6th European Conference on Metal Organic Frameworks and Porous Polymers

EUROMOF



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Plenary Lectures

CHEMISTRY AND APPLICATION OF DYNAMIC MOF/PCP BEYOND RIGIDITY AND INTO THE REALM OF SOFT POROUS CRYSTALS

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Keywords: *soft porous crystal, hybridization, dynamics, storage, separation, isotopologue mixture*

As the promising materials to address global issues of clean energy technologies and environmental sustainability, the emerging class of crystalline microporous materials, porous coordination polymers (PCPs) or metal-organic frameworks (MOFs),[1] have been applied in fields of gas storage and separation, delivery vessel, sensors, catalysis, supercapacitors, FETs, batteries, proton conduction, and so on. We have found the 3rd generation (3G) PCPs/MOFs (Soft porous crystals, SPCs[2]) that possess flexible or dynamic porous frameworks reversibly respond to external stimuli, not only chemical but also physical, unlike robust PCPs/MOFs (2G).[3,4] In particular, by controlling the local motion of organic ligands that construct the framework, we discovered and developed an effective mechanism for separating gas mixtures with similar properties, such as oxygen/argon,[5] alkane/alkene,[6,7] and light water/heavy water isotopologue mixtures.[8]

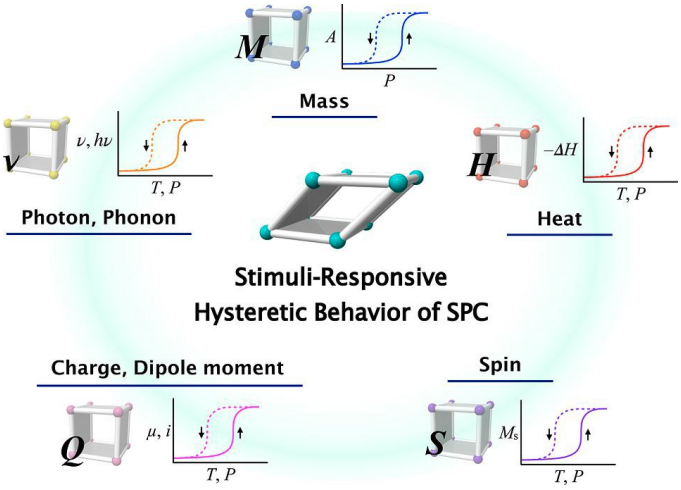


Figure 1. PCP/MOF-based soft porous crystals with superior features that differentiate them from other porous materials

This talk provides an essential and accessible overview of the chemistry of SPCs, their current features, and the outlook of further developed materials as 4th generation PCPs/MOFs, which exhibit multi-functions simultaneously or alternately in combination.[9,10]

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UNRAVELLING TRANSIENT POROSITY: STRUCTURAL AND THERMODYNAMIC INSIGHTS INTO FLEXIBLE POROUS MATERIALS

Len Barbour,[a,b]

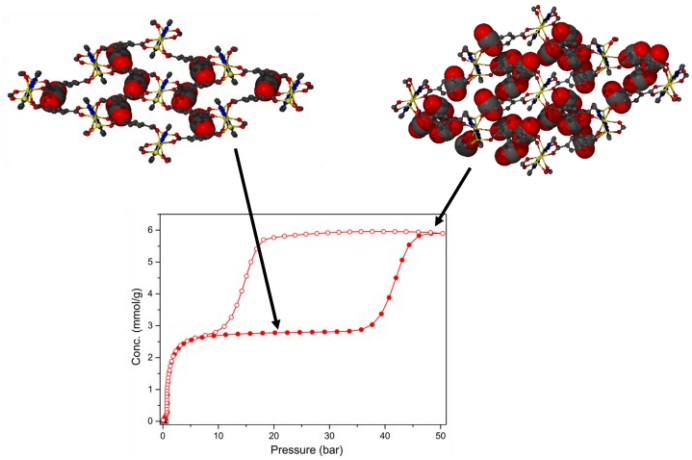
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Keywords: *in situ structural analysis, transient porosity, flexible materials, sorption calorimetry*

The past three decades have seen remarkable progress in the design and characterisation of new classes of porous materials. Yet, deciphering the complex interplay between molecular-level structure and physico-chemical properties—particularly in systems that undergo structural transformations upon guest uptake or release—remains a significant challenge. This is especially true for flexible porous materials with 0D pores, which exhibit *transient porosity*: the ability to transport guest molecules despite lacking permanent channels. These behaviours, often indicated by stepped sorption isotherms, call for innovative analytical approaches. This presentation will describe laboratory-based *in situ* single-crystal and powder diffraction techniques developed in our group to probe guest-induced structural changes. It will also highlight a relatively straightforward adsorption calorimetric method for determining the enthalpy changes associated with individual sorption and desorption events during gate-opening and -closing transitions.[1] Drawing on two decades of work, the presentation will demonstrate how these methods have yielded deep insights into the behaviour of soft porous crystals and clarified key mechanisms underlying transient porosity.[2-10]



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COMBINING SPECTROSCOPIES AND MOLECULAR MODELLING TO DISCLOSE COMPLEXITY IN MOFS

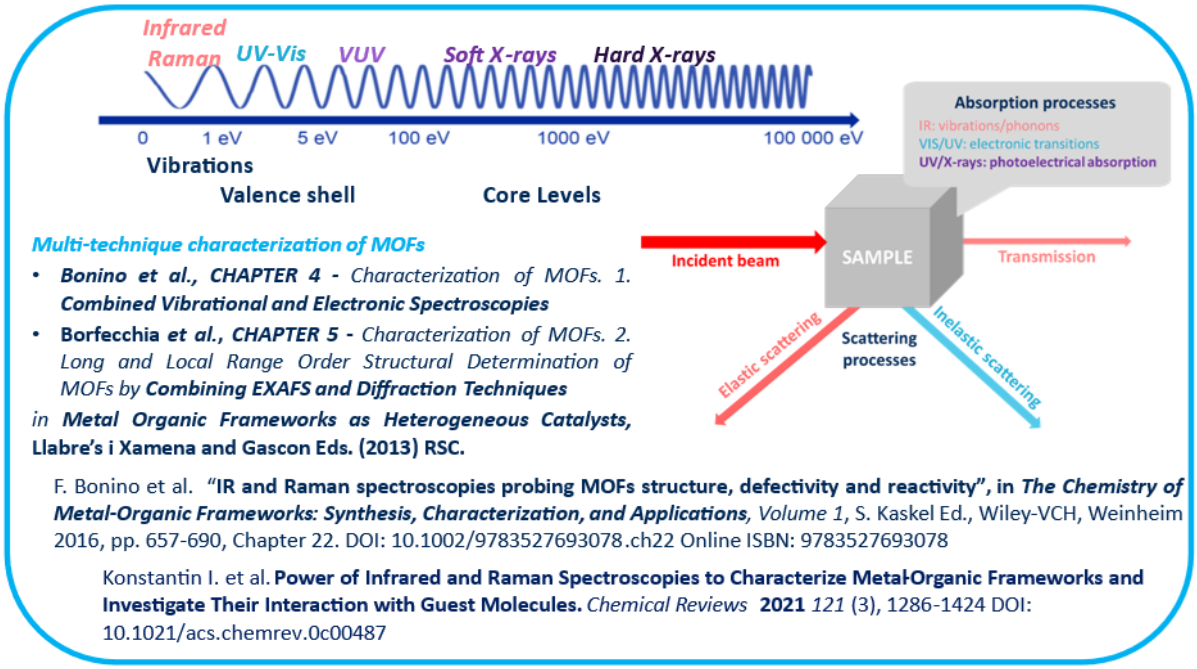
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Keywords: MOFs, Spectroscopies, Molecular Modelling

Spectroscopic techniques, combined with molecular modeling, have emerged as powerful tools to investigate the complex nature of MOFs. The availability of different energy probes allows us to monitor spin states, vibrations, valence or core electronic transitions, through a series of spectroscopies (NMR, EPR, Raman, IR, UV-Vis, XAS). Furthermore, the possibility of performing experiments under a wide variety of conditions (in terms of pressure and temperature) lets to study surface phenomena that occur during a reaction or when a selective adsorption phenomenon takes place. Spectroscopies provide detailed information on the structural and electronic properties of MOFs, as well as on their dynamic behavior under reaction conditions. Techniques such as infrared spectroscopy (IR), Raman spectroscopy, X-ray absorption (XAS), X-ray photoelectron spectroscopy (XPS), and ultraviolet-visible spectroscopy (UV-Vis), to name a few, enable the observation of key intermediates, reaction mechanisms, and changes in the active sites of catalysts and selective adsorbents. Furthermore, operando spectroscopy, which enables measurements under real reaction conditions, has significantly improved our understanding of their real-time behavior. The combination of these spectroscopic and molecular modeling approaches has been instrumental in unraveling the molecular-level interactions between these complex materials and reagents, identifying reaction pathways, and guiding the design of more efficient, selective, and durable sorbents or catalytic systems. The present contribution aims to illustrate potentialities and limits of IR, Raman, UV-Visible and XAS in Metal Organic Frameworks characterization. Case studies will be selected in respect to the use of MOFs as heterogeneous catalysts or selective adsorbers.



NANO SOLUTIONS FOR GLOBAL CHALLENGES: THE PROMISE OF METAL-ORGANIC FRAMEWORKS

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Eighty years ago, polymers were largely unknown to the general public. However, in the late 1930s, one polymer—nylon—became a household name almost overnight. Nylon's debut revolutionized the women's hosiery market, marking the beginning of a materials revolution that would take decades to unfold. Over time, polymers became indispensable, finding applications in clothing, kitchenware, electronics, building materials, medicine, and beyond. Today, they are recognized as one of the defining materials of the 20th century.

Looking ahead, porous metal-organic frameworks (MOFs)—often referred to as "smart and programmable sponges"—are poised to become a hallmark material of the 21st century. Although this class of multidimensional crystalline materials is still in its early stages, their potential is vast. Fifty years from now, MOFs could be as integral to human life as polymers are today.

MOFs can be envisioned as nano-scale Tinker Toy assemblies, with metal nodes and organic linkers forming highly ordered, periodic structures. This modular design gives MOFs remarkable versatility and tunability, enabling a wide array of applications. Researchers worldwide have already explored their relevance in drug delivery, water harvesting, gas storage, chemical separations, and the destruction of toxic agents such as nerve gases.

Significantly, the commercialization of MOFs has begun, with start-up companies driving the transition from lab-scale research to practical, real-world applications. This talk will delve into the transformative potential of metal-organic frameworks, highlighting their role as enabling materials for environmental applications. From basic scientific discovery to implementation and commercialization, MOFs are paving the way for innovative solutions to some of society's most pressing challenges.

INSIGHTS INTO ADSORPTION OF WATER IN METAL-ORGANIC FRAMEWORKS FROM MOLECULAR SIMULATION

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Keywords: *Adsorption, molecular simulation, water*

Adsorption of water plays an important role in many applications of metal-organic frameworks (MOFs), including CO_2 capture and atmospheric water harvesting. Molecular simulations can predict adsorption properties and provide useful molecular-level insights into observed behavior. However, simulations of water pose challenges due to uncertainty in the force field (the model) as well as in efficient sampling of molecular configuration. We will discuss how these challenges can be overcome in the context of recent examples from our work.

For CO_2 capture, competitive adsorption of water can decrease the working capacity. One potential way to reduce water uptake is to make the MOF more hydrophobic. Wang et al. [1] introduced a variant of CALF-20 featuring hydrophobic methyltriazolate linkers. This material retains the ability to adsorb CO_2 at 70% relative humidity (RH) – a threshold at which CALF-20 shows negligible CO_2 uptake. Grand canonical Monte Carlo (GCMC) simulations reveal that the methyl group hinders water network formation in the pores of the material and enhances the CO_2 selectivity over N_2 in the presence of a high moisture content [1]. Calculated radial distribution functions suggest that introducing the methyl group into the triazolate linker increases the distance between water molecules and Zn coordination bonds, offering insights into the origin of the enhanced moisture stability observed for CALF-20M. We have also used GCMC simulations and machine learning to screen thousands of MOFs to find additional candidates that can capture CO_2 in the presence of humidity.

For atmospheric water harvesting, high adsorption of water is desired, especially at low RH, but moderate enthalpies of adsorption are also required, making it challenging to find good candidate materials. Xie et al. [2] recently showed that several phosphonate-based MOFs exhibit high water uptake at low RH and are exceptionally stable. Molecular simulations predict the water isotherms in very good agreement with experiment and provide insights into the excellent sorption performance of these materials [2]. In NbOFFIVE-1-Ni, we find that framework flexibility plays an important role in water uptake [3]. We have also investigated the adsorption mechanism of water in NU-1000 [4]. We found that details related to the termination of the zirconium nodes can have a big impact on the shape and pressure of the condensation step in the water adsorption isotherm. Our analysis reveals that rotational mobility of aquo ligands, often neglected in computational studies, can shift the condensation step by up to 20% in RH. By examining the adsorption modes and interaction sites, we demonstrate that configurational changes in the Zr_6O_8 node affect water adsorption significantly and can change the nature of the interactions from hydrophobic to hydrophilic. We propose a robust, transferable approach to account for these changes in simulations, achieving good agreement with experimental results.

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THE BEAUTY OF CRYSTALLINE HYBRID MATERIALS: FROM CRYSTAL ENGINEERING TO DEVICE FABRICATION

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Keywords: *crystalline hybrid material, crystal engineering, organic-inorganic, metal-organic framework, hydrogen-bonded framework, copper halide hybrid semiconductor, light-emitting diode*

Crystalline hybrid materials, such as metal-organic frameworks (MOFs), metal-halide and metal-chalcogenide based hybrid semiconductors (HSCs), hydrogen-bonded coordination frameworks (HCFs) and hydrogen-bonded organic-inorganic frameworks (HOIFs), have attracted enormous attention over the past two decades. This interest stems not only from their diverse and rich structural chemistry, but also from their unique functionalities, systematic tunability, and promising physicochemical properties that underpin a broad range of potential applications.

In this presentation, I will discuss our recent progress in the design and optimization of several structurally and functionally distinct classes of crystalline hybrid materials, including MOFs, HOIFs, and hybrid copper iodides [1-12]. Our studies are guided by crystal engineering principles and strategies and aim to tailor and enhance properties for targeted applications. I will also outline our efforts in translating some of these materials into prototype devices through simple, solution-based thin-film fabrication processes.

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Keynote Lectures

ORDERING CHEMICAL FUNCTIONALITY IN POROUS MATERIALS FOR FUNCTION

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The diversity of metals and linkers complicates identification of metal-organic framework components that lead to desired topologies and internal surface chemistries. We have used machine learning to predict the synthesisability and the pore dimensions of a metal-organic framework solely from the identity of the metal and the linker, which is the selection the experimentalist must make (*Angew. Chem. Int. Ed.* **61**, e202114573, 2022; *Digital Discovery* **3**, 2509, 2024). Even with that choice made, there is considerable diversity of synthetic conditions to navigate, which can be addressed by automated synthesis. High-throughput brute force exploration of a large synthetic parameter space affords an ordered arrangement of two linkers on the well-known zirconium oxo carboxylate UiO-66 network, opening a new direction for the chemical control of guest access to porosity. (*Angew. Chem. Int. Ed.* **60**, 26939, 2021).

The ordering of multiple sidechains over a common structural framework is a route to tailoring the guest response of a porous material that draws on analogy with the precise sequence of common amino acid building units over the common polypeptide backbone of proteins. We demonstrate the ordering of different sidechains over a common porous scaffold through recognition of their distinct chemistries during synthesis by the conformations that the building units adopt in order to form the framework. This conformationally-directed sidechain order enhances separation performance over that of a single sidechain framework, associated with distinct locations of the separated molecules driven by the differentiated environments created by the ordered sidechains. (*Angew. Chem. Int. Ed.* **63**, e202411960, 2024).

NEW FRONTIERS IN MODELING ADSORPTION IN METAL-ORGANIC FRAMEWORKS ACCOUNTING FOR FLEXIBILITY AND ACCURATE INTERMOLECULAR INTERACTIONS

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Keywords: *machine learning potentials, adsorption, Monte Carlo simulations, flexible Metal-Organic Frameworks*

Adsorption technology is essential for important technologies such as energy storage, separation, catalysis. Reticular materials like metal-organic frameworks (MOFs) and covalent-organic frameworks (COFs), have been widely explored for adsorption and separation technologies due to their modular design capabilities.[1] Computational simulations are instrumental to screen large sets of MOFs. One can obtain quantitative properties such as the adsorption isotherm, the Henry constant and isosteric heats of adsorption, which can then be compared with experiment. However, modeling also provides a strong vehicle to deduce qualitative features such as preferential adsorption sites or clustering of guests in confined pockets crucial for future design of new materials.[2]

To obtain adsorption isotherms one currently typically relies on grand canonical Monte Carlo simulations (GCMC), which allows to dynamically vary the number of adsorbents at given conditions of temperature and chemical potential. The main drawback of these GCMC simulations for adsorption in framework materials is their assumption of rigid frameworks, making them unsuitable for flexible structures. Furthermore, energy evaluation are typically performed using classical force fields thanks to their computational efficiency. GCMC simulations often require a million number of energy evaluations which is not feasible with quantum mechanical based methods. Adsorption isotherms are extremely sensitive to the level of theory used to describe the intermolecular interactions. Methods giving errors of only 4kJ/mol – known in the field as chemical accuracy – may not reliably predict the true shape of the isotherm.[3] Accurate adsorption simulations require both accurate intermolecular interactions and proper treatment of framework flexibility.

Within this talk, I will show new frontiers to meet these challenges and will highlight the importance of making the adsorption data available for the community. Firstly, we have developed novel methodologies to train accurate machine learning potentials (MLP) to calculate adsorption properties based on very accurate underlying quantum mechanical data.[4,5] It is important to emphasize that, particularly for adsorption, the training process must also include high-energy configurations to ensure that trial moves with high energy can be reliably rejected during Monte Carlo simulations. Second, we have recently developed an alternative sampling procedure as alternative for GCMC simulations, namely the Transition Matrix Monte Carlo (TMMC) method combined with molecular dynamics (MD) trajectories to fully capture framework flexibility.[3] Additional MD simulations furthermore allow to obtain insight into preferential adsorption positions.[2] I will illustrate how these methodological developments have enabled simulation of adsorption properties of realistic MOFs fully accounting for flexibility and for dynamic behavior of the framework. Examples comprise CO_2 adsorption in MOFs with open metal sites (Mg-MOF-74), flexible frameworks (CALF-20),[6] water adsorption in flexible MOFs (MOF-303),[3] olefin/paraffin adsorption in zeolitic imidazole frameworks.[7] Finally, I will highlight how to make the essential adsorption metadata and primary data available in a digital format. In 2021 IUPAC established a task-force for the standardization of adsorption data based on a human readable STAR format, the adsorption information file (AIF).[8] Reporting adsorption data as AIF allows to make all essential primary and metadata findable, accessible, and interoperable, which is essential for reproducibility and future analysis.

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ELECTROACTIVE METAL-ORGANIC FRAMEWORKS FOR SENSING, ELECTROCATALYSIS AND IONTRONICS

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Keywords: *redox active MOFs, electrocatalysis, photochromic, iontronics*

Electroactive MOFs have received considerable attention in recent years.[1] Their electronic conductivity and redox chemistry is crucial for performance. In particular, redox hopping mechanisms coupled with ionic motion offer new chances for iontronic devices.[2]

Triphenylene-based conductive metal-organic frameworks are intensively studied for HER, CO2RR, ORR and other electrocatalytic reactions. They are highly sensitive for glucose and urea sensing.[3] However, under oxidative potential the role of framework is not entirely understood and stability depends on reaction conditions. These two-dimensional materials are easily electronically tailored by ligand-design achieving high performance in the electrocatalytic glycerol oxidation.[4] In situ methods such as NMR and Raman spectroscopy shed light on the mechanistic aspects of this rather complex reaction.

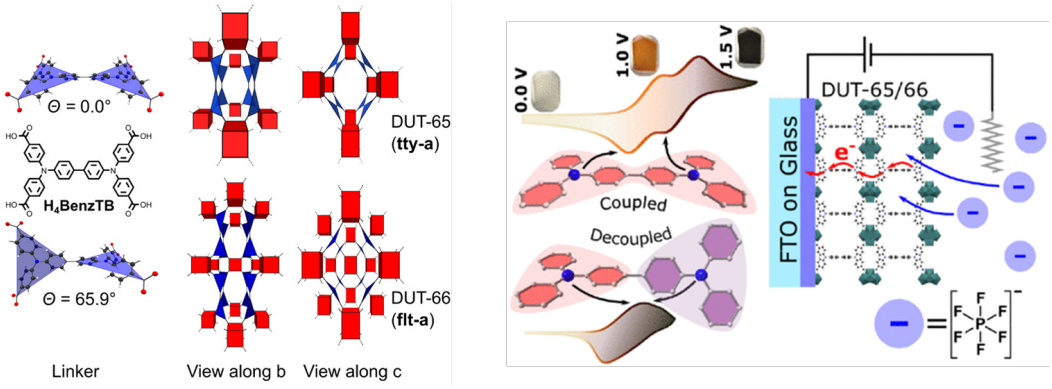


Figure 1: Redox-active Zr-based frameworks DUT-65 and DUT-66 enable redox-engineering via topology-design.[6]

Redox active MOFs open new avenues for photochromic devices and iontronics.[5] Piccard-type ligand systems (N,N,N′,N′-benzidinetetrabenzoate) are easily integrated into Zr-MOFs to obtain electrochromic materials.[6] Their redox chemistry can be controlled via topology design. Redox active MOFs for iontronic applications are an emerging field enabling capacitive diodes (CAPodes) and their integration into capacitive logic gates in future.

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ADVANCING MOF SIMULATIONS WITH MACHINE-LEARNED POTENTIALS

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Keywords: *MLP Training, MLP-Molecular Dynamics, MLP-Monte Carlo, MOF Flexibility, Guest Adsorption, Guest diffusion*

Machine-learned potentials (MLPs) are transforming materials science by enabling accurate and efficient modeling of complex materials, such as metal-organic frameworks (MOFs). These data-driven approaches overcome the limitations of traditional methods like density functional theory (DFT), which are computationally prohibitive for large-scale simulations. MLPs offer a hybrid alternative by learning the potential energy surfaces from quantum mechanical data, thereby providing rapid and precise predictions of material properties across extended length and time scales.
One area where MLPs prove especially valuable is in the modeling of flexible MOFs, which can exhibit phase transitions and mechanical deformations in response to external conditions (thermal, mechanical pressure). Using MLPs, we explore the MOF CALF-20's phase space with unprecedented efficiency, revealing distinct two-step elastic deformation and high fracture strain, which are critical for potential applications in flexible electronics and sensors. Furthermore, MLPs extend their utility to adsorption simulations, particularly for MOFs with open metal sites (OMS), where strong host-guest interactions are challenging for classical force fields to describe accurately. We demonstrate this by developing an MLP for H_2 adsorption in Al-soc-MOF-1d, an OMS-containing framework. The MLP accurately models H_2 binding and diffusion, offering insights into adsorption performance that can guide the design of MOFs for hydrogen storage applications. We will deliver in this presentation several examples illustrating the potential of ML-based approaches to advance the computational modeling of MOFs.

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ADVANCED POROUS MATERIALS FOR LIQUID SEPARATION MEMBRANES

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Keywords: *Metal-Organic Frameworks, Covalent Organic Frameworks, Liquid Separation Membranes, Water Purification, Alcohol Dehydration, Organic Solvent Nanofiltration*

The recent decade has witnessed the booming development of advanced porous materials (APMs) such as metal-organic frameworks (MOFs) and covalent organic frameworks (COFs). Unlike their conventional counterparts (e.g., silica, activated carbon, zeolite), APMs have well-ordered structures, uniform yet tunable pore sizes, and versatile chemical compositions suitable for various modifications. Membrane technologies have attracted increased attention recently because of their important applications in clean energy and environmental sustainability. The combination of APMs in membrane technologies would generate innovative solutions and tremendous impacts. In this talk, I will present our group's studies on APMs as membrane materials for liquid separations, including water purification, alcohol dehydration, and organic solvent nanofiltration. Through strategies including postsynthetic defect healing, judicious selection of secondary building units, and adopting flexible substrates, we have gradually revealed the potential of APMs for industrial liquid separations.

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WATER STABILITY IN MOFS: FROM PRINCIPLES TO PRACTICE

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Keywords: *water stability, heat transfer, water harvesting*

Metal-organic frameworks (MOFs) have emerged as serious contenders as advanced materials for enabling water sorption-based applications in energy efficiency and climate control technologies. These include atmospheric water capture, heat pumps, desiccation, humidity control, and thermal batteries. Here, I will discuss the fundamental chemical principles that allow MOFs to display water stability as would be required in such applications [1]. I will show how thermodynamic principles allow the derivation of "isoreticular curves", which predict the relationships between the pore features of a given material and the measurable water sorption properties, namely critical relative humidity for condensation, maximal capacity, and pore size or temperature for the onset of water sorption hysteresis [2]. Through this analysis, we propose guidelines for the maximization of sorption capacity at a given relative humidity with minimal hysteresis and discuss the theoretical limits for capacity at low relative humidity.

On the application side, I will show how MOFs have enabled a new design for efficient air-conditioning systems that are commercially deployable in both industrial and residential settings.

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BREAKING BONDS, BUILDING CHEMISTRY

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Historically, innovations in synthetic methods and chemical reactions have transformed how scientists design and synthesize molecules and materials. Indeed, novel reactions or synthetic strategies not only enable access to previously unattainable structures but also inspire new paradigms for constructing materials that address global social, economic, and industrial challenges.

In this talk, I will introduce the concept and recent advances in Clip-off Chemistry. This approach is based on the design and synthesis of novel molecules and materials with well-defined compositions and structures via bond cleavage within molecular frameworks. Clip-off Chemistry thus represents a new synthetic methodology in which programmed, selective disassembly leads to the formation of new molecules and materials. This molecular disassembly is achieved through chemical reactions; in a first approach, via ozonolysis, which enables the cleavage of organic building blocks or linkers through direct breaking of alkene or alkyne bonds. I will present the fundamental principles of Clip-off Chemistry and recent examples of molecules and structures obtained through controlled bond fission in porous reticular materials.

PHOTOACTIVE METAL ORGANIC FRAMEWORKS FOR HYDROGEN PRODUCTION

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Keywords: *metal-organic frameworks, hydrogen production, photocatalysis*

Metal Organic Frameworks, a versatile class of porous hybrid solids with a large chemical and structural diversity, have been proposed to date for a wide range of applications.[1] In the field of catalysis, although MOFs bear a limited thermal and/or chemical stability, the careful spatial distribution of active sites enables to reach unprecedented achievements in this field.[2] Despite recent progresses, the use of MOFs in photocatalysis is still at its infancy with challenges both in terms of performances and stability.[3] Metal(IV) based MOFs (M=Ti, Zr, Ce) are among the most promising candidates in this field due to their intrinsic photoactive features and high chemical stability.[3]

These past two decades we devoted a particular effort to decipher the complex chemistry of Ti-MOFs.[4] This led to the discovery of series of Ti oxoclusters or metal oxide chains polycarboxylate microporous MOFs, some of them exhibiting exceptional photoconductive properties.[5, 6] Among other achievements, this was associated with either an outstanding production of hydrogen from the photocatalytic decomposition of formic acid in water,[7] or an improved photocatalytic performance from the decomposition of water.[6] This is in part associated to their specific photophysical features such as their sometimes long life charge separation.[8] Cu-embedded MOFs are another class of photoactive MOFs; however, most Cu based MOFs exhibit a very limited chemical stability preventing from their use in aqueous solution. An alternative consists in building heterometallic MOFs where high valence oxoclusters are combined with Cu clusters in order to construct porous water stable photoactive MOFs; this paves the way for their utilization in photocatalytic hydrogen production from water.[9]

Through a large international consortium of materials' chemists, experimentalists or theoreticians, in part related to the ongoing EU project MOF2H2,[10] we have been studying the behavior of these new classes of MOFs for the photocatalytic production of hydrogen. In this presentation will be disclosed some of the main findings and remaining challenges in this field.

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FROM FRAMEWORK-DYNAMICS ENGINEERING TO SCINTILLATION PROPERTIES AS DEMONSTRATED BY SOLID STATE NMR AND SYNCHROTRON SOURCE X-RAY DIFFRACTION

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Keywords: *framework dynamics, hetero-ligand MOFs, solid-state NMR, synchrotron radiation PXRD*

Engineering coordinated rotational motion in porous architectures enables the fabrication of molecular machines in solids.[1,2] MOFs offer great opportunities to integrate multiple fast-rotating molecular entities in the framework endowed with geared mechanism, resembling a prototype of molecular machines. Specifically, pillared Zn-MOFs comprising bicyclopentane–dicarboxylates (BCP) in 2D sheets separated by bipyridine pillars allow to arrange orthogonally the two distinct molecular rotors in arrays and generate a dynamic cascade mechanism concerted with oscillating motion of the framework. Following this strategy, the insertion of azobipyridine as a pillar enabled to introduce a further degree of freedom and a crank-like motion in the solid-state machinery, as shown by MAS NMR down to 90 K.[3] External stimuli could modulate dynamics: CO_2 and I_2 vapors diffusing into the pores drive a piston-like 0.5 A dislocation of the two subnetworks and, in turn, change motional scenario (Figure 1). The rotary dynamics, intrinsically coupled with the framework flexibility, was followed by complementary evidence, such as multinuclear solid-state NMR and NMR relaxation times down to very low temperatures, synchrotron radiation XRD and gas sorption.
With the aim of switching material properties on-command, we fabricated fast-reorientable dipoles integrated into molecular rotors to produce materials responsive to static or oscillating electric fields.[4] The combination of high-resolution synchrotron-source XRD and solid-state NMR spectroscopy at temperatures down to 4 K, along with DFT and phonon calculations, unveiled a concerted dance of C-F rotating dipoles in Al-MOFs triggered by the interaction among nearest-neighbour rotors.
Additionally, by fabricating *hetero-ligand* MOFs containing two scintillating linkers endowed with the same length and complementary emission-absorption spectra, set in close intimacy (1-2 nm), the scintillation properties were greatly enhanced. These Hf-MOFs capture and concentrate radioactive isotopes of gases, such as Xe and Kr, which transfer their ionizing radiation to the framework which, in turn, produce a visible light signal with improved performances.[5-7] The homogeneous distribution of the two pillars in the framework was highlighted by high sensitivity *hyperpolarized* ^{129}Xe NMR (2% dilution of Xe in He/N_2), showing the quick exploration of favorable Xe sites. Multiple investigation techniques, such as synchrotron-radiation X-ray diffraction, Xe adsorption isotherms and Grand Canonical Monte-Carlo (GCMC) simulations, corroborated the favorable Xe sites and determined the interaction energy with the pore walls.

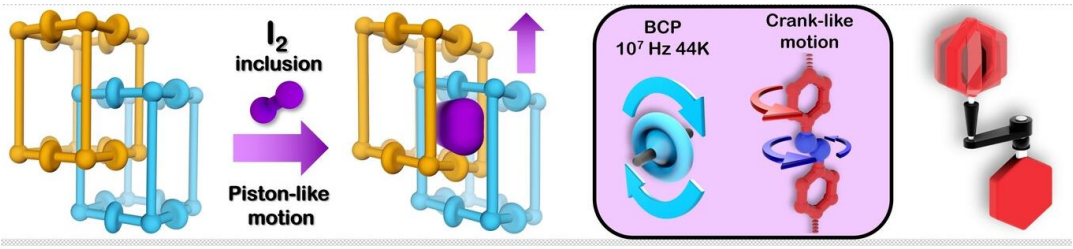


Figure 1. Pillared MOF: structural transformation upon I_2 diffusion into the pores (left), rotor dynamics and crank-like motion of azobipyridine pillar (right).

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TAILORING CATALYTIC SURFACES *OF* AND *WITH* COVALENT ORGANIC FRAMEWORKS

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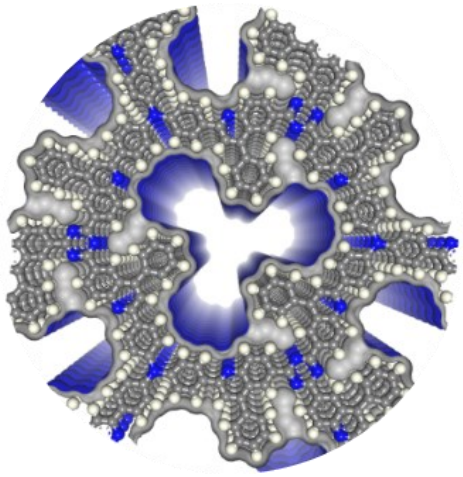
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Keywords: *Covalent Organic Frameworks, Photo/Electrocatalysis, Multicomponent-Reactions*

Catalysis is a crucial technology with significant implications for both economic and ecological sustainability. It plays a central role in developing resource-efficient, sustainable processes for energy and material conversion. Porous functional materials, characterized by large accessible surface areas and well-defined surface functionalities, are vital as catalysts in a wide range of viable chemical reactions.

Among these materials, are covalent organic frameworks (COFs). They combine the advantages of organic polymers with those of conventional inorganic or hybrid porous materials, such as zeolites, activated carbon, or metal-organic frameworks.[1] COFs feature ordered pore structures and tunable pore sizes, along with exceptionally high porosity and surface area. Moreover, their exclusively organic composition allows for precise control over both the chemical properties of their surfaces and the physical characteristics of the overall framework.

These unique features make COFs highly attractive for emerging applications, including freshwater generation,[2] energy storage,[3] and also opens up innovative prospects in electro- and photocatalysis.[4] In this presentation, we demonstrate how the surface of COFs can be precisely tailored to meet the requirements of specific catalytic applications. We also show how COFs can be used to modify the surfaces of inorganic catalysts and to stabilize biological catalysts.



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AI-DRIVEN DESIGN OF MOFS FOR CARBON CAPTURE

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Keywords: *AI, Machine Learning, Carbon Capture, molecular simulation*

Metal-Organic Frameworks (MOFs) represent one of the most promising classes of materials for applications in gas separation, storage, sensing, and catalysis. Their modular nature allows for nearly infinite structural diversity. However, despite remarkable progress in synthesis and simulation, the holy grail of MOF science—designing the optimal material for a specific application—remains elusive. This challenge is rooted in several fundamental issues. First, the design space of MOFs is effectively infinite, making brute-force experimentation and high-throughput simulations inherently limited. Second, optimality is often multi-objective, requiring trade-offs between performance metrics like selectivity, capacity, stability, and cost that resist simple ranking schemes. Third, even when simulations predict an ideal structure, its practical synthesis may prove impossible or unscalable.

AI and data-driven approaches are transforming the landscape of MOF discovery.[1,2] By leveraging extensive experimental and computational databases, we can address chemical questions that have long resisted classical theory. Furthermore, we investigate how AI models can uncover the underlying structure–property relationships that define high-performance materials, particularly in the context of carbon capture.[3] Instead of replacing human expertise, AI enhances it—helping us navigate complex design spaces with increased precision and creativity. This integration of AI into MOF design signifies a fundamental shift in our approach to materials discovery.

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TAILORING THE MORPHOLOGY OF MOF NANOCRYSTALS BY USING SELF-ASSEMBLED MATERIALS

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Keywords: *MOFs, nanostructures, composites, (bio)polymers, carbon-based materials, self-assembly*

Precise control over nanomaterial morphology and dimensions is crucial for tuning their physico-chemical properties. Advances in DNA and protein nanotechnology, inorganic crystallization, and polymer/surfactant self-assembly have enabled unprecedented synthesis of anisotropic nanoparticles—such as 1D nanotubes, nanowires, 2D platelets, rings, and stars.[1] This crystal engineering has not only enabled the exploration of novel physical, chemical, and biological phenomena but also spurred the development of advanced applications. In recent decades, MOFs have attracted considerable interest, as this family of porous solids offers a unique opportunity to design a wide range of architectures with modulated porosities and chemical functionalities. Most MOF research has focused on discovering new structures, assessing their properties, and developing MOF-based composites, while less attention has been paid to the control of MOF crystal size and morphology. Progress in this area has primarily relied on carefully chosen synthesis conditions and the use of structure-directing agents or modulators. [2,3] However, these methods often yield powdered samples consisting of spherical, isotropic nanocrystals with limited size control. The rare existing 1D MOF architectures in the forms of nanowires, nanotubes and nanorods were synthesized through a bottom-up solution route or hydrothermal process eventually templated by polymer or inorganic 1D nanostructures. [3,4]

Herein, we present our progress in the development of MOFs based composites to address environmental and energy-related applications. The assembling of MOFs with biopolymers and carbon based materials was envisaged not only to process MOFs composites and impart novel functionalities but also to control the diameter/shape of MOFs nanocrystals and their spatial organization within the support matrix.[5,6] We have taken profit of the self-organization properties of biopolymers and carbon-based materials and liquid-liquid phase separation processes to tune the organization, nanostructuration and porosity of composites.[5,6] Advanced characterization tools (X-ray diffraction, N_2 porosimetry, TEM analytical and imaging techniques, HAADF-STEM, electron diffraction…) were combined to provide a complete picture of these composites at the nanoscale and describe their mechanical, interfacial and dynamic properties. Recently, by using graphene oxide nanoscrolls as structure directing agents, a series of 1D Al MOFs nanostructures differing in their crystal dimension and aspect ratio as well as structural flexibility upon guest molecules adsorption were prepared. All these materials were investigated for the capture of pollutants, gas separation or (bio)catalysis.[5-7]

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6th European Conference on Metal Organic Frameworks and Porous Polymers

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Invited Lectures

RETICULAR DESIGN OF QUANTUM MATERIALS: EMERGENT PROPERTIES IN METAL–ORGANIC NETS

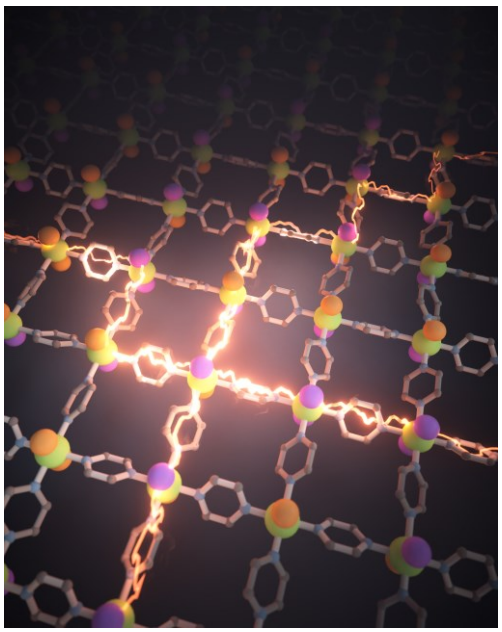
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Keywords: *Quantum materials, low-valent MOFs, magnetism, electrical conductivity, valence tautomerism*

Quantum materials exhibit exotic phenomena arising from the intricate interplay between electronic, magnetic, and lattice degrees of freedom. Traditionally, most such materials are purely inorganic and synthesized under conditions dominated by thermodynamic control. Reticular chemistry, however, provides complementary tools for quantum materials discovery, enabling the design, synthesis, and understanding of systems with unique symmetries and electronic structures.



Metal–ligand assemblies featuring variable or inseparable valence states (“non-innocence”) are widespread in coordination chemistry and offer a route to harness strong electron–electron correlations in extended networks. This strategy provides a realistic means to challenge the current state-of-the-art approaches to quantum materials.

In this lecture, I will present our recent findings in the search for genuinely new symmetries in MOFs and coordination solids, along with their emergent properties. These include metallicity, geometric frustration, valence tautomerism, and exceptionally strong magnetic correlations that give rise to high-temperature magnetic ordering.[1–8]

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CONTROLLED INCORPORATION OF MULTIPLE METALS INTO MOFS: STRATEGIES TO ENHANCE CHEMICAL AND STRUCTURAL COMPLEXITY

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Keywords: *Metal–Organic Frameworks, Multimetal Systems, Messenger Building Units, Structural Complexity, Iridium*

The ability to precisely control the distribution of multiple metal cations within a single metal-organic framework (MOF) opens new avenues for tuning reactivity, stability, and electronic properties. In particular, MOFs that integrate multiple metal cations within their structures offer a suitable platform for increasing both the chemical and structural complexity of the materials, which can give rise to novel or enhanced properties and behaviors. However, the controlled incorporation of selected combinations of different metal elements remains a major synthetic challenge.

We have explored several strategies to synthesize MOFs incorporating different combinations of various metal elements. Through one-pot synthetic approaches we have investigated rare-earth-based MOFs and demonstrated that both the crystallization mechanism and the initial metal composition have a critical influence on the final cation distribution within the secondary building units (SBUs), leading to outcomes ranging from compositional segregation to well-defined atomic arrangements.[1]

In addition, we have developed a synthetic route to incorporate iridium atoms into MOF structures. Following a multimetal strategy, we synthesized a novel family of MOFs featuring two distinct SBUs: one composed of Ir centers and another formed by In or Sc atoms. This approach enables the expansion of reticular chemistry toward previously unexplored metal elements, incorporating new types of active sites and broadening the spectrum of accessible reactivity.[2]

Furthermore, we have shown that specific combinations of metal atoms can be incorporated into MOFs by using heterometallic molecular complexes as *messenger building units* (mBUs). These preassembled clusters encode the desired metal composition and transfer it to the framework during synthesis. By combining these mBUs with di-, tri-, and tetratopic organic linkers, we have synthesized MOFs with distinct topologies. In all cases, the controlled integration of metal pairs, such as Ga/Ni or Ga/Co, was successfully achieved.[3-4]

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POROUS IONIC LIQUIDS FROM STABLE MOF SUSPENSIONS: WHAT THEY ARE, HOW THEY WORK, AND WHY THEY MATTER

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Keywords: *porous liquids, ionic liquids, MOFs, gas absorption, suspension stability*

Porous ionic liquids [1] — comprising stable suspensions of microporous solids such as metal-organic frameworks (MOFs) in sterically hindered ionic liquids — are emerging as a powerful class of materials for the capture, separation, and transformation of small molecules [2]. By preventing pore blockage through the use of bulky ion pairs, these suspensions preserve MOF accessibility while benefiting from the chemical versatility of ionic liquids.

These systems demonstrate exceptional performance in gas absorption, with uptake capacities that scale with MOF content and often surpass those of the individual components. When properly formulated — such as ZIF-8 suspensions in phosphonium acetate or levulinate ionic liquids — CO_2 uptake can be more than twice as high and significantly more selective than in the pure MOF at 1 bar and 303 K. Thermodynamic analyses and molecular simulations help elucidate the underlying mechanisms driving this behaviour. The enhanced performance arises from a combination of gas chemisorption within the ionic liquid, increased free volume in the suspension, and favorable gas–solid interactions that also contribute to the suspension's stability [3,4].

Crucially, efficient gas absorption underpins improved reactivity in catalytic and electrocatalytic processes [2,5]. Porous ionic liquids enable higher local gas concentrations in the liquid phase, which can accelerate reaction rates and enable milder operating conditions. This is exemplified by the direct transformation of absorbed CO_2 into cyclic carbonates at room temperature and atmospheric pressure using ZIF-8/phosphonium halide systems [5].

Altogether, porous ionic liquids represent a modular and sustainable platform for designing advanced separation and reaction media. Their tunable composition, enhanced gas uptake, and capacity to facilitate downstream chemical transformations make them particularly promising for applications in gas capture and gas-phase catalysis.

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SYNERGISTIC EFFECT IN HETEROMETALLIC TITANIUM-ORGANIC FRAMEWORKS IN CATALYSIS

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Keywords: *Synergy, Titanium-Organic Frameworks, Heterogeneous Catalysis.*

Heterometallic metal-organic frameworks (MOFs) are increasingly relevant as they offer customizable functions linked to specific metal combinations. These frameworks provide significant advantages over their homometallic counterparts by enabling targeted modifications in adsorption, structural response, electronic structure, and chemical reactivity. However, achieving precise control over the metal distribution in these solids presents a challenge.[1] Synthetic control of cluster composition, rather than indirect framework modification, allows direct access to catalytic activities that are unique to particular metal combinations.

In this context, combining highly stable heterometallic titanium frameworks with other metals to create heterometallic secondary building units (SBUs) with the general formula TiM_2 [M = Mg, Fe, Co & Ni] exemplifies the benefits of controlling the specific metal distribution within the framework for use as heterogeneous catalysts. The catalytic activity observed in these materials is not merely due to the presence of two metals but arises from their synergistic cooperation, creating a catalytic entity that is more efficient than the simple sum of its parts.

Using an integrative experimental-computational approach, we explore how these metals influence each other, realizing a synergistic catalytic effect in a variety of reactions, including: *i)* the degradation of a nerve agent simulant in non-buffered conditions,[2] *ii)* the aminolysis of epoxides,[3] and *iii)* for the formation of carbon-carbon bonds via the 1,4-radical conjugate addition.[4] The importance of precise metal distribution at the atomic level is underscored, extending the applicability of heterometallic MOFs to a broad range of cascade and tandem reactions. These advances highlight the transformative potential of heterometallic MOFs in catalysis, offering innovative solutions and efficiency improvements across diverse chemical processes.

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MICROWAVE AND FLOW PROCESSING FOR SUSTAINABLE SYNTHESIS OF METAL-ORGANIC FRAMEWORKS AND COMPOSITES

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Keywords: *microwave, flow chemistry, metal-organic frameworks, magnetic composites.*

The tunable characteristics of metal-organic frameworks (MOFs) offer substantial potential for both economic and environmental benefits, with applications spanning molecular separations, catalysis, environmental remediation, sensing, and healthcare.[1] Despite this promise, challenges in manufacturing, such as poor reproducibility and high energy and capital demands, have limited their broader industrial adoption. Advancing technologies that enable more reproducible, cost-effective and sustainable production is essential for transitioning MOFs from academic research to commercial application.[2]

Microwave and flow technologies are considered sustainable due to their high efficiency and rapid heating resulting in reduced energy consumption and processing times compared to conventional methods. This presentation outlines our work on synthesizing MOFs and novel magnetic framework composites (MFCs) using scalable continuous flow methods.[3,4] Our custom-built flow reactors are capable of producing these materials within seconds to minutes, achieving exceptionally high space-time yields (STY) of 2.07 × 10^3 kg/m^3/day for MOFs and 6.32 × 10^5 kg/m^3/day for MFCs. These values represent the highest reported STY and fastest synthesis routes reported for these materials to date.[3,4] Notably, we have demonstrated precise control over key properties such as surface area, morphology, particle size and phase, and magnetic behavior.[3,4] This is made possible by optimizing energy input[5] and mixing conditions during the reaction—critical parameters for scaling up the production of these materials for real-world use.

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COMPUTATIONAL MODELLING STRATEGIES FOR GAS SEPARATION IN COF ADSORBENTS AND MEMBRANES

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Keywords: *Covalent organic frameworks, adsorbent, membrane, simulation, gas separation.*

Covalent organic frameworks (COFs) are promising adsorbents and membranes for industrial gas separations, but accurately predicting their performance requires careful selection of computational methods.

This talk compares two key approaches for evaluating gas transport in COF membranes: the non-equilibrium method, Concentration Gradient-Driven Molecular Dynamics (CGD-MD), and the conventional grand canonical Monte Carlo and equilibrium MD (GCMC+EMD) hybrid approach. For COFs with pore-limiting diameters (PLDs) < 10 Å, we find the choice of method significantly impacts predicted selectivity.[1] GCMC+EMD hybrid approach suggests methane selectivity, while CGD-MD reveals preferential hydrogen permeation. We aim to quantify the competitive relationship between adsorption and diffusion timescales via Density Functional Theory (DFT) calculations, showing how this balance governs the method-dependent selectivity predictions in membrane separations.

The second part of this talk focuses on high-throughput computational screening of COF adsorbents for acetylene/carbon dioxide/methane separation, where atomic charge assignment methods significantly impact accuracy. While quantum chemistry-derived charges are reliable, their computational cost limits scalability. We demonstrate that machine learning (ML) methods can rapidly predict atomic charges (within seconds) while preserving accuracy.[2] A systematic analysis of Coulombic and van der Waals interactions further reveals that PLD alone cannot fully capture gas selectivity trends in adsorbents.

The methodologies discussed in this talk will be useful for the design of novel adsorbents and membranes for industrial gas separation applications.

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DYNAMIC COVALENT ORGANIC FRAMEWORKS FOR SOLAR ENERGY HARVESTING AND PHOTOCATALYSIS

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Keywords: *Covalent Organic Frameworks (COFs); Dynamic response; Solar Energy; Photocatalysis; water splitting*

Sunlight-driven photocatalysis is regarded as one of the most promising strategies for renewable energy conversion. Recent studies have demonstrated that dynamic structural twisting of photocatalysts in their excited states can suppress charge recombination and enhance photocatalytic efficiency. Covalent Organic Frameworks (COFs), crystalline porous materials constructed via strong covalent bonds between organic building blocks, offer tunable light-harvesting and charge-transport properties, making them attractive candidates for heterogeneous photocatalysis under visible light. In this talk, we present the atomic-level observations of rotational and translational dynamics in single-crystal COFs upon adaptive guest inclusion of various organic molecules. These dynamics involve multiple rotamers of covalent linkages and switchable interframework noncovalent interactions. Such dynamic COFs exhibit concerted structural transformations in response to guest molecules, a property that has been widely studied for applications in gas storage, selective adsorption, heterogeneous catalysis, and molecular sensing. Recently, we have designed a dynamic COF with modulated structural flexibility in aqueous environments, which demonstrated enhanced performance in solar energy harvesting and photocatalytic activity.

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MECHANICAL PROPERTIES OF MOF CRYSTALS AND MONOLITHS

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Keywords: *Anisotropy, Elasticity, Plasticity, Fracture, Nanoindentation, Nanospectroscopy*

Given the vast structural, chemical and physical variability of MOFs, the resultant framework materials exhibit an astonishingly varied mechanical properties straddling the classical borders defined by conventional solids (Figure 1), namely the metals, ceramics, and polymers. 'MOF mechanics'[1] is the new science underscoring the discovery and understanding of the rich structure-mechanical property relationships evidenced in MOF crystals, glasses, monoliths and composites. This talk will highlight the opportunities and challenges in determination of mechanical behavior and modeling of mechanical response, by employing a combination of experimental and computational techniques. The basic questions of elasticity, yielding, plasticity, adhesion and fracture toughness (resistance to cracking) will be addressed by means of several exemplars below. (i) Micropillar compression and breakage of highly anisotropic single crystals;[2] (ii) Structural defects and collapse of open frameworks interrogated by nearfield nanospectroscopy[3]; (iii) Elasticity, plasticity, and heterogeneity of nanocrystalline MOF monoliths[4] versus amorphous glasses; and (iv) AFM nanoindentation of 2-D layered MOF bound by *van der Waals* interactions.[5] Collectively, the results enable us to better elucidate the physical phenomena and mechanical trends that control the functions of framework solids.

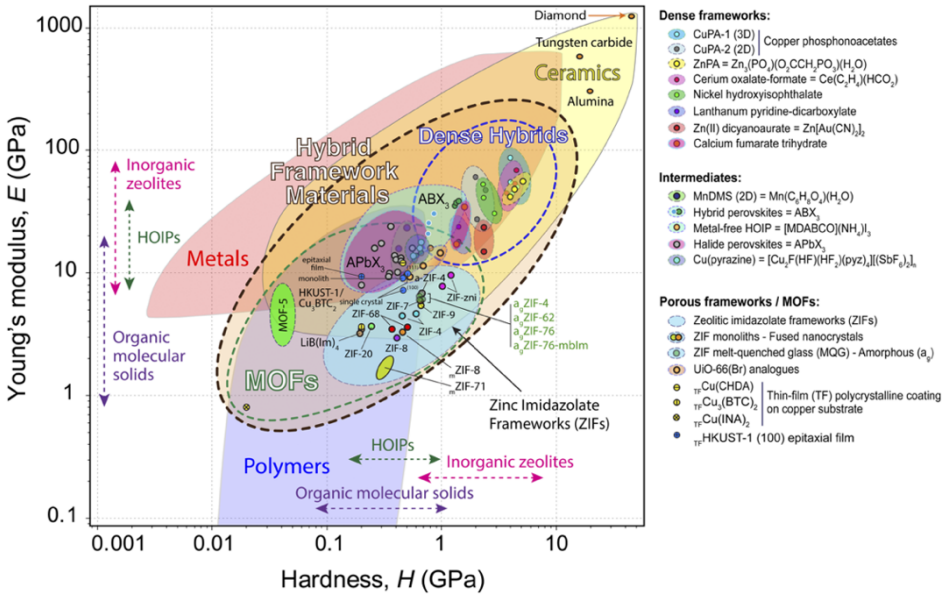


Figure 1: Ashby-style materials selection chart of the mechanical stiffness (given by Young's modulus) versus the hardness values of the representative MOF structures, plotted alongside the conventional classes of engineering materials. Adapted from ref [1].

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USING FRAMEWORK TOPOLOGY AND PORE NETWORK TO BETTER UNDERSTAND FRAMEWORK MATERIALS

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Topology is key to the determination of many physical and chemical properties of materials, such as electrical and optical properties, magnetic properties, thermal and mechanical behaviour, etc. This is particularly true for framework materials, and we have recently developed the open source CrystalNets.jl software library (and an associated web application) in order to provide researchers in the field with tools to easily and systematically characterize the topology of materials.[1]

More recently, we have started applying this methodology at large scale, to databases of materials. In a first example, we have performed high-throughput analysis of topology of materials on a large scale databases of existing and hypothetical materials, the Materials Project[2] data set of more than 170,000 structures (see workflow presented in Figure 1). Beyond the statistical analysis of the most frequent topologies and coordination environments, the publication of this topological data will allow researchers to search for materials by topology and chemical environment, paving the way to enhanced performance in materials screening for applications.[3]

In a second example, we have applied this systematic determination of topology to the upcoming version of the CoRE MOF database of curated experimental structures for computational purposes. The incorporation of topological information, among many other rich geometrical, physical and chemical features in the database, makes it easier for the community to build material screening and machine learning workflows.[4]

Finally, for nanoporous materials such as porous MOFs, it is also important to characterize the topology of the porous space. We will demonstrate our on-going efforts in this direction of research.

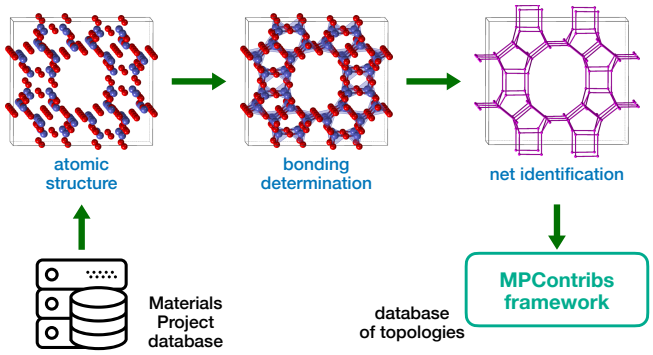


Figure 1: Large-scale characterization of chemical bonding and topology in the Materials Project database, by systematic analysis of 170,000 inorganic structures.

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COVALENT ORGANIC FRAMEWORKS – UNDERSTANDING THE PHOTOCYCLE FOR ADVANCED PHOTOCATALYSIS

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Keywords: *photocatalysis, photocycle, Covalent Organic Framework, COF*

Covalent Organic Frameworks (COFs) are essentially crystalline, porous, and photo-active polymers which are widely recognized for their high stability, metal-free nature, visible-light compatible bandgaps, and tunability towards a targeted photocatalytic reaction. Their synthesis is guided by dynamic covalent chemistry, which employs reversible bonding mechanisms to enhance the crystallinity and order within their structures. Typically, two-dimensional photocatalycally active COFs (2D-COFs) are synthesized through the strategic assembly of 2 or more aromatic precursors, typically a donor and an acceptor unit (see Figure 1). The properties of these diverse building blocks can be meticulously tailored, based on electronic properties, planarity, conjugation and additional functional groups. Once the COF is hit by light, several processes occur on ultrafast timescales that are all important to the final photocatalytic activity and selectivity, such as the creation of an exciton, the splitting of the exciton in separate charges, the movement of the charges to the surface and the interaction of the charges (electron and holes) with the substrates. A thorough understanding of this photocycle (Figure 1, right) is important to further improve the photocatalytic properties of the COFs.

In this presentation I will discuss a few very recent case-studies on the photocatalytic applications of COFs: (i) on metal-free H_2O_2 production[1] and (ii) on nitrobenzene reduction[2] and (iii) on [4+2] cycloadditions [3].

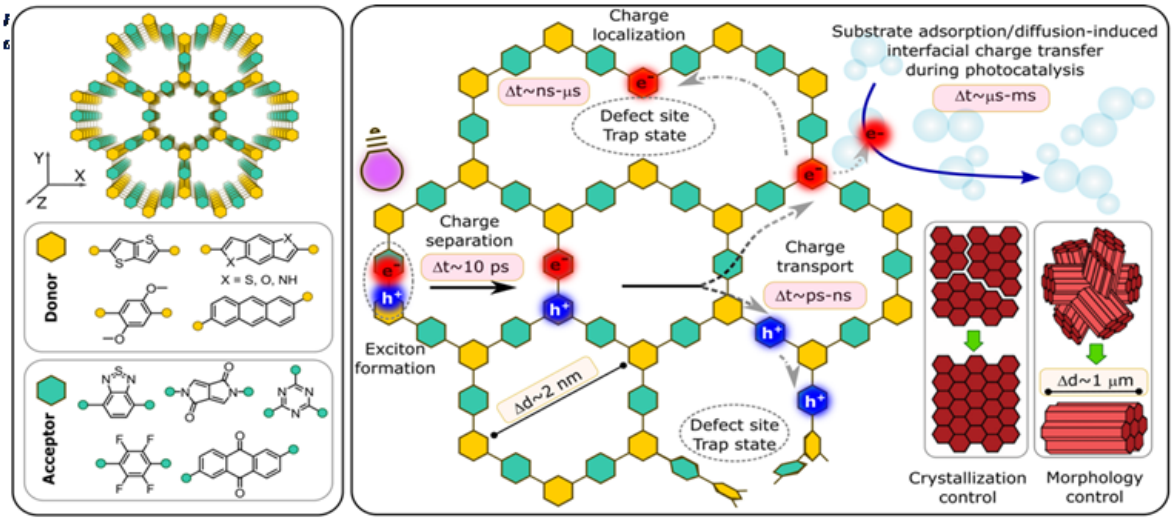


Figure 1: (left) a 2D Covalent Organic Framework and some typical donor and acceptor units, (right) some phenomena occurring on ultrafast time scale in the so-called photocycle.

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SMART MEMBRANES FOR SIMULTANEOUS DETECTION, FILTRATION, AND DETOXIFICATION OF HAZARDOUS GASES

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Keywords: *conductive MOFs, layered materials, air purification, smart membranes, e-textiles*

Ensuring ubiquitous access to clean air is paramount for protecting human health and promoting climate equity. Aside from drinking water protection and security, inadequate access to clean air poses one of the greatest threats to human health in the coming century. Air pollution represents the fourth greatest risk factor for human health worldwide, only trailing factors based on genetics or lifestyle choices, such as high blood pressure, diet, and smoking. Among the list of air pollutants outlined by the Environmental Protection Agency, toxic gases such as SO_2, H_2S, NO_x, NH_3, and CO stand out as particularly hazardous with permissible exposure limits at part-per-million concentrations that can lead to acute toxicity effects, as well as chronic issues stemming from prolonged low dose exposure. While some of these gases originate from anthropogenic sources, such as the burning of fossil fuels and industrial processes, some of them can also be generated from natural sources, like wildfires and volcanic eruptions, making the detection and protection from toxic gas emissions a complex task.

Smart membranes—materials with tailored properties capable of responding to external stimuli—hold tremendous promise in environmental remediation and the design of personal protective equipment through combined capabilities in separating and detecting specific gases. This presentation will highlight the potential utility of conductive layered 2D metal–organic frameworks (MOFs) on textiles to serve as multifunctional materials to achieve simultaneous chemical detection and filtration of toxic gases.[1-3] An emphasis will be placed on the fundamental understanding and molecular design of modular structure–property relationships within this class of MOFs. The use of these materials paves the way towards scalable smart membrane design that merges ultrasensitive, selective, and low-power sensor technology with scalable methods for high-performance fabrication strategies.

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MOLECULAR RECOGNITION-INDUCED STRUCTURAL FLEXIBILITY IN ZIFS

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Keywords: *ZIFs, gas adsorption, structural changes, fluorinated materials*

The removal of emerging and persistent contaminants (e.g., PFOAs, solvents, etc.) in industrial effluents require the design of porous materials combining a highly developed porous structure, and a dedicated surface chemistry to promote specific interaction with the target molecules. Among them, metal-organic frameworks (MOFs) represent promising candidates due to their tailorable structure, engineered porosity and designed surface chemistry. Zeolitic-imidazolate frameworks (ZIFs) are a subclass of MOFs characterized by fascinating reversible structural transformations upon an external stimulus (heat, adsorption, pressure, etc.).[1] The high degree of framework flexibility identified to date, allows to design crystalline networks with molecular-induced selectivity, depending on the nature of the organic ligands, the functional groups associated, the pore structure, among others. Overall, it depends on the competition between strong non-bonding interactions, that promote the formation of highly dense structures, and bonding interactions, that favour the formation of high symmetry, low-density crystal structures.[2,3] Furthermore, these intracrystalline interactions can be altered/modified, depending on the nature of the adsorbate molecules, thus opening the gate to unexplored adsorption phenomena in gas and liquid-phase processes. In this communication we will summarize some examples of structural changes in ZIFs (**Figure 1**), their sensitivity to the nature of the probe, and how the knowledge of the associated mechanism can be used to design porous materials with an enhanced performance in a wide variety of applications from gas storage/separation to mechanical energy storage, and liquid-phase selective separation processes.[4,5] Special attention will be given to liquid-phase adsorption processes to emphasize the crucial role of the solvent, and how the associated solvent-adsorbate and solvent-framework interactions will determine the appearance of structural changes in ZIFs. (e.g., breathing phenomena).[6]

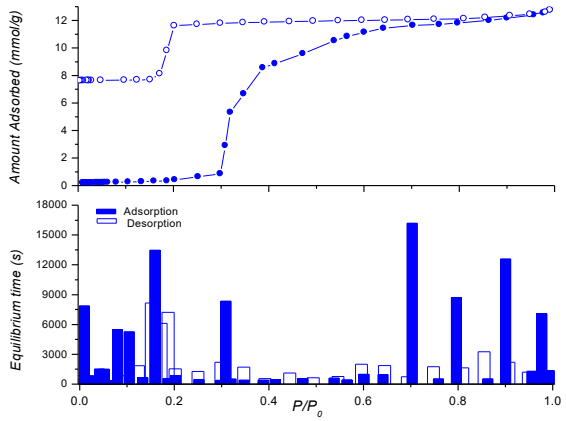


Fig. 1. N_2 adsorption/desorption isotherm for ZIF-7 at 77K (upper panel). Time required to reach equilibrium for each of the adsorption and desorption points (lower panel).

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STRUCTURE MEETS FUNCTION: POROUS NETWORKS ENGINEERED FOR ENVIRONMENTAL IMPACT

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Keywords: advanced characterization, synchrotron techniques, environmental applications

Metal- and Covalent-Organic Frameworks (MOFs and COFs), constructed from molecular components that assemble into highly porous architectures, have traditionally been perceived as static entities. This perception, rooted in conventional views on crystallinity, has long shaped our understanding and design of these materials. However, a growing body of evidence reveals that this view is incomplete—these frameworks are, in fact, dynamic, and their performance is tightly coupled to this structural responsiveness.

With applications spanning catalysis, sensing, health, separations, and beyond, MOFs and COFs operate under complex, often non-ideal environments (Figure 1). Under such conditions, their real atomic structure can deviate significantly from the idealized models, revealing distortions, disorder, and dynamic rearrangements that are critical to function. Key questions emerge: What is the true structure of these materials during operation? How do local atomic changes influence their catalytic or adsorptive behaviour?

In this talk, we will present how cutting-edge X-ray scattering techniques—particularly Pair Distribution Function (PDF) analysis—are transforming our understanding of these materials. Unlike traditional diffraction methods, PDF analysis allows us to probe short- and medium-range order in both crystalline and disordered systems,[1] offering a powerful window into the structural dynamics of MOFs, COFs, and their hybrids under working conditions. By capturing these hidden distortions, we can unravel how structural flexibility impacts performance in applications such as energy conversion, pollutant capture, and environmental remediation.[2-3]

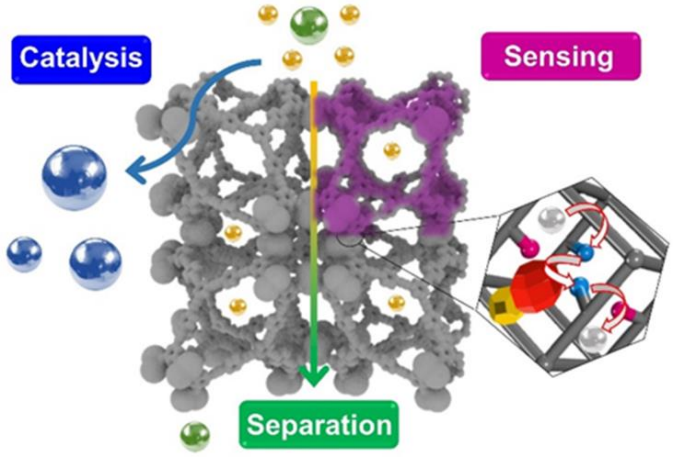


Figure 1. Porous reticular nanomaterials with diverse applications, including catalysis, sensing, and separation, highlighting their versatility in addressing critical challenges in energy, environmental, and health-related fields.

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MOF AND HOF NANOSHEET CRYSTALS ASSEMBLED AT THE AIR/WATER INTERFACE: UNIQUE STRUCTURES AND GAS SORPTION/ELECTRONIC PROPERTIES

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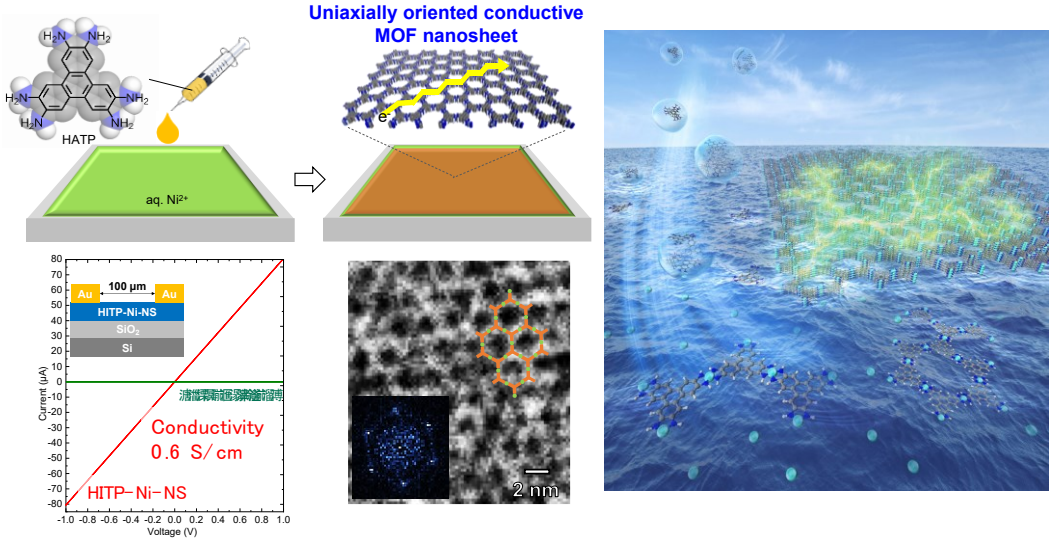
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Keywords: *Nanosheets, 2D materials, Air/water interface, Electrically conductive, Oriented films*

Development of rational methods for creating ordered two-dimensional (2D) structures with nanometer scale precision is one of the central issues in the nanoscience and nanotechnology fields because of their intrinsic physical-chemical properties which are seen in those of their equivalent bulk state. Inclusion of highly regulated nanopores into the nanosheet structure will further open the possible applications such as nanosieves, molecular/ion storage and sensor devices as well as introducing guest molecules into the nanopores tune variedly the sheet properties (electric conduction, nanoheterojunction). Utilizing molecular building units are suitable for creating such porous nanosheets because of rich variety of design and facile modification of size and shape.

Here, I introduce a facile bottom-up synthesis of molecular nanosheets with both positional and size regulated nanopores utilizing air/liquid interfaces [1-5]. By applying liquid interfaces, growth direction of the object can be well controlled with utilizing self-assembly feature of the molecules under mild conditions. We have succeeded to tune finely the nanosheet structures by rational modification of molecular building units. The highly crystalline structure remains after transferring a solid substrate from the liquid surface as well as without any supports. Notably, such highly oriented porous crystalline structure is obtained specifically by applying bottom up synthesis at air/liquid interfaces, not by other techniques.

I also present detailed insights into the formation process of electrically conductive MOF nanosheets composed of 2,3,6,7,10,11-hexaiminotriphenylene (HITP) and Ni (II) ions (HITP-Ni-NS) at the air/liquid interface [6-8]. The morphological and structural features of HITP-Ni-NS strongly depend on the standing time—the time without any external actions involved, but leaving the interface undisturbed after setting the ligand solution onto the metal-ion solution. We find that the fundamental features of HITP-Ni-NS are determined by the standing time with conductivity sensitively influenced by such pre-determined HITP-Ni-NS characteristics. These findings will lead towards the establishment of a rational strategy for creating MOF nanosheets at the air/liquid interface with desired properties, thereby accelerating their use in diverse potential applications.



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INVESTIGATIONS INTO INTERMEDIATE SPECIES IN ZEOLITIC IMIDAZOLATE FRAMEWORK FORMATION

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Keywords: *Zeolitic imidazolate framework, synthesis, crystallization, metastable, dynamics.*

Metal–organic frameworks (MOFs) have promising properties for several applications, including water harvesting, carbon capture, chemical sensing and environmental remediation. However, fundamental material characteristics, such as phase, purity, particle size and yield are extremely challenging to control or predict a priori without a better understanding of how MOFs form. In particular, the intermediate species present before and during MOF crystallisation, which are transient by nature but critical to nucleation and crystal growth,[1] are extremely elusive.

We have developed a simple approach to controlling the formation of a model subset of MOFs, the zeolitic imidazolate frameworks (ZIFs), which has allowed us for the first time to isolate and characterise a series of intermediate phases using X-ray crystallography, NMR spectroscopy and DFT simulations. We show that the major species immediately preceding crystallisation are structurally most similar to the secondary building units (SBUs) found in the crystalline phase (Fig. 1), but nucleation of the MOF requires intermediates to be involved in dynamic equilibria. With this knowledge, we are able to rationalise the phase selection of competing framework isomers based on calculated reaction energies from DFT and qualitative observations from pH monitoring data.[2]

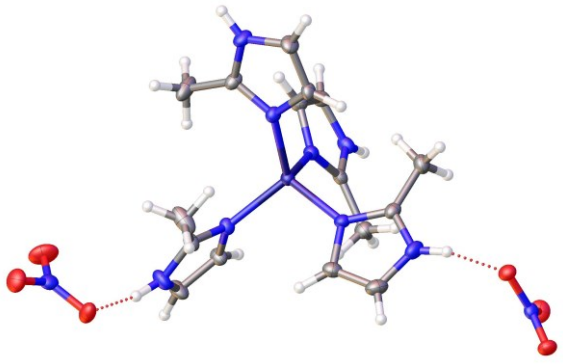


Figure 1. Crystal structure of a ZIF SBU-like intermediate formed from the reaction of metal nitrate and 2-methylimidazole.

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ROOM TEMPERATURE REDUCTION OF NITROGEN OXIDE ON IRON METAL-ORGANIC FRAMEWORKS

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Keywords: *Fe-MOFs, NOx removal, heterogeneous catalysis*

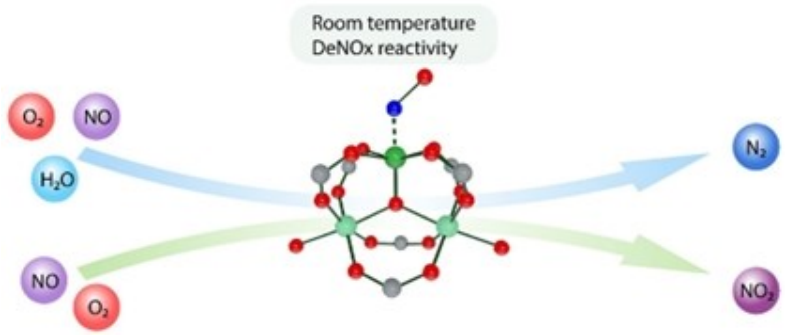
Air pollution remains a critical global concern, closely linked to combustion processes that release nitrogen oxides (NOx), major contributors to environmental degradation and serious threats to human health. Although NOx decomposition is thermodynamically favorable at ambient temperature and pressure, the reaction is kinetically hindered due to its high activation energy.

To date, no heterogeneous catalyst has demonstrated the ability to lower this activation barrier without the aid of co-reactants or elevated temperatures. In contrast, nature efficiently addresses denitrification through a suite of iron- and copper-based metalloenzymes, including nitrate reductase, nitrite reductase (NIR), nitric oxide reductase (NOR), and nitrous oxide reductase, that sequentially reduce nitrate to dinitrogen via nitrogen oxide intermediates.

Inspired by these enzymatic systems, we have developed a catalyst capable of decomposing NO at room temperature, in the presence of oxygen and water, and without the need for reducing agents. This achievement was made possible through a combination of density functional theory (DFT) calculations, rational material design, advanced synthesis, and cutting-edge characterization techniques.

The resulting nanostructured catalyst is based on MIL-100(Fe), an iron trimesate metal-organic framework (MOF) that is biocompatible, scalable via green synthesis, and well-suited for practical application. Its reaction mechanism has been elucidated using *operando* infrared spectroscopy.

This work represents a significant advancement in understanding the deNOx process, bridging the gap between heterogeneous and enzymatic catalysis, and offering a cost-effective, sustainable solution for air purification in confined polluted environments.



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ELECTRIC-FIELD MANIPULATION OF MOF AND COF COLLOIDS FOR ENHANCED PERFORMANCES AND DYNAMIC STRUCTURAL COLOR

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Keywords: *Electric field control, crystal orientation, dynamicity*

Biological composites bear complex designs and hierarchical structures that are key to their specific function and exceptional properties. However, the structural and functional complexities of natural materials are difficult to integrate into synthetic composites, as the control of materials across multiple length scales is a major scientific challenge. We work on the preparation, assembly, and multi-length scale structuring of Metal-Organic Frameworks (MOFs) and other colloidal materials and composite systems for optical and ion conduction applications, using an interdisciplinary approach. Most MOFs possess non-cubic lattices and anisotropic functionality dependent upon crystallographic direction and are generally synthesized in bulk as loose as microcrystalline powders. As such, for practical purposes, general methods to manipulate and orient free-standing MOF crystals would be useful to harness their anisotropic functionality. This talk will focus on our exploitation of physicochemical interactions at air/liquid/solid interfaces, as well as top-down processing methods and external fields to manipulate MOF materials, ranging from tuning MOF crystal size and shapes to the dynamic alignment of NU-1000 MOF microrods as well as E-field assisted liquid crystalline assembly of MOF particle superstructures. Examples of the impact of MOF orientation and positioning on their performances for sensing and actuation will be given. We also extend our examples to include COF materials, and demonstrate the use of E-fields to achieve dynamic structural color based on MOF and COF colloidal materials.

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HARNESSING MOLECULAR MODELING, MACHINE LEARNING, AND EXPERIMENTS FOR THE DESIGN AND DISCOVERY OF NOVEL MOFs

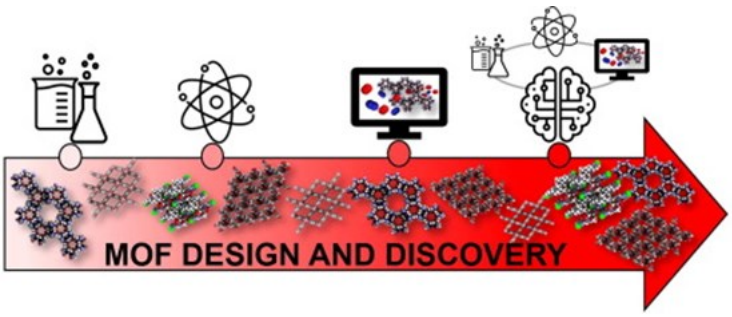
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Keywords: *metal-organic frameworks, molecular simulations, machine learning, gas separation*

Metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) hold immense potential for a wide range of applications, particularly in gas adsorption and separation. The number of synthesized MOFs and COFs has been rapidly increasing in addition to the emergence of thousands of hypothetical materials. Evaluating millions of materials through random selection, iterative experimental testing, or brute-force computational simulations is simply impractical. In this talk, I will discuss how the integration of atomistic calculations, molecular simulations, machine learning, and data science prior to experimental work can significantly accelerate the discovery and design of materials tailored for specific applications. I will present case studies where our strategy, combining molecular modeling with data-driven aproaches, successfully guided experimental efforts toward synthesizing novel MOFs and MOF-based composites with record-setting carbon capture performance. I will also share recent results demonstrating how we use molecular simulations and machine learning to comprehensively screen MOF and COF databases to identify the most promising candidates for gas separations such as CO_2/CH_4 (natural gas purification), CO_2/N_2 (flue gas separation), and CO_2/H_2 (hydrogen recovery). Finally, I will highlight how machine learning enables the development of structure–performance relationships, guiding the rational design of new materials with exceptional CO_2 separation capabilities. These insights are expected to inspire and accelerate experimental advances in the development of next-generation MOF adsorbents, membranes, and composites for a variety of gas separation applications.



MODULATION OF THE TEMPERATURE AND GAS SENSING PROPERTIES OF NEW METAL–ORGANIC FRAMEWORKS BASED ON HEXANUCLEAR RARE EARTH SECONDARY BUILDING UNITS THROUGH SINGLE-CRYSTAL-TO-SINGLE-CRYSTAL TRANSFORMATION REACTIONS

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Keywords: *Metal Organic Frameworks, Crystal structures, Gas Sensing, Temperature Sensing, Single-Crystal-to-Single-Crystal Transformations*

Metal-Organic Frameworks (MOFs) have attracted a tremendous research interest because of their significant potential for practical applications in areas such as gas storage and separation, drug delivery, sensing, catalysis, etc.[1] MOFs with fine-tuned properties can be prepared through a process called post synthesis modification (PSM). PSM allows the introduction/exchange of functional groups of a MOF and is preferable to proceed in a single-crystal-to-single-crystal (SCSC) fashion because with this way direct structural information can be provided for the achieved structural modifications via single crystal x-ray crystallography.[2]

We shall discuss two families of trivalent rare earth (RE^{3+}) MOFs based on a hexanuclear $(RE^{3+})_6$ SBU and their exchanged analogues. The first one involves 8-connected 2-D MOFs based on an angular dicarboxylic ligand 4,4'-(hydroxymethylene)dibenzoic acid (H_2BCPM), **UCY-17**(RE). A series of exchanged analogues **UCY-17**(Tb)/L produced from linker installation SCSC reactions of **UCY-17**(Tb) with selected dicarboxylic ligands shall also be discussed which resulted to the turn-on of the thermometric properties of these materials.[3] The second family of compounds with the general formula $\{((CH_3)_2NH_2)_2[Y_6(\mu_3\text{-}OH)_8(bpydc)_6]\}_n$ is based on the linear dicarboxylic ligand H_2bpydc= [2,2'-bipyridine]-5,5'-dicarboxylic acid. Its subsequent metalation with transition metal ions was achieved giving rise to a series of exchanged analogues with various metal ions. Gas sensing studies of the pristine and metalated compounds revealed a variety of different gas sensing capabilities. Thus, SCSC transformation reactions allowed not only the targeted modification of the structures of the two MOFs but also the modulation of their temperature and gas sensing properties.

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ELECTROACTIVE FRAMEWORK MATERIALS FOR ENERGY STORAGE: REDOX-ACTIVE COF-BASED ELECTRODES AND PROTON-ELECTRON DUAL-CONDUCTIVE MOF

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Keywords: *Redox-active COF electrodes, dual-conductive MOFs, energy storage, organic batteries.*

Energy storage devices that are based on earth-abundant elements, environmentally friendly, and possess high energy density are essential for storing electricity generated from renewable sources. Conventional cathodes based on transition metal oxides need to be replaced to reduce reliance on critical raw materials such as cobalt. Redox-active metal-organic (MOFs) and covalent organic frameworks (COFs) have emerged in recent years as auspicious electrode materials for energy storage applications due to their high stability, porosity to facilitate ion diffusion, and huge chemical and structural versatility.[1,2] Besides their inherent porosity, MOFs and COFs may also incorporate electronic functionalities such as electrical conductivity, becoming attractive for their implementation as components in different devices.[3] In this direction, the development of mixed ionic-electronic conductors is of great interest for energy storage applications. In the first part of the talk, I will present one of the first examples of a proton-electron dual-conductive MOF based on tetrathiafulvalene (TTF)-phosphonate linkers (Figure 1).[4] In the second part of the talk, I will present some examples of electrode materials based on redox-active COFs used as high-capacity organic cathodes in Li and Mg batteries.[5,6] Finally, the synthesis and electrochemical properties of a series of redox-active TTF-based COFs that were explored as high-voltage organic cathodes for lithium batteries will be presented.[7]

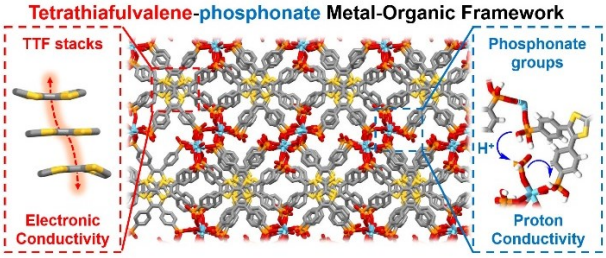


Figure 1: Schematic representation of the dual conductive MOF based on TTF-phosphonate linkers.

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6th European Conference on Metal Organic Frameworks and Porous Polymers

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Oral Presentations

STABILISE COMPRESSIBLE LIQUIDS BY HYDROPHILIC MESOPORES

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Keywords: *compressible liquids, porous liquids, water intrusion, water stability, colloidal stability, hierarchical structures, mesopores.*

A critical bottleneck for the use of metal-organic frameworks (MOFs) in practical applications has been the long-term stability, especially in moisture atmosphere or aqueous environment. For example, porous liquids, which have been emerging as promising candidates for separation and energy applications, require the formulation of stable colloids with permanent porosity. Compressible liquids, a category of porous liquids, can be produced by dispersing MOF particles with hydrophobic pores in water.[1] Due to water intrusion into the large porosity of MOFs under pressure, such liquid suspensions exhibit significantly greater compressibility than traditional liquids, *e.g.*, 20 times higher than water, making them suitable for energy storage and absorption applications.[2] However, MOFs in water are prone to hydrolysis or separation from the liquid phase, even for ZIFs that are known for their excellent hydrothermal stability compared to other MOFs.

In this presentation, we will introduce a new strategy to simultaneously improve the physical and chemical stabilities of hydrophobic MOFs in liquid water, ultimately yielding highly stable compressible liquids. This is achieved by introducing a hydrophilic mesoporosity that is hydrated at ambient conditions, in addition to the existing hydrophobic micropores that are kept empty unless sufficient pressure is applied. Creating new mesopores with favourable solvent interaction allows water to effectively 'dissolve' the crystal, resembling the solubility of large macromolecules based on exothermic interactions, so the physical stability can be improved. The chemical stability will be improved by the altered surface on the additional mesopores.

We will demonstrate two approaches on the prototypical ZIF-8, where the mesopores are introduced to the crystal interior and exterior, respectively. The first approach (Figure 1a) produces nanoparticles of mesoporous ZIF-8 via a template-directed synthesis,[3] where the highly favourable hydrogen bonds between the new mesopore surface and the solvating water molecules contribute to colloidal stability and resistance to hydrolysis. The second approach (Figure 1b) protects ZIF-8 crystals with a mesoporous silica shell,[4] which keeps the ZIF-8 micropores accessible for water intrusion, maintaining the high compressibility, and meanwhile enables long-term stability in water for at least 180 days at room temperature.

The proposed approaches are scalable and can in principle be applied to other MOFs. Compressible liquids stabilised in these ways can be used for a longer time, at harsher conditions, and undergo a larger number of compression cycles with the reversibility of water intrusion in the micropores. This work can also inspire future endeavours to developing porous liquids for practical uses and enabling various applications of MOFs in aqueous environment.

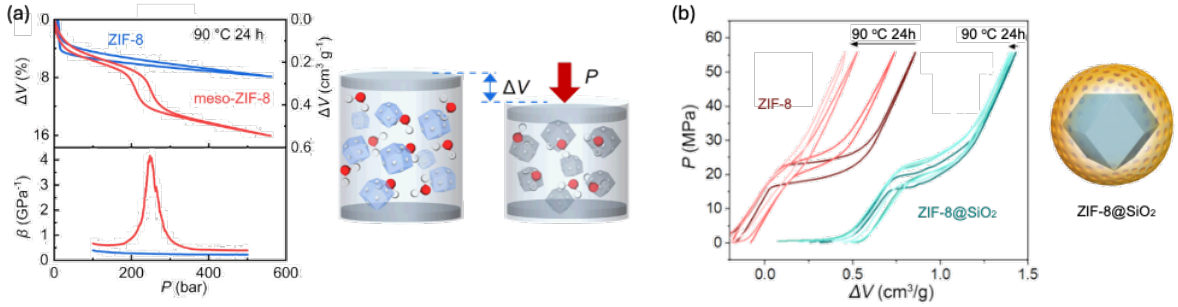


Figure 1. ZIF-8 compressible liquids after 24 hours in hot water at 90 °C, with improved stability by using (a) ZIF-8 with hydrophilic mesopores,[3] and (2) ZIF-8 coated with a mesoporous SiO_2 shell.[4] The pristine ZIF-8 has lost almost all its pore volume and compressibility in water under the same condition.

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CONTROLLING THE FUNCTIONALITY OF HYBRID GLASSES

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Keywords: *glasses, metal−organic frameworks, hybrid organic-inorganic perovskites.*

Hybrid materials are formed from inorganic metal ions or clusters connected by organic bridging linkers – examples of which include metal–organic frameworks (MOFs) and hybrid organic-inorganic perovskites (HOIPs).[1]

While research has traditionally focused on their crystalline forms, glasses formed from hybrid materials have gained significant interest in recent years, where research into their fundamental and applied properties has shown exciting structural and adsorptive behaviours.[2,3] Notably, the chemical tuneability so prominent in their crystalline precursors is retained in the glasses, allowing targeted materials design.

This presentation will focus on recent developments in the physical and adsorptive properties of hybrid glasses, including strategies towards the retention of porosity in glass-forming MOFs, and the notable adsorptive and uptake behaviour of glasses formed from HOIPs.

MOF glasses are typically formed via melt-quenching, though this usually leads to a reduction in porosity.[3] Here, we investigate the use of mixed-linker strategies as a route to modulate framework structure, porosity, and glass-forming ability. By systematically varying linker size and shape, we examine the impact on crystallinity, thermal behaviour, and pore retention in both the crystalline and glass states. The findings demonstrate the potential of mixed-linker approaches to tune the properties of MOF-derived glasses.[4]

Due to their non-porous nature in the crystalline state, the adsorptive properties and uptake behaviours of HOIP-based materials have not been extensively studied. Here, we show that the glass forms of these materials intriguingly show enhanced CO_2 and water uptake when compared to their crystalline precursors - a behaviour which contrasts with MOF glasses, where densification upon glass formation usually reduces uptake. This exciting behaviour in a class of materials previously not considered for their adsorptive properties, combined with the exceptional stability of the glasses and their tuneable optical band gaps, position glasses formed from HOIPs as promising candidates for applications which require long-term resistance to external stimuli, such as moisture.[5]

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THE INTIMATE RELATIONSHIP BETWEEN MECHANOCHEMISTRY AND MOF GLASSES

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Keywords: *MOF glasses, mechanochemistry, glass-ceramics, proton conduction, melt-processing*

Metal–organic framework (MOF) glasses, particularly those derived from zeolitic imidazolate frameworks (ZIFs),[1,2] are an emerging class of amorphous hybrid materials that preserve the versatile chemistry of crystalline MOFs while offering the mechanical flexibility of glass. However, the scope of melt-processable MOFs remains narrow, primarily due to the thermal decomposition of most imidazolate-based frameworks before reaching their melting point. Mechanochemistry has emerged as a game-changing strategy to overcome this limitation. By applying high-energy ball milling, one can introduce significant structural disorder, reduce particle and crystallite sizes, and enhance defect densities in crystalline MOFs—collectively lowering their melting temperatures and expanding the thermal gap between melting and decomposition.[3] These mechanically activated states facilitate otherwise inaccessible glass transitions, thereby offering new synthetic routes for MOF glasses.

In our recent study, we reported the first successful melt-quenching of cadmium-based MOF, $Cd(im)_2$, into a dense, optically translucent monolithic MOF glass.[4] The key enabler was mechanochemical synthesis, which destabilized the crystal lattice enough to allow liquefaction prior to decomposition. Upon reheating, this $Cd(im)_2$ glass undergoes partial recrystallization, yielding the first MOF-based glass–ceramic, which displays markedly enhanced mechanical properties such as hardness and elastic modulus (Figure 1). Extending this mechanochemical strategy further, we also synthesized a proton-conducting coordination polymer glass based on Al^{3+} and Zr^{4+} nodes, using linker systems amenable to glass formation. This water-stable glass exhibits an impressive anhydrous proton conductivity exceeding 10^{-2} S cm^{-1} at 150 °C, surpassing many crystalline MOFs and state-of-the-art polymer-based electrolytes. Thanks to its amorphous nature, the material can be thermally reshaped into defect-free monoliths or thin films, offering excellent formability for integration into solid-state electrochemical devices. The high conductivity stems from dense hydrogen-bonding networks and highly mobile proton carriers confined in the disordered framework matrix.

Altogether, these findings illustrate the dual role of mechanochemistry: not only as a synthetic gateway to new meltable MOF systems but also as a tuning tool for developing functional hybrid glasses with tailored properties. This synergy between solid-state chemistry and materials processing opens up novel directions for hybrid glass design in fields such as ionics, photonics, and energy conversion.

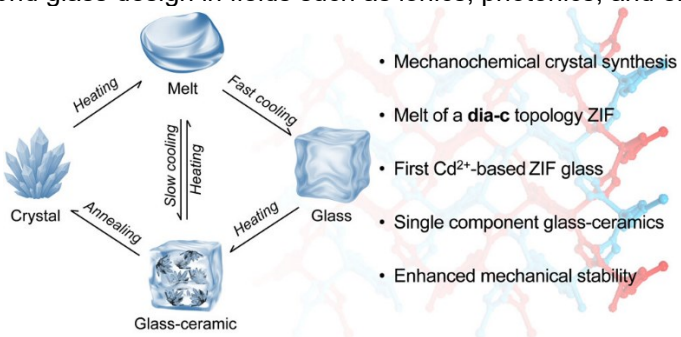


Figure 1. Schematic diagram of the phase transition of the Cd-based MOF.

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RAPID DEVELOPMENT OF A VAST FAMILY OF IONIC MOF STRUCTURES FACILITATED BY STRUCTURE-DIRECTING AGENTS AND 3D ELECTRON DIFFRACTION

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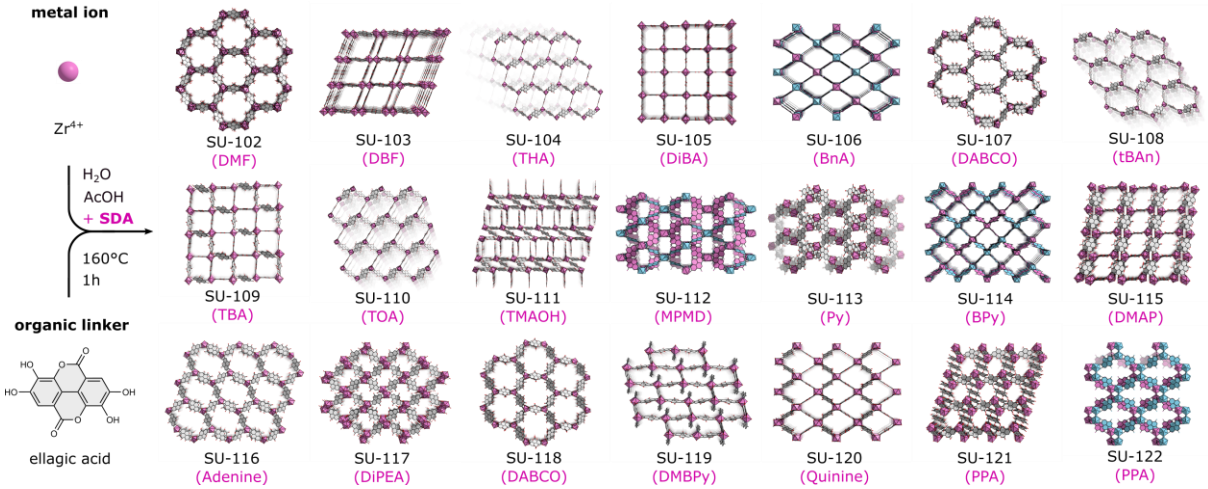
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Keywords: *structure directing agents, 3D electron diffraction, natural products, wastewater treatment*

The vast majority of MOF linkers are based on synthetic carboxylate, azolate and pyridyl functional groups. In comparison, catecholate linkers are underrepresented in MOF literature. Due to strong metal-ligand interactions facilitated by stronger electrostatic interactions and a wide ligand bite angle, catecholate-based MOFs can demonstrate high chemical stability.

Ellagic acid is one of the building units of plant-based polyphenols: tannins. It is quite inexpensive, biocompatible and common in fruits, nuts, berries and tree bark. We have explored the use of ellagic acid as a catecholate linker to develop stable and biocompatible MOFs. The first metal-ellagate MOF, SU-101, was developed under green synthesis conditions at room temperature by mixing nonhazardous Bi^{3+} sources with edible pomegranate-sourced ellagic acid in water.[1] By changing the metal ion to Zr^{4+} and reacting it with ellagic acid in a DMF/H_2O/acetic acid mixture, we developed the robust anionic MOF SU-102, which we utilized in capturing pharmaceutical pollutants in real municipal wastewater.[2] By only changing DMF for other organic molecules that behave as structure directing agents (SDAs) that reside as guests in the pores, an additional 20 zirconium-ellagate MOFs, all with unique frameworks, were synthesized.[3] Due to small crystal size, all structures were determined by 3D electron diffraction (3D ED). With a short MOF synthesis protocol (1h) and fast structure determination by 3D ED (few minutes per crystal), three of these MOFs were synthesized for the first time on the same day, and their crystal structures were determined later that day. This demonstrates how advances in structural characterization can rapidly accelerate the development of novel materials.



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CONTROLLING THE SPATIAL ARRANGEMENT OF ACTIVE SITES IN HETEROGENEOUS CATALYSIS

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Keywords: *MOF-specific catalysis, hydrosilylation, active site arrangement, hydrogenation*

Heterogeneous catalysis can offer substantial practical advantages, especially for large-scale reactions, but rational optimization of catalytic performance remains challenging. While homogeneous catalysis involves identical transition metal centers with a well-defined ligand set, traditional heterogeneous catalysts feature a plethora of distinct sites with distinct activity and selectivity. Since metal centers can interact with one another over extended distances, not only the primary coordination environment of the metal needs to be carefully controlled, but also the arrangement of metal centers throughout the catalyst. Synthetic strategies that permit selective synthesis of multiple distinct metal arrangements with precision present substantial opportunities to increase catalyst performance. We found that structural differences between materials that are removed from the active site by 8 chemical bonds or more have drastic effects on active site activity.[1]

For metalloradical catalysis with Rh(II) porphyrin centers, precise spatial organization of the Rh(II) active sites enables access to distinct mechanistic pathways.[2,3] Radical intermediates can give rise to fascinating reactivity, but their generation commonly requires substantial energy input. We are interested in enabling energy-efficient radical transfer reactions that do not require the formation of high-energy free radical intermediates. MOF-based catalysts are able to catalyze olefin hydrosilylation at room temperature via a concerted radical transfer pathway, while molecular analogues proved ineffective even at 140 °C. Access to novel 3-center-3-electron silane σ-adducts proved crucial to enable the assembly of a tri-component transition state through which silyl radicals can be transferred to olefins with an activation barrier that is 15 kcal·mol^{-1} lower than the minimum barrier required for the formation of free silyl radicals. Metal-organic frameworks provide a pore environment that can be engineered with atomic-level precision, which can be leveraged to stabilize new intermediates and transition states.[4]

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ELECTRON HOPPING THROUGH METAL-ORGANIC FRAMEWORKS: FUNDAMENTALS AND APPLICATIONS

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Keywords: *conductivity, diffusion, electrochromism, electrical rectification, transport*

Owing to their large internal surface area, their porosity and synthetic tunability, metal-organic frameworks (MOFs) have become appealing research targets for a variety of applications, including energy storage, catalysis, and as (opto)electronics components. Amongst MOFs that are electrically conducting, those that propagate charge transport by a diffusional electron hopping mechanism are a rich research field, both from a fundamental as well as applied viewpoint.[1]

In this contribution, we will briefly discuss some key experiments that can be performed to unambiguously identify such redox-conducting MOFs. We will illustrate the theory of cation-coupled electron diffusion through redox-conducting MOFs on a couple of selected examples.[2] We will show that electric conductivity through redox conducting MOFs is strongly dependent on the redox composition of the MOF, and can be tuned by up to four orders of magnitude.[3] The presentation will culminate in recent findings that redox-conducting MOFs can be leveraged for electrical rectification.[4]

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REVEALING INVISIBLES: ANALYSIS OF FRAMEWORK MATERIALS BY 3D ELECTRON DIFFRACTION

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Keywords: *metal-organic framework; covalent organic frameworks; structure-property relationship; electron crystallography; electron diffraction*

Metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) are known for their versatile physicochemical properties, which offers immense opportunities in a wide range of applications. However, MOFs and COFs are often synthesized as nanocrystals and/or multiphasic powders, which are challenging for studies by X-ray diffraction methods. Three-dimensional electron diffraction (3DED) has been developed to tackle these challenges. By taking advantage of the strong interaction between electrons and matter, 3DED allows single crystal structural analysis even when the crystal sizes are down to the range of nanometers.

In this talk, I will give an overview of the development of low-dose 3DED method for analyzing MOFs and COFs, where we overcome the challenges of electron beam damage to these compounds[1,2]. Using 3DED, I will give an example of taking the high-throughput advantage of 3DED on discovery of new MOF materials among phase mixtures[3], and discovery of unknown layer stacking behavior in a 2D COF[4]. Furthermore, I will talk about using 3DED to probe molecular motions in MOF nanocrystals[5]. Last but not least, I will present using 3DED to study host-guest interactions, including organic molecules[6] and our recent development of studying CO_2 sorption process in MOF-74. We believe that using 3DED as a powerful analytical tool for discovering new MOFs and COFs and revealing their unique properties at an atomic level would help to accelerate research in this community.

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UNDERSTANDING STRUCTURAL COMPLEXITY IN M-CAU-64, AS A FUNCTION OF TEMPERATURE AND HUMIDITY, USING LABORATORY X-RAY DIFFRACTION METHODS

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Keywords: *flexible frameworks, variable temperature, humidity, powder X-ray diffraction*

The structures of many Metal-Organic Framework (MOF) compounds change in response to the application of external stimuli, including pressure, temperature and the adsorption/desorption of guest molecules.[1,2,3] This structural flexibility makes analysis of the structures of these compounds challenging. High-resolution synchrotron powder diffraction has been widely applied to obtain structural parameters, under both ambient and non-ambient conditions.[4] Getting access to such facilities can, however, be difficult. Laboratory diffractometers, equipped with non-ambient chambers (e.g. temperature or humidity) offer a more convenient way to collect diffraction data.

We present here a complete structural characterisation of the M-CAU-64 family of compounds ($[NaM(III)(H_2O)_2(C_2H_2O_3)_2]\cdot xH_2O$; M = Al, Fe, Ga; CAU – Christian-Albrechts-Universität). This family of mixed-metal MOFs is synthesised with glycolic acid as the linker [5] and demonstrates a complex series of phase transitions in response to temperature and humidity. The framework compounds were discovered using high-throughput methods, with the phases identified using a laboratory powder diffractometer. The structures of the compounds were solved using either laboratory single crystal or powder diffractometry. M-CAU-64 is porous to water vapour (up to 360 mg g^{-1}), showing a two-step absorption process, but is non-porous to N_2. To understand the differences in sorption behaviour, variable temperature and variable humidity studies were performed using BTS-500 and CHC+ chambers, respectively, mounted on laboratory instruments. These studies revealed a rich phase transition behaviour, with five additional phases identified and analysed.

The use of laboratory powder diffraction data, and specifically non-ambient studies, was crucial to the analysis of this structurally complex family of materials. This study demonstrates the important contribution that laboratory diffraction can make to the study of flexible frameworks.

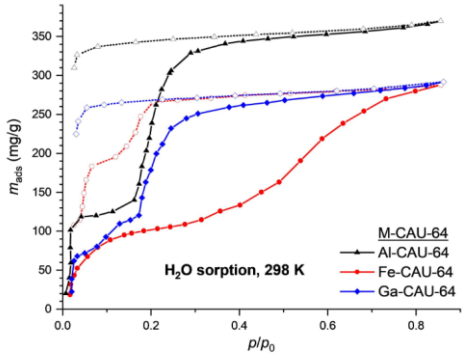


Fig. 1: Water sorption isotherms of M-CAU-64 at 298 K, showing stepped absorption behaviour.

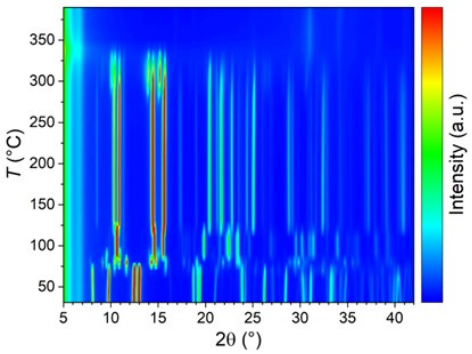


Fig. 2: Variable temperature X-ray diffraction study of Al-CAU-64 performed with a BTS-500 mounted in a Bruker D6 PHASER benchtop diffractometer.

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DISORDER STRUCTURE DETERMINATION BY 3D PAIR DISTRIBUTION FUNCTION ANALYSIS: THE CASE STUDY OF UoB-100(Dy)

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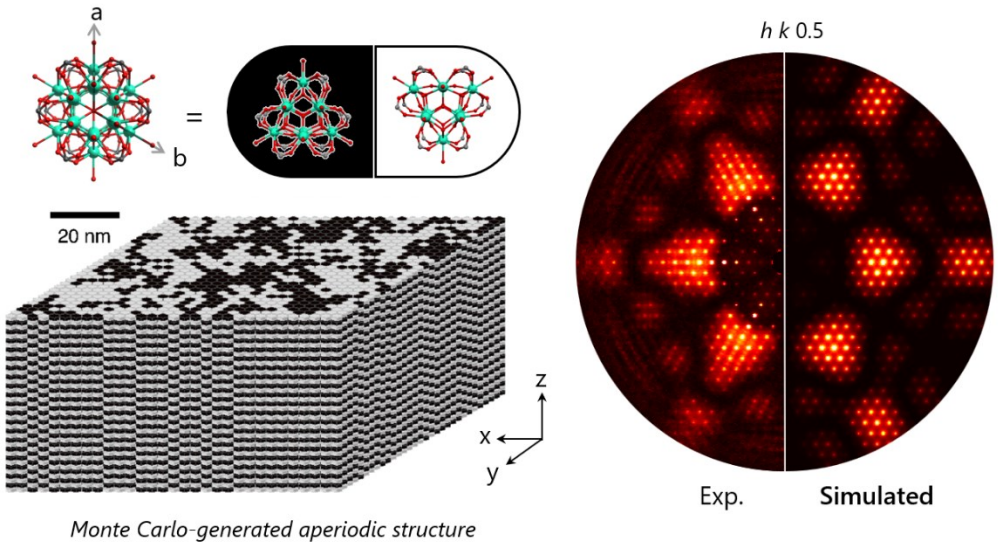
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Keywords: 3D *total scattering, structural disorder, 3D pair distribution function, UoB-100*

A novel lanthanide MOF, UoB-100, containing Dy based metal nodes was found disordered in its average crystal structure. Inspection of the diffraction planes reconstructed from laboratory single crystal X-ray diffraction data revealed structured broad intensities containing information on the local arrangement of cluster disorder. A combination of single crystal 3D delta pair distribution function [1] and Monte Carlo simulations afforded a realistic nonperiodic model for the atomic structure of UoB-100, which reproduces the total scattering observed in diffraction experiments [2]. This case study exemplifies the power of 3D total scattering analysis for the combined structure determination of average and real structure of MOFs, thereby providing essential information for tuning distribution of species, defects and disorder towards finer control over their complex emergent properties [3].



Monte Carlo-generated aperiodic structure

Simulated realistic distribution of cluster orietations in the disordered UoB-100 (left), and resulting diffuse scattering pattern, side by side with the experimentally observed one (right).

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DIRECT OBSERVATION OF THE DEHYDRATION OF A METAL HYDROXIDO CLUSTER TO A METAL OXIDO CLUSTER IN A METAL-ORGANIC FRAMEWORK

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Keywords: *Phase transformation, Cluster chemistry, in-situ investigation, X-ray diffraction*

Some metal-organic frameworks (MOFs) exhibit single-crystal-to-single-crystal transformations during removal or exchange of the guest molecules in the pores. Crystal structure determination of such samples is a powerful technique to elucidate the host-guest properties of the MOF. Typically, adsorption sites or configurational changes in network arrangement can be identified. Cases where the constitution of the network changes are much rarer.

Here, we present the desolvation and dehydration of a zinc-organic framework $[Zn_4(OH)_2(solv)_2]L{\cdot}solv$ (L = organic linker, solv = solvent molecules), in which the constitution and geometrical arrangement of the inorganic secondary building unit (SBU) is completely changed upon heating of the material. In as-synthesized state, the inorganic SBU has coordinated solvent molecules on zinc cations. Originally, we expected that solvent removal at elevated temperature would result in these coordination sites becoming available as open metal sites for host-guest interactions. However, a single crystal X-ray diffraction experiment at 363 K revealed that not only the solvent molecules were removed, but also the rest of the inorganic cluster had transformed significantly from a butterfly shaped $[Zn_4(OH)_2]^{6+}$ to tetrahedral $[Zn_4O]^{6+}$ (Figure 1) due to an additional dehydration step ($2OH^- \rightarrow O^{2-} + H_2O$). Thus, instead of open metal sites, the coordination number of the zinc ions had changed. Variable temperature powder X-ray diffraction confirms the phase transformation occurs in the bulk. Gas sorption of CO_2, C_2H_4, and C_2H_6 succeeded on the transformed phase, which requires specific pre-treatment conditions.

A similar dehydration reaction occurs in the zirconium-based inorganic SBU of UiO-66 [1]. Rarely, has such a constitutional change been observed as directly as in this case and with as large structural rearrangement of the atoms in the SBU. Both clusters, $[Zn_4(OH)_2]^{6+}$ and $[Zn_4O]^{6+}$, are frequently observed in MOF structures (like MOF-5), and it stands to reason that the transformation observed here in the solid state can also occur in solution and determine the SBUs found in the product.

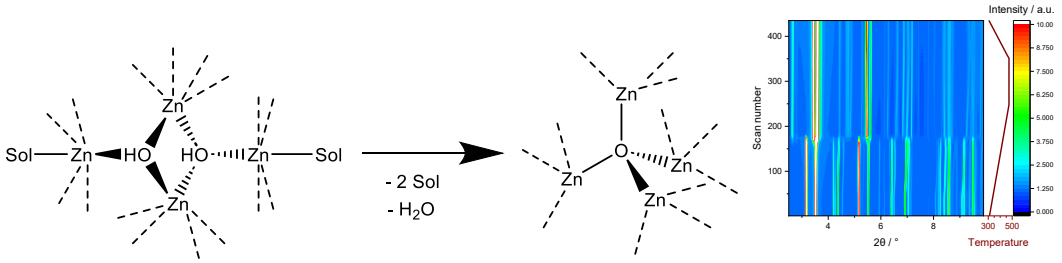


Fig.1. Left: Constitutional change of the inorganic SBU during desolvation and dehydration. Right: Observation of the phase transition in the variable temperature powder XRD pattern.

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CONTROLLING THE MECHANISM OF NUCLEATION AND GROWTH ENABLES SYNTHESIS OF UIO-66 METAL–ORGANIC FRAMEWORK WITH DESIRED MACROSCOPIC PROPERTIES

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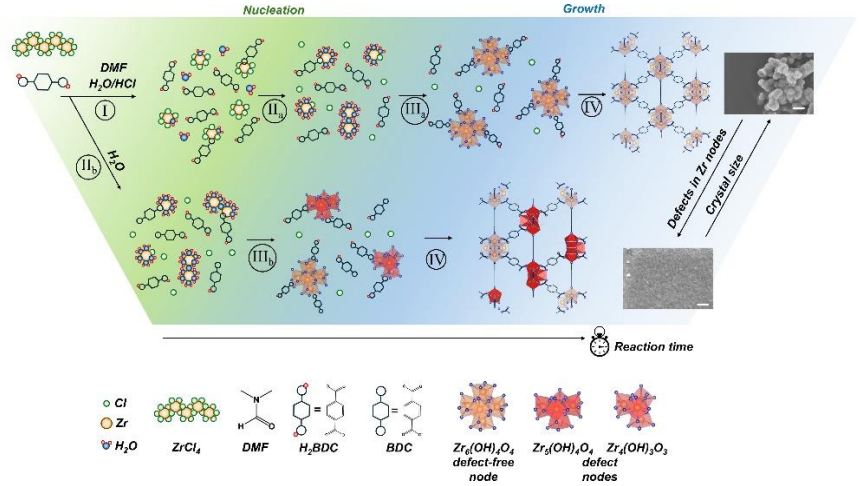
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Keywords: *mechanism of synthesis, in situ XAS, in situ NMR, nucleation and growth*

Background and motivation. Metal-organic frameworks (MOFs) have been studied in depth by chemists and material scientists because of their tunable adsorption and (electro) catalytic properties as well as diversity of discovered topologies like MIL-53, UiO-66, ZIF-8, HKUST-1, etc. However, after more than twenty years of research, understanding of mechanisms of their synthesis is still lacking, hence hindering further progress in reproducible synthesis.[1,2] The present work links the detailed molecular-level nucleation and growth mechanism of the UiO-66 crystallization with the variation of the macroscopic properties of MOF crystals, achieved by manipulating the amount and nature of synthesis modulators.

Results and discussion. By combining in situ time-resolved XRD, Zr K-edge XAS and ^{1}H and ^{13}C NMR spectroscopy, we show that the properties of the final MOF are influenced by H_2O and HCl which affect the nucleation and crystal growth at the molecular level.[3] The nucleation implies hydrolysis of monomeric zirconium chloride complexes into zirconium-oxo species, and this process is promoted by H_2O and inhibited by HCl, allowing to control crystal size by adjusting the H_2O/Zr and HCl/Zr ratios in the synthetic mixture. The rate-determining step of crystal growth is represented by the condensation of monomeric and oligomeric zirconium-oxo species into clusters with the structure identical to that in secondary building units (SBU) of UiO-66 framework. The rapid crystallization in the absence of HCl leads to the formation of defective SBUs with missing zirconium atoms, providing a pathway to control the number of defects in UiO-66 crystals. Remarkably, we have shown that assembling of the metal nodes and linkers into the UiO-66 structure is not the rate-limiting step, and the degree of deprotonation of the linker has no direct effect on the crystallization kinetics or crystal size of final MOF. Finally, we demonstrate inapplicability of redissolution–crystallization mechanisms for the formation of defect free UiO-66.



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STABILITY OF MOF IN PRESENCE OF WATER : NEW INSIGHTS FROM HIGH-FIELD SOLID-STATE NMR

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Keywords: *NMR, water, ^{17}O, ^{91}Zr, stability, steam, UiO-66*

The stability of MOFs in the presence of water is a key factor for their performance in applications such as freshwater production, dessication, humidity control and gas capture. Solid-state nuclear magnetic resonance (ssNMR) with its atomic-level resolution, is a powerful local probe for exploring the structural defects of MOFs under such conditions. In particular, quadrupolar nuclei like ^{17}O and ^{91}Zr offer unique insight into the inorganic cluster of MOFs such as the Zr-based UiO-66. However, ssNMR studies of these nuclei are challenging due to the low natural abundance of ^{17}O (0.037%) and the ultrawide line of ^{91}Zr spectra.

To address this challenge, we explore isotopic enrichment strategies for ^{17}O using either $H_2{}^{17}O$ or a ^{17}O-enriched terephthalate ligand synthesized by mechanochemistry[1]. Solid-state ^{17}O NMR reveals distinct isotope distributions among the μ_3-OH, μ_3-O^{2-}, and carboxylate (COO^-) oxygen sites, depending on the enrichment route. Furthermore, hydrothermal treatments reveal dynamic oxygen exchange between these sites, highlighting the lability of Zr–O bonds even in structurally intact frameworks.

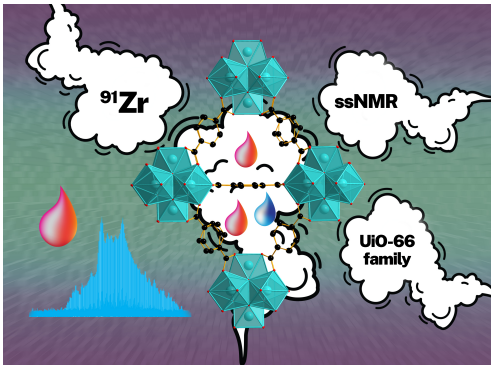


Figure 1. ^{91}Zr NMR helps in the characterization of the structural behavior of the cluster of MOF in presence of steam water at different temperatures

We also demonstrate the possibility of acquiring ^{91}Zr ssNMR spectra on UiO-66, UiO-66-Fumarate and UiO-67-NH_2, in presence of steam at different temperatures, using advanced NMR pulse sequences, high magnetic field (18.8 T) and cryogenic conditions (140 K).[2] When combined with more conventional analytical techniques, such as N_2 adsorption, X-ray diffraction, IR, and ^1H and ^{13}C ssNMR, ^{91}Zr ssNMR provides valuable information in both framework integrity and guest molecule adsorption. We notably show that UiO-66(Zr) and UiO-66-Fum(Zr) remain stable under steam exposure at various temperatures for at least 24 h and up to 7 days for UiO-66(Zr). In contrast, UiO-67-NH_2 containing a 2-amino-[1,10-biphenyl]-4,40 -dicarboxylate linker exhibits structural degradation between 80-150 °C but surprisingly remains intact at 200 °C. The lower stability of UiO-67-NH_2 stems from its larger pores and its weaker Zr–O coordination bonds, whereas its preservation at 200 °C results from a more limited condensation of water in the pores.

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CHEAP AND EFFECTIVE: ALUMINUM FORMATE (ALF) AS THE ULTIMATE SIMPLEST MOF FOR CARBON CAPTURE, GAS SEPARATION, AND LONG-DURATION HYDROGEN STORAGE

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Keywords: *Adsorption, Air and Inert Gas Separation, Carbon Capture and Hydrogen Storage*

In this talk, we present our recent findings on carbon capture, air gas separation, and long-duration hydrogen storage using Aluminum Formate (ALF), studied via high-pressure isotherms, neutron scattering, and computational methods. ALF, the simplest MOF with small pores and narrow connecting channels, displays unexpectedly strong performance in CO_2 capture, O_2/N_2 separation, and H_2 storage. We also describe synthetic strategies to enhance the kinetics of ALF compounds, particularly through Al/Fe solid solutions.

Our results show that ALF's gating effect arises from the temperature-dependent dynamics of formate linkers that modulate pore apertures. As temperature increases, these dynamics enable access to new kinetic adsorption regimes, marked by adsorbate-specific kinetic inflection temperatures (KITs). Identifying KITs is crucial for designing kinetic or absolute gating separations efficiently.

Combining gas sorption, crystallography, spectroscopy, and modeling, we explore how thermodynamics and kinetics interact in ALF and can be exploited for separation design. We rationalize the origin of temperature-regulated gating and demonstrate how DFT calculations and temperature-programmed desorption can predict real-world separation conditions. Our work offers a framework for characterizing materials with similar gating behavior, particularly ultramicroporous systems.

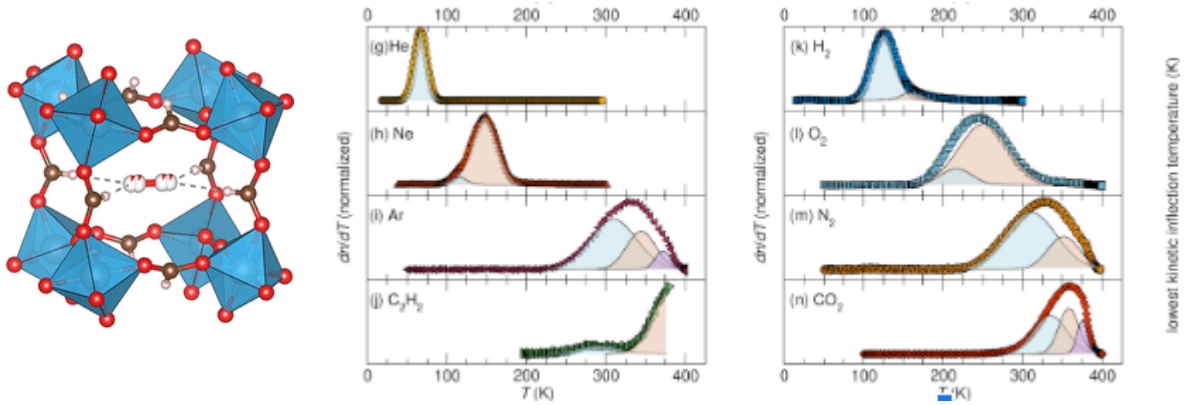


Figure 1. Structure of ALF and Temperature Desorption Plots for various gases, with desorption temperatures from 80 K (for He) to 400 K (for C_2H_2), enabling efficient gas separation by ALF.

*The work was done in collaboration with Hayden A. Evans, Gavin A. McCarver, Thuc T. Mai, Yongqiang Cheng, Zeyu Deng, Ryan A. Klein, Dan Zhao, Pieremanuele Canepa, Angela R. Hight Walker, Anthony K. Cheetham, and Craig. M. Brown.

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TAILORED MOLECULAR DIFFUSION IN NANOPOROUS MATERIAL FOR SEPARATION AND CATALYSIS

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Keywords: *MOF thin film, diffusion, catalysis*

Chemical separation and catalysis are vital industrial processes, with porous materials playing a central role in these applications. Over the past two decades, significant attention has been given to exploring the potential of crystalline porous materials, such as metal-organic frameworks (MOFs) and covalent organic frameworks (COFs), due to their unique structural and chemical properties. Among the critical factors influencing their performance is molecular diffusion, which directly impacts the efficiency of chemical separations, turnover frequencies, and selectivity in catalytic reactions.

In my talk, I will provide an overview of our research focused on fine-tuning molecular diffusion within nanoporous MOF thin films.[1-2] I will highlight a recently developed methodology for controlling chemical diffusion, which enables the achievement of maximum catalytic efficiency.[3] This includes optimizing turnover frequency and geometric selectivity, demonstrated using a MOF catalyst for a condensation-type organic reaction.

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ADSORPTION-DRIVEN CATALYSIS IN METAL-ORGANIC FRAMEWORKS

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Keywords: *adsorption, catalysis, hydroformylation, CO2, methanol*

The chemical-flexibility, tunable pore size and chemical and structural stability of MOFs can be used to design active sites at the molecular level and to produce heterogeneous catalysts.[1] In this contribution, we demonstrate how the chemistry, topology and the adsorption properties of MOFs can be harnessed in catalysis to achieve catalytic performance not possible with either homogeneous or heterogeneous systems.

MOFs can affect selectivity in the hydroformylation of olefins, one of the most important homogeneous catalytic reactions to obtain linear or branched aldehydes from olefins in the presence of syngas. We show how MOFs with MOF-74 and UMCM-1 topologies push Co-catalyzed hydroformylation into kinetic regimes not available under standard conditions[2]. Montecarlo simulation, powder in-situ neutron crystallography combined with adsorption and IR spectroscopic studies support the idea that micropores of MOFs increase the olefins density beyond neat conditions and partially prevent the adsorption of syngas allowing branched selectivity up to 90% using olefins with no directing groups, which is not achievable with existing Co catalysts.[3] We also demonstrate that adsorption in MOFs can be exploited to promote tandem Co-catalyzed hydroformylation/aldol condensation leading to a bifunctional homogeneous/heterogeneous catalyst that increases the aldol products by a factor of 14 compared to the corresponding homogeneous counterpart [4].

MOFs also exhibit promise in CO2 conversion to methanol at a low partial pressure. Two systems were developed: the first utilized a ruthenium-based PNP-pincer complex (Ru-Macho-BH) integrated with amine-functionalized Mg2(olz), achieving methanol yields much higher than its homogeneous counterpart at low CO2 pressures of 0.5 bar. The second system employed UiO-66 functionalized with Cu-Zn, enabling selective methanol synthesis at lowCO2 partial pressures and temperatures. This approach significantly outperforms conventional industrial catalysts, such as CZA, under comparable conditions. This work highlights the critical role of MOF-based adsorption in driving catalytic activity and selectivity beyond the state of the art. MOFs enable catalytic systems to achieve exceptional levels of performance and selectivity, establishing them as essential tools in advanced catalysis research.

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HARNESSING THE SUNLIGHT FOR PHOTOCATALYTIC WATER SPLITTING

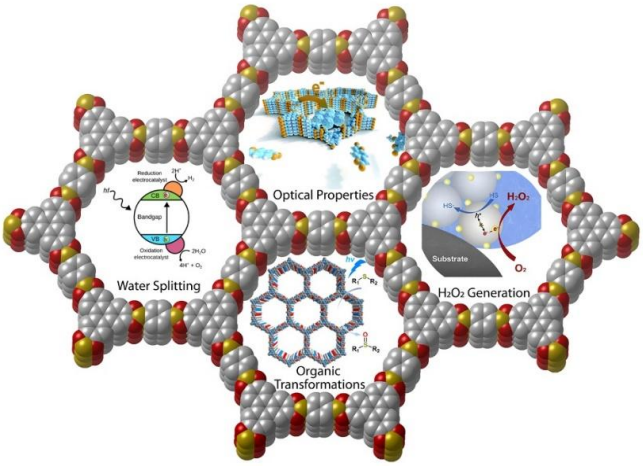
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Keywords: *covalent organic frameworks, photocatalysis, water splitting, hydrogen peroxide, catalysis*

Covalent organic frameworks (COFs) are two- and three-dimensional crystalline and porous materials known for their customizable topologies and functionalities.[1,2] Those with intrinsic micropores are gaining significant traction due to their adaptable pore sizes, large surface areas, enhanced chemical stability, and streamlined large-scale synthesis. In contrast to their boron-linked counterparts, imine, and *β*-ketamine COFs offer superior chemical stability, paving the way for various applications, including gas storage, heterogeneous catalysis, energy storage devices, and proton-conducting membranes.[3] In our quest to prepare efficient and recyclable COFs for photocatalytic water splitting to generate hydrogen, we have demonstrated the synthesis of crystalline and porous *β*-ketoenamine COFs functionalized with acetylene (-C≡C-) and diacetylene (-C≡C-C≡C-) moieties.[4] In further efforts to achieve efficient hydrogen generation via water splitting, we have presented the synthesis of heptazine COFs, achieving efficient and consistent hydrogen generation. Finally, we have demonstrated the utility of hydrazine COFs for the photosynthesis of hydrogen peroxide from pure water, demonstrating the versatility of COFs in photochemistry.[5,6]



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TAILORED TI-BASED METAL-ORGANIC AEROGELS: A VERSATILE PLATFORM FOR POST-SYNTHETIC DOPING AND PHOTOCATALYTIC HYDROGEN PRODUCTION

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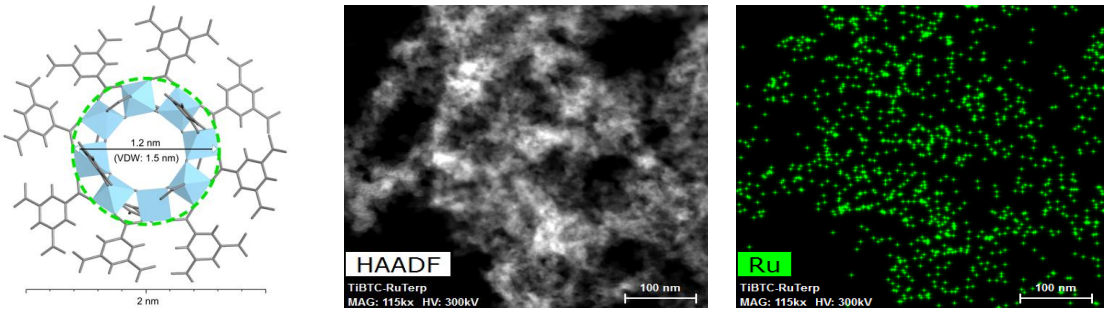
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Keywords: *titanium oxo-clusters, metal-organic aerogels, post-synthetic doping, photocatalytic hydrogen production*

Metal-organic gels (MOGs) and their derived aerogels (MOAs) are emerging as an alternative to crystalline MOFs, combining the coordination-driven tunability of the latter with the flexibility, hierarchical porosity, and easy processability of sol–gel networks. Their non-crystalline nature enables the integration of functional units without crystallization constraints, making them attractive for diverse applications. Recent studies have highlighted their potential for photocatalytic CO_2 reduction and hydrogen production.[1,2] Herein we report the design of a new approach to prepare a titanium-based MOA, noted as TiBTC, synthesized via a two-step strategy involving a pre-formed titanium oxo-cluster ($[Ti_8O_8(benzoato)_{16}]$), and a subsequent ligand exchange with benzene-1,3,5-tricarboxylato ligands (BTC). This synthetic approach, performed under mild conditions, preserves the structural integrity of the Ti_8-core, as evidenced by thorough characterization including PXRD, FTIR, NMR, TGA, SEM/TEM, N_2 adsorption, and XPS. Additionally, near edge X-ray absorption fine structure (NEXAFS) spectroscopy confirms the retention of the Ti_8 cluster after gelation and post-synthetic modification (Figure 1a and 1b). Exploiting the abundance of uncoordinated –COOH groups in the framework, we achieved the incorporation of single-atom site co-catalysts via coordination with Ru, Co, Ni, and Cu complexes bearing terpyridine (TPY), bipyridine (BPY), and phenanthroline (PHEN) N-ligands. Elemental mapping and XRF confirmed homogeneous dopant distribution (Figure 1c) and UV-Vis diffuse reflectance spectroscopy revealed enhanced light absorption in the visible range, particularly for TPY-based systems.

Photocatalytic hydrogen evolution under 365 nm LED irradiation demonstrated significant activity for TiBTC (111 $\mu mol \cdot g^{-1} \cdot h^{-1}$), which further increased upon functionalization. The RuTPY@TiBTC hybrid showed the highest performance (167 $\mu mol \cdot g^{-1} \cdot h^{-1}$), surpassing even Pt-loaded analogues and highlighting the role of TPY in facilitating multielectron storage and transfer. Notably, CuTPY@TiBTC reached comparable activity (164 $\mu mol \cdot g^{-1} \cdot h^{-1}$), offering a non-noble metal alternative. Additionally, they showed stable long-term performance up to 16 hours.

These results underscore the potential of Ti-based aerogels for light-driven hydrogen evolution reaction, where the combination of a well-defined oxo-cluster core, tunable surface chemistry, and accessible doping sites enables rational catalyst design beyond crystalline MOFs.



(a) (b) (c)

Figure 1. (a) Pre-formed Ti_8 oxo-cluster in TiBTC systems. (b) High-angle annular dark-field STEM micrograph and (c) Ru elemental mapping of the RuTPY@TiBTC aerogel.

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TAILORED IMMOBILIZATION OF OXIDATION ENZYMES ONTO METAL-ORGANIC FRAMEWORKS (MOF) TO SYNTHESIZE STABLE BIO-HETEROGENEOUS CATALYSTS FOR METHANE-TO-METHANOL

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Keywords: *metal-organic framework, oxidation enzymes, bio-heterogenous catalysis*

The selective oxidation of light-chain alkanes, such as methane, to methanol is a significant challenge with profound implications for sustainable energy and chemical production. Over the years, several approaches have been explored to achieve this transformation.[1] These approaches offer unique advantages, but none have yet achieved the combination of high yield, selectivity, and sustainability required for implementation.

Enzymes compared to traditional catalysts operate under mild conditions while providing exceptional selectivity and precision. This makes them one of the most promising tools available. Methane-to-methanol transformation is interestingly found in nature and is performed mainly by methane monooxygenases (MMOs), while some *unspecific peroxygenases* (UPOs) were described on longer alkanes. However, despite their incredible capabilities, enzymes face significant challenges when applied outside their natural environments. In general, such as many enzymes, these suffer from poor stability over time, making them unsuitable for industrial processes, especially in flow.

All these challenges can be addressed by immobilizing enzymes on supports. As such, these enzymes can be used multiple times and in a continuous process. Immobilizing enzymes onto more advanced materials, such as metal-organic frameworks (MOFs), offers distinct advantages over other commonly used supports. Their dynamic structural flexibility can be adjusted to maximize enzyme loading and enhance mass diffusion from and to enzymes.[2] Unlike conventional supports, MOFs offer strategic positioning of enzymes, (on the surface, within the pores, covalent linkage on linker or metal cluster) making them suitable candidates for this tailor-made biocatalysts.

Currently, only enzymes with small dimensions have been immobilized on MOFs or very stable ones that can tolerate encapsulation during the MOF's synthesis.[3] Therefore our project focuses on the immobilization of more sensitive enzymes, prioritizing those capable of methane-to-methanol reaction, extending the family of bio-heterogenous catalysts. To achieve this, we recently prepared a new collection of MOFs with tailored properties for different immobilization methods, including entrapment via larger pores (PCN-222, MIL-101), covalent linkage (MOF-808-NH_2, MOF-808-acetate, UiO-66-$(COOH)_2$, UiO-66-NH_2,). Additionally, new water-based synthesis at higher pH has been developed (MOF-808, UiO-66-NH_2, MIL-101) for *in situ* immobilization. These biocatalysts were characterized for activity, stability, recyclability, and enzyme positioning within the material, using advanced techniques like circular dichroism and fluorescence spectroscopy to analyze enzyme-MOF interactions that influence their performance.

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METAL-ORGANIC FRAMEWORKS (MOFS) FOR CAPTURING AND SENSING VOLATILE ORGANIC COMPOUNDS (VOCS) IN INDOOR AIR

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Keywords: *VOCs, Capture, Sensing, QCM, experiment/modeling*

Volatile organic compounds (VOCs) are identified by the World Health Organization (WHO) as significant pollutants that contribute to the decline of indoor air quality. These compounds originate from construction and finishing materials such as paints, wallpapers, flooring, adhesives, combustion processes, as well as cleaning and preservation products. Even at low concentrations in indoor air, VOC emissions can pose risks to human health and damage sensitive machinery. Consequently, detecting and mitigating trace levels of airborne contaminants (ranging from parts per billion to parts per million) remains a critical challenge for ensuring a safe and clean environment in both residential and workplace settings.

In this context, porous materials such as Metal-Organic Frameworks (MOFs) show great potential due to their tailorable chemical and physical properties and highly porous structures, making them effective as sorption media for direct air contaminant capture[1] or as components in electronic devices designed to monitor contaminant concentrations.[2] However, given the vast number of synthesizable frameworks,[3] the selection of a material for a specific contaminant often stems from a trial-and-error approach, resulting in performances that are far from optimal.[4]

To address this challenge, we propose an integrated computational and experimental approach to identify the most suitable MOFs for adsorbing specific VOC contaminants. This method combines high-throughput molecular simulations to pinpoint promising materials with advanced adsorption experiments at very low contaminant concentrations, complemented by sensing tests. Using this approach, we highlight several MOFs identified as effective for capturing and/or detecting various contaminants, including aromatics, halogenated hydrocarbons, terpenes, and more challenging substances such as siloxanes and phthalates.

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TUNING ADSORPTION KINETICS FOR SELECTIVE GAS SEPARATION IN FLEXIBLE MOFS

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Keywords: *Structural flexibility, Selective sorption, Insitu X-ray studies, Thermal Analysis*

Structurally flexible metal–organic frameworks (MOFs), referred to here as FMOFs, exhibit fascinating properties, as they can adopt different, interconvertible structures in response to external stimuli such as heat or guest adsorption/desorption [1]. This unique behavior offers significant advantages for applications like efficient gas separation and transport. The structural responsiveness of these soft frameworks results from a balance between the energy cost of framework deformation and the energy gain from guest–framework and guest–guest interactions.

Despite these advantages, developing FMOFs with high molecular recognition performance for mixtures or dilute gases at room temperature remains a challenge, primarily due to the typically weak interactions between gas molecules and the porous framework. This limitation underscores the need for strategies to construct porous platforms capable of selectively responding to gas adsorption under ambient conditions.

To overcome this challenge, we have conducted a systematic study on the molecular design principles required to modulate both the deformation energy of the framework and the interaction energy with guest molecules [2–3]. Using in situ single-crystal X-ray diffraction (SCXRD) and powder X-ray diffraction (PXRD), we closely examined the structural changes that occur during gas sorption. In parallel, we also investigated adsorption kinetics, which provide critical insights into how quickly and selectively these transitions occur.

Our studies reveal that the control of adsorption kinetics can be just as important as thermodynamic affinity in achieving difficult separations. By tuning the rate of gas uptake and release, it becomes possible to separate mixtures that are otherwise challenging to distinguish, such as water isotopologues, CO_2/C_2H_2, and light hydrocarbons [4–7]. These findings suggest that kinetic selectivity is a powerful, and often underutilized, design strategy.

To further understand these dynamic processes, we use a range of in situ characterization techniques, including time-resolved XRD, thermogravimetric analysis (TG), and differential scanning calorimetry (DSC), under controlled gas environments. These methods allow us to probe the structural and energetic changes that occur during sorption in real time.

In this talk, I will present our recent findings on the structure–sorption property relationships in FMOFs. I will discuss how framework flexibility and adsorption kinetics work together to enable selective gas separation, and how our integrated approach has provided new insights into the fundamental mechanisms of structural responsiveness in flexible MOFs.

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CHARACTERIZATION OF SHAPED FLEXIBLE MOFS FOR GAS SEPARATION

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Keywords: *Flexible MOFs, Shaping, Organic binders, Gas Separation*

A notable feature of certain MOFs, in addition to their characteristic high surface area, molecule-sized pores, and facile tunability, is their flexibility [1]. In response to gas adsorption or other external stimuli, such as mechanical pressure, these materials exhibit a variation in their pore size and crystal structure [2]. The conventional synthesis of MOFs typically yields a fine powder form, which poses significant challenges for industrial-scale applications due to its tendency to induce high pressure drop, clogging, and heat and mass transfer issues. For practical applications, adsorbent powders are formulated using a binder, leading to mechanically and abrasion resistant structures. The formulation of flexible MOFs poses a particular challenge – flexible behavior needs to be retained for the formulated material [3].

We developed ZIF-8 and MIL-53 flexible MOFs millimeter-sized extrudates while preserving their flexibility. Different binder recipes were screened, using polymeric organic polyalcohol-based and cellulose-based binders. The shaped materials were compared on the basis on the retention of the textural properties and of their structural flexibility by nitrogen sorption (77 K) and XRD. As in one of the rare cases in open literature, the mechanical strength of the extrudates was quantified. Thermogravimetric analysis was employed to assess the thermal properties of the shaped MOFs in comparison to their powder-based precursors. It was shown that the formulation process modifies the heat transfer properties of the formulated material. The adsorption properties of the most promising materials were evaluated for the adsorption of water and alcohol vapors and the dynamic separation of alkane / alkene mixtures. The presented work gives new insights into the effects of material formulation using organic binders on the flexibility of MOFs and its impact on gas adsorption properties.

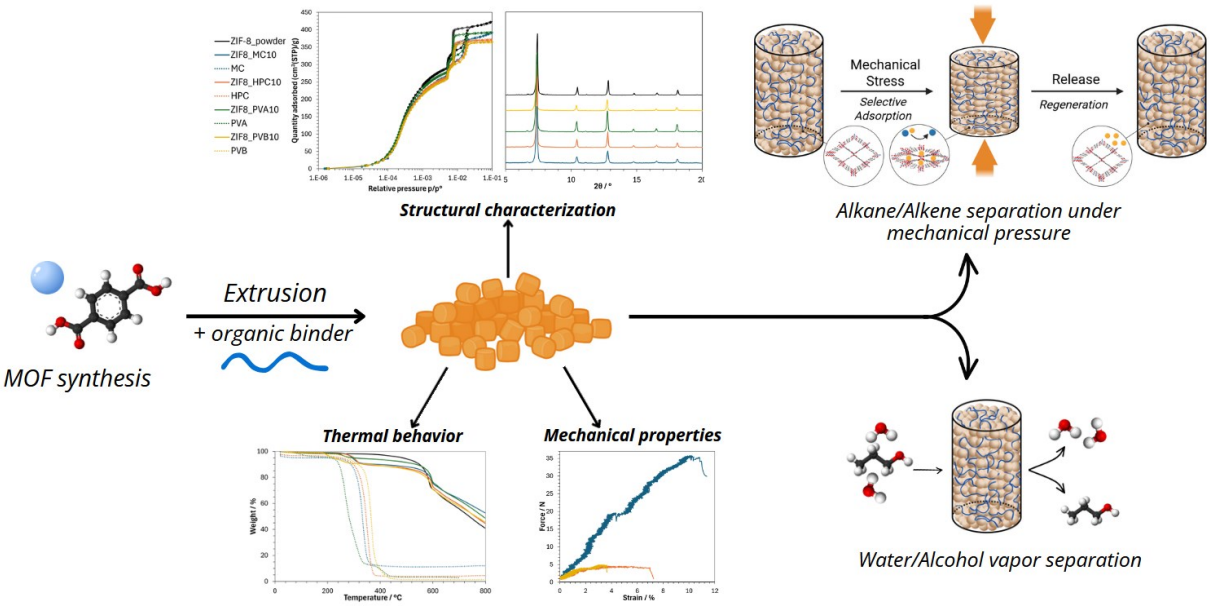


Figure 1 - Graphical abstract

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A SOFT BEGINNING: REVISITING THE FIRST PCP TO REVEAL ITS HIDDEN FLEXIBILITY

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Keywords: soft porous crystals, gas adsorption, global flexibility, local flexibility

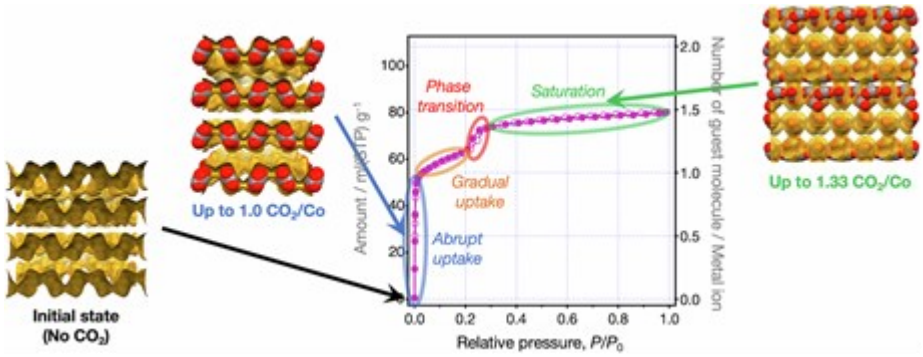
Porous Coordination Polymers (PCPs), also known as Metal–Organic Frameworks (MOFs), have long attracted attention due to their remarkable gas adsorption properties and highly tunable pore structures. In 1997, Kitagawa and co-workers reported the first PCP capable of adsorbing significant amounts of gas molecules, establishing a foundational milestone in the field.[1] However, the mechanism by which gas molecules, larger than the narrow bottlenecks in the structure, could access the internal pore space remained a long-standing enigma.

In this study, we revisit the “first PCP” with modern experimental tools and perspectives. By combining low-temperature gas adsorption measurements with in situ single-crystal X-ray diffraction (XRD) techniques, we uncover a progressive adsorption mechanism driven by local structural flexibility, termed “squeeze adsorption.” At initial adsorption stages, CO_2 molecules penetrate into the seemingly inaccessible pore cavities by locally widening the narrow channels—akin to opening a semi-flexible molecular gate. Upon further adsorption, a cooperative structural transformation is triggered, enabling enhanced CO_2 uptake via a phase transition characteristic of soft PCPs.[2]

The material, $[Co_2(4,4'\text{-bipyridine})_2(NO_3)_4]$, exhibits a layered “tongue-and-groove” architecture forming one-dimensional beanpod-shaped pores with constricted necks smaller than the kinetic diameter of gas molecules. In situ structural analysis during CO_2 exposure at 195 K reveals that initial gas molecules induce a twist in the 4,4’-bipyridine linkers, enabling pore opening without disrupting the crystalline framework. This local deformation propagates to a lattice-level transition at higher pressures, reflected as a two-step adsorption isotherm typical of soft porous crystals.

This work not only solves a decades-old puzzle but also redefines the origin of the field: the first PCP was already a soft PCP. Our findings offer a new historical perspective and underscore the importance of structural flexibility in gas adsorption phenomena. Moreover, they demonstrate the utility of in situ structural techniques in elucidating dynamic behaviors in porous materials, which are key to applications in gas separation, storage, and responsive functions.

By bridging historical discoveries with state-of-the-art methodology, this research exemplifies how revisiting foundational materials can yield transformative insights, ultimately redefining the trajectory of an entire field.



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UNVEILING THE CALORIC RESPONSE OF FLEXIBLE MOFS UNDER VACUUM: A NEW AVENUE FOR ECO-FRIENDLY REFRIGERATION

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Keywords: *Thermomaterials, MOFs, Refrigeration, Pressure, Vacuum, Calorimetry, Thermometry.*

Global warming is increasing the demand for refrigeration, which ironically contributes further to climate change. The use of CO_2 as a refrigerant is a promising eco-friendly alternative due to its favorable thermodynamic properties and low global warming potential.[1] However, CO_2-based systems face challenges such as lower efficiency, high operating pressures, and limitations at elevated temperatures, requiring further innovation to compete with existing technologies.[2]

On this basis, thermal effects triggered by CO_2 pressure on flexible MOFs such as MIL-53(Al)[3] and MOF-508b[4] have recently been described as a '*breathing-caloric"* effects. This phenomenon is part of a potential new eco-friendly and efficient refrigeration technology. Both MOFs undergo a stimulus-induced solid–solid phase transition between a closed-pore (*cp*) and an open-pore (*op*) phase. This solid-solid transition, driven by CO_2 pressure variations, produces a colossal thermal change (ΔH > 100 kJ kg^{-1}) at room temperature (298 K)—comparable to conventional refrigerant gases and even exceeding the thermal change of CO_2 gas alone in the case of MOF-508b. Notably, this occurs under CO_2 pressure ranging between 1 - 30 bar, in contrast to the ~150 bar typically required when CO_2 is used as a refrigerant gas alone.

Currently, only a few examples of MOFs exhibiting this effect have been reported in the literature, and these generally occur in the high gas pressure range (p > 1 bar). However, given that a significant number of MOFs demonstrate guest-induced flexibility, it is of great interest to explore whether the breathing-caloric-like effect could also be achieved in MOFs with phase transitions triggered by applying vacuum (p < 1 bar), in contrast to the typically required high pressures. Vacuum-driven operation presents several advantages over conventional high-pressure systems, including lower energy consumption, access to lower temperatures beyond the reach of traditional technologies, reducing risk related to pressurized systems and significantly lower gas consumption.

To carry out these non-standard calorimetric measurements, we designed and built a custom-modified variable-pressure differential scanning calorimeter (VP-DSC), along with a bespoke thermometric setup. These tools enable in-depth characterization of the thermal behavior of MOFs under controlled CO_2 (or other gases) pressure and vacuum, quantifying enthalpy, entropy, and temperature changes under different conditions of external temperature and pressure/vacuum. Our preliminary results demonstrate the achievement of colossal caloric effects under vacuum conditions, opening new pathways for exploring a wide range of flexible MOF materials with potential applications beyond high pressure-induced systems.

Acknowledgments

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ACCURATE *AB INITIO* PREDICTION OF ADSORPTION ISOTHERMS FOR WATER IN MOFS

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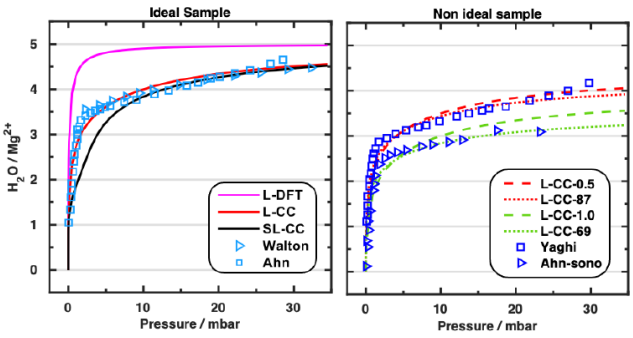
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Keywords: *Water harvesting, water isotherm, Mg-MOF-74, ab initio quantum chemistry*

MOFs are versatile platforms for various applications including water harvesting and carbon capture and storage. The design of improved MOFs requires the reliable prediction of adsorption isotherms with "chemical" accuracy (±4 kJ/mol). While density functional theory (DFT) has provided atomistic understanding of the H-bonded structures involved in the water-filling mechanism of MOF-303,[1] chemical accuracy for adsorption energies is rarely achieved with DFT even if dispersion is taken into account. Here, we employ wavefunction methods (Coupled Cluster theory) within a hybrid QM:QM approach (QM – quantum mechanics) to get accurate adsorption energies.[2] Gibbs free energies are then obtained from vibrational partition functions ("analytical sampling") and used as input for predictions of adsorption isotherms based on multi-site or multi-step Langmuir models.

For Mg-MOF-74 (also known as CPO-27-Mg), water adsorption isotherms measured on different samples and predicted computationally using different methods vary widely.[3] It is experimentally known that the fully loaded structure contains five water molecules per Mg^{2+} ion (composition $Mg_2(dobdc)\cdot 10H_2O$, dobdc = 2,5-dioxido-1,4-benzenedicarboxylate).[4]



The figure (left panel) shows that our approach yields close agreement with experiments (Walton,[5] Ahn,[6] blue symbols) when Coupled Cluster energies are used for the multi- and stepwise-Langmuir models (L-CC and SL-CC, respectively), whereas DFT (PBE+D3) predicts much too high loadings for a given pressure and full loading is reached already at much too low pressures. The right panel shows experimental isotherms (Yaghi,[7] Ahn-sono[6]) which do not reach full loading, only 3 to 4 H_2O per Mg^{2+}. Our accurate multi-site Langmuir Coupled Cluster calculations show that agreement with those experiments is reached if we assume (i) that only about 70 to 90 % of the adsorption sites of the ideal structure are accessible (L-CC-69 and L-CC-87), or (ii) that water had not been completely removed from the Mg^{2+} sites (to which water binds most strongly) and that all or half (L-CC-1.0 and L-CC-0.5, respectively) of the Mg^{2+} sites remained occupied.

We conclude that *ab initio* QM:QM simulations have reached a level of accuracy that deviations between theoretical predictions and experiments indicate sample imperfections.

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THE OPEN DAC PROJECT: DATASETS AND MODELS FOR SORBENT DISCOVERY IN DIRECT AIR CAPTURE

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Keywords: *direct air capture, adsorption, machine learning*

The Open DAC 2023 project (ODAC23) introduced a publicly available dataset of more than 38 million density functional theory (DFT) single point calculations for CO_2 and H_2O adsorption in metal-organic frameworks (MOFs).[1] The work improved upon prior high-throughput computational studies (HTS) of MOFs by performing all calculations at the DFT level of theory instead of relying on physics-based classical force fields (FFs) that often fail to accurately describe chemisorption. ODAC23 identified promising MOF candidates and chemical motifs for direct air capture (DAC) from humid air. State-of-the-art machine learning architectures were also trained on ODAC23 and were shown to be more effective at describing CO_2 and H_2O adsorption in MOFs than other FFs. The Open DAC 2025 dataset (ODAC25) expands upon ODAC23 and incorporates several improvements to address the limitations of the original dataset.

The ODAC25 dataset expands upon both the diversity of adsorbates and the types of sorbent materials compared to ODAC23. ODAC25 includes more than four million new DFT single point calculations for N_2 and O_2 adsorption to ensure a complete description of air-based separations. Although N_2 and O_2 are typically treated as inert or neglected in many HTSs, respectively,[2] we find instances of both N_2 and O_2 chemisorption in several MOFs. This addition will help address the challenge of predicting selectivity in MOFs where CO_2 is chemisorbed because sites that are highly reactive toward CO_2 are more likely to be reactive toward other competing adsorbates. ODAC25 also expands upon the library of more than 8,000 pristine and defective MOFs studied in ODAC23 by introducing ~10^3 MOFs featuring diamine functionalization of linkers and of open-metal sites. Nucleophiles are known from experimentation to strongly bind CO_2,[3] but computational defect engineering and functionalization remain underdeveloped areas of research.[4] We intend for these new MOFs and the associated functionalization algorithm to serve as a useful starting point for future work focused on nucleophilic functionalization of MOFs.

Lastly, ODAC25 updates two methods from ODAC23 to improve accuracy and reproducibility. The ODAC23 DFT calculations were performed using gamma point k-spacing for efficiency. We introduce heuristics to improve DFT accuracy by increasing k-point densities for MOFs with small unit cells. Unlike most HTSs, all ODAC DFT calculations permit the MOF to deform upon the introduction of a guest molecule. This caused more than 75% of ODAC23 MOFs to achieve a new energetically favorable reference state relative to relaxation with only the empty MOF. Selecting the lowest energy MOF from all relaxations performed with a given MOF is vital to accurately compute adsorption energies, and we systematically performed additional DFT relaxations to account for this phenomenon. ODAC25 improves upon the size, diversity, and accuracy of ODAC23 and represents the most complete dataset of DFT calculations for DAC-related adsorption in MOFs to date.

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DYNAMICS AND CONFORMATIONAL ENERGETICS OF GUEST MOLECULES IN CRYSTALLINE SPONGES

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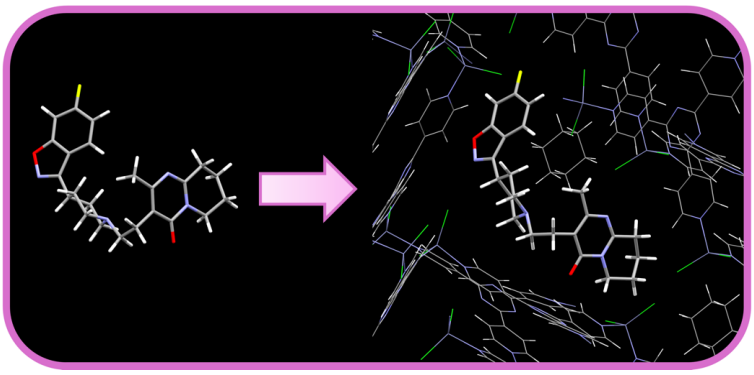
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Keywords: *crystalline sponge, computational, modelling, energetics, dynamics*

The crystalline sponge (CS) method has become an important technique in the structural elucidation of compounds considered to be “uncrystallisable”. The technique removes the necessity of crystallisation for single-crystal X-ray diffraction by utilising the crystallinity and porosity of metal-organic frameworks (MOFs) to form host-guest complexes with the compound to be analysed. Despite gaining significant attention from the research community, work has primarily focused on the determination of molecular structures and the improvement of experimental procedures. The study of MOFs and host-guest complexes by computational methods is not a novel concept, however studies directed specifically at CS structures are lacking. This project seeks to provide a fundamental understanding of the type of environment that is present in the pores of CS structures and the extent to which the CS impacts the geometry and dynamics of guest molecules.

Recently published work**[1]** has employed a density functional theory (DFT) based computational approach to drive a conformational study of guest molecules within the pore environment. To understand the influence of the host framework, guest conformations from experimental structures are compared to the global conformer landscape generated by a conformer search algorithm. The distortion of any molecule away from its idealised (gas phase) molecular geometry involves an increase in the total energy of the molecule. Quantification of the change in the total molecular energy has provided insight into the distortions of guest molecules induced by interactions within the pores of the CS. Guest molecules in the CS have been found to be closer in energy to the conformational ground state than those found in organic crystal structures, suggesting a greater freedom of movement of molecules and that the environment in the CS pores is more similar to liquid phase than typical crystal packing.

Furthermore, to understand the type of environment within the CS pores, a more dynamic molecular study is required. To gain insights into the behaviour of molecules in the pores of the CS, it is necessary to understand whether they are either static, i.e. restricted to their exchange sites, or dynamic i.e. have freedom to move around the pore with other guest and/or solvent molecules. Current work is utilising Monte Carlo simulations combined with machine-learned force fields to simulate the pore environment. These simulations will enable an understanding of the dynamics of guest molecules in the CS and how the presence of non-interacting solvent affects guest molecule behaviour. These insights will aid the interpretation of molecular structures obtained from the CS method and will form the basis of future work in predicting the arrangement of molecules within the CS.



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COMPUTATIONAL ELUCIDATION OF POLLUTANT BINDING MECHANISMS IN FUNCTIONALIZED ZR-MOFS

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Keywords: *Density Functional Theory, Molecular Dynamics, Grand Canonical Monte Carlo, Environmental Remediation, Pollutants.*

The family of metal-organic frameworks (MOFs) holds great promise for applications in catalysis, sensing and the adsorption or capture of environmentally relevant species such as carbon dioxide, nitrogen oxides and water contaminants.[1] In this work, we present a multiscale computational study to elucidate the adsorption mechanisms of two key pollutants: (i) nitrogen dioxide (NO_2)[2] and (ii) perfluorooctanoic acid (PFOA)[3], in functionalized zirconium-based MOFs (Zr-MOFs). PFOA is an emerging, persistent anthropogenic pollutant that poses a serious threat to water quality, while NO_2 is a hazardous gas commonly released during high-temperature combustion processes. By employing a combination of computational techniques, including Density Functional Theory and Grand Canonical Monte Carlo simulations, we investigate the molecular interactions and binding mechanism between these pollutants and the functionalized Zr-MOF. Furthermore, we explore the influence of functionalization on adsorption performance and interaction mechanisms. Finally, novel functionalization strategies are proposed and computationally assessed with the aim of designing new materials with enhanced adsorption capabilities.

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NEGATIVE THERMAL EXPANSION OF A MIXED-LINKER ZR-MOF SYSTEM

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Keywords: *thermal expansion, vibrational spectroscopy, molecular modeling*

Thermal stresses due to temperature fluctuations can lead to the formation of cracks or plastic deformations. Therefore, a precise control of thermal expansion is critical to mitigate thermal stress in materials for applications such as dental fillings, thin films or high-precision optics. This can be achieved by designing novel composite materials, in which the positive thermal expansion of the functional material for the target application is neutralised by adding a material exhibiting negative thermal expansion to obtain a net-zero thermal expansion of the composite material during normal operating conditions. Materials which have been reported to exhibit negative thermal expansion include nanoporous metal-organic frameworks (*e.g.*, MOF-5, HKUST-1, UiO-66 and derivates). The volume contraction of these materials at rising temperatures can be explained by the excitation of low-frequency transverse vibrations of the flexible organic linkers.[1]

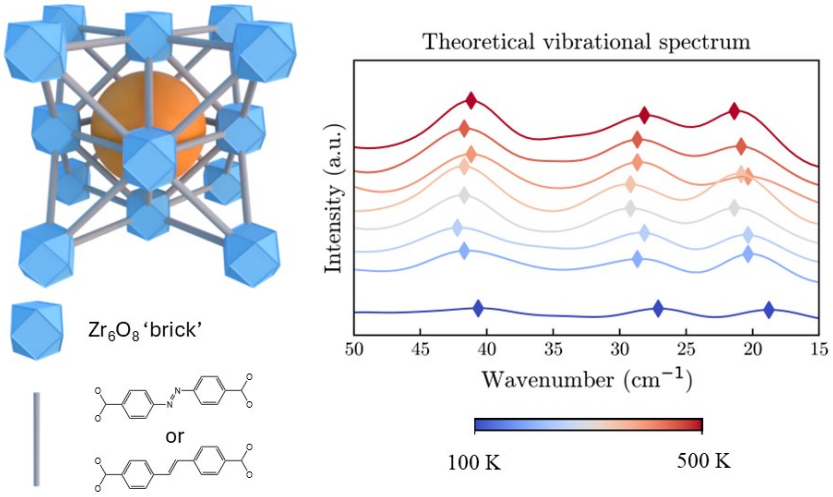


Figure 1: Left: topology of mixed-linker Zr-MOF system. Right: Vibrational spectra at different temperatures from molecular dynamics simulations, the diamond symbols indicate the local maxima of the spectra. From low to moderate temperatures, the peaks move to higher wavenumbers. From moderate to high temperatures, the peaks move back to lower wavenumbers.

A mixed-linker solid solution of geometrically similar building units in a single framework has the potential to precisely manipulate the mechanical and thermal properties of metal-organic frameworks.[2] In this contribution, we aim to use vibrational spectroscopy in experiment and theory to study the displacive vibrational modes of the flexible organic linkers and the subsequent thermal expansion behaviour of a high-symmetry mixed-linker Zr-MOF system with geometrically frustrated azobenzene and stilbene linkers. We constructed a series of representative structural models of mixed-linker MOFs by varying the relative linker content and used machine learning-accelerated molecular dynamics simulations to derive vibrational spectra at realistic operating conditions. A direct comparison between the predicted vibrational spectra and experimental Raman spectra will deliver a precise structural description at the atomistic scale to unravel the balance between phonon-driven negative thermal expansion and conventional positive thermal expansion.

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SYNTHESIS OF THREE-DIMENSIONAL COVALENT ORGANIC FRAMEWORK FILMS AND THEIR ELECTROACTIVITY

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Keywords: thin films, covalent organic frameworks, organic electronics

The high porosity and crystallinity of covalent organic frameworks (COFs) hints to a great potential for this class of material in both mass and charge transport. However, the powdered state of COFs from the conventional solvothermal synthesis hampers applications that require internal continuity, *e.g.* electroactive COFs where grain boundaries interrupt the successive charge transportation.[1] We have explored two methods to solve this problem, which we have successfully applied to make two and three-dimensional COFs, both of which builds upon a spatial kinetic control of bond formation. The first method is based on a solid-liquid interface. Anchoring groups are chemically attached to a surface, and as reagents are flown over the surface, the polymerization reaction occurs predominantly on the surface. We have shown that the key for making smooth films is to work at low concentrations.[2] This because the reaction between monomers and the surface follows first order kinetics,[3] while the coupling between monomers in the bulk follow second order kinetics. We have further shown that by flowing different monomers sequentially over the surface, it is possible to achieve layered COFs,[4] potentially enabling a method to incorporate different functions in different layers in a film. The electroactivity of the made COFs has also been explored.[3, 5] The second method is based on a liquid-liquid interfacial approach.[6] By distributing reactants into separate phases using hydrophobicity, the chemical reaction is confined to an interface that orients the crystal growth. A molecular-smooth interface combined with in-plane isotropic conditions enables the synthesis of films on a centimetre size scale with a uniform thickness of 10-100 nm, and with the lattice alignment clearly seen under transmission electron microscope.[6a] The fabricated films exhibit considerable mechanical robustness, for instance a 13 nm homogenously thick film can have a free-standing length of 37 µm. The explored method is supposed to be universal to all imine type three-dimensional covalent crystal films since it is based on general chemical considerations.

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STIMULI RESPONSIVE COVALENT ORGANIC FRAMEWORKS (COFS)

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Keywords: *Covalent Organic Framework, Stimuli Responsive, actuator, sensing*

Smart materials that can undergo reversible changes in their structures or properties in response to external stimuli, such as light, pH, heat, or redox reagents, have emerged as a thriving area of research due to their diverse applications. These applications include shape memory devices, information storage, and light-controlled molecular machines. Immobilizing organic molecular switches into covalent organic frameworks (COFs), a class of robust organic porous crystalline materials, offers an attractive approach for achieving reversible switching. In this context, we present three families of COF materials incorporating viologen, azobenzene, and spiropyran molecular switches (Figure 1). These materials exhibit diverse properties, including solid state reversible photochromism, light-responsive surfaces with controllable wettability, excellent stability under solvent-free conditions, and the ability to capture and release rhodamine B under light control. Additionally, they demonstrate reversible chromism induced by heat or pH.

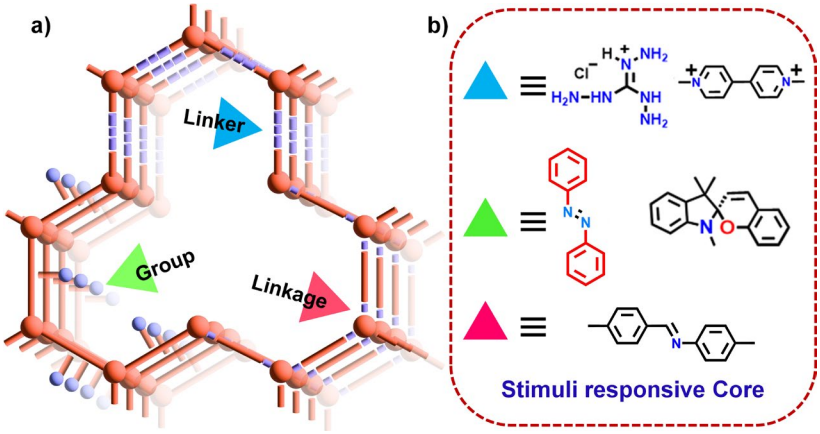


Figure1: Stimuli responsive COFs

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ASYMMETRIC PORE ENGINEERING IN COVALENT ORGANIC FRAMEWORK FOR ION EXCHANGE MEMBRANES

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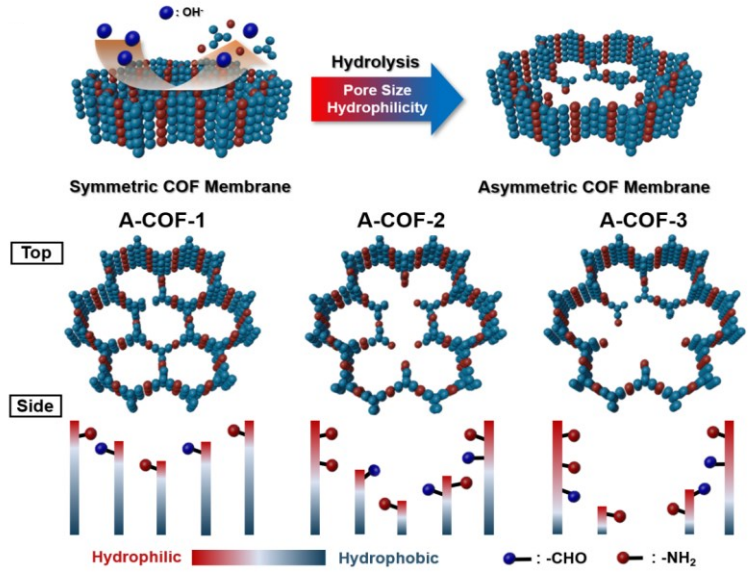
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Keywords: *covalent organic framework, osmotic power generation, pore engineering, asymmetric channel structure*

Reverse electrodialysis (RED) directly produces electrical energy from salinity gradient by selective ion permeation through channels of membranes. Covalent organic framework (COF) is regarded as a promising membrane material due to a well-defined porous architecture originating from its formation of continuous covalent bonds between organic precursors. Particularly, imine-based COF membranes possess advantages for RED processes such as excellent structural stability by virtue of intramolecular hydrogen bonds in pores and aligned channel structures, resulting in high ion selectivity. However, as the hydrogen bond network inside the COF pore disturbs the interaction with water molecules, the ionic conductivity is low due to the induced hydrophobic environment in the nanochannel. Here, we developed an imine-based COF membrane with asymmetric channel structures to improve the RED performance by regulating the ion transport behavior along the diffusion channels. The asymmetric channel is formulated by treating an alkaline solution on one side of the COF membrane to induce gradual changes in the aligned channel structure, partially decomposing imine bonds into original functional groups. The asymmetry along the channel is controlled by reaction conditions, and the resulting channel exhibits hydrophilic properties due to the breakage of hydrogen bond networks. Thus, high ionic conductivity can be achieved through the hydrolyzed channel, while maintaining moderate ionic selectivity attributed to the crystalline pore structure. In the optimal channel structure, the output power density can reach up to 5 W/m^2 under a 50-fold salinity gradient. It is expected that this strategy of inducing gradual changes in characteristics through asymmetric variations in channel structure has the potential to alter the ion diffusion behavior of nanochannels in other membranes, with promising applications in environmental and energy fields.



SYNTHESIS STRATEGIES TO π-EXTENDED COVALENT ORGANIC FRAMEWORKS

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Keywords: *covalent organic frameworks, vinylene linkage, π-conjugation, three-component synthesis*

π-Conjugated materials are highly attractive due to their unique optical and electronic properties. Among these, 2D covalent organic frameworks (COFs) stand out for offering the opportunity to precisely arrange monomers in sheets, which further extend into ordered crystalline and porous 3D networks through aromatic interlayer interactions.[1] Recent progress in the synthesis of π-conjugated 2D COFs has been driven by the development of effective π-bridging linkages (e.g., vinylene, benzoxazole, and pyrazine), either directly or through post-synthetic modification (PSM) approaches. In addition, careful choice of building blocks with π-conjugated structures and topology design to augment the overlapping of π-orbitals have proven to be vital in achieving frameworks with extended electron delocalization.

Herein, we discuss our work in the synthesis of COFs featuring extended conjugation. Our recent results on the rapid synthesis of vinylene-linked COFs will be presented,[2] where strong dipole moment of a phenanthroline building block was found to drive the rapid formation of a crystalline network (Figure). Building on this study, we will also present results on extending this approach to other vinylene-linked COFs. On the other hand, we have previously reported on a three-component synthesis strategy to boronic ester-linked COFs,[3] where azaacene formation between pyrene dione building block and an aromatic diamine occurs simultaneously with framework formation. We will present our new results on the extension of this strategy to other framework classes.

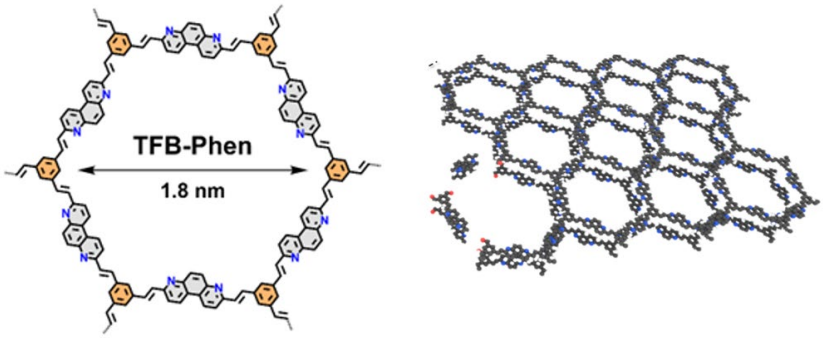


Figure. Vinylene-linked COF forms rapidly using a phenanthroline-based building block.[2]

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HIGH-THROUGHPUT SYNTHESIS OF COFS FOR SUSTAINABLE APPLICATIONS

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Keywords: *Covalent Organic Frameworks, Processability, Scalability, Photocatalysis, Electrochemical CO_2 reduction*

Covalent organic frameworks (COFs) are highly tunable, crystalline porous materials with significant potential in applications ranging from membrane separations and photocatalysis to ion transport and electrochemical energy conversion. However, their broader adoption is hindered by persistent challenges in synthesis scalability, processability, and integration into functional devices.

This talk outlines recent efforts to address these limitations and advance the practical deployment of COFs for sustainable water and energy applications. I begin by introducing a synthesis approach that yields stable, homogeneous suspensions of crystalline COF nanoparticles, enabling solution-processable formats such as thin films via casting.[1] Real-time mechanistic insights into COF nucleation and growth, gained through liquid-cell transmission electron microscopy (TEM), reveal how homogeneous conditions influence crystallinity and morphology.[2]

Building on these insights, I present a high-throughput continuous-flow synthesis strategy capable of producing highly crystalline COFs in diverse macroscopic forms—including membranes, monoliths, and packed beds—with space-time yields approaching ~60,000 kg m^{-3} day^{-1}.[3] This platform overcomes conventional batch-processing limitations and enables direct integration of COFs into scalable systems.

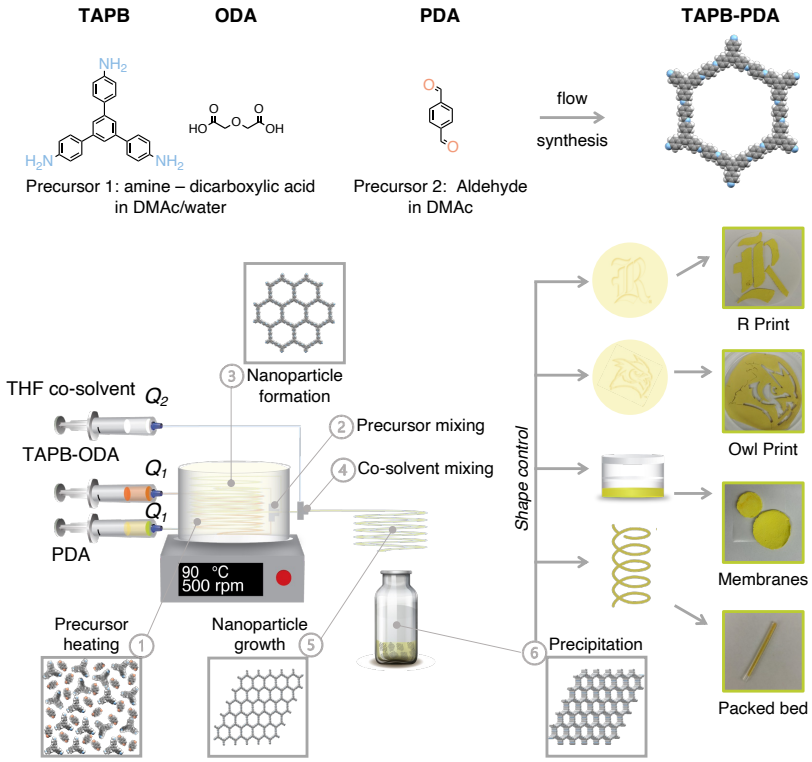


Figure 1. Overview of flow microreactor for the continuous high throughput synthesis and processing of a prototypical imine-linked COF. Top: amine and aldehyde precursor solutions used for flow synthesis of FrCOF-1. Bottom: schematic of microreactor modules and reaction setup. The red and blue dashed boxes indicate the microY mixers at 90 °C and room temperature, respectively. The numbers 1−6 illustrate the evolution of precursors injected into the microreactor to final COF bulk samples sequentially across the reactor modules. Right: controlled precipitation of FrCOF-1 to various macroscopic formats.

MODULATING OPTOELECTRONIC PROCESSES IN COVALENT ORGANIC FRAMEWORKS

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Keywords: *Covalent Organic Frameworks, Donor-Acceptor Frameworks, Conjugation, Optoelectronic Properties, Charge Separation*

Heteroaromatic molecular building blocks can be assembled in the highly ordered spatial environment of covalent organic frameworks (COFs), forming two-dimensional (2D) and 3D crystalline architectures with intriguing optoelectronic properties. Here, we will discuss different strategies aimed at creating electroactive networks capable of light-induced and electrochemical charge transfer. For example, we create interpenetrated donor-acceptor COF phases with novel dibenzochrysene-based building blocks that can be viewed as constrained propeller-shaped tetraphenylethylene with reduced curvature engaging in very tight π-stacking.[1] Thienothiophene- (TT) and benzodithiophene-2,6-dicarboxaldehyde based 2D kagome COFs were synthesized *in situ* with a fullerene derivative to create interpenetrated electron-donor/acceptor host-guest systems showing efficient charge transfer within ps from the COF to the fullerene guest. Considering light harvesting features, synthetic efforts have led to several COFs integrating extended chromophores capable of efficient harvesting of visible and near infrared light, for example.[2] Notably, heterocyclic isometric donor-acceptor-donor moieties that can be embedded in the same COF crystal structure allow for fine-tuning of optical absorption and luminescence, as well as photoelectrochemical activity.[3]

Extending thin film growth methodology to create solvent-stable oriented 2D COF photoabsorber structures, COF films can serve in photoelectrochemical water splitting systems.[4] The detailed mechanism of excited state dynamics in light-harvesting conjugated COFs has been revealed by means of transient absorption spectroscopy,[5] while ongoing work establishes efficient excited state diffusion – even across grain boundaries – in 2D COF thin films.[6] Wurster-type structural motifs are attractive building blocks for imparting high conductivity in the corresponding COFs,[7] which feature tunable optical properties upon integrating donor-acceptor moieties. COF films can also act as ultrafast solvatochromic chemical sensors,[8] as photodetectors,[9] and show very efficient electrochromic response.[10]

Intriguingly, the lattice of COFs can be rendered dynamic. We have recently developed dynamic two-dimensional COFs that can open and close their pores upon uptake or removal of guests while fully retaining their crystalline long-range order.[11] Here, a *wine rack* design based on rigid, π-stacked columns of perylene diimides (PDIs) interconnected by non-stacked, flexible bridges shows stepwise phase transformations between contracted pore and open pore forms, as well as striking modulation of excitonic coupling. Ongoing work focuses on the design of ultra-large pore donor-acceptor COFs with extended light-harvesting abilities and optimized charge separation, illustrating their intriguing structural diversity leading to enhanced optoelectronic functionality.[12]

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The functional potential of these materials is further demonstrated through two case studies: (1) a modular photocatalytic system for PFOA degradation with approximately 20% conversion to fluoride ions,[2,3] and (2) proton-conductive COF foams functioning as solid electrolytes for electrochemical CO_2 reduction (CO_2RR). The latter enables low-voltage CO_2RR operation with selective production of formic acid and C_2+ products at industrially relevant current densities, while maintaining long-term recyclability and stability.[2]

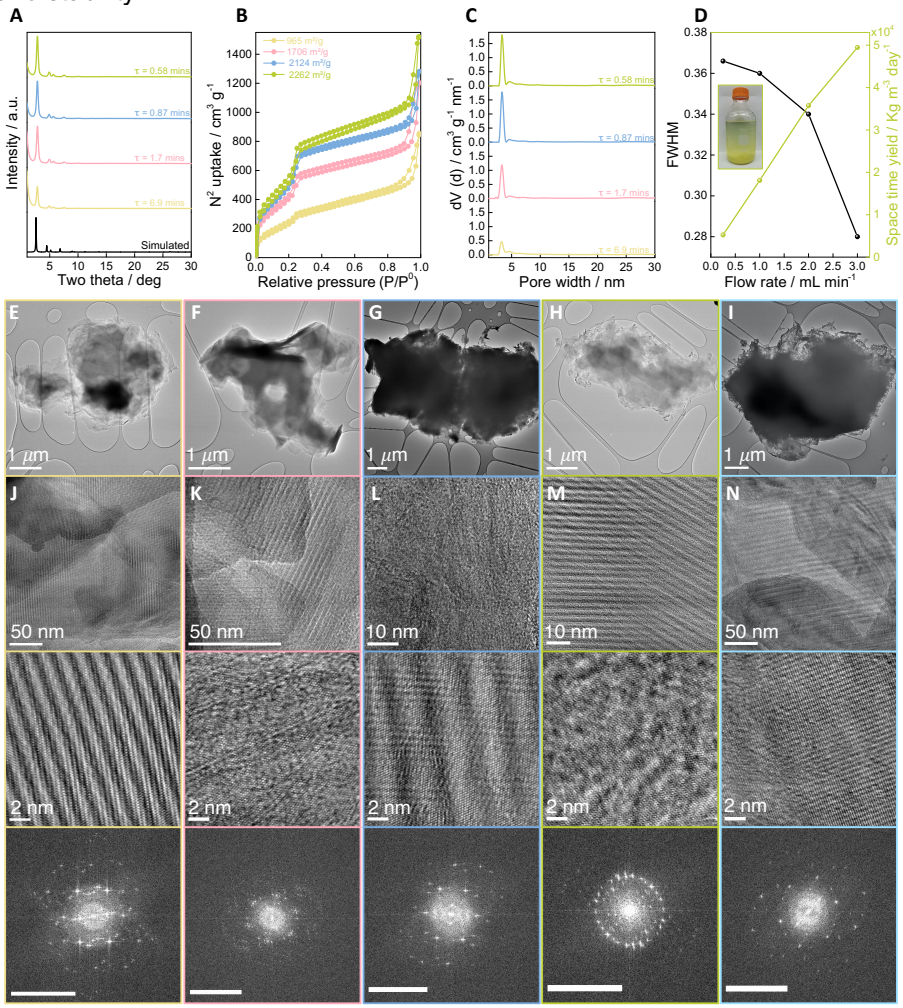


Figure 2. Effect of residence time and concentration on the prototypical FrCOF-1 ("TAPB-PDA") synthesized by microreactor. (a) PXRD patterns show full crystallinity regardless of operating flow rate. (b) N_2 adsorption isotherms showing increasing porosity at shorter residence times. (c) Total pore volumes increase with reducing residence time. (d) fwhm (black) decreases and STY (mint) increases for higher flow rates. TEM and HRTEM images with fast Fourier Transforms (FFT) for FrCOF-1 synthesized at inlet precursor flow rates of (e,j) 0.25 mL min^{-1}, (f,k) 1 mL min^{-1}, (g,l) 2 mL min^{-1}, (h,m) 3 mL min^{-1}, and (i,n) 3 mL min−1 (1/2 concentration), respectively. The scale bar of all FFTs is 10 nm^{-1}.

Together, these results establish a path toward COF technologies that are not only chemically precise but also **engineerable at scale**, enabling real-world deployment in clean water and clean energy systems.

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INSIGHTS INTO DECOUPLED SOLAR ENERGY CONVERSION AND CHARGE STORAGE IN A 2D COVALENT ORGANIC FRAMEWORK FOR SOLAR BATTERY FUNCTION

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Keywords: *Covalent Organic Framework, Solar Battery, Charge Storage*

To mitigate our reliance on fossil fuels and facilitate energy transition, efficient conversion and storage of ubiquitous solar energy is a key strategy. Despite significant research progress in photovoltaics, energy storage in decentralized batteries requires the decoupling of energy conversion and storage, which causes major energy loss and higher cost. Seamless integration of a photoconversion system and an energy storage system in a single device can effectively store the excess energy. Materials that can demonstrate light harvesting, effective charge carrier separation for long-term charge storage, and on-demand charge retrieval as electrical energy, would be the most suitable choice. Such properties have been demonstrated in graphene-, carbon-nitride-, polyoxometalate-, and metal organic frameworks- based materials; however, the charge storage capacity remains uncompetitive. Driven by the need for earth-abundant and sustainable materials for solar energy storage, covalent organic frameworks (COFs) have emerged as a new generation of molecularly defined semiconductors with tunable optoelectronic properties. Herein, the rational integration of an electron reservoir in a polyimide two-dimensional COF unlocks the unique combination of light harvesting and electrical energy storage. When used as an aqueous solar battery anode, the COF demonstrated a capacity of ~38 mAh g^{-1} operating as a pseudocapacitor, which stores charge as long-lived radical anions for days. With photo-electrochemical measurements in conjunction with detailed spectroscopic studies and theoretical support, we attempt to unravel the mechanism of long-term charge stabilization. We present a holistic study revealing the role of solvents, electron donors, and external ions in determining the long-term charge storage capability and overall capacity. Our findings indicate that charge trapping in NDI-COF is mediated by dielectric screening via dipolar interactions and hydrogen bonding, thus rendering water the solvent of choice for long-term charge trapping. Furthermore, on-demand release of long-lived electrons with a suitable co-catalyst unlocks the prospects of dark photocatalysis, which will be investigated in the future.

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STABILIZING SUPRAMOLECULAR POM ASSEMBLY WITHIN POROUS ORGANIC POLYMER MATRIX FOR WATER OXIDATION REACTION

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Keywords: *porous organic polymer, polyoxometalate, quantasome, photocatalysis, water oxidation*

Solar-driven water splitting offers a direct pathway to the production of "solar hydrogen," as an ideal renewable, carbon neutral, energy vector. In particular, Photosystem II (PSII) is the natural machinery that can split the strong O-H water bonds, abstracting electrons and protons, while evolving oxygen using low energy photons.[1] Recently, we introduced the biomimetic concept-design of totally artificial quantasomes (QS) based on the self-assembly of deca-anionic oxygen-evolving catalyst Ru_4POM within a multichromophoric "corolla" of cationic perylenebisimides (PBI) that display a hierarchical supramolecular and integrated architecture where PBI antennas surround the oxygen evolving catalysts, thus enabling water oxidation using visible light quanta, and emulating the oxygenic function of PSII.[2]

To further reinforce the supramolecular architecture against operational stress under oxygenic turnover, we introduce herein the on-surface photo-polymerization of the QS units by installation of styrene terminals on the PBI antennas.[3] In this work, a tailored polymerizable PBI chromophore has been implemented by the synthesis of a bis-cationic PBI scaffold, decorated with two terminal styrene groups (PBI-S, Figure 1).

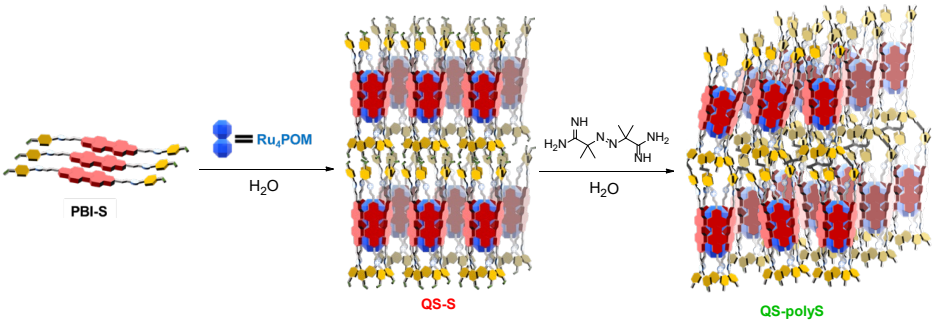


Figure 1. Self-assembly of QS-S upon Ru_4POM intercalation with aggregated PBI-S in water followed by their light-induced cross-polymerization to yield QS-polyS.

The formation of the quantasome assembly occurs readily in water leading to lateral aggregation (QS-S) followed by the photo-polymerization of the styrene groups, yielding the corresponding porous polymer made by quantasomes monomers (QS-polyS). This methodology of cross-linking QS is shown to improve the robustness of the photoanodes. Notwithstanding the fact that the reticulation occurs with apolar styrene moieties, water physisorption has been retained in these materials. Albeit the precise mechanism of water delivery to the catalytic quantasome center is still unknown, this water affinity is expected to play a significant role in the catalytic performance observed in water photooxidation. A significant improvement of the photocatalytic performance (up to 290%) and stability is obtained thanks to photo-cross linking, forming a polystyrene backbone while reinforcing the quantasome connectivity. These findings hold promise for the development of quantasome-based photoanodes whose efficiency could be further improved thorough a tailored engineering of the co-polymer residues, by regulating the hydrophilic/hydrophobic domains, to boost water transport.

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ENHANCEMENT OF TWO-PHOTON ABSORPTION IN METAL-ORGANIC FRAMEWORKS VIA SYNERGISTIC EFFECTS INDUCED BY ASSEMBLY

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Keywords: *metal-organic frameworks, multiphoton absorption, nonlinear optics, structure-property relationships, density functional theory*

An interesting concept permitting the study of a variety of new photophysical phenomena is based on the assembly of modulated light- and electron-responsive materials. Metal-organic frameworks (MOFs) offer unique advantages in this respect, including the ability to control aggregation effects and enhance the stability of chromophores. The three-dimensional structure of such materials is often driven by coordination with the secondary building units (SBUs) and noncovalent interactions that control intermolecular interaction patterns, triggering new functionalities of such assemblies[1,2]. However, the resultant optoelectronic response may also be significantly impacted by the vibrational flexibility of molecules in an assembly[3,4] and polarization effects induced by SBUs[5,6]. In addition, highly specific light-induced phenomena in molecules and materials may involve a multitude of photophysical and photochemical processes that lead, as an example, to luminescence, photon upconversion, photoconduction, as well as nonlinear optical (NLO) properties. The factors driving diversity of exceptional performances, especially multiphoton absorption (MPA), remain poorly understood, limiting the development of design principles for MPA-optimized MOFs.

In my talk, I will explain the origin of MPA in perylene- and pyrene-based MOFs[7,8] and demonstrate the role of MOF topology, chromophore packing, intermolecular interactions, conformational locking and electronic coupling effects on their optical properties and MPA functionality. I will explain the quantum mechanical calculation of their photophysical properties, as well as the molecular bases of light-induced phenomena. I will provide insights into the role of charge transfer and highlight structure-property relationships, aiding the development of design principles for MPA-active MOFs, offering insights for designing advanced functional MOF materials tailored for photonic applications.

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CHARGE TRANSFER MECHANISMS IN SINGLE-CRYSTAL GROWTH AND BATTERY APPLICATIONS OF METAL-ORGANIC FRAMEWORKS

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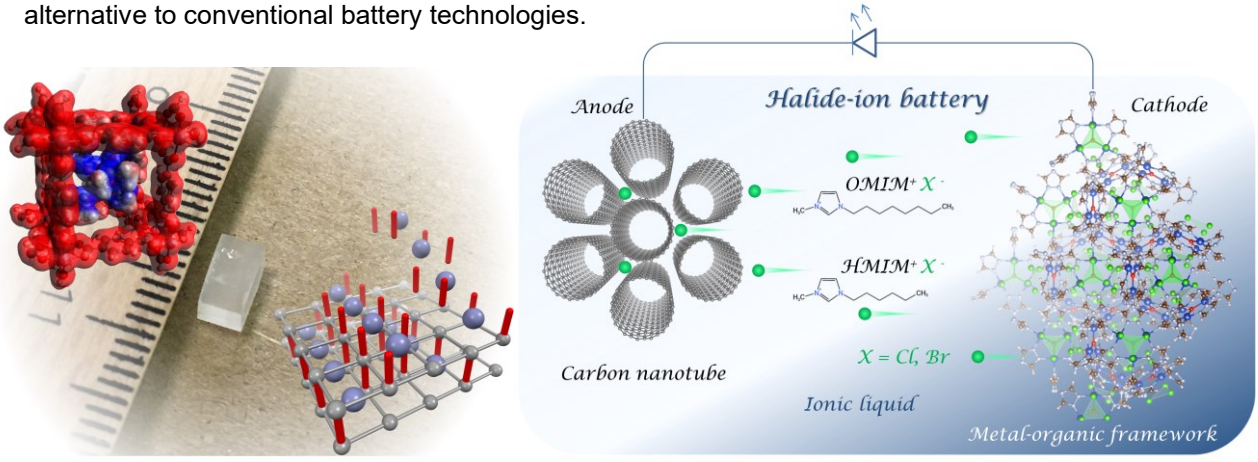
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Keywords: *Single crystal growth, charge-transfer MOF, redox-active MOF, halide-ion battery*

Methods for growing large crystals form the foundation of materials science and technology. Our research focuses on understanding charge transfer mechanisms in single-crystal growth and in the halide-ion battery applications of metal-organic frameworks (MOFs). We recently reported a scalable approach for growing single crystals of a charge-transfer MOF composed of zinc, acetate, and terephthalate ions [1]. This framework encapsulates arrays of octahedral zinc-dimethyl sulfoxide (DMSO) complex cations within its one-dimensional (1D) channels, forming an extended three-dimensional (3D) structure. The reproducible and scalable epitaxial growth enabled the MOF to form square cuboids that grow stepwise to centimeter-scale dimensions (see left panel in Figure). This continuous single-crystal growth, with no apparent size limit, is attributed to the ionic nature of the anionic framework and its cationic 1D molecular fillers.

Another crystalline MOF we synthesized is a water-stable and redox-active framework composed of trinuclear copper clusters and triazole ligands [2]. We demonstrated that redox reactions within the MOF [3] can be harnessed to design and fabricate a halide-ion battery, which charges via halogenation of the MOF at the cathode (see left panel in Figure). The battery employs a pure imidazolium-based ionic liquid electrolyte and binder-free carbon nanotube (CNT) electrodes, one of which hosts microcrystals of the MOF. It exhibits redox potentials exceeding 0.6 V, energy densities up to 7 Wh/kg, and specific capacitances as high as 10 mAh/g, along with excellent cycling stability over 100 cycles. Raman spectroscopy combined with electrochemical analysis reveals the redox states responsible for energy storage. This rechargeable battery is non-flammable, moisture-resistant, and constructed entirely from earth-abundant elements, making it a promising and sustainable alternative to conventional battery technologies.



Left: Single crystal of a charge-transfer MOF with Zn, BDC linkers, acetate pillars, and $Zn(DMSO)_6^{2+}$ fillers. Insets: electrostatic potential of a cuboidal subcell (top left) and epitaxial growth (bottom right).
Right: A halide-ion battery employing a redox-active, water-stable Cu-triazole MOF as the cathode material, a carbon nanotube (CNT) anode, and imidazolium-based ionic liquid electrolytes.

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ALKALINE STABLE METAL ORGANIC FRAMEWORKS FOR ENERGY APPLICATIONS

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Keywords: *metal organic framework, alkaline stability, energy application*

Metal Organic Frameworks (MOFs) with high porosity and tailorable chemical components have drawn increasing interest in gas storage and energy conversion in the past decades. MOFs are formed by chemical bonds between organic ligands (linkers) and metal ions (nodes), generating periodic crystalline network structures with high porosity and large surface area [1]. These properties make MOFs of interest for potential applications in energy, such as storage media for gases (H_2 and CH_4), thin film devices, and catalysis [2]. Degradation of MOFs is usually associated with metal–ligand bond breaking, and the formation of products that are more stable as compared with pristine MOFs. Chemical stability of MOFs depends strongly on the choice of metal/ligands, the connection numbers of metal ions/clusters, and hydrophobicity/hydrophilicity of the ligands [3]. Therefore, it is crucial to enhance the connectivity of the MOF´ s building unit.

In general, high valent metals (Zr^{4+}, Al^{3+}) tend to coordinate with O donor ligands (hard bases) to form MOFs with strong coordination bonding; Low pK_a of carboxylate linkers provide decent level of acidic stability [3]. On the other hand, low valent metals (Zn^{2+}, Fe^{2+}, Ni^{2+}) can construct stable MOFs with N-containing linkers (soft bases); High pK_a of azoles and strong coordination bonds, gives remarkable stability in basic solutions [3].

To explore the suitability of Metal-Organic Frameworks (MOFs) for electrochemical devices operating under mild alkaline conditions, we subjected the two categories of MOFs to degradation in KOH solutions. Following comprehensive characterization, certain MOFs have emerged as promising candidates for energy applications in mild alkaline environments, such as fuel cells, electrolysis or redox flow batteries. These MOFs exhibit notable crystalline stability even after being exposed to mild alkaline conditions, making them potentially valuable materials for various applications including catalysts and electrodes in such settings.

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HYBRID FRAMEWORKS WITH MULTIPLE KINDS OF LINKAGES

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Keywords: *reticular chemistry, structure synthesis, multiple linkages, proton conductivity*

Development of the framework chemistry has entered a new era that is defined by the tremendous research interests in the frameworks' hierarchical complexity, structural variance, and their potentials in performing multiple functions[1]. In this talk, I will first discuss new tools to synthesize metal-organic frameworks (MOFs) with as many as five components in strict order using multiple kinds of coordinative linkages[2], and further utilize linkage-selective editing method to modify the frameworks for enhanced properties[3]. In addition, research progress that combines coordinative linkages with dynamic covalent linkages[4] and hydrogen bonding linkages[5], either simultaneously or in sequential manner, to construct multicomponent frameworks will be introduced. These new methods create framework structures that can be viewed as hybrids of MOFs and hydrogen-bonded organic frameworks (HOFs) or covalent organic frameworks (COFs). The spatial compatibility between different nets locks the units into patterned arrangements, thereby giving rise to structures that integrate the advantages of different categories. Their potential applications in gas adsorption, proton conduction, and cascade catalysis will be discussed.

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CENTRING STRUCTURE DIRECTING AGENTS FOR MOFS DESIGN: CONCEPT, CHALLENGES AND OPPORTUNITIES

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Keywords: *mix-ligand, rational design, topology, geometry mismatch, synthesis*

Developing innovative tools for the rational assembly of materials[1] is key in a field now fed by millions of yet to be made, hypothetical structures[2] for which simply combining the needed metal(s) and ligand(s) gives no success guarantee on the assembly of the desired product. We recently demonstrated that mastering *geometry mismatch*[3] with the use of pyridyl and imidazole based *centring Structure Directing Agents* (cSDA) allowed for the design and assembly of a series of 30+ sodalite (**sod**) based zeolite-like-MOFs (ZMOFs),[4] pseudo-polymorphs of the MIL-100/PCN-333 family with **mtn** topology.

We now expanded the concept to *ca.* a dozen additional "classical" topologies (**flu**, **hmc**, **hex**, **ydq**, etc.) and increased complexity from the foundation study,[4] combining various types of supermolecular building blocks (SBBs), but also exploring a novel class of topologies coined *merged nets*[5] (**stn**, **pop**, etc.).

The use of the cSDAs goes beyond the assembly itself. Similarly as for architecture and construction, the cSDA yields more robust frameworks, less prone to collapse upon guest removal. By capping some windows in the framework, it can also prevent self-interpenetration, and in the case of flexible nets, rigidify the outcome. Aside from these evident possibilities, we also demonstrate that cSDAs can also be used to guide the specific orientation of the main ligand in a structure, therefore bringing the possibility to control pore dimensions to the next level.[6] Additionally, we show that cSDAs can also help arranging 1-periodic metal-organic rods in space.[6] Finally, depending on the targeted application, the cSDAs can be fully removed or exchanged to achieve higher porosity, wider windows, or left in place for separation purposes.



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CHANGING METAL SEQUENCES IN MULTIVARIATE METAL-ORGANIC FRAMEWORKS INCORPORATING CARBORANE LIGANDS

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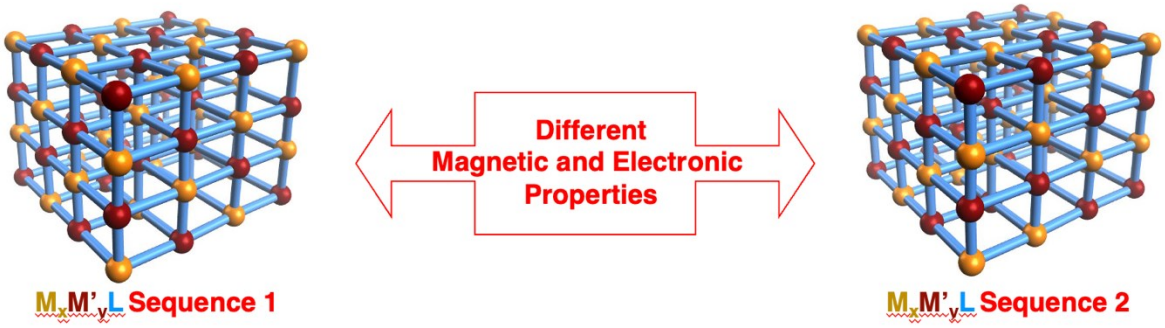
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Keywords: *Boron clusters, Porous Materials, Multi-metallic.*

Carboranes (CB), polyhedral boron clusters, have emerged as a fascinating class of 3D ligands for the construction of metal-organic frameworks (MOFs) due to their unique properties, such as thermal stability, chemical inertness, tunable electronic and steric characteristics. Carborane-based MOFs have gained significant attention in recent years as promising materials for various applications.[1] The versatility of carboranes allows for the design and synthesis of MOFs with diverse structures and properties, offering exciting opportunities for fundamental research and practical applications.

We are currently exploring the integration of lanthanide and transition metal ions with CB ligands to create a range of innovative multifunctional materials. Our recent work demonstrated that the bulkiness and acidity of CB linkers enables the synthesis of multi-metallic multivariate (MTV) MOFs incorporating flexible combinations of multiple lanthanides. This strategy has produced Tb/Eu MOFs for anticounterfeiting,[2] GdLn MOFs with magnetocaloric and luminescent properties,[3] and the first-ever MOF containing eight different lanthanides.[4]

We will show our most recent results on CB-based MOFs incorporating transition metals (***m*CB-Co** and ***m*CB-Ni**).[5] Using these isostructural MOFs, we generate two multi-metallic MTV MOFs with different Ni/Co sequences, resulting in distinct magnetic and semiconducting properties (see Figure). These findings pave the way for the rational synthesis of functionally tunable multi-metallic frameworks, opening new avenues for novel materials with tailored properties.



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DATA-DRIVEN DISCOVERY OF RETICULAR MATERIALS

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Keywords: *Up-down Approach, Reticular Chemistry, Materials Discovery*

Reticular materials such as metal–organic frameworks (MOFs), metal–organic polyhedra (MOPs), zeolitic imidazolate frameworks (ZIFs), and covalent organic frameworks (COFs) represent a diverse and modular class of solids with broad utility in gas storage, separation, catalysis, and sensing. Three-dimensional (3D) frameworks offer enhanced structural complexity, tunability, and functional diversity compared to their lower-dimensional counterparts. Despite the vast range of available metal nodes and organic linkers, the chemical space explored for 3D frameworks—especially in COFs and ZIFs—remains limited.

To address this gap, we extend the data-driven Up–Down Approach (UDA)—a rational design strategy originally developed for Zr_6-based MOFs—to systematically explore the underutilized chemical space of 3D framework materials. In contrast to traditional bottom-up synthesis, UDA begins by identifying feasible topologies and subsequently maps them to synthetically accessible building blocks. This topology-first methodology enables the systematic generation of novel framework architectures that are often inaccessible through conventional design strategies.

Applying the UDA across multiple framework families, we discover and validate over 100 novel 3D COF structures. These frameworks exhibit both chemical plausibility and experimental feasibility, demonstrating the approach's robustness and versatility. Our findings show that UDA significantly expands the accessible chemical space of framework materials and provides a unified, data-driven platform for high-throughput discovery across reticular chemistry.

By leveraging the interplay of modularity, topology, and algorithmic design, the Up–Down Approach opens new avenues for rational exploration and targeted synthesis in both metal–organic and covalent systems, redefining the boundaries of structural diversity in framework chemistry.

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RETICULAR CHEMISTRY FOR FUNCTIONAL CRYSTALLINE POROUS FRAMEWORKS

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Keywords: *Reticular chemistry, metal–organic frameworks, highly connected nets, gas storage*

Reticular chemistry has developed into a powerful tool for the design and synthesis of porous, crystalline framework materials such as metal–organic frameworks (MOFs).[1-3] In this presentation, I will report on our recent progress with quasicrystal approximants in isoreticular **mcm**-MOFs and the assembly of highly connected 3,12,24-connected **uru**-MOFs.[4-5] In addition, I will introduce how fundamental reticular chemistry can be applied to the precise synthesis of targeted stable porous MOFs based on iron- or chromium-based inorganic nodes.[6-7] We also studied these MOF materials for water vapor capture and the onboard storage of clean-energy gases such as hydrogen and methane. In the end, I will report a scalable approach for integrating photosensitive MOFs onto textile fibers for the high-efficiency antimicrobial applications.[8-10]

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MOCOFS: RETICULAR INTERSECTION OF MOF AND COF CHEMISTRY TOWARD ELEVATED CRYSTALLINITY, STABILITY, AND COMPLEXITY

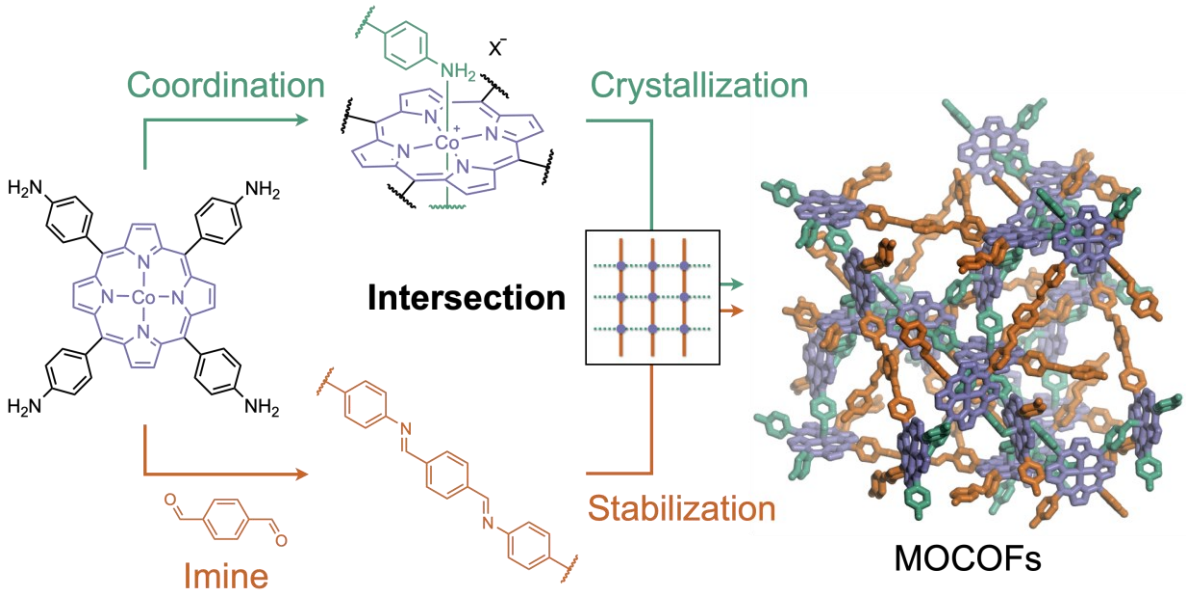
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Keywords: *MOFs, COFs, crystallization, chemical stability, topology*

Reticular chemistry, or linking molecular building blocks through strong bonds into crystalline frameworks, is a powerful strategy for creating porous materials with tailored structures and properties.[1] As prominent exemplars, MOFs and COFs have been developed in recent decades based on metal–organic coordination and covalent organic linkages, respectively. However, these two types of linkages exhibit distinct tendencies: Metal–organic linkages are usually highly reversible and directional, facilitating high crystallinity in MOFs; Covalent organic linkages, such as imines, tend to be less reactive with many chemicals, providing high chemical stability to COFs. Here, we introduce metal–organic–covalent–organic frameworks (MOCOFs), constructed by the intersected extension of metal–organic and covalent organic linkages, which combine the crystallinity of MOFs with the stability of COFs in a complex framework.[2] The first MOCOFs were synthesized by reacting cobalt aminoporphyrin with dialdehydes, forming cobalt–amine coordination and imine linkages simultaneously from each porphyrin node. The extended framework comprises a complex chiral topology **lvz**, confirmed by single-crystal X-ray diffraction. The MOCOFs exhibit larger crystal sizes than related COFs and greater chemical stability than related MOFs, owing to the cooperation of the two types of linkages. In addition, they have high porosity and demonstrate specific adsorption of acid molecules. Therefore, MOCOFs represent a novel design strategy for reticular materials with enhanced properties.



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SULFUR-FUNCTIONALIZED ZR^{4+} MOFS FOR CAPTURE AND RECOVERY OF GOLD IONS AND GOLD NANOPARTICLES

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Keywords: *MOFs, gold capture, gold nanoparticle recovery*

The increasing demand for gold may lead to resource depletion and raise environmental concerns due to the mass production of electronic waste (e-waste) generated from the disposal of electronic and electrical equipment, which typically has a short lifespan of only a few years. Therefore, recycling e-waste and recovering gold from industrial wastewater is economically essential and environmentally significant. Despite ongoing progress, most materials developed for gold recovery focus on dissolved gold ions, often overlooking gold nanoparticles (AuNPs). However, AuNPs are increasingly used in various industrial products and represent a significant source of gold, as each nanoparticle contains thousands of gold atoms.

In this study, we present two sulfur-functionalized Zr^{4+} metal–organic frameworks (MOFs), whose crystal structures were determined via PXRD and microcrystal electron diffraction (MicroED). These materials were evaluated for their ability to remove Au ions and AuNPs from water. Their sorption performance was investigated through comprehensive studies, including sorption kinetics, isotherm analysis, and tests using natural waters with varying matrix complexity and e-waste simulants. In all cases, the MOFs demonstrated exceptional ability to capture both gold ions and nanoparticles, with rapid sorption kinetics (<1 hour) and impressive sorption capacities (up to 890 mg of Au ions and 43 mg of AuNPs per gram of MOF). XPS studies revealed that the gold recovery mechanism involves chemical interactions between gold species and the sulfur-containing groups in the MOFs. MOF–alginate and MOF–cotton fabric composites were prepared. They effectively removed AuNPs from distilled water and e-waste simulant solutions under continuous flow. Notably, gold can be recovered from the Au-loaded MOFs using mildly acidic thiourea solutions, and the regenerated sorbent can be reused for gold capture at least three times. Finally, the excellent performance of these MOFs in capturing gold ions and nanoparticles from complex solutions enabled the development of the first passive sampling device for long-term monitoring and recovery of AuNPs from environmental waters.

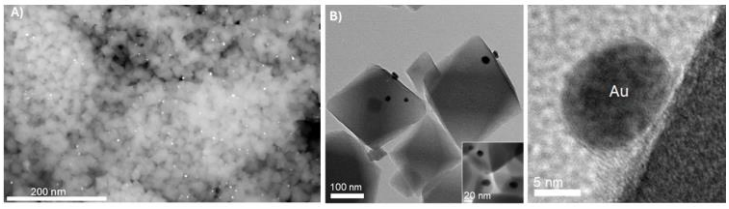


Figure 1. A) FE-SEM image of the MOF loaded with AuNPs appeared as bright spots. B) TEM image of the same material, showing Au NPs (dark spots) attached to the surface of MOF particles. C)A high-resolution TEM image of an individual Au NP.

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CONTINUOUS FLOW SYNTHESIS OF HIGHLY STABLE, WATER-BASED MOFs FOR EFFICIENT TOXIC GAS CAPTURE

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Keywords: *metal-organic framework, hydrothermal, flow synthesis, porous material, gas capture*

Metal-organic frameworks (MOFs) show huge promise for capturing harmful gases such as H_2S, SO_2, and CO_2. Through adjustments in pore dimensions, MOFs can be optimized to selectively capture and remove targeted molecules while excluding others [1]. Nevertheless, challenges arise in maintaining MOF stability, particularly when exposed to gases such as H_2S and SO_2, due to strong interactions that can potentially lead to irreversible connections, such as metal-sulfur bonds, causing structural degradation. Furthermore, in the presence of humidity, the generation of highly acidic species can accelerate MOF structure deterioration [2]. Although MOF synthesis has advanced from research to practical applications, commercialization remains in its early stages due to challenges in scaling up and maintaining material properties. Traditional batch solvothermal synthesis, common in lab-scale MOF research, is restricted to milligram/ gram-scale and typically requires long reaction times. In addition, most MOFs have been synthesised using toxic solvents such as DMF, posing significant environmental and safety risks that hinder large-scale production [3].

This study focuses on the water-based synthesis and scale-up of MOF-303, an environmentally friendly metal-organic framework reported to exhibit exceptional adsorption performance for polluting oxides such as CO_2 (10.7 mmol·g^{-1}) and SO_2 (7.86 mmol·g^{-1}), as well as excellent water and thermal stability up to 400 °C [4]. In this work, MOF-303 was successfully synthesised for the first time in continuous flow, a scalable route which provides efficient mixing, heat transfer, and minimizes energy input.

The optimization of MOF-303 synthesis focused on evaluating the effect of reaction temperature, time, and molar ratio of the used base (NaOH) on the morphology, surface area, structure, and yield. The synthesis was carried out in a hydrothermal flow system at temperatures ranging from 25 to 250°C with a residence time of 2.7 to 3.5 minutes. Results revealed that higher base molar ratio (1:1:3; metal: linker: base) led to an increase in the average yield from 38% to 67%. Increasing the reaction temperature from 150°C to 200°C raised the BET surface area from 910 to 1120 m²/g producing well-defined rod-like crystal shapes. The synthesised MOF-303 showed remarkable adsorption stability over 20 cycles with a high CO_2 uptake (17 wt.% at 25 °C and 1 bar). Optimizing the synthesis process parameters is clearly a key to achieving the desired characteristics and performance as well as for enabling the scalable production of MOF-303 at an industrial level.

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METAL ORGANIC FRAMEWORK FOR CRITICAL METAL SEPARATION

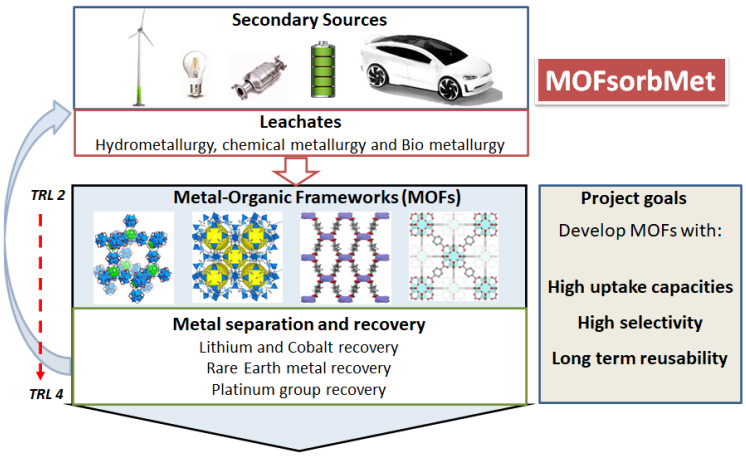
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Keywords: *Functional MOFs, Metal Separation,*

Metal-Organic Frameworks (MOFs) have emerged as a highly promising material for various applications such as gas absorption, gas separation, catalysis, drug delivery, sensors, and several others.[1] MOF's potential in critical metal separation is a topic of significant interest. Critical metals such as Cobalt, Lithium, Rare earth elements (REEs) and Platinum group elements play a pivotal role in strategic technologies such as energy, e-mobility, digitalisation and aerospace etc. Due to supply constrained and environmental challenges, particularly in light of current geopolitical developments, ensuring a secure and sustainable supply of critical metals is top priority. Extensive research is carried out to develop efficient technology for extracting and reusing critical metals from both the primary and secondary resources. Given the tunability of MOFs with desired functionality, pore size and geometry, they can serve as an exceptional adsorbent for the separation and purification of metals. [2]



MOFsorbMET project aimed at validating the MOFs for critical metal separation, addressing the benefits and limitations quite often exploring them for real leachate samples. We have investigated MOFs for Nickel, Cobalt, Silver and lithium adsorption separation. We have also developed new functional MOFs targeted towards a specific group of metals. This presentation will discuss our findings from MOFsorbMET project, highlighting the performance, opportunities and limitations of MOFs.

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A NOVEL ANILATO- BASED FAMILY OF 3D MOFs FOR ENVIRONMENTAL APPLICATIONS

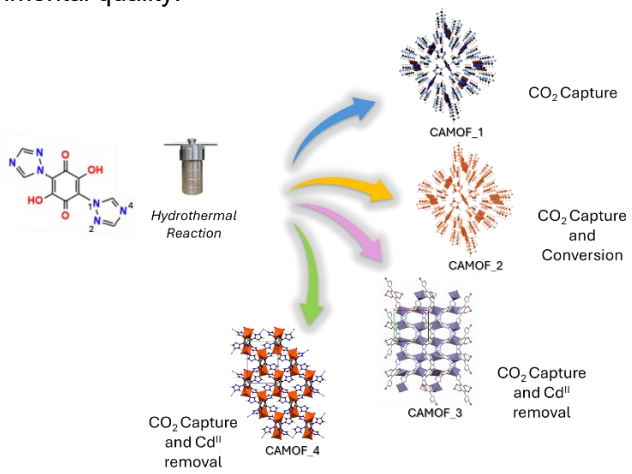
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Keywords: *Metal Organic Frameworks, Anilate, CO_2 Capture and Conversion, Cd^{II} removal*

Capturing CO_2 from the atmosphere represents a key challenge, since CO_2 has been recognized as the primary anthropogenic greenhouse contributor to the increase of earth's average temperature. Their high porosity, tunable pore size and large surface area make Metal-Organic Frameworks (MOFs) promising candidates to uptake and separate CO_2 from gaseous mixtures. In particular, the ultramicroporosity (pore size < 0,7 nm) and the presence of amine groups are crucial requirements in the design of MOFs for CO_2 separation. In 2021, some of us synthesized, *via* hydrothermal approach, a new microporous MOF, formulated as $[Co(trz_2An)]n{\cdot}2.5H_2O$ (CAMOF-1) [1], by combining 3, 6-*N*-ditriazolyl-2,5-dihydroxy-1,4-benzoquinone (trz_2An, An=anilate=2,5-dihydroxy-1,4-benzoquinone), as organic linker, with Co^{II} metal node in a 1:1 stoichiometric ratio. This MOF showed a favourable balance of high selectivity, high adsorption capacity and high regenerability, thus being a promising candidate for CO_2 gas separation processes; its framework is capable to sieve larger molecules, such as methane or nitrogen, to reach very high CO_2 selectivity values in different conditions of temperature and concentration. We report herein the synthesis, crystal structure and performance studies of three new microporous MOFs obtained by combining trz_2An with Cu^{II}, Zn^{II} and Fe^{II} metal nodes, formulated as $[Cu(trz_2An)]{\cdot}nH_2O$ (CAMOF-2), $Zn(Trz_2An){\cdot}3H_2O$ (CAMOF-3) and $Fe(Trz_2An){\cdot}\ 3H_2O$ (CAMOF-4). CAMOF-2-4, show a 3D robust structure, with a pore size of 3.46 Å for CAMOF-2 and 3,89 Å for CAMOF-3,4, consistent with the kinetic radius of CO_2 [2] and absorption capacity of 2 molecules of CO_2 / unit formula confirmed by pore analysis data.

Static and Dynamic Adsorption Measurements revealed *i*) remarkable carbon dioxide uptake, *ii)* high selectivity in CO_2:N_2 gas mixtures, *iii)* easy regeneration in mild conditions.
Furthermore, *i)* preliminary CO_2 electroreduction studies showed a good capability of CAMOF-2 to convert carbon dioxide into ethylene and *ii)* adsorption test removal, performed on CAMOF-3 and CAMOF-4, revealed a good performance to remove Cd^{II}, well known as highly toxic heavy metal ion, at different pH range and concentrations. In conclusion, trz_2An is a strategic organic linker, which combined with different transition metal ions, gave rise to a novel thermal stable, robust, microporous 3D MOFs family employing for environmental quality.



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SCALABLE METAL PHOSPHONATE FOR THE CAPTURE OF ACID MOLECULES UNDER INDUSTRIAL-RELEVANT CONDITIONS

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Keywords: *metal phosphonate, CAU-60, large-scale synthesis, reversible adsorption, and separation*

Metal-organic frameworks (MOFs) show great promise in gas sorption, molecular separation, and water harvesting, but their large-scale use is limited by high production costs, synthesis challenges, and poor stability under harsh conditions, especially in strongly acidic and basic media. Nevertheless, some MOFs are already used industrially for CO_2 removal and atmospheric water harvesting [1]. Metal phosphonates, a relatively underexplored class of MOFs, are particularly valued for their chemical robustness. This stability is enhanced when coordinated with trivalent or tetravalent metal ions, owing to the stronger binding affinity of phosphonate compared to carboxylate groups, a result of their higher charge [2].

Herein we report the results on CAU-60, a porous aluminum phosphonate of composition $[Al_2H_6(PMP)_3]\cdot 9H_2O$, synthesized from Al^{3+} ions and N, N′-piperazinebis(methylene- phosphonic acid) (H_4PMP) as the linker which can reversibly adsorb HCl from solution [3]. Large-scale synthesis of CAU-60 and synthesis optimization with a yield of 90-95% from a few milligrams to a few hundred grams as well as reversible sorption of HCl gas and HNO_3 from solution phase are demonstrated. The performance of CAU-60 was further evaluated for trace HCl removal from hydrogen gas, where even low concentrations (50–200 ppm) can cause equipment corrosion and catalyst deactivation [4]. Structured CAU-60 pellets demonstrated efficient HCl capture (1.75 mmol HCl/g) under industrially relevant conditions - high gas velocities (>0.3 m/s), 10 bar pressure, room temperature, and <100 ppm HCl using a fixed-bed breakthrough (BT) setup. The material showed rapid water-induced HCl desorption and stable performance over six adsorption–regeneration cycles, out-performing conventional non-regenerable sorbents (Figure 1).

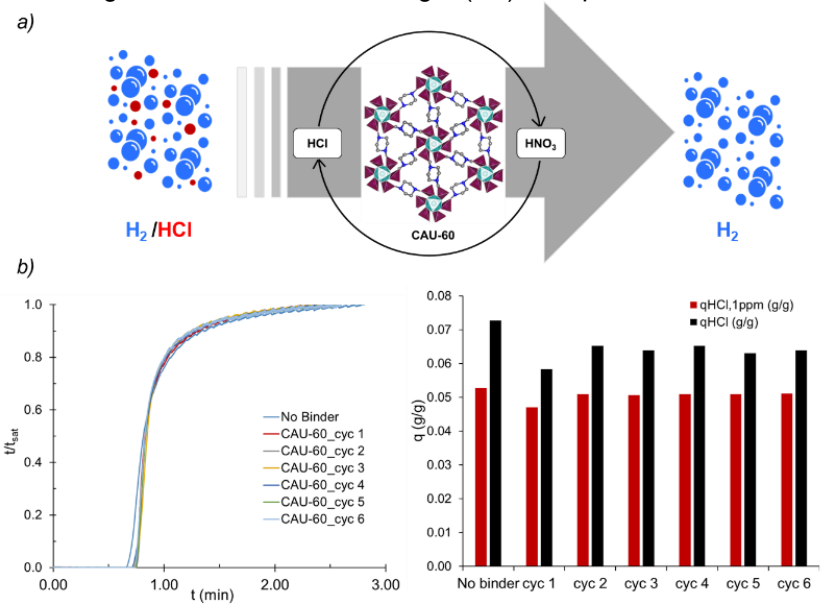


Figure 1: **a)** Graphical representation of selective reversible adsorption of CAU-60 towards HCl and HNO_3 in solution and separation of HCl in gas phase from H_2/HCl mixture. **b)** BT curves of CAU-60 with H_2/HCl mixture in different cycles and bar diagram shows the uptakes at saturation and one ppm HCl concentration.

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COLORIMETRIC DETECTION OF COLORLESS ACID VAPORS USING A MOF-BASED SENSOR

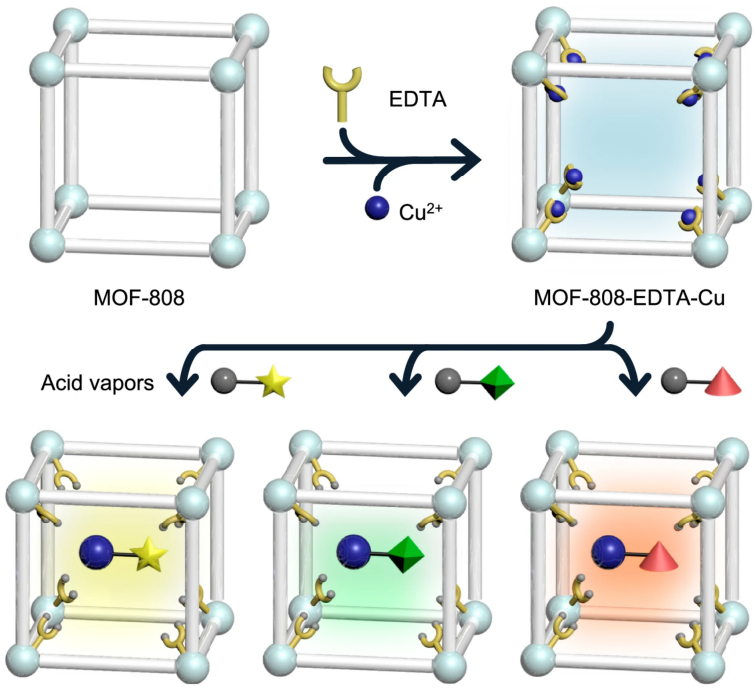
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Keywords: *Colorimetric sensor, Acid vapor discrimination, MOF-808-EDTA-Cu*

The rapid and accurate identification of hazardous gaseous acid chemicals is essential for ensuring safety, effective evacuation, and timely first aid in various industrial and environmental settings. Despite ongoing efforts, existing methods have struggled to differentiate between multiple acidic vapors and remain limited in practical applicability. In this presentation, we introduce a novel colorimetric sensor, MOF-808-EDTA-Cu, engineered by integrating the robustness of MOF-808 with Cu-EDTA, resulting in a proton-triggered decoder capable of converting corrosive acid anions into distinguishable colorimetric responses. Notably, the sensor exhibits a vivid cyan-to-yellow shift upon exposure to HCl vapor and demonstrates the ability to visually differentiate various acidic vapors (HF, HBr, and HI) through unique color changes. Moreover, by exploiting the compatibility of the MOF-based sensor with multiple metal ions in an atomically dispersed state, we achieved the discrimination of up to six different colorless acid vapors within a single sensor domain. Additionally, the integration of a flexible polymer has enabled the fabrication of a portable, miniaturized acid sensor capable of continuous 24-hour monitoring with simple visual detection via the naked eye or camera sensors.



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MICROPOROUS AL-MOF FOR CO2 CAPTURE: FROM FUNDAMENTAL STUDIES TO LARGE SCALE SYNTHESIS AND LAB-PILOT TESTING

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Keywords: *MOF, CO_2 capture, large scale, lab-pilot testing.*

Among the many existing MOFs, only few are promising adsorbents for Carbon Capture due to their excellent working capacity and selectivity for CO_2 over other gases present in the industrial gas streams, with good stability to moisture/steam and other impurities. Recently, CALF-20 has emerged as an alternative benchmark to standard zeolite 13X for physisorption-based CO_2 capture from high CO_2 concentration flue gases.[1] Despite this huge leap forward in the field, also de-risking the use of MOFs at the industrial scale, CALF-20 cannot be the unique solution because of the gigantic amounts of CO_2 to be treated together with the diversity of the possible capture processes/conditions. Thus, there is still a real need to search for other "realistic" cost-effective sorbents as alternative to CALF-20.

In this regard, we will report on a robust microporous Al-carboxylate framework, MIL-120(Al), (MIL: Institute Lavoisier), which exhibits high CO_2 uptake (1.9 mmol g^{-1} at 0.1 bar, 298 K).[2] *In situ* Synchrotron X-ray diffraction measurements and molecular simulations revealed that the structure of MIL-120(Al) offers a favorable configuration for the CO_2 capture where pores being decorated with a high density of μ_2-OH groups and accessible aromatic rings. Besides, based on calculations and experimental evidences, moderate host-guest interactions ($Q_{st}(CO_2)$ ≈ 40 kJ mol^{-1}) is deduced, suggesting a relatively low regeneration energy penalty. Moreover, an environmentally friendly ambient pressure green route was developed to prepare the MIL-120(Al) at the kg-scale (with an estimated production cost of ca.13 USD/Kg among the lowest for MOFs) while the MOF was further shaped into stable beads. First evidences of its efficient CO_2/N_2 separation ability were validated by breakthrough experiments while IR *operando* studies indicated a kinetically favorable CO_2 adsorption over water. Furthermore, 3 Kg of shaped (beads) MIL-120(Al) were tested on the VPSA pilot with a flue gas containing 15/85 CO_2/N_2 mixture, which showed that an optimal experimental CO_2 purity of 97% and recovery of 90% were obtained, exceeding the performance of MIL-160(Al).[3]

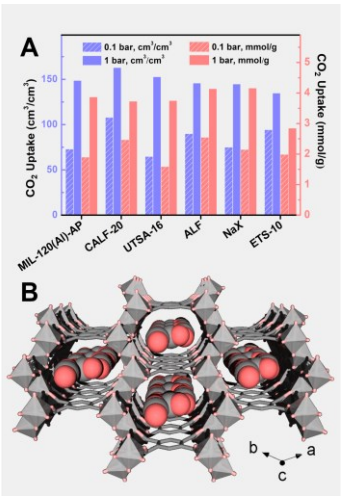


Figure 1. (A) CO_2 uptakes of MIL-120(Al) and benchmark sorbents. (B) Crystal structure of MIL-120(Al) showing CO_2 molecules packed in the 1D-

In this communication, we will present more in details our study highlighting the technical details and performances which makes MIL-120(Al) an excellent adsorbent candidate for industrial scale CO_2 capture processes.

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AMINO ACID-BASED METAL-ORGANIC FRAMEWORKS DERIVATIVES FOR DIRECT AIR CAPTURE: TOWARD NET-ZERO CO_2 EMISSIONS

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Keywords: *Amino acid-based MOFs derivatives, CO_2 Capture, Direct Air Capture*

Over the years, economic and population growth have driven increased energy production, largely met by the use of fossil fuels. This has resulted in a significant rise in global greenhouse gas emissions, with $MtCO_2eq$ released into the atmosphere annually.[1] Since the launch of European Green Deal[2] in 2019 by the European Union (EU), new regulations and actions have been implemented to combat climate change and steer the EU towards becoming climate neutral and resilient by 2050. The development of carbon capture, utilization, and storage (CCUS) technologies has emerged as a promising alternative to conventional mitigation strategies, enabling the reduction and reuse of CO_2 emissions. Typically, CCUS technologies aim to lower CO_2 emissions from large and stationary sources (e.g. industrial plants such as cement), which emit gas mixtures with relatively high concentrations of CO_2, thus, preventing their release into the atmosphere.[3] Recently, Direct Air Capture (DAC) methodology has gained more attention owing to its ability to extract CO_2 directly from the atmosphere, acting as a direct mitigator of climate changes. However, lower concentrations of CO_2 in air (≈ 0.1%) compared to the stationary sources (5-15%), excess of moisture and inadequate temperature and pressure conditions, make the development of efficient DAC systems a significant challenge.[4] Among various approaches, adsorption-based methods have been highlighted as promising for both CCUS and DAC, due to their low energy consumption, easy implementation and low operational cost. Metal-Organic Frameworks (MOFs), known for their high porosity, excellent crystallinity and tunability, have emerged as strong candidates to be used as adsorbents for CO_2 capture.[5] Despite their high adsorption capacity in CCUS applications, in real DAC conditions, with low CO_2 partial pressure, at room temperature and in the presence of humidity, MOFs showed a low adsorption efficiency for CO_2.[6] Therefore, the development of more stable and efficient MOFs derivatives tailored for DAC applications is of critical importance. Amino acids, owing to their oxidative resistance, low toxicity and strong reactivity with CO_2 have been explored as CO_2 capture promoters. However, their typical use in liquid phase systems limits their practical applicability.

In this study, taking advantage of the post-synthetic modification strategy, DL-proline amino acids were anchored to the pristine MOFs, NH_2-MIL-125 and UiO-66-NH_2, through a simple condensation reaction, to produce a proline-based MOF derivatives, MIL-125-Pro and UiO-66-Pro. When compared to pristine MOFs, the introduction of the proline unit into the MOF structure led to a 2-fold and 5-fold increase in the CO_2 capture efficiency of MIL-125-Pro and UiO-66-Pro, respectively (1 bar and 25 ºC). Their ability to be used in DAC conditions with improved efficiency has been demonstrated, highlighting the potential of MOF derivatives for boosting CO_2 capture.

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BREATHING EASIER: CAN ADSORBENTS HELP CAPTURE CO_2 INDOORS?

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Keywords: *CO_2-removal, breakthrough, dynamic sorption*

Indoor air quality is receiving increasing attention due to its direct impact on human health, cognitive performance, and well-being. One often-overlooked component of indoor air pollution is carbon dioxide (CO_2), which can easily reach concentrations around 1500 ppm in poorly ventilated or densely occupied spaces such as offices, classrooms, or homes. At these levels, CO_2 has been associated with symptoms like headaches, drowsiness, and reduced decision-making performance. Addressing elevated indoor CO_2 concentrations is therefore essential not only for comfort but also for maintaining a healthy and productive indoor environment.

In this study, we explored the potential of an amine-functionalized industrial resin, Lewatit® VP OC 1065, for use in room air purification systems. This material has been previously reported as a promising candidate for direct air capture (DAC) due to its high affinity for CO_2. Here, we shift the context to indoor environments, focusing on its performance at CO_2 concentrations of approximately 1500 ppm, which are typical in real-world indoor scenarios.

We conducted a series of breakthrough experiments under both dry and humid conditions, using single- and multicomponent gas mixtures to comprehensively evaluate the material's sorption behavior. These experiments provide a robust dataset for further modeling and system design, tailored to indoor air purification needs.

Beyond the health-related benefits, capturing CO_2 indoors before it is released into the atmosphere also offers an additional environmental advantage—contributing to decentralized and passive CO_2 mitigation strategies, and potentially supporting the development of CO_2-neutral buildings.

This work emphasizes the value of reproducible, application-driven characterization and demonstrates a transferable methodology for assessing porous materials in real-world air purification scenarios.

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AL-FUMARATE ANALOGUE MOFS BASED ON C4 LINKERS WITH DIFFERENT FUNCTIONALITIES. STRUCTURAL INSIGHTS AND CO_2 ADSORPTION PROPERTIES

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Keywords: *Aluminum MOFs, Synthesis, CO2 adsorption, Characterization*

Aluminum based MOFs have been extensively studied in the recent past for their enhanced stability and easy scalability. The most famous aluminum MOF, which was developed at industrial scale is the Al-fumarate (Al-FUM), sold under the commercial name of Basolite A520 by BASF chemical company. Al-FUM, of formula $Al(OH)(FUM)\cdot 4H_2O$ (FUM^{2-} is the fumarate anion) is isostructural with the terephthalate analogue MIL-53 MOF but having a more rigid structure respect to this latter and smaller pores.[1] Al-fumarate has been employed for many applications ranging from gas storage and separation, pollution remediation, heterogeneous catalysis and as filler for Mixed-Matrix Membranes.[2] In this contribution we report on the syntheses, performed by using a solvent-free approach or by using green solvents derived from biomasses such as γ-Valero Lactone (GVL), of novel Al-MOFs based on C4 linkers, namely tetraflurosuccinic acid (H_2-TFS) and L-aspartic acid (H_2-L-Asp). The two MOFs Al-TFS and Al-L-ASP here reported are isostructural to Al-FUM but the presence of a perfluorinated chain, in the case of Al-TFS, and of an amino group in the case of Al-L-Asp, strongly influences their structure/properties features. Al-TFS of formula $Al(OH)(TFS)1.5H_2O$ undergoes a phase transition upon water removal due to a conformational change of one of the two ligand of the asymmetric unit.[3] Despite the presence of F atoms, the MOFs resulted very hydrophylic if compared to Al-FUM. CO2 adsorption properties were also evaluated in term of total capacity and selectivity. On the contrary Al-L-Asp MO, of formula Al(OH)(L-ASP), does not undergo any structural change upon water removal and it display a good thermal resistance up to 300 °C. Remarkably, the CO_2 adsorption properties are largely improved respect the fumarate analogue reaching a value as high as 3.2 mmol/g at 273 K with a IAST selectivity over 80 probably due to favorable interaction of CO_2 with basic amino groups.

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PILOT-SCALE TESTING OF AL-MOF FOR POST-COMBUSTION CO_2 CAPTURE AT TECHNOLOGY CENTRE MONGSTAD (TCM)

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Keywords: *CO_2 capture, VPSA Pilot, MOF, Experiments, Simulations*

Carbon capture and storage (CCS) or Use (CCU) has emerged as a leading approach for CO_2 mitigation, particularly in carbon-intensive for achieving net zero emissions by 2050. However, the current amine-based absorption process has limitations such as high energy demands and solvent degradation. CO_2 separation by adsorption is a promising alternative due to potential lower energy consumption and reduced environmental impact. Although extensive lab-scale studies highlight the potential of MOFs for CO_2 capture, industrial-scale application remains limited, and the effects of real operational conditions on factors like productivity, purity, and energy consumption are not yet fully understood.

Addressing the issue, a consortium of 14 partners from 8 different countries has collaborated to establish the MOF4AIR project. The initiative aims to develop and demonstrate the performance of promising MOF materials in post-combustion CO_2 capture contexts. Technology Centre Mongstad (TCM) is one of the three selected demonstration sites to test the MOF-based CO_2 capture technology at industrial scale as part of the MOF4AIR project.

The Vacuum Pressure Swing Adsorption (VPSA) demonstration pilot setup at TCM is designed to treat 50 to 100 Nm^3/h of flue gas coming from a residual fluid catalytic cracking unit (RFCC) or from a steam boiler (Mongstad heat plant (MHP)). The VPSA pilot includes (i) a scrubber, (ii) a dryer unit, (iii) a contaminants removal unit, and (iv) the MOF section, which comprises three 41 L columns filled with 55 kg of pelletized MOF MIL-160(Al) $Al(OH)(O_2CC_4H_2OCO_2)$) [1-2] provided by MOFTech. The VPSA pilot operates a 6-step cycle composed of an adsorption step, heavy reflux, co-current evacuation, counter-current evacuation, light reflux and light product pressurization [3].

This VPSA demonstration unit was firstly optimized with a simulation model developed with the results obtained with the laboratory scale VPSA pilot using an aliquot of the sample [4]. Optimization of the VPSA unit using a genetic algorithm (NSGA-II) was performed to maximize purity and recovery while minimizing energy consumption [5].

Performance tests were carried out based on an experimental plan derived from VPSA simulations. Various VPSA adaptations were tested to improve CO_2 recovery and purity. During the test campaign, parameters such as co-current evacuation time, co-current flow rate, and counter-current flow rate were found to significantly influence the adsorption process. However, achieving the target levels for CO_2 capture and purity has been challenging, with fine-tuning hindered by the process's inherent complexity.

The VPSA unit was extensively modified to enhance performance. After more than one year of tests and improvements, current results indicate solid overall performance of both the VPSA system and the plant's operational flow. The maximum CO_2 purity achieved was 95.6 ± 3.6 % with a recovery of 91.1 ± 0.3 % and with an energy consumption of 743 ± 12.2 kWh/ton. The data was calculated based on a 2-hour operating period representing 35 consecutive cycles.

The results from the TCM site demonstration reach the project objectives with a recovery higher than 90% and a purity higher than 95% and demonstrates the feasibility of using MOFs in a post-combustion CO_2 capture process.

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TAILORED FUNCTIONAL METAL-ORGANIC FRAMEWORKS FOR ENHANCED OPTICAL GAS SENSING

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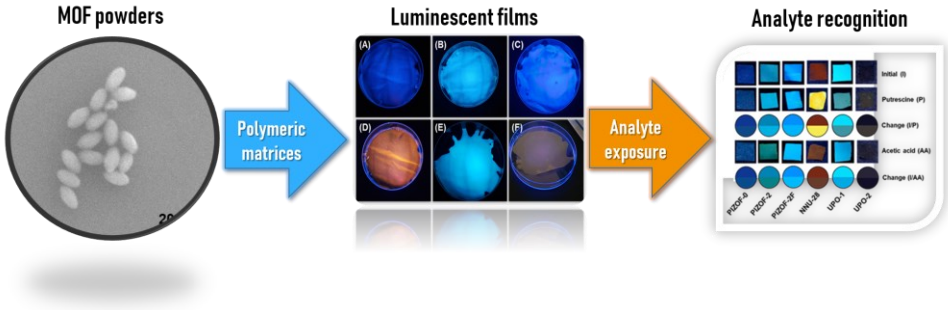
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Keywords: *Metal-organic frameworks, Polymeric Films, Photoluminescence, Absorbance, Sensor*

In this contribution, we present the exceptional sensing capabilities of tailor-designed metal-organic frameworks as active materials in optically functional thin films. These coordination polymers are either directly immobilized as thin films or embedded in optically inert polymeric matrices to create advanced sensing devices for gaseous analytes. Matrices such as polydimethylsiloxane (PDMS) and polyvinylidene fluoride (PVDF) offer mechanical stability and preserve the optical properties of the MOFs, making them ideal platforms for sensing applications. Among the materials explored, luminescent metal-organic frameworks (LMOFs) with selective sensitivity to target analytes are particularly promising. For example, post-synthetically Cd^{2+} modified ZIF-8 nanocrystals, integrated into PDMS films, have demonstrated selective detection of hydrogen sulfide [1]. Similarly, trimetallic 2D rare-earth LMOFs (RE = Y, Eu, Tb) with emission bands spanning across the visible spectrum [2] and Porous Interpenetrated Zr-Organic Frameworks (PIZOFs) featuring chemically functionalized linkers [3], have been embedded in PVDF films to produce image-based recognition patterns for a variety of volatile organic compounds (VOCs), highlighting their versatility as multi-responsive gas sensors. In parallel, porphyrinic MOFs have been effectively employed for colorimetric sensing. Specifically, nanosized PCN-223 crystals incorporated into PDMS films [5], as well as M-TCPP MOF nanosheets (NAFS) assembled at the air-water interface, enable multi-analyte recognition through absorbance-based responses without light scattering in the sensor array. Unlike conventional solution-based methods, the use of solid-state MOF films supports the development of miniaturized devices incorporating LED–CCD/CMOS technology, allowing precise gas detection with reduced interference. This approach significantly expands the application potential of MOF-based sensors across a wide range of environments and practical scenarios.



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LUMINESCENT MOFS FOR FLUOROCHROMIC DETECTION OF MULTIPLE EXTERNAL STIMULI

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Keywords: *Luminescent MOFs, Photophysics, Proton-Transfer, External Stimuli Detection*

Metal-organic frameworks (MOFs), a class of porous crystalline hybrid organic-inorganic materials, have emerged as one of the most significant materials in the last two decades.[1] Their exceptional physicochemical properties have enabled their integration into a wide range of applications and technologies. A notable subclass of MOFs, known as luminescent MOFs (LMOFs), is distinguished by its ability to emit light and has demonstrated great potential for advanced photonic applications, such as light-emitting diodes (LEDs) and luminescent sensors.[2] Beyond the intrinsic emission properties of LMOFs, their accessible porosity provides a platform for encapsulating a diverse array of luminescent compounds.[3] This offers several advantages including the mitigation of aggregation-induced quenching in certain dyes — thereby enhancing their luminescent quantum yield — and the ability to modulate the emission color as well as their sensing capabilities.

Herein we present the synthesis, structural characterization, steady-state, and photodynamics properties of different LMOFs, in which proton-transfer or charge-transfer dyes are part of the MOF (as organic linkers) or encapsulated within the pores of the material. Then, we have proved the potential of these materials to detect different chemical (vapors of toxic acid and base compounds) and physical (changes in temperature and applied uniaxial pressure) external stimuli. For instance, we encapsulated for the first time two different proton transfer dyes within the pores of two well-known MOFs, ZIF-8 and UiO-66. By a combination of steady-state and photodynamics characterization, we proved that both molecules are encapsulated as anions in the ZIF-8 and as the enol tautomer in the UiO-66 MOF. Their interaction with HCl (acid) or Et_3N (base) vapor induces a change in the emission color of these materials (Fig. 1a). The detection mechanism was unveiled by time-resolved emission spectroscopy measurements. We also fabricated another LMOF using 2,5-dihydroxyterephthalic acid (DHT) as the organic linker and proved its potential for detecting multiple external stimuli (Fig. 1b). These results may open a new avenue for the development of more efficient LMOF-based sensors.

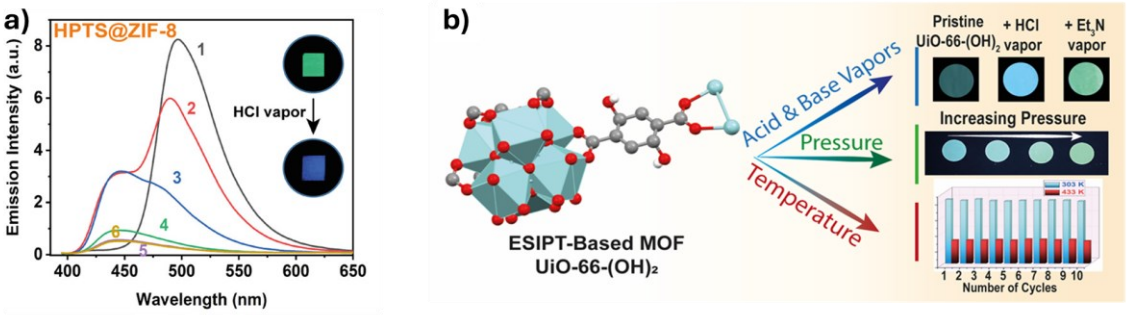


Figure 1. a) Emission spectra of HPTS@ZIF-8 after different times of exposition (1 = pristine material, 6 = 30 min) to a saturated atmosphere of HCl. b) Schematic illustration of the fluorochromic detection capabilities of UiO-66$(OH)_2$ MOF in response to multiple external stimuli.

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THIAZOLE-, THIOPHENE- AND SELENOPHENE-CONTAINING ZIRCONIUM MIXMOFs AS LUMINESCENT SENSORS AND ADSORBENTS OF PERSISTENT ORGANIC POLLUTANTS IN WASTEWATER

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Keywords: *Thiazole, selenophene, thiophene, zirconium, mixed-linker MOFs, wastewater treatment, luminescence sensing, adsorption*

Access to safe water, sanitation and hygiene is the most basic human need for health and well-being. The increase in concentration of Persistent Organic Pollutants (POPs) in waters around the globe is a problem that should be urgently addressed to avoid the possibility of adverse effects on health and the environment. The ideal material for water remediation should combine high POPs adsorption capacity and sensitive light-responsive behavior for selected contaminants. Due to the vast library of nodes and spacers conceivable, MOFs show exceptional chemical and structural versatility combined with permanent porosity and represent the ideal materials for this task.[1] While MOFs featuring fully carbocyclic spacers are ubiquitous, much fewer examples are found with (N,S,Se)-containing heterocycles like thiazole, thiophene and selenophene. These are electron-deficient (thiazole) or electron-rich (thiophene, selenophene) systems bearing a basic sp^2-N atom and a sp^3-hybridized S/Se atom; they are intrinsically fluorescent[2] and they can be found in several naturally occurring biomolecules like luciferin (the active component generating luminescence in fireflies). Some representative examples of Zr^{IV} mixed-linker MOFs decorated with tailored heterocyclic linkers will be presented, along with their exploitation in the field of luminescence sensing and adsorption of Ibuprofen Sodium, Diclofenac Sodium and PFAS in wastewaters (Figure 1).[3,4]

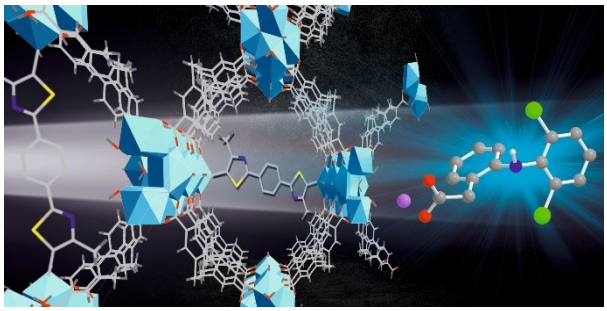


***Figure 1**. Diclofenac Sodium adsorption by [**TzPhTz^{Me}**@PCN-700]. From reference [4].*

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RARE EARTH MOFS IN POTENTIAL CANCER THERAPIES

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Keywords: *rare earth, adsorption, metal organic framework, drug uptake*

Although mostly studied for their gas capture and catalytic properties, metal organic frameworks exhibit remarkable qualities as a potential new generation of drug delivery systems. The intrinsic porosity and ability to adsorb drugs at greater drug loading capacities than comparable technologies, whilst also demonstrating unparalleled tunability, has made many researchers consider therapeutic uses of MOFs.[1]

We have explored the realm of rare earth (RE) MOFs with a view to using them as a delivery vehicle for FDA approved frontline anticancer drugs. The high magnetic moments within RE-MOFs provide a high contrast for magnetic imaging techniques, potentially providing a direct mechanism by which to view the precise location of drug release in vivo. A study of drug loading using 4 different anticancer drugs was found to deliver a high drug loading capacity of up to 29% w/w, across families of different RE-MOF structures.

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ENVIRONMENTAL REMEDIATION AND RATIONAL USE OF MOFS IN AGRICULTURE

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Keywords: *Water purification, Water decontamination, Agrochemicals, Pesticides*

The convergence of population growth and climate change threatens food security on a worldwide scale. Current trends in population growth suggest that global food production is unlikely to satisfy future demand as predicted. In order to accomplish these significant objectives, the use of agrochemicals (fertilizers, pesticides, plant hormones, etc.) becomes inevitable to ensure quality and high yields. However, their intensive application has resulted in the deterioration of ecosystems. making necessary to develop more efficient and less toxic methods against pests and infections, while improving crops productivity. Importantly, large quantities of agrochemicals do not reach their intended objectives due to application practices (between 10-75% do not reach their target) and their widespread use, contributing to the deterioration of ecosystem quality, adversely affecting the health of living beings, water and soil.

Among the novel technologies considered, Metal-Organic Frameworks (MOFs) appeared as innovative and promising materials for environmental applications.[1] In this regard, MOFs can be used in water treatment or in the controlled release of agrochemicals. For example, in agriculture, we take a further step and use organic agrochemicals as linkers in the preparation of MOFs, what we have called AgroMOFs (Figure 1). Through this original strategy, we aim to achieve a controlled agrochemical delivery and enhance crop production and quality, while reducing contamination.[2] All these studies evidenced the potential of MOFs in agriculture without damaging our environment.

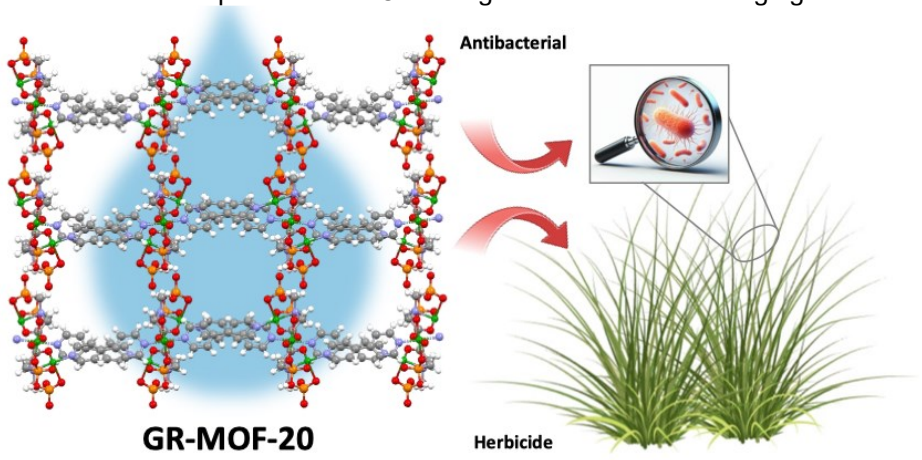


Figure 1. GR-MOF-20 based on Cu^{2+} and glyphosine, and its dual effect as antibacterial and herbicidal agent.

Acknowledgments

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UNLOCKING THE POTENTIAL OF PHYSISORPTION FOR DIRECT AIR CAPTURE VIA THE PRISMA PLATFORM

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Keywords: *Direct Air Capture, physisorbents, MOFs, holistic approach*

Direct Air Capture (DAC) technologies are essential for achieving global net-zero carbon targets, yet current systems predominantly rely on chemisorption, which poses challenges due to high energy requirements and material degradation. Physisorption, in contrast, offers advantages such as lower regeneration energy and potential scalability, but suffers from weak CO_2 binding at atmospheric concentrations, limiting its standalone viability. This work investigates the potential of physisorption for DAC by adapting the PrISMa (Process-Informed design of tailor-made Sorbent Materials) platform—a holistic framework integrating material simulations, process modeling, techno-economic analysis (TEA), and life-cycle assessment (LCA)—to the DAC context.[1]

We assess the limitations of physisorbents under ultra-dilute CO_2 conditions. By simulating a wide range of metal–organic frameworks and other porous materials, we find that when integrated into a desiccant unit, they can approach or even outperform chemisorbents on key performance indicators such as net carbon avoidance cost (nCAC), energy efficiency, and environmental impact.

Furthermore, using machine learning within PrISMa enables rapid screening and iterative refinement of candidate materials based on DAC-specific targets. Our findings indicate that with careful design and system-level integration, physisorption can emerge as a competitive alternative for DAC, particularly in scenarios where sustainability and modular deployment are prioritized. This study underscores the power of combining advanced chemical engineering with data-driven material selection to accelerate the development of next-generation carbon removal technologies.

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2.5-DIMENSIONAL COVALENT ORGANIC FRAMEWORKS: THE STRUCTURE AND SUPERIOR CO2 CAPTURE PROPERTIES

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Keywords: *COFs, new geometry, CO_2 capture, substoichiometric, thermodynamics*

Covalent organic frameworks (COFs) have been classified into 2-dimentional (2D) and 3-dimentional (3D) subclasses. Overall, the definition of 2D-COF is those made from building block monomers that have (i) a "linear or planar" conformation[1,2] and (ii) a shape that is geometrically expected to cause two-dimensionally extending network, generating "stacked layer" material with "1D pores"[1,2]. The definition of 3D-COF is those made from monomers with "connectivity in three dimensions," achieved typically using nonplanar monomers with tetragonal (T_d) symmetry[1-3], forming 3D network and "granular" material; 3D-COFs have either 1D or 3D pores depending on the case[1-3].

Herein, we report a new geometrical type that do not follow the above definitions of 2D and 3D COFs (Fig. 1). We call them 2.5D-COFs based on the following reasons: These COFs are made using a monomer with T_d symmetry (Fig. 1a), from which formation of 2D network is not expected. These COFs are made by "connectivity in three dimensions," but generated 2D network and "stacked layer" material (Fig. 1b-e). These COFs do not have 1D pores. Therefore, such COFs do not match present definitions of 2D- and 3D-COFs; we thus propose to call such intermediate structure 2.5D-COFs.

The 2.5D-COFs are sub-stoichiometric COFs (ss-COFs), but the distinct difference from existing ss-COFs is that, in our COFs for which we used tetrakis(4-aminophenyl)methane (**TAM**) as a tetrahedral monomer, all unreacted amines (-NH_2) of **TAM** point normal to the network plane, *i.e.*, to the third dimension[4] (Fig. 1b-d). Notably, owing to the ultrahigh-density primary amines (> 4×10^5 μm^{-2} $layer^{-1}$) regularly set in the 3D pores, these COFs exhibited high CO_2/N_2 selectivity, very low heat of adsorption (*ca.* 25 kJ mol^{-1}) (Fig. 1f), high thermal stability in air (to 300 °C), and fast CO_2 adsorption rate (equilibrium time < 10 s)[4], which are superior properties as solids to capture and separate CO_2.

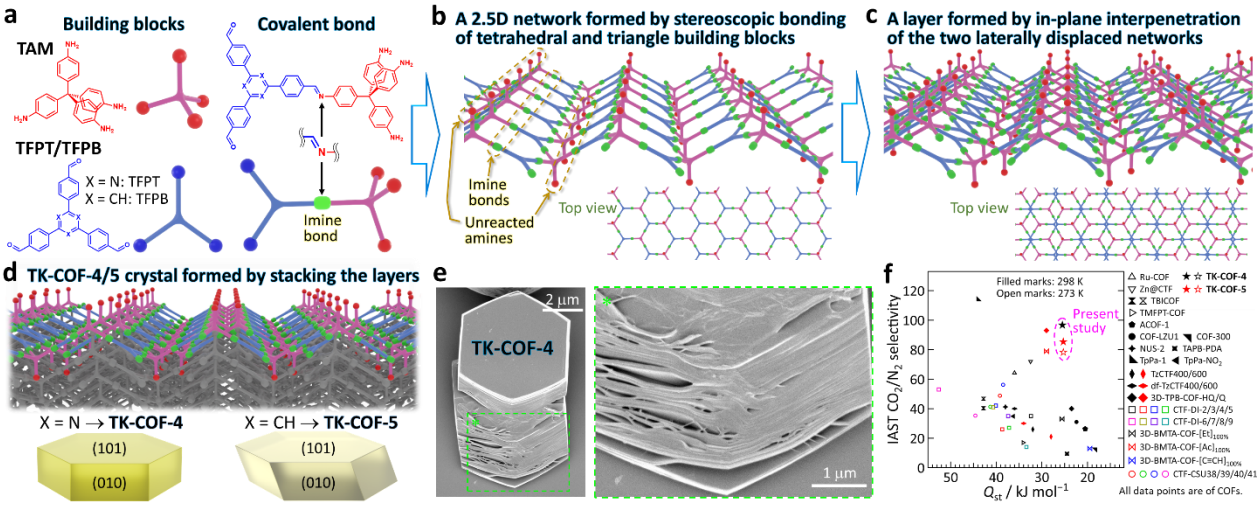


Figure 1 (a) Monomers used, (b-d) schematic of the 2.5D-COFs, (e) SEM image, (f) CO_2/N_2 selectivity *vs.* CO_2 adsorption heat.

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IN-SITU INVESTIGATION OF WATER HARVESTING BY CAU-10-OH METAL ORGANIC FRAMEWORK: A 2-STEPS PROCESS

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Keywords: *water harvesting, In-situ XRD, relative humidity*

MOFs exhibits interesting harvesting water capabilities from the air or as heat pumps as they demonstrate a steep increase in water uptake in the range 10-30 RH%[1]. Optimal water isotherms are represented by an alternation of moderately hydrophilic and hydrophobic sites. However, even within MOFs exhibiting such alternation, the required steep uptake of water relevant for real applications is quite scarcely met[2]. Recently, we have studied the CAU-10-X (H = H, CH_3) members and unravelled the materials' structural deformation and water ordering during absorption[3]. We have shown that the steric hindrance of the -CH_3 group lowers the number of average hydrogen bonds from 3.3 to 2.3 explaining the difference in the water uptake behavior.

Among the various members of the CAU-10-X family, X = OH is particularly interesting as this is the only composition where a steep 2-step process is taking place within the isotherm[2]. Aiming to determine a conceptual understanding of the mechanism resulting from this water absorption to design "de novo" water harvesting materials, we have investigated the members X = OH using in-situ relative humidity powder diffraction. We present in Fig. 1 our results for X = OH. These results demonstrate for the first time the existence of an intermediate phase.

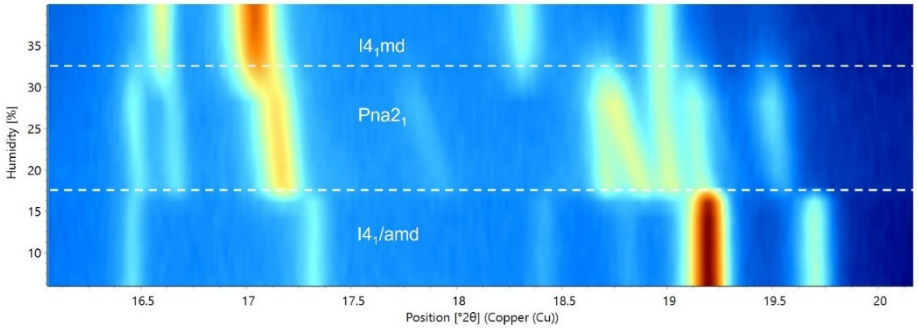


Figure 1: In-situ relative humidity study of CAU-10-OH carried out at T = 60°C

The existence of this intermediate phase stabilized under temperature and moderate RH shed some new light in our understanding and call for further investigation of the water uptake mechanism. The possibility to stabilize and study an intermediate phase enables us to have further understanding of the water uptake mechanism.

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CRYSTAL ENGINEERING OF AZOLATE COORDINATION NETWORKS FOR CLEANING AIR AND FRESHWATER

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Keywords: *coordination network; transient porosity; crystal engineering; air purification; freshwater*

State-of-the-art for commodity purifications, *i.e.*, cleaning commodity chemicals, air, and freshwater is highly energy-intensive. Traditional physisorbents, including zeolites, and > 100,000 metal-organic frameworks (MOFs, composed of organic ligands) can reduce this energy footprint, but are limited by cost, performance and/or stability issues.[1] To address this, our group is developing a new class of energy-efficient azolate coordination networks, ACNs, that feature *the best of both Worlds*: A) inorganic ligands and azolates-derived hybrid compositions (composed of inorganic ligands) that offer electrostatically strong binding sites for gas sorbates like carbon dioxide and light hydrocarbons (*e.g.*, acetylene, propyne); B) ultramicropores, *i.e.*, narrow pore sizes < 0.7 nm, ideal for tightly binding to the foregoing sorbates of relevance.[2] Amenability to bottom-up design approaches along both aspects, following the first principles of crystal engineering is found to deliver (and control) several high-volume gas and freshwater purifications. Specifically, harnessing transient porosity to elicit temperature-independent microporosity to CO_2 *vs.* temperature-dependent microporosity to C_2H_2 has been identified.[3] The (partly unpublished) findings, reinforced by solid-state ^{13}C CP/MAS NMR data and molecular dynamics results, establish azole-pyridyl bifunctional ligands' versatility in the crystal engineering of azolate coordination networks.

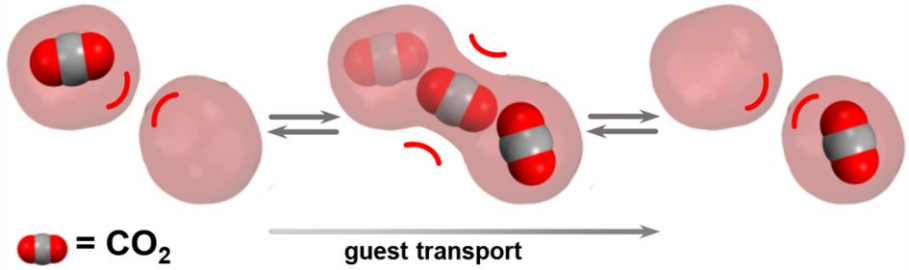


Figure 1: Porosity “without pores”: we uncover a crystal engineering strategy with potential to enable the design of transient porosity in an array of underexplored coordination networks.[3]

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DESIGN OF A MOF FEATURING AN ALIPHATIC CARBOXYLATE LINKER FOR LITHIUM-ION TRANSPORT IN SOLID-STATE BATTERIES

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Keywords: *Ion conductivity, Solid State Electrolytes, Aliphatic linkers, Lithium-ion transport, Energy storage*

Aliphatic carboxylate linkers remain a relatively underexplored class of building blocks in the design of metal-organic frameworks (MOFs), despite their potential to introduce dynamic behavior and structural adaptability.[1,2] In contrast to aromatic linkers commonly employed in MOF synthesis, aliphatic linkers offer segmental flexibility, enabling conformational rearrangements that can promote ion transport.[3] This molecular flexibility supports the formation of continuous ion-conduction pathways and tunable pore environments, both critical for enhancing ionic mobility in solid-state electrolytes. In this work, we report the synthesis and characterization of a coordination polymer constructed from 1,2,3,4-butanetetracarboxylic acid (BTCA), an aliphatic tetracarboxylic acid featuring a flexible, saturated four-carbon backbone. The combination of multiple coordination sites and molecular flexibility enables the formation of a framework that supports efficient lithium-ion transport, demonstrating its promise as a solid-state electrolyte for lithium battery applications. This study highlights the promising potential of aliphatic linkers to expand the design space of functional MOFs for energy storage technologies and beyond.

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COST-EFFECTIVE HYBRID DFT METHODS TO ADDRESS SIZE AND COMPLEXITY IN METAL-ORGANIC FRAMEWORKS

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Keywords: *modeling giant MOFs, hybrid DFT, cheap sol-3c methods*

The chemical versatility and modular nature of Metal–Organic Frameworks[1,2] (MOFs) make them unique materials for a wide range of possible applications[3-10]. However, from a computational view point, ab initio modeling of MOFs is a challenging and demanding task, in particular, when the system reaches the size of giant MOFs as MIL-100 [11] and MIL-101[12] with several thousand atoms in the unit cell. Here, we show how such complex systems can be successfully tackled by a recently proposed class of composite electronic structure methods revised for solid-state calculations [13]. These methods rely on HF/density functional theory hybrid functionals (i.e., PBEsol0, HSEsol and r2SCAN0) combined with a double-zeta quality basis set. They are augmented with semi-classical corrections to take into account dispersive interactions (D3 scheme[14]) and the basis set superposition error (gCP[15]). The resulting methodologies, dubbed “sol-3c,” are cost-effective yet reach the hybrid functional accuracy. Here, sol-3c methods, implemented in the CRYSTAL code[16], are effectively applied to predict the structural, vibrational, electronic, and adsorption properties of some of the most common MOFs. Calculations are feasible even on very large MOFs containing up to 3700 atoms in the unit cell as MIL-100 and MIL-101, with small-scale computing resources (e.g. 80 cores). We propose to use our composite methods for the routine In Silico screening of MOFs targeting properties beyond plain structural features.

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INVESTIGATION OF MOF MECHANICS WITH BRILLOUIN LIGHT SCATTERING AND MACHINE LEARNED INTERATOMIC POTENTIALS

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Keywords: *MOF mechanics, spectroscopy, machine-learned potentials, structure-to-property relationships, elastic moduli*

Due to their open framework architecture combined with the flexibility of their building-units, MOFs are substantially more mechanically compliant than conventional inorganic materials. The low elastic moduli of (activated) MOF structures make them particularly susceptible for structural collapse under applied pressures [1]. As such a structural collapse can cause gradual degradation of performance over time, it is clear that a fundamental understanding of structure-to-mechanical-property relations are of crucial importance for virtually any practical application of MOFs.

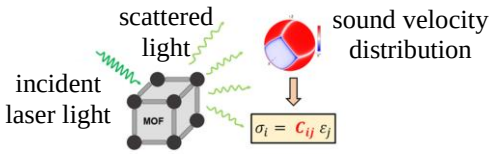


Figure 1. Measurement principle in Brillouin experiments to determine the full elastic tensors from direction dependent sound velocities.

From an experimental point of view the mechanical properties of MOFs are typically characterized using (powder) X-ray diffraction (PXRD) or indentation methods. However, these methods are either lacking the ability of giving insights into direction dependent mechanical properties or are prone to errors when the anisotropy of the probed samples is not correctly accounted for. In stark contrast, Brillouin light scattering (BLS) [2] is a promising optical and completely non-invasive method that allows the measurement of directionally dependent sound velocities in not too opaque materials. These correspond to the group velocities of ultra-low frequency acoustic phonons, from which the full elastic tensor of the sample under scrutiny can be derived, see Figure 1. For MOFs this was first demonstrated in the seminal work of Tan et al. [3]. From the elastic tensor, the full elastic behavior of the studied sample can be derived, including, e.g. the directionally dependent elastic moduli. In this contribution we demonstrate how a tight combination of BLS experiments and simulations, namely state-of-the-art DFT calculations and machine learned interatomic potentials (MLIPs) [4] can be used to investigate mechanical properties of MOFs [5]. We demonstrate how insights from simulations on various levels of theory can help to interpret spectra obtained from as-synthesized single MOF crystals, which are often comparably small in size and, thus, limit the range of accessible experimental data. For the investigated Zn-based MOF GUT-2 this allows the determination of values for the components of the elastic tensor in the cubic approximation to be C_{11} = 18.4 GPa, C_{12} = 12.7 GPa and C_{44} = 5.2 GPa from which Young's modulus were calculated to be 11.2 GPa. These experimentally determined values are in excellent agreement with the results obtained from our simulations and allow us to immediately characterize the investigated MOF as a more rigid system compared to other well-studied systems like MOF-5 or HKUST-1.

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EXPERIMENTAL VALIDATION OF A MULTI-SCALE SIMULATION MODEL FOR OPTICAL PROPERTIES OF CHIRAL SURMOFS

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Keywords: *Chiral SURMOF, Infrared spectroscopy, multiscale workflow*

Surface-Anchored Metal-Organic Frameworks (SURMOFs) were developed to offer reproducible and homogenous deposition of MOFs on solid substrates. Good adhesion to the substrate can be achieved with adequate surface functionalization and crystallinity and thickness of the SURMOFs can be controlled by varying the growth parameters [1].

Among SURMOFs, the ones with chiral linkers have recently attracted interest for their potential in enantioselective separation and sensing [2]. Given the demand for high-efficiency enantiomer recognition in pharmaceutical and food industries, understanding and optimizing the optical properties of chiral SURMOFs is crucial for their application in this field. Advanced theoretical models can help guiding experimental efforts efficiently, since they can help predict optical properties and streamline material design. However, for these theoretical models to be reliable, their predictions must be validated against experimental data.

We present here the validation of a multi-scale modeling approach to simulate the optical properties of the chiral SURMOFs of Cu- and Zn-camphoric acid-Dabco, through experimental comparison [3]. The model spans multiple length scales, from single-unit-cell simulations to thin-film modeling. A comprehensive set of optical characterizations - including infrared reflection and transmission measurements and electronic circular dichroism (ECD) - were conducted and compared with theoretical results. To confirm the orientation-dependent IR response predicted by the simulations, infrared scattering-type near-field optical microscopy (IR-SNOM) was employed. The agreement between model and experiment demonstrates the accuracy of the approach and highlights its potential for accelerating the design of chiral SURMOFs for enantioselective applications.

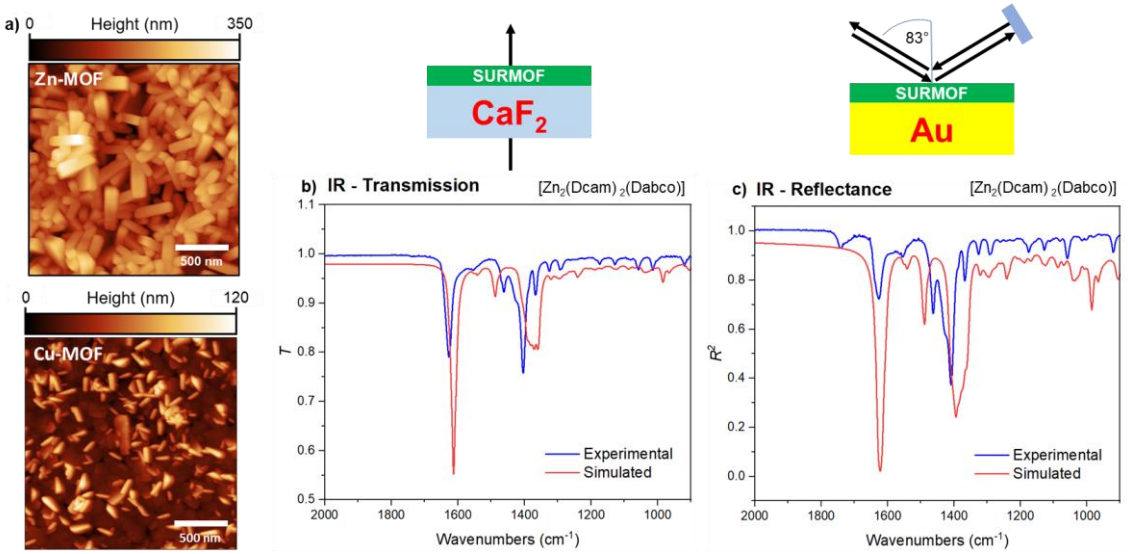


Figure 1: a) AFM images of both SURMOF films; Comparison of experimental and simulated IR spectra in b) Transmission and c) Reflectance modes

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DEVELOPMENT OF TWO-COMPONENT LIQUID-PHASE ADSORPTION SIMULATION OF DRUG ADSORPTION IN MOFS

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Keywords: Liquid-phase adsorption, Monte Carlo simulation, Drug adsorption, *Chemical potential*

Introduction

Metal–organic frameworks (MOFs) are expected to be used as carriers for drug delivery systems (DDSs). Drugs adsorption in MOFs is necessary to utilize MOFs as a drug carrier. Drugs are generally adsorbed in MOF pores by stirring MOF particles and drugs in solvent [1]. It is essential to identify the involved mechanism of drug adsorption in MOFs. Our previous study investigated the effects of solvent-induced interactions on drugs loading capacity of MOFs [2]. For further investigation of the drug adsorption mechanism in liquid-phase, the molecular simulation should be effective. Although simulation of the adsorption of various drugs on MOFs has been performed [3], it has been quite difficult to obtain calculation conditions and adsorption amounts that are consistent with experimental results. Therefore, in this study, we developed a simulation method that can simulate two-component liquid-phase adsorption using Monte Carlo simulation. The interaction among MOF, drug, solvent, radial distribution function, and adsorption site of drug were analyzed in detail.

Simulation details

The present study combined canonical Monte Carlo (CMC) and grand canonical Monte Carlo (GCMC) methods to simulate two component liquid-phase adsorption of drug and solvent to MOFs. We selected UiO-66 series as model MOFs and 5-fulorouracil (5FU) as a model drug. For GCMC calculations, the chemical potential or fugacity of each component in liquid-phase adsorption should be determined. First, the Widom insertion method was performed with a CMC method using only drug and solvent in a box. The conditions such as the number of drug/solvent, box size, and temperature were corresponded to conditions at experimental adsorption equilibrium. The excess chemical potentials $\mu_{ex,i}$ and fugacity, f_i, of each of the drug and solvent were calculated from Eqs. (1), (2).

$$\mu_{ex,i} = -k_B T \ln\langle W_{r,i}\rangle \quad (1)$$

$$f_i = \frac{W_{I,i} k_B T N_i}{V\langle W_{r,i}\rangle} \quad (2)$$

$W_{r,i}$, $W_{I,i}$, k_B ,T, and N_i are the Rosenbluth factor of the system, the Rosenbluth factor of the ideal gas, Boltzmann's constant, the temperature of the system, and the number of particles in the system, respectively. The obtained fugacity of drug and solvent were set to performe GCMC simulations. The LJ potential and Coulomb potential were employed for the atomic interactions. The CMC-GCMC simulation were performed and The LJ interaction parameters ε_{MOF} were modified in range of 0.5-1.5 to obtain the experimental values for 5FU adsorption in UiO-66s.

Results and discussion

In CMC simulation, $\mu_{ex,5FU}$ = −65.39 and $\mu_{ex,EtOH}$ = −12.83 kJ/mol were obtained using Eqs. (1), (2) in case of ethanol solvent. GCMC simulations were performed with the fugacity calculated from the μ_{ex}. The adsorption amount of 5FU tended to increase as ε_{MOF} increased. For ε_{MOF} = 0.75, the adsorption amount of 5FU in CMC-GCMC was almost the same as the experimental adsorption amount of 5FU. Density distribution analysis suggested that 5FU molecules were more likely to be stabilized in the large octahedral pores than in the small tetrahedral pores of UiO-66s. Furthermore, based on radial distribution function, it was suggested that 5FU molecules were localized in the MOF pores while solvent molecules were widely distributed. These results supported the presence of adsorption sites in density distribution analysis.

Conclusion

In this study, CMC-GCMC simulation method was developed to correspond liquid-phase adsorption. It was suggested that the adsorption amount of 5FU in the experimental values in various solvents were reproduced. This methodology could be adapted to liquid-phase adsorption of various other solvent/drug/MOFs systems.

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DECODING WATER SORPTION IN MOFS: SINGLE-CRYSTAL INSIGHTS FROM SPECTROSCOPY AND MODELING

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Keywords: *in-situ vibrational spectroscopy, host-guest interaction, water harvesting*

Climate-induced droughts are becoming an increasing problem worldwide. Water harvesting from the atmosphere using metal-organic frameworks (MOFs) has emerged as a promising solution to access clean drinking water, particularly in arid regions. In this process, MOFs act as local concentrators of water molecules, facilitating their phase transition from gas to liquid. While the role of the crystal structure in MOFs' performance has been well-studied, the influence of particle morphology and composition on water uptake and release is less understood. However, understanding how intrinsic properties such as defect density, metal composition, and guest molecules affect water sorption behavior in MOFs is challenging due to the complex interactions at the single-particle level, frequently suffering from polycrystalline regions, defects, and inter-crystalline adsorption. Conventional characterization methods overlook these microstructural variations, leading to incomplete or misleading conclusions about the material's true potential.

To address these challenges, we employed our recently developed MOSAIC imaging system, which enables high-resolution *in-situ* characterization.[1] This multi-modal system combines space-resolved Raman and fluorescence spectroscopy with advanced nonlinear imaging techniques, enabling us to investigate local water uptake and release within MOFs.[2] Correlating Raman mapping with Four-wave mixing and coherent Raman imaging we can localize, quantify, and monitor the uptake and distribution of guest molecules inside the framework. In this contribution,[3] we discuss how metal substitution in MOF-801 and MOF-808 influences water uptake, kinetics, and long-term stability. Using MOSAIC in combination with NMR and DFT calculations, we disentangle how residual guest molecules, metal composition, and defects modulate the material's water adsorption behavior.

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TUNING ADSORPTION-INDUCED BREATHING: HOW FLUORINATION REDEFINES FLEXIBILITY IN MIL-53(Al)

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Keywords: *adsorption-induced flexibility, breathing, MIL-53(Al), fluorination, in situ characterization*

The dynamic response of MIL-53-type Metal-Organic Frameworks (MOFs) has inspired extensive research into flexible porous materials.[1] In this work, we present the first comprehensive *in situ* characterization of a fully perfluorinated variant of MIL-53(Al), synthesized via a green, solvent-free route.[2] Despite retaining the archetypal MIL-53(Al) topology, F_4-MIL-53(Al) exhibits a profoundly different adsorption-driven flexibility due to the presence of four fluorine atoms on the organic linker. By integrating *in situ* powder X-ray diffraction (PXRD), *in situ* infrared spectroscopy (IR), *in situ* solid-state NMR (SSNMR), and gas adsorption measurements, we have disclosed the complex, multi-step phase transitions (*np* → *lp'*→ *lp*, Figure 1-left) of F_4-MIL-53(Al) upon exposure to different gas molecules (H_2O, CO_2, CO, Ar, N_2). Notably, water adsorption does not induce contraction, as in hydrogenated MIL-53(Al), but rather a two-step expansion, with a very low uptake (<1 mmol/g till to 60% relative humidity), revealing a drastic alteration in host–guest interactions caused by per-fluorination. Most intriguingly, CO_2 adsorption triggers a reversible breathing process, including an unexpected phase transition, followed by the appearance of a second large-pore phase at higher CO_2 pressures, suggesting the existence of multiple intermediate states (Figure 1-right). These transitions are not observable via *ex situ* techniques, demonstrating the necessity of our *in situ* approach to fully capture the dynamic nature of flexible MOFs. To further explore the effect of fluorination on flexibility a set of F_x-MIL-53(Al) (x<4) are also synthesized and characterized, discovering how the number and position of fluorine atoms on the aromatic ring significantly affect the breathing behavior. Our findings underline the profound impact of fluorination on framework flexibility and adsorption properties of MIL-53(Al), offering new insights into the structure-property relationships governing MOF dynamics and opening new directions for the rational design of next-generation flexible materials with tailored adsorption responses.

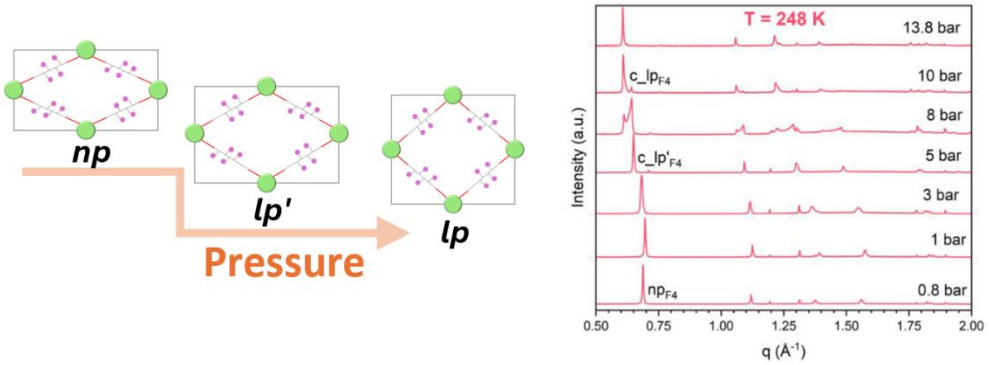


Figure 1. Left. Multi-step phase transitions of F_4-MIL-53(Al): narrow pore (*np*), intermediate large pore (*lp'*), large pore (*lp*). Right. *In situ* PXRD patterns of F_4-MIL-53(Al) during CO_2 adsorption at 248 K.

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CHEMICAL-ENGINEERING OF THE BREATHING-CALORIC EFFECTS IN MOFS: SOLID TRANSITIONS, GAS ADSORPTION AND HYDROGEN-BONDING

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Keywords: *eco-friendly refrigeration, breathing-caloric effect, functionalization, phase transitions*

In the last years, MOFs have emerged as a very promising family of materials for eco-friendly refrigeration and heating.[1] Recent reports have found very large thermal changes associated with breathing transitions –named as "*breathing-caloric*" effects–, which are of great interest for thermal management technologies. This effect has been studied in depth for MIL-53(Al)[2] and MOF-508b[3] demonstrating thermal changes similar to those of refrigerant gases used in conventional heating and cooling applications, without the environmental hazards associated with these traditional refrigerant gases.

In these first studies, the breathing-caloric effect was attributed to a combination of thermal changes due to the solid-solid phase transition and to CO_2 sorption processes.

Now, in this work we explore the **functionalization of MOFs as a key tool for understanding the fundamental origins and enhancing the caloric response**. We study different MOFs with different functional groups onto the organic linkers, so the caloric effects can be rationally tailored, attending to the thermal contribution of the CO_2 sorption, to the thermal contribution of the volume change of the solid-solid phase transition, and also to thermal contributions of hydrogen-bonding and π–π stacking, two new contributions that had not been explored yet in the pressure-induced caloric effects. With these studies we seek to establish structure-property relationships that will enable the rational design of MOFs with enhanced thermal responses for more efficient and environmentally friendly climate control applications.

In summary, we found that the functionalization of MOFs can be a powerful strategy to tune their thermal and caloric properties, and also to understand these changes as crucial aspect towards the chemical-engineering of breathing-caloric effects.

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IN-SITU TEM INVESTIGATION OF PHASE TRANSITIONS IN ZEOLITIC IMIDAZOLATE FRAMEWORKS UNDER WORKING CONDITIONS

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Keywords: Zeolitic Imidazolate Frameworks, TEM, Diffraction, in-situ heating.

Zeolitic imidazolate frameworks (ZIFs), have garnered significant attention due to their promising applications in gas separation and catalysis. To gain crucial insights into their chemical behavior and performance, in-situ transmission electron microscopy (TEM) has proven to be a powerful tool for studying the structural evolution of ZIFs under operating conditions. However, investigating these delicate soft materials using TEM is challenging due to the potential radiation damage caused by the high-energy electron probe.

In our study, we systematically examined the stability and phase transformations of ZIFs under various temperature and gas environments using advanced in-situ environmental TEM techniques. Initially, we assessed the stability of ZIF crystals under electron beam exposure by measuring the attenuation of relative intensities in Bragg planes over time as a function of the total electron dose applied. We established a critical electron dose threshold of 30 $e^{-}Å^{-2}s^{-1}$ at room temperature for ZIF-8 and ZIF-L [1]. Exceeding this critical dose during any TEM experiment results in electron-beam-induced structural degradation. Additionally, we investigated the effect of elevated temperatures and found that ZIF-L undergoes structural collapse and amorphization at temperatures above 550°C. Using energy-dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS) mapping in scanning TEM (STEM), we tracked changes in composition and chemical state.

We further investigated the pyrolysis of ZIF-L at temperatures between 700°C and 1100°C to establish structure-property correlations for its performance in the oxygen reduction reaction (ORR). We discovered that nitrogen-doped graphitic carbon, formed during pyrolysis, is a key factor in enhancing the properties of pyrolyzed ZIF-L.

Moreover, we explored the stability of ZIF-8 in an oxygen atmosphere. Under 2.7 mbar O_2 pressure and temperatures ranging from 350°C to 550°C, we observed the transformation of ZIF-8 into ZnO nanoparticles, identified by contrast changes in TEM bright-field images and confirmed by selected area electron diffraction (SAED) patterns.

Our comprehensive study demonstrates the effectiveness of in-situ TEM techniques in elucidating structure-property relationships, overcoming the challenges associated with electron-beam experiments on beam-sensitive MOFs. Our findings provide valuable insights into the behavior of ZIFs under realistic operating conditions and contribute to the development of more efficient and stable MOF-based and derived materials for various applications.

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EXPLORING THE REVERSIBLE DYNAMICAL BEHAVIOUR OF NANOCRYSTALLINE INTERPENETRATED DIAMONODOID METAL-ORGANIC FRAMEWORKS

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Keywords: *Pollutant Removal, Mechanochemistry, Dynamic Behaviour, 3D Electron Diffraction*

Metal-Organic Frameworks (MOFs), hybrid organic-inorganic crystalline materials formed by the self-assembly of metal ions or clusters coordinated with organic linkers, have earned significant attention due to their exceptional tunability, large surface area, and potential for applications in various fields, including gas storage, catalysis, drug delivery, environmental remediation, energy storage and water purification.[1]

MOFs are typically synthesized via solvothermal reactions; however, more environmentally friendly methods to avoid the massive use of organic solvents are desirable. In this respect, Mechanochemistry has emerged as a promising green alternative, as it minimizes solvent consumption and excess reagents while enabling the formation of unique phases or structures that are difficult or impossible to achieve via conventional methods.[2]

In this study, we report the mechanochemical synthesis of a highly interpenetrated MOF with a diamond-like network, achieved by combining the TPPM (tetra-4-(4-pyridil)phenylmethane) linker with Cu(II) paddle wheels or discrete octahedral complexes as metal nodes.[3] Due to challenges in growing large single crystals, 3D electron diffraction (3D ED) analysis was crucial for the structural elucidation of the nanocrystalline materials. This characterization, combined with powder X-ray diffraction analysis, allowed us to identify both open and closed pore forms of the frameworks. The MOFs thus obtained, which show a dynamic behaviour (Figure 1), were further functionalized by introducing specific secondary building units (SBUs) to investigate their effects towards the absorption of fluorinated volatile anaesthetics (VAs) and per- and polyfluoroalkyl substances (PFAS).

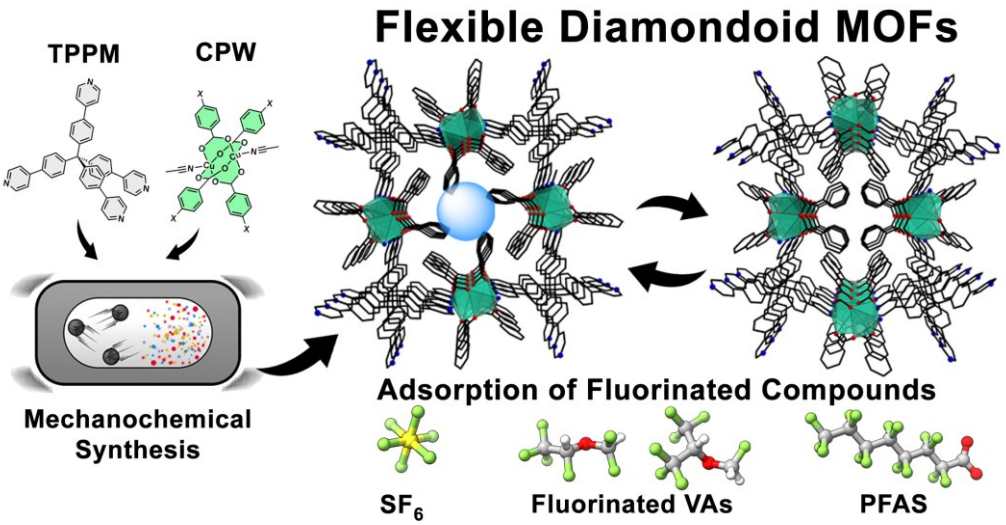


Figure 1. Scheme of the synthetic process, dynamic behavior, and applications of TPPM-based MOFs.

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FUNCTIONALIZED TRIAZOLATE-BASED MOFs FOR ENHANCED DILUTED CO_2 CAPTURE

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Keywords: *indoor CO_2 capture, triazolate MOFs*

Capturing low-concentration CO_2 is crucial for mitigating indoor air pollution and advancing next-generation carbon capture technologies, particularly in environments where trace CO_2 levels can adversely impact air quality and human health. In this work, we present a newly developed metal-organic framework, NICS-24, which incorporates diaminotriazolate and oxalate linkers, forming a distinctive two-channel structure with square-shaped pores. To benchmark its performance, NICS-24 was compared with two compositionally related materials—zinc triazolate oxalate (CALF-20) and zinc 3-aminotriazolate oxalate (CALF-15). While CALF-20 showed the highest CO_2 uptake at elevated pressures, NICS-24 outperformed both materials at lower CO_2 concentrations, achieving a notable capacity of 0.6 mmol/g at 1000 ppm.

The low-pressure performance of NICS-24 is additionally enhanced to 1.1 mmol/g by post-synthetic ligand modification using trifluoromethyltriazole and thiomethyltriazole linkers. Enhancement is most probably attributed to defect-formation which foster stronger CO_2-framework interactions and improve selectivity over gases such as N_2 and O_2. The framework's narrower channels, compared to CALF-20, further contribute to selective CO_2 adsorption by creating a more size-discriminating pore environment. To gain insights into performance under realistic conditions, we investigated the adsorption behavior of NICS-24 in the presence of humidity—a common challenge in practical applications. Using a combination of breakthrough experiments, solid-state NMR spectroscopy, and density functional theory (DFT) simulations, we found that water molecules preferentially occupy the framework due to hydrogen bonding with amine groups, leading to reduced CO_2 uptake under humid conditions. These findings underscore the role of competitive adsorption and suggest potential for further framework modification to enhance performance in moisture-rich environments.

Finally, we assessed the regenerability of NICS-24 through vacuum and temperature swing adsorption (VSA and TSA) protocols. While VSA resulted in a partial loss of working capacity due to strong CO_2 binding, TSA enabled complete regeneration and preserved structural integrity over multiple cycles, confirming the material's durability and practical potential for indoor air purification and industrial applications.

DEVELOPMENT OF ELECTROCATALYSTS FROM TOPOTACTIC TRANSFORMATION OF MOFS

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Materials Science and Engineering
Cornell University

Metal-based catalysts are indispensable in a wide range of clean energy technologies from water electrolysis for sustainable hydrogen production to the electrochemical reduction of CO_2 to produce value-added fuels and chemicals. Recent advances have demonstrated that the ability to control the size and bonding of the active sites to produce single atom catalysts, SACs, can significantly boost catalytic activity, selectivity, and durability, paving the way for cost-effective alternatives to precious metal catalysts.

In this talk, I will present our recent efforts to develop a new family of monometallic and bimetallic SACs supported on nitrogen-rich porous carbons from the topotactic transformation of MOFs. This approach preserves key structural motifs from the MOFs while enabling precise dispersion of single atoms in the support. In addition, I will present in operando spectroscopic and electrochemical characterization techniques that directly probe reaction intermediates, elucidate the catalytic mechanism, and correlate active site dynamics with product selectivity under realistic operating conditions. Lastly, I will discuss how the interplay between atomic dispersion, local coordination environment, and electronic structure controls their electrocatalytic performance and compare to the state-of-the-art systems.

TAILORED INTEGRATION OF A CU(I) CATALYTIC SITE INTO UIO-67 FOR OXYGENATION REACTIONS

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Keywords: UiO-67 *MOF, bipyridine ligands, copper complex, oxygenation reaction, GC-MS and NMR catalytic tests*

The precise integration of catalytic units within metal–organic frameworks (MOFs) represents a powerful strategy for developing efficient heterogeneous catalysts with excellent performance. We first synthesized a well-defined bipyridine-based Cu(I) molecular complex, coded CuBPA, (previously shown to be effective in the oxygenation of cyclohexene), and then, drawing inspiration from homogeneous catalysis, we afforded its heterogeneous counterpart within the robust, crystalline framework of UiO-67, obtaining the so-called UiO-67-BPY-Cu-BPA material.[1],[2],[3] Key to this strategy was the incorporation of a tailored percentage of properly substituted bipyridine linkers in addition to the conventional linker 4,4′-biphenyl dicarboxylic acid, taking advantage of their ability to coordinate the copper center, introduced and stabilized with finely tuned post-synthetic modifications. The material was thoroughly characterized by PXRD, TGA, and BET analyses to confirm its textural properties, whereas UV-Vis-NIR and XAS provided evidence of the Cu(I) oxidation state and local coordination environment, validating the successful immobilization of the metal within the MOF pores.

The catalytic performance of this system was evaluated in the oxygenation reaction of cyclohexene mediated by the *tert*-butyl hydroperoxide, with exciting results. It is worth noticing that in addition to traditional GC-MS analysis, an ex-situ study by using ^{1}H-NMR spectroscopy was implemented, enabling insight into the mechanistic behavior of the catalyst, better allowing the identification of the products.[3] Encouraged by these promising results, we further explored the catalyst's reactivity under varying atmospheric conditions (air, oxygen, and nitrogen), revealing the profound impact of fine-tuned parameters on catalytic performance. Very interestingly, the catalytic results obtained for the UiO-67-BPY-Cu-BPA material were also used for comparison with its homogenous counterpart (CuBPA complex) as well as with a broader family of UiO-67-based materials, each presenting differently decorated copper metal sites and used in oxygenation reactions of light hydrocarbons.[4][5][6] This approach allowed us to draw a clearer picture of the deep impact of the copper environment, paving the way for a conscious design of copper-based catalysts used in oxygenation reactions of light hydrocarbons.

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TEXTILE FUNCTIONALIZED BY METAL-ORGANIC CAGES FOR THE CAPTURE AND DEGRADATION OF CHEMICAL WARFARE AGENTS

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Keywords: *Metal-organic cage, functionalized textile, toxic molecules degradation*

For more than ten years, the world has seen a resurgence in the number of armed conflicts and an increase in terrorist risks.[1] This threat is reflected in particular by the use of old and new generation chemical weapons. Among these chemical warfare agents (CWA) used are nerve agents (Sarin gas), blisters (Yperite), or suffocants (phosgene). Civilian or military personal protective equipment (PPE) developed to date generally offers passive protection (capture). A transition to active protection (degradation) is particularly interesting, especially if it provides improved protection while maintaining comfort, lightness, washability, mechanical characteristics, IR stealth, and fire protection. Farah has pioneered this field of research by integrating MOFs onto textile composites for the degradation of CWA.[2] This research aims to develop a textile functionalized by Zr-based metal organic cages (MOCs) capable of capturing and degrading model toxic agents of the NRBC type. This very recent class of materials has many advantages (compared to zeolites, activated carbons, and MOFs), particularly due to their solubility.[3] However, several scientific challenges remain in particular regarding the **integration of MOCs into textiles** as no studies have explored their deposition on textile fibers. Their nanoparticle nature (10^{-9} m) should simplify this integration compared to conventional porous materials (MOFs, zeolites). Another improvement is necessary to **enhance the strength of functionalized textiles**. Unlike microparticulate materials (10^{-6} m), nanoscale MOCs could offer better abrasion resistance. Here we demonstrated that the solubility of Zr-based MOC ensure (i) their efficient deposition on textile fiber by a one pot synthesis method, by impregnation or by spray dryer technique (Figure 1), (ii) the capture and degradation of model toxic agents, and (iii) the excellent compatibility with natural textile fibers tested. The resistance (mechanical and aging) of the functional textile was evaluated by aging studies, to obtain a fiber maintaining its degradation capacities under rigorous conditions (UV, H_2O, temperature, abrasion, perspiration, etc.). This compromise between efficiency and textile properties leads us closer to active protection for PPE.

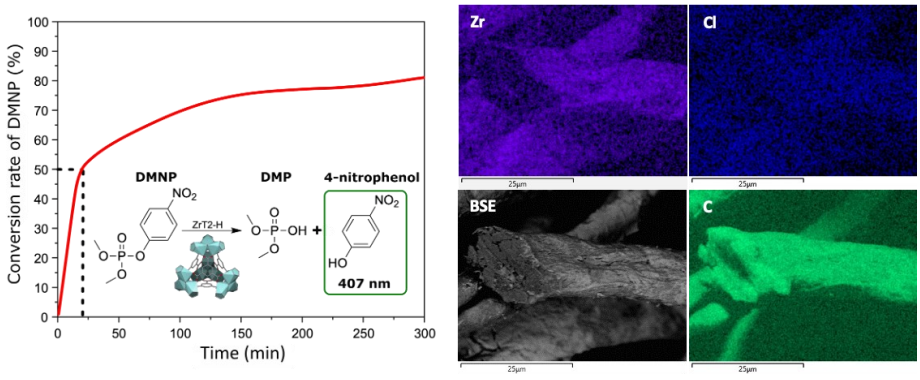


Figure 1. (Left) Conversion rate of simulant CWA (DMNP) as function of time using ZrMOCs as catalyst. (Right) Elemental analysis on SEM images of textile fiber integrating MOCs.

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METAL-ORGANIC MATERIALS FROM MOPS TO MOFS AND MELTABLE MATERIALS

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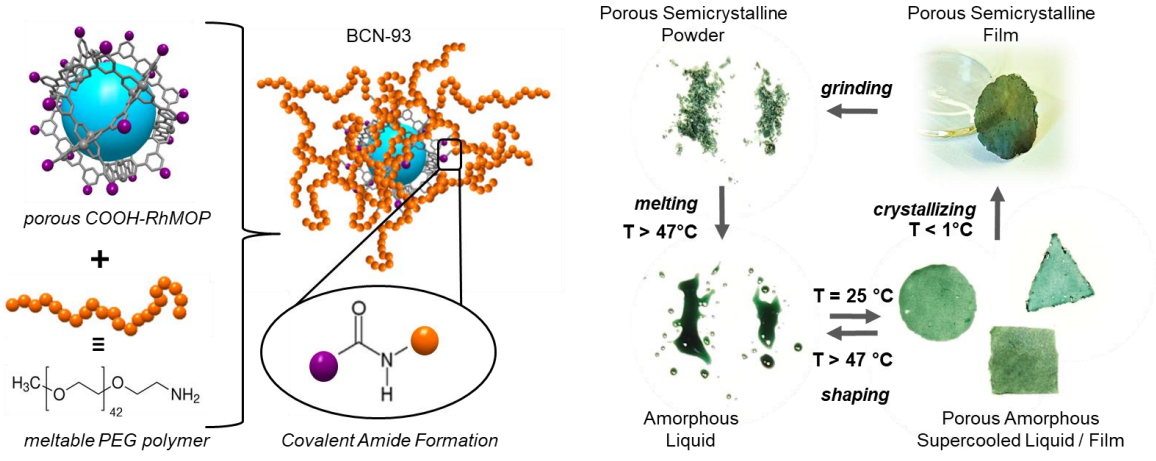
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Keywords: *metal-organic polyhedral, meltable, porous materials*

Metal-organic materials represent a cutting-edge category of functional materials wherein metal ions or clusters are intricately linked by organic ligands, creating a network structure. The ultimate strategy to shrink porous metal-organic materials down to the sub-5-nm scale is the isolation of single, zero-dimensional, discrete metal-organic polyhedra (MOP) units, which define the cavities in metal-organic frameworks (MOFs). These materials possess remarkable attributes such as a substantial surface area, customizable pore size and shape, and a diverse array of functional groups.[1] These qualities render highly versatile across numerous applications, including gas storage and separation, (photo)catalysis, sensing, and drug delivery.[2] But, can we change the physical state of a metal-organic material retaining its porosity? Porous melts, porous liquids and porous glasses are all new and emerging classes of porous materials, which offer great opportunities due to their unique characteristics. Herein, a simple and straightforward way to produce heteroleptic and heterometallic MOPs as well as a new type of metal-organic material; a porous and meltable MOP (named BCN-93) will be presented.[3]



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CRADLE-TO-GATE ENVIRONMENTAL IMPACT ASSESSMENT OF COMMERCIALLY AVAILABLE METAL-ORGANIC FRAMEWORKS MANUFACTURING

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Keywords: *Metal–organic Frameworks, Environmental impact, CO_2 emission, Greenhouse effect, Impact assessment.*

Metal-organic frameworks (MOFs) are a promising next-generation crystalline porous material with exceptional structural, chemical, and application diversity. Since their discovery, the reticular tunability and physiochemical properties of MOFs have been studied and carefully manipulated to make them suitable for a wide variety of applications. After decades of research, these materials are moving from the benchtop to commercial, industrial-scale production. The fact that the global MOF market size was US$ 271.14 million in 2021 and is anticipated to reach a readjusted value of US$ 1188.59 million by 2028 explain its supremacy as the next-generation porous material. [1] Although MOFs are now widely explored, the overall environmental impacts of these emerging materials are still underexplored. In this work, we present the first example of overall assessment of ten industrially produced and widely explored MOFs considering 18 diverse environmental impact categories such as global warming potential, fossil resource scarcity, water consumption, ecotoxicity etc. via cradle-to-gate life cycle assessment.[2] Importantly, our study presents a comprehensive comparison between different synthetic methods of each MOFs and compiles the environmental impacts associated only with the individual “synthesis” or “washing” steps. This study highlights the critical importance of using of green solvents over organic to reduce the overall environmental footprint. By identifying the synthetic drawbacks associated with different methods, this work provides a blueprint for the sustainable design and required future development of MOF synthesis.

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6th European Conference on Metal Organic Frameworks and Porous Polymers

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Poster

HEAVY METALS ABSORPTION INTO THE AMINO-RICH PORE SPACE OF CUBIC AND ORTHORHOMBIC VARIANTS OF ZR(IV) AND CE(IV)-IMIDOACETATE METAL-ORGANIC FRAMEWORKS

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Keywords: *Green and scalable synthesis, new MOF structures, heavy metals absorption*

Metal-organic frameworks (MOFs) have emerged as a highly versatile class of crystalline porous materials for heavy metal removal from aqueous systems, due to their tunable porosity, high surface area, and chemical encodability [1,2]. Among the diverse family of MOFs, frameworks built from high-valent metal nodes such as Ce(IV) and Zr(IV) show exceptional hydrolytic stability, making them ideal candidates for water remediation applications [3,4]. In this work, we report a green, water-based, and scalable synthesis of two new Ce(IV)- and Zr(IV)-based metal-organic frameworks (MOFs) fabricated from iminodiacetic acid (IDA) as a bidentate linker and an amino-rich organic ligand. As expected, the addition of monocarboxylic acid modulators not only facilitates controlled crystallization but also directs the formation of distinct structural variants, yielding cubic and orthorhombic phases of the resulting materials.

The IDA ligand, bearing both amine and carboxylate functional groups favor the coordination to the archetypal $[Zr_6\mu_3\text{-}O_4(\mu_3\text{-}OH)_4]$ clusters during the MOF synthesis, whilst let the amino bridging groups of the IDA linkers free for a metal absorption through a strong metal chelation chemisorption mechanism. [5,6]. The Ce-MOF exhibited a well-defined cubic structure, whereas the Zr-MOF crystallized into an orthorhombic phase, as revealed by the structural model obtained from the Rietveld analysis of the synchrotron X-ray diffraction data. The needle like morphology of the crystals of the Zr(IV)-based orthorhombic phase correlates with the linker defective and dynamic structure, showing significant dynamic and reversible breathing upon absorption and desorption of different solvents.

These frameworks demonstrated excellent performance in removing Cr(VI), As(III), and As(V) ions from water, with high absorption capacities and fast kinetics under static conditions. The performance is attributed to both the chemical functionality and the defectivity of the linker, specially of the Zr(IV)-based MOF variant, which provide accessible binding sites and pathways for ion diffusion [7]. Altogether, our results highlight the potential of IDA-functionalized Ce(IV) and Zr(IV) MOFs as effective, water-stable materials for the remediation of toxic metal ions. Their green synthesis routes and superior adsorption behavior offer a promising avenue toward the development of next-generation adsorbents for environmental purification.

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AMINO ACID FUNCTIONALIZATION OF METAL-ORGANIC FRAMEWORKS TO ENHANCE CO_2 CAPTURE

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Keywords: *metal-organic frameworks, DUT-67, amino acids, CO_2 capture*

Developing efficient and environmentally responsible materials for CO_2 capture remains a key challenge in the context of climate change.[1] Here, we present a green post-synthetic approach to functionalize the zirconium-based MOF DUT-67[2] using amino acids as dual-functional ligands. The interplay between amino group accessibility, pore environment, and specific CO_2 interactions is explored.

Incorporation of L-proline and L-tryptophan was achieved under mild conditions. Structural and spectroscopic analyses confirm successful coordination of the amino acids to the Zr_6O_8 clusters while preserving the crystallinity of the pristine framework. Primary CO_2 adsorption results show a marked increase in gas affinity for the functionalized materials. Notably, DUT-67-Trp exhibits adsorption enthalpies similar to those of high-performance amine-functionalized MOFs.[3] Breakthrough experiments under controlled humidity reveal distinct water–sorption interactions, with both materials maintaining CO_2 capture capacity even at elevated relative humidity (up to 50%). These findings highlight the potential of amino acid–modified MOFs as efficient and environmentally safer sorbents for CO_2 capture.

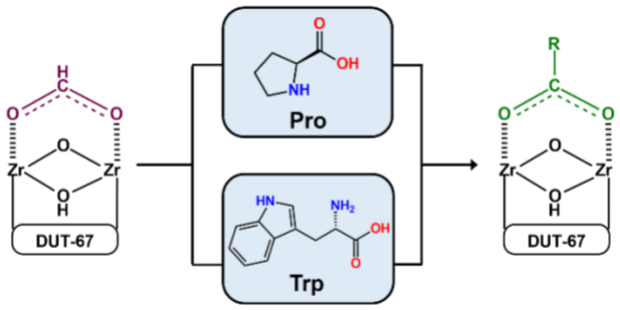


Figure 1. Schematic amino-acid functionalization of the inorganic node in DUT-67.

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CONFINED GEOMETRY EFFECTS ON THE SUPERCRITICAL ADSORPTION BEHAVIOR OF HYDROGEN

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In recent decades, growing concerns about global climate change and the increasing frequency of extreme natural disasters have led society to prioritize the search for low-polluting and renewable energy sources. As a result, hydrogen is emerging as a promising clean energy alternative.
However, the efficiency and safety of H_2 storage are challenging. Several methods for storing hydrogen fuel are currently being researched or are already in practice: compressed hydrogen, liquefied hydrogen, cryo-compressed hydrogen, metal hydrides, complex metal hydrides, liquid organic hydrogen carriers (LOHC), and physisorption-based storage in porous materials [1].

For physisorption-based hydrogen storage supercritical high-pressure adsorption is important, but there is still a lack of understanding of how key textural properties such as surface area and confinement (e.g., pore size/pore geometry) affect details of the shape of supercritical high-pressure adsorption isotherms. A key feature is that experimentally determined surface excess adsorption isotherms may exhibit a characteristic maximum at a certain pressure. For a given temperature and adsorptive/adsorbent system, the surface excess maximum (and the corresponding adsorbed amount) is related to the storage capacity of the adsorbent. In order to investigate the effect of confinement on the supercritical adsorption behaviors, in previous work [2] a systematic experimental study assessing the effect of pore size on the supercritical adsorption isotherms of pure fluids such as C_2H_4, CO_2, SF_6 had been conducted over a wider range of temperatures and pressures utilizing a series of mainly mesoporous model materials exhibiting well-defined pore size. A fundamental result of this work is a unique, fluid-independent correlation between the pressure of the surface excess maximum (at a given temperature) and the effect of confinement.

In this study, we expand our investigations from the mesopore range to the micropore range with the focus on supercritical hydrogen adsorption, i.e., exploring the effects of pore size, geometry, and pore-network characteristics on hydrogen adsorption behavior at 77 K. To achieve this, we employ selected metal-organic-framework materials, which have been characterized through a combination of argon adsorption at 87 K and dedicated non-local-density-functional theory (NLDFT) methods. Additionally, we perform complimentary grand canonical Monte Carlo (GCMC) simulations to to investigate the effect of confinement of supercritical hydrogen adsorption on a molecular level. Our systematic study reveals significant structure-property relationships, enabling us to determine optimal operating conditions for hydrogen storage applications under specific thermodynamic conditions.

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EXPANDING THE FAMILY OF MULTICOMPONENT ULTRAPOROUS MOFS VIA FACILE TOPOTACTIC SINGLE-CRYSTAL-TO-SINGLE-CRYSTAL METAL EXCHANGE REACTIONS

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Keywords: *ultraporous MOFs, hierarchical porosity, single-crystal-to-single-crystal topotactic metal exchange, gas storage*

Metal-organic frameworks (MOFs) are crystalline porous materials constructed from metal cations or clusters- known as secondary building units (SBUs) - connected by multitopic organic linkers. Their structural versatility, large pore sizes, high surface areas, and tunable porosity make MOFs ideal for a wide range of applications, including gas storage, separation, and catalysis. Post-synthetic modification (PSM) is a versatile approach for introducing new functionalities into pre-formed MOFs by altering the linkers or exchanging the metal nodes. These chemical transformations or exchanges not only improve the physicochemical properties of the frameworks but also enable the formation of MOFs that are otherwise inaccessible via direct synthesis due to functional group instability or incompatibility under standard conditions.

Recently, we reported a new series of ultraporous MOFs, denoted as Fe-**tbb**-MOFs-x (x = 1, 2, 3), constructed from a distinctive ternary, trigonal prismatic building block.[1] These materials exhibit hierarchical porosity, making them highly suitable for cryogenic gas storage, including hydrogen and methane[1]. To further expand this family of important materials we targeted the Al-analogues because of their anticipated enhanced stability due to stronger Al-carboxylated bonds as well as improved gravimetric gas storage properties due to the lighter framework. However, direct synthesis attempts to isolate these analogues resulted in either amorphous or mixed phases. To overcome these problems we developed a facile topotactic single-crystal-to-single-crystal transformation of Fe-**tbb**-MOF-x into Al-**tbb**-MOF-x (x = 1, 2, 3) under controlled reaction conditions (Figure 1)[2]. Complete metal cation exchange was confirmed via energy dispersive spectroscopy (EDS), and the resulting crystal structures were determined using synchrotron single crystal X-ray diffraction measurements. Argon sorption measurements at 87 K revealed that the Al-**tbb**-MOF-x series exhibits higher porosity compared to their iron-analogues. Important structural insights and gas storage properties will be presented and discussed.

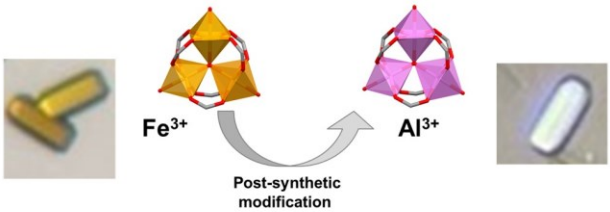


Figure 1. Single crystals of Al-**tbb**-MOF-x (right) were obtained through a facile topotactic metal exchange reaction directly from Fe-**tbb**-MOF-x (left).

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PYROLYTIC REARRANGEMENT OF SILVER(I) METAL-ORGANIC FRAMEWORK VIA SCSC TRANSFORMATION

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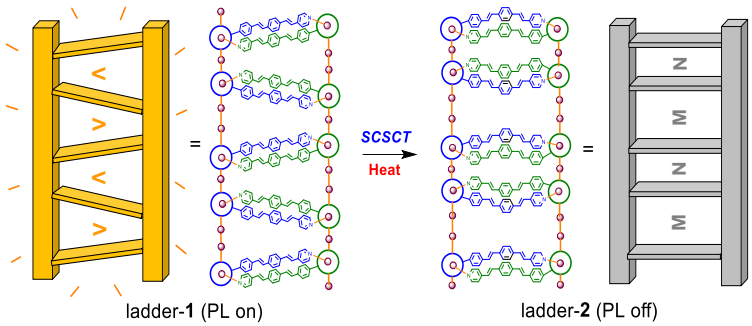
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Keywords: pyrolytic rearrangement, olefin ligand, single-crystal-to-single-crystal (SCSC) transformation

We herein report a unique thermal rearrangement of a coordination polymer accompanying photoluminescence (PL) on-off behavior via single-crystal-to-single-crystal (SCSC) transformation. Self-assembly of a multitopic olefin-armed NOS_2-macrocycle **L** and silver(I) trifluoroacetate gives rise to an orange emissive ladder-like coordination polymer (ladder-**1**) in a Λ-V-Λ-V pattern (where "Λ" is a trapezoid and "V" is a reverse trapezoid). Upon heating at 80 °C, surprisingly, ladder-**1** undergoes a drastic SCSC transformation to non-emissive ladder-**2** with an N-M-N-M pattern (where "N" is a narrow rectangle and "M" is a wide rectangle). A mechanistic pathway for converting ladder-**1** to ladder-**2** via the bond-breaking/making and pedal motion is proposed. In addition, the PL on-off behaviors are discussed based on the structure-property relation. Both ladder-**1** and ladder-**2** were photo inactive even though the olefin bonds in the face-to-face alignment were separated by 3.7-3.8 Å. Consequently, the multiple functions of the olefin-armed macrocycle work cooperatively via communications to satisfy the conformational and electronic conditions.



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SOLVENT-INDUCED SCSC CONVERSION OF HETEROBIMETALLIC TO HOMOMETALLIC 2D MOFS VIA AN ADD-AND-REMOVE STRATEGY

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Keywords: SCSC*, MOFs, copper iodide, exocyclic coordination, self-assembly*

Constructing high-dimensional metal-organic framework (MOF) materials unattainable by direct methods is demanding. We herein report the construction of a two-dimensional (2D) copper(I) iodide MOF via an *add-and-remove* strategy of a second metal component (HgI_2).[1] The networking reaction of an O_2S_2-macrocycle (**L**) with CuI via a bridging exocyclic coordination under the direct condition was unsatisfactory because of its one-dimensional (1D) product $\{[(\mu_4\text{-}Cu_3I_3)(\mathbf{L})_2]\cdot 2CH_3CN\cdot CH_2Cl_2\}_n$ (**1**) with low-yield. Alternatively, the self-assembly of **L** with a mixture of CuI and HgI_2 allows the generation of a 2D heterobimetallic Cu(I)/Hg(II)-MOF $\{[Cu_2(\mu\text{-}Hg_2I_4)(\mathbf{L})_2(CH_3CN)_2I_2]\cdot\text{toluene}\}_n$ (**2**, *brick wall*) crosslinked by μ-Hg_2I_4 square dimers via the bridging exo-coordination mode. When the crystals of **2** were immersed in methanol, the crystals were converted to a desired 2D Cu(I)-MOF $[(\mu_4\text{-}Cu_2I_2)(\mathbf{L})_2]_n$ (**3**, *square grid*) by the replacement of the crosslinker μ-Hg_2I_4 with μ_4-Cu_2I_2 via the solvent-assisted etching. Interestingly, this 2D-[1D]*-2D conversion process that proceeds in an SCSC mode is completed by the dimerization of open coordinating sites CuI* to form a μ_4-Cu_2I_2 node ($2CuI^* \rightarrow Cu_2I_2$), preserving the 2D dimensionality. The conversion process is discussed based on PXRD, EDX, AFM, TGA, and NMR data.

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MERGED NETS AS A PLATFORM FOR DESIGNING AND SYNTHESIZING TOPOLOGICALLY DIVERSE MOFS

Salma Benzaria,[a] Hao Jiang[a] and Mohamed Eddaoudi[a]

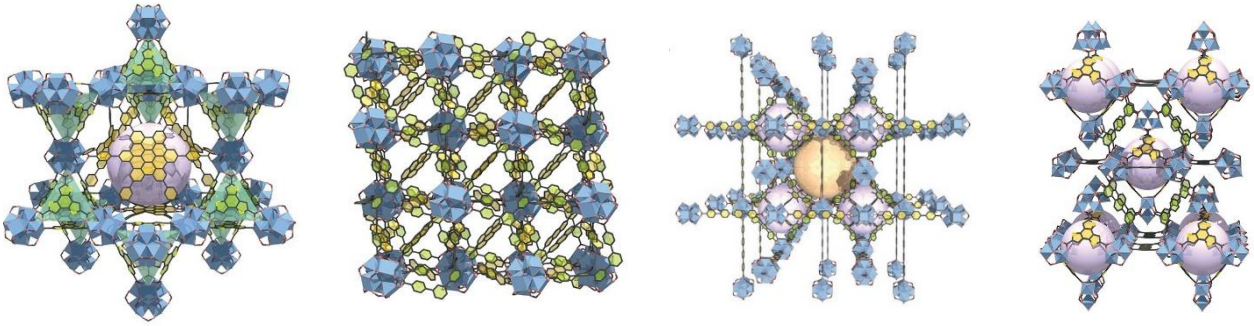
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Keywords: *Structure design, merged nets, topology prediction, ordered-disordered structures*

Designing complex materials made from multiple components is often limited by a lack of suitable blueprint nets. To solve this, we developed a *merged-net*[1] *approach* that balances design ability and complexity. We studied relationships between 53 edge-transitive nets and created a map to find compatible pairs, leading to 353 merged nets. Using this, we built a design method and proposed over 100 new metal-organic framework (MOF) structures. The effectiveness of this approach was confirmed by successfully synthesizing four types of materials (figure 1), each representing a different category of merged nets: **sph** from three-periodic edge-transitive nets (3p-3p), **pch** from three-periodic net and two-periodic edge-transitive layer (3p-2p), **thw** from three-periodic net and one-periodic rod (3p-1p), and **nam** from three-periodic net and zero-periodic edge-transitive polyhedra (3p-0p). Furthermore, we successfully synthesized materials that are based on the derived-merged **pck** net and related-merged **nih** net, demonstrating the extensibility and versatility of the merged-net approach[2].

Beyond structure generation, controlling order within disordered positions remains a major challenge. Using the merged-net strategy, we demonstrated precise control over both ordered and disordered structures, where the framework is maintained by one net and the ordering is tuned by another. By guiding the arrangement of linkers, we achieved the deliberate positioning of a tetratopic rectangular linker within hexagonal nodes. Out of over 43 million possible configurations, we identified 33 uniform arrangements corresponding to four distinct topologies. Remarkably, experimental synthesis confirmed the formation of one of these predicted structures, showcasing the unprecedented accuracy of our structural prediction. Theoretical calculations further support the feasibility of the remaining three topologies as viable synthetic targets. Notably, the ordered structure exhibits superior methane storage capacity compared to both single-linker and saturated-linker analogs[3].



Tb-**sph**-MOF-6 RE-**pch**-MOF-1 Zr-**thw**-MOF-1 Fe-**nam**-MOF-1

Figure 1. Synthesized MOFs based on enumerated merged nets.

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DESIGN AND SYNTHESIS OF α-TYPE LAYERED AND PILLARED ZIRCONIUM PHOSPHITE PHOSPHONATES WITH HIGH SPECIFIC SURFACE AREA AND POROSITIES

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Keywords: *zirconium phosphonates, sol-gel, porous structures*

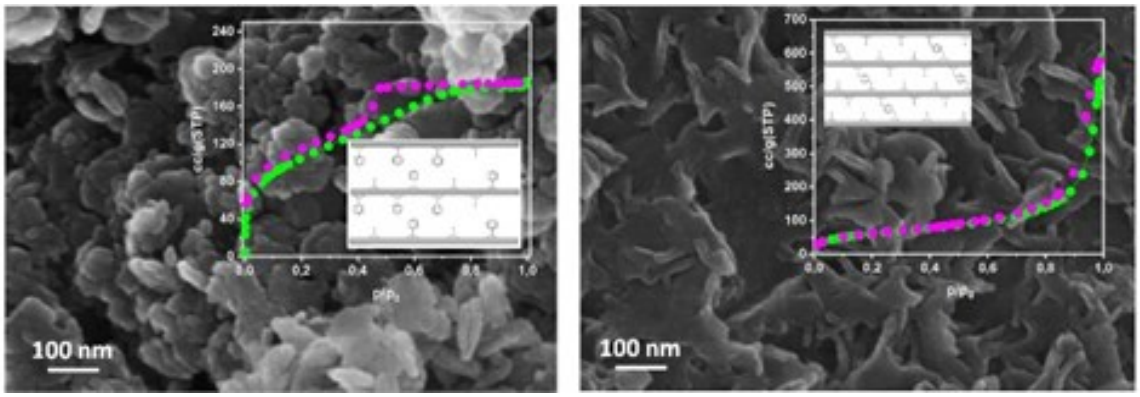


Fig. 1: SEM image of zirconium phosphite phenylphosphonate and zirconium phosphite p-xylenediphenylphosphonate, with the N_2 absorption (magenta) and desorption (green) curve and the representation of the interlayer region of zirconium phosphite–phosphonate materials.

The sol-gel method[1] allows the controlled synthesis of layered or pillared nanostructures based on zirconium phosphite–phosphonate, through the combined use of phosphorous acid and aromatic phosphonic acids[2,3]. By varying the nature of the ligand and the molar ratio between the components, it was possible to obtain materials with tunable porosity (micro- meso- and macroporous) and with surface areas up to 352 m²/g.

These new materials were characterized by various techniques (^{31}P MAS NMR, XRPD, SEM, FTIR, N_2 and H_2 adsorption isotherms), and thanks to them it was observed that the microporosity and the interlamellar distance directly influence the gas adsorption capacity.

In particular, the zirconium phosphite phenylphosphonate $Zr(O_3PH)_{0.5}(P1)_{1.5}$ compound showed the highest hydrogen uptake, equal to 1.43 mmol/g at 77 K, thanks to the high microporosity. Instead, the zirconium phosphite p-xylenediphosphonate $Zr(O_3PH)_{1.0}(P2)_{0.5}$ material, despite having a smaller surface area, reached the highest adsorption capacity for vapor phase dichloromethane, up to 1300 mg/g at 30 °C, thanks to the significant interparticle macroporosity.

The combination of synthetic simplicity, structural versatility and functional performance makes these materials promising candidates for applications in hydrogen storage and selective removal of VOCs.

Work in progress to setup the synthesis of similar materials by the mechanochemical approach.

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BINARY SOLVENT MIXTURES IN ZIF-94 SYNTHESIS: TOWARDS CONTROLLABLE PARTICLE SIZE

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Keywords: *ZIF-94, green synthesis, particle size control, CO_2 capture*

Zeolitic imidazolate frameworks (ZIFs), a subgroup of metal-organic frameworks (MOFs), have in recent years been extensively studied for sorption applications due to their superior stability and kinetics for vapour/gas adsorption if compared to some carboxylate-based MOFs. The ZIF-94 (also known as SIM-1) is a broadly studied ZIF with potential uses in CO_2 capture (2.2 mmol @25°C 1bar) and CO_2/N_2 separation when used as part of Mixed Matrix Membranes. One of the problems with utilizing some ZIFs, including ZIF-94, in sorption and separation applications is that the metal coordination flexibility and particular linker and metal combinations lead to the coappearance of multiple stable phases with different topologies. This includes ZIF-93/94 system with 5-methyl-imidazole-4-carbaldehyde as a linker and ZIF-71/72 system with 4,5-dichloroimidazole as a linker. The two co-existing phases in such systems show either vastly different porosity (ZIF-71/72) or a significant change in gas isotherm shape and final gas/vapour uptake (ZIF-93/94). In this context, a crucial problem when trying to optimize the reported ZIF-94 synthesis is that often, mix phase systems form. Nanoparticulate ZIF-94 can be prepared using THF (usually mixed with MeOH). The downside of this synthesis is THF's low volatility and subsequent entrapment in the pores of ZIF-94. This requires a solvent exchange step, where ZIF-94 is refluxed in EtOH for faster solvent exchange. Ideally, the use of a smaller, volatile solvent would eliminate the need for this workup step.

Herein, we report the mechanochemical and solvothermal synthesis of phase-pure ZIF-94. The final solvent mix utilized two cheap, readily available volatile solvents, where one directs structure and the other impacts kinetics. Using the binary solvent mixture under solvothermal conditions, both nanoparticles and larger particles could be prepared by varying the temperature and stirring times of the synthesis mixture prior to heating.

Initially, mechanochemistry was used for solvent screening due to its short synthesis times. This included water and various alcohols (methanol to butanol). In the case of water and methanol, after milling and aging of the sample for a day, we observed only the RHO phase of ZIF-93. Prolonged aging without washing led to the slow formation of a mixed phase system. Ethanol and isopropanol led to the formation of ZIF-94, while butanol, due to its size, led to the formation of ZIF-93. he optimal solvent mixture derived from mechanochemistry was then tested in solvothermal synthesis at room temperature at 60°C and 85°C. By changing the ratio of the solvents or the temperature, we were able to obtain various particle sizes of ZIF-94. All ZIF-94 samples prepared with the binary solvent system showed CO_2 uptake comparable or better than one of ZIF-94 prepared using THF. Therefore, we successfully shifted the synthesis from THF/MeOH to EtOH/H2O, eliminating the need for the solvent exchange step.

SYNTHESIS AND CHARACTERIZATION OF WATER-STABLE MOFS DESIGNED FOR PHOTOCATALYTIC APPLICATIONS

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Keywords: *MOFs, single-crystal X-ray diffraction, water-stable MOFs, photocatalysis*

Mimicking natural photosynthesis by using synthetic photocatalysts and natural sunlight as the energy source, could produce new methods for dye/pollutant degradation, carbon dioxide reduction and hydrogen production applications. Metal-organic frameworks (MOF) have been studied as photocatalysts for these various reactions with their advantages being in having large specific surface areas, porous structures and precise modifiability of the structures. While inorganic semiconductor compounds have been studied more extensively for photocatalysis they usually suffer from poor visible light absorption, large band gaps or photocorrosion. However, MOFs can be modified to overcome these problems due to their characteristic structure containing both inorganic metal centers and organic ligands. Therefore, it is a promising strategy to develop new visible light active MOFs for photocatalytic applications. [1,2]

One of the most important properties of MOFs required for their large-scale utilization in photocatalysis and many other applications is their water stability. It is especially important in catalytic reactions made in aqueous media like in photocatalytic water splitting. Therefore, it is important to create new MOFs which would be both stable in water and have good photocatalytic properties. In addition, it is beneficial to synthesize MOFs in water or water mixtures which would indicate their stability in water and at the same time would improve the economical and safety aspects of their syntheses. [3,4]

In this work, we present the synthesis and characterization of a series of new mixed ligand MOF structures based on highly aromatic carboxylate and N-donor ligands. We have been able to crystallize and synthesize multiple new MOF structures from aqueous solutions and characterize their structures by single-crystal X-ray diffraction (SCXRD) (Figure 1). Structural characteristics and thermal stability of the MOFs have been confirmed by powder X-ray diffraction (PXRD) and thermal analyses. In addition, some of the syntheses have been optimized to produce pure crystalline MOF phases with a newly developed green and rapid synthesis route using solely water as the solvent. Finally, preliminary results demonstrate the potential of these MOFs in photocatalytic hydrogen production applications.

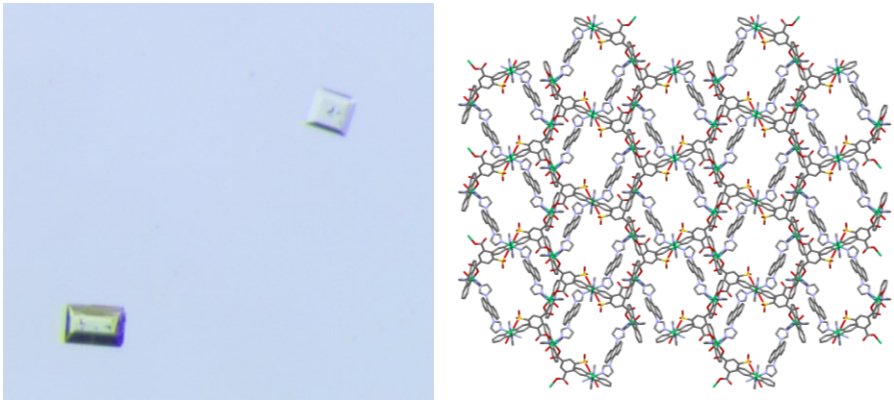


Figure 1. Microscope image of MOF single crystals (left) and an example of a characterized 3D-MOF crystal structure (right).

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TOP-DOWN APPROACHES FOR THE DE-RETICULATION OF METAL-ORGANIC FRAMEWORKS

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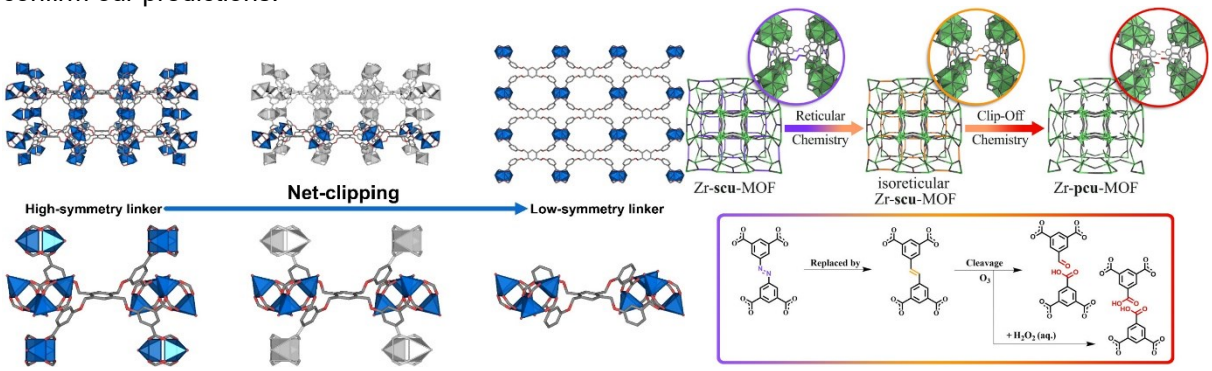
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Keywords: *De-reticulation, Prediction, Top-down approaches, Synthesis, Rational design*

The principles of reticular chemistry based on bottom-up approaches cannot cover certain limits of prediction in the assembly of MOFs related to the polymorphism in nets that require the same building units. In addition, current methods for structural prediction in reticular chemistry are insufficient for desymmetrized MBBs.[1-3]

Herein, we present two top-down approaches for the de-reticulation of reticular materials. The first top-down approach, *net-clipping*, is based on the de-reticulation of MOFs and edge-transitive nets by clipping MBBs or nodes of higher connectivity and symmetry by half.[4-5] We select the clippable MBBs with 4-connected (4-c) square/rectangular, 4-c tetrahedral, 6-c hexagonal, 8- c cubic, and 12-c hexagonal prismatic linkers to decrease its symmetry into less-regular MBBs. By applying net-clipping to all the nets constructed with nodes with these connectivities and shapes, 141 derived and 56 clipped nets are anticipated, being 39 of them described for the first time. We validate our strategy with the synthesis of 6 novel MOFs constructed with less-symmetric MBBs and several literature examples that confirm our predictions.



Then, we introduce a new synthetic approach, *Clip-off Chemistry*, based on the de-reticulation of MOFs via bond breaking for the obtention of novel molecules or materials.[6] We validate our strategy with the synthesis of two topologically different tridimensional (3D) MOFs (Zr-**pcu**-MOF and Sc-**pcu**-MOF) from other two different 3D MOFs as precursors (Zr-**scu**-MOF and Sc-**soc**-MOF, respectively). Using the ozonolysis reaction and double bonds as our cleavable reaction/groups, respectively, we demonstrate that this transformation can be performed quantitively, selectively, and periodically, occurring in a single-crystal-to-single-crystal fashion.

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DIMETHYLFORMAMIDE-FREE, RAPID SYNTHESIS OF LARGE SINGLE CRYSTALS OF MOF-5 AS AN UNDERGRADUATE LABORATORY EXERCISE

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Keywords: *Synthesis, Crystallography, Metal-Organic Frameworks, Undergraduate Teaching*

Metal-Organic Frameworks are well-known among researchers but may be unfamiliar to undergraduate students of chemistry and material science. An engaging way for students to understand MOFs is to provide them with hands-on experience in MOFs synthesis and structural characterization. Synthesis of MOFs can be carried out with relative ease in an undergraduate chemistry laboratory session. Single crystal X-Ray Diffraction (SCXRD) would be an ideal way to visualize the structure of MOFs, but requires the growth of large and well-diffracting crystals which can be challenging to achieve within the limited timeframe dedicated to laboratory course. Reciprocally, demonstrating the power of SCXRD on student grown crystals of a topical and modern material is also a challenge.

This work presents an easy and rapid method for the solvothermal synthesis of large crystals of MOF-5 using N,N-diethyl-meta-toluamide as a solvent.[1] The crystals, including their morphology, can be readily observed by the naked eye, see Figure 1. The synthesized MOF-5 crystals can be characterised SCXRD in minutes (depending on the diffractometer).

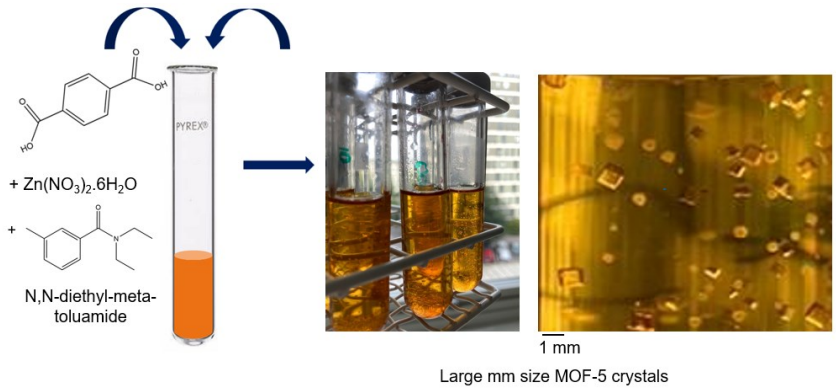


Figure 1, reaction schematic of the dmf-free synthesis of MOF-5 crystals, and the reaction mixture showing the presence of the large crystals.

Naturally, the synthesized MOFs can be further characterized by other techniques such as scanning and transmission electron microscopy, thermogravimetric analysis and gas sorption measurements. An overview of the expected results is also provided. This simple, safe and cost-effective protocol can be valuable to promote Metal-Organic Frameworks and crystallography, and support teachers in the introduction of materials chemistry techniques to their students[2,3].

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CHARGED TETRATOPIC BORATE-BASED FRAMEWORKS CONSTRUCTED FROM COVALENT AND COORDINATION BONDS

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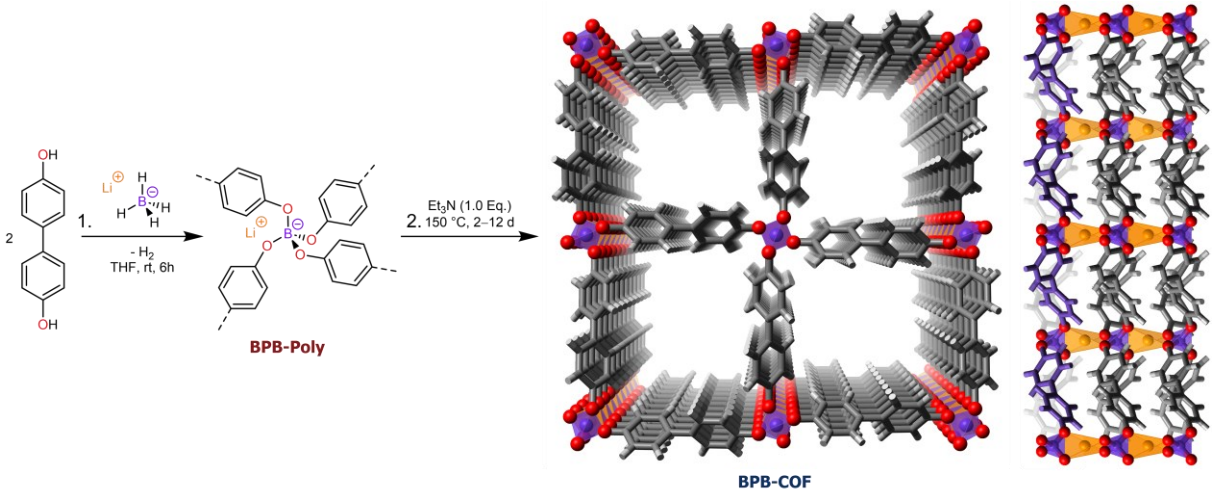
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Keywords: *Metal-organic frameworks, Covalent organic frameworks*

Framework materials are typically classified by the elements and types of bonds they are composed of. Two classes of particular interest are metal-organic frameworks (MOFs) and covalent organic frameworks (COFs). While MOFs use metal atoms coordinated by ligands as linkers via coordination bonds, COFs are constructed from organic building blocks connected by covalent bonds. Due to these fundamental differences, a hard line is often drawn between these classes. They both, however, share common features such as crystallinity, porosity, and high tunability, which can be designed *ab-initio*. In a toolbox-like fashion, aspects such as building units, linkages, and topology can be selected to generate a material tailored for a specific task. The curation of the linkage, in particular, is an essential tool to control the resulting properties of the material.

By exploring new linkage chemistry, we present frameworks constructed from anionic tetratopic borate units, which enable the rational design of hybrid materials, that combine features from both metal-organic and covalent-organic frameworks.[1] The charged frameworks were found to possess unprecedented structures, utilizing both covalent and coordination bonds. Here, anionic layers are obtained by covalently linking the phenoxy groups to the borate centre. To efficiently compensate the anionic charge, the alkali metal counterion resides in the interlayer space, coordinated by the phenoxy groups. As a result, the overall framework relies on ionic coordination bonds to give pillared anionic layers.

The interplay between weak ionic and strong covalent bonds presents an attractive design strategy to modify the bulk material. By selectively targeting the ionic interaction, the material can be exfoliated into sub-nm thin nanosheets. This provides a useful pathway towards the processability of framework materials, which are often obtained as poorly processable powders. Furthermore, the synthesis from simple, commercial lithium borohydride and dihydroxyaryls makes tetratopic borate-based materials an attractive platform for solid-state conduction, gas storage and separation.



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ESTABLISHING POROSITY IN MULTINODAL MOFS BASED ON AN OCTATOPIC ORGANIC LINKER VIA FACILE TOPOTACTIC CATION EXCHANGE REACTIONS

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Keywords: *Metal-Organic Framework (MOFs), Post -Synthetic Metalation, Gas Sorption*

Metal-Organic Frameworks are highly crystalline porous materials consisting of organic ligands and inorganic clusters, which are connected together via strong coordination bonds. Gas storage and separation, catalysis and drug delivery are only some of the interesting applications of MOFs. The variety in both the organic and inorganic building unit can lead to the design and development of a great number of novel frameworks with desired properties. However, the de novo synthesis does not always lead to the formation of MOFs with the targeted structure, thus post-synthetic modification could be the proper approach [1].

In this work, we explored a new octatopic carboxylated-based linker for the reticular synthesis of novel MOFs. A highly crystalline material was obtained under controlled solvothermal reactions with $Zn(NO_3)_2.6H_2O$ in the form of single crystals.[2] Remarkably, the structure features three different types of Zn^{2+}-based inorganic building units resulting in a unique multinodal framework. However, efforts to activate this material were unsuccessful, presumably due to incompatible geometries of the resulting solvent-free Zn^{2+} cations. To address this problem, the Cu^{2+}-analogue was targeted due to the anticipated stable coordination in the activated structure, associated to the Jahn-Teller effect. Interestingly, direct solvothermal reactions using $Cu(NO_3)_2.6H_2O$ resulted in amorphous products. To access the desired Cu^{2+}-based MOF, we developed a facile topotactic metal cation exchange methodology during which Zn^{2+} cations were quantitatively replace by Cu^{2+}, as confirmed by X-ray diffraction measurements and EDS spectroscopy. Successful activation the Cu^{2+}-analogue was achieved by supercritical CO_2 drying. Important structural details and extensive gas sorption properties will be presented and discussed.

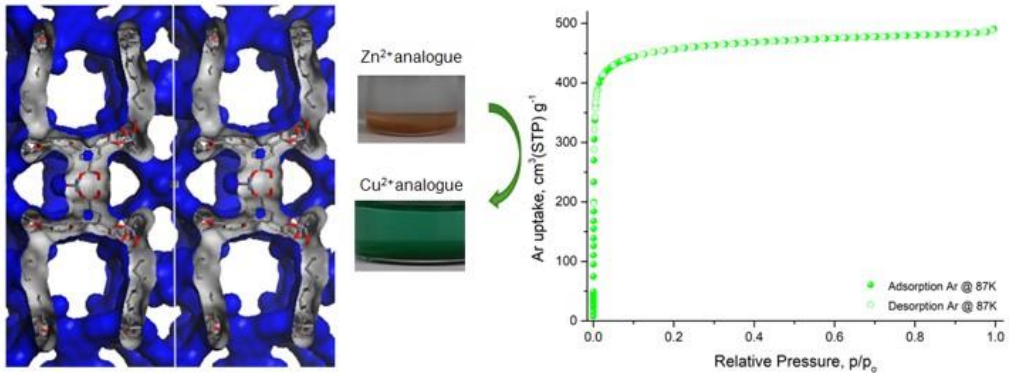


Figure 1. Controlled topotactic reaction during which Zn^{2+} cations were quantitatively replaced by Cu^{2+} provided access to the highly porous structure of a novel multinodal MOF based on a new octatopic linker.

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TRIAZINE-PHOSPHONATE BASED LINKERS: EXPLORING SYNTHETIC METHODOLOGIES AND THEIR DIVERSE COORDINATION NETWORKS

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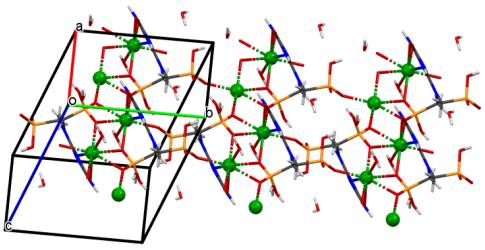
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Keywords: *metal phosphonates, heterocyclic rings, triazine*

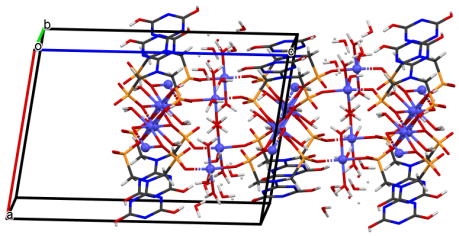
Phosphonate-based heterocyclic ligands combine the structural versatility of heterocycles with the strong metal-binding ability of phosphonate groups, making them attractive candidates for the construction of functional coordination materials. In this work, we synthesized two such ligands: (((4,6-dioxo-1,4,5,6-tetrahydro-1,3,5-triazin-2-yl)azanediyl)bis(methylene))diphosphonic acid (Tr-1ABMP) and (3-((4,6-dihydroxy-1,3,5-triazin-2-yl)amino)-1-hydroxypropane-1,1-diyl)bis(hydrogenphosphonate) (Tr-1PAM), using a simple aqueous S_NAr reaction between cyanuric chloride and phosphonate precursors at low temperature (0–5 °C) [1].

Both ligands were reacted with a variety of metal ions to form metal–phosphonate compounds. From these reactions, four single-crystal structures were successfully isolated and characterized by single-crystal X-ray diffraction (SC-XRD): three involving Tr-1ABMP coordinated with Ca^{2+}, Sr^{2+}, and Cu^{2+}, and one involving Tr-1PAM coordinated with Ca^{2+}. The Tr-1ABMP-based compounds with Ca, Sr, and Cu form two-dimensional (2D) coordination polymers, while the Ca–Tr-1PAM compound forms a one-dimensional (1D) coordination polymer. All compounds were fully characterized by a variety of techniques.

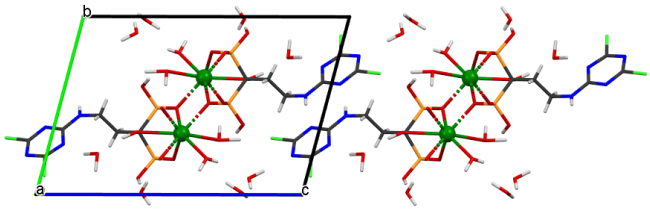
The presence of multiple phosphonate groups and the triazine core enables versatile coordination modes and structural motifs, making these ligands promising candidates for catalytic applications. Future work will focus on exploring their catalytic activity in biodiesel synthesis and evaluating their stability under conditions relevant to renewable energy applications, with the goal of developing efficient and reusable catalytic materials.



Ca-Tr-1ABMP



Cu-Tr-1ABMP



Ca-Tr-1PAM

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FACILE ONE POT SYNTHESIS OF A BIMETALLIC Fe/Ni-soc-MOF: STRUCTURAL INSIGHTS AND GAS STORAGE APPLICATIONS

Emmanouil Paragioudakis,[a] Konstantinos G. Froudas,[a] Constantinos Tsangarakis,[a] Pantelis N. Trikalitis [a]

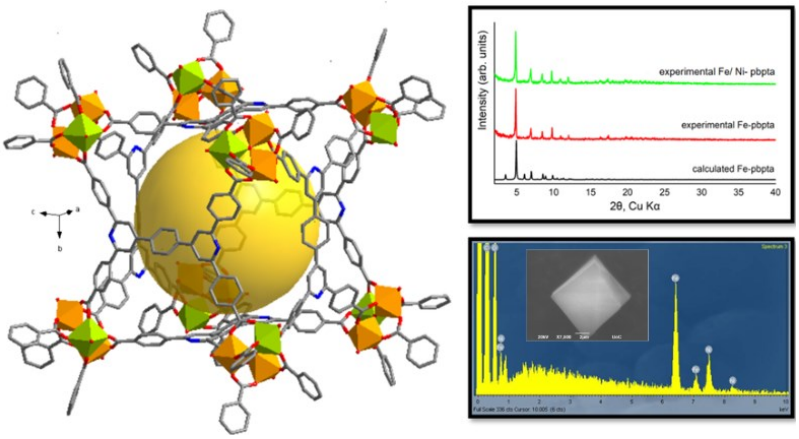
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Keywords: *Metal-Organic Frameworks, Mixed-Metal MOFs, Synergism, Complexity, Gas Storage*

Metal-Organic Frameworks (MOFs) represent an important class of porous, crystalline materials that have undergone remarkable development over the past three decades, driven by their potential in a wide range of applications. Mixed-Metal-Organic Frameworks (MM-MOFs) constitute a subclass of these materials, incorporating two or more different metal ions into the framework structure.[1] MM-MOFs have attracted considerable interest due to the enhanced properties they can exhibit compared to their homometallic counterparts, arising from the complexity and the synergism introduced by the presence of different metal ions, especially in the case of heterometallic clusters.[2] Trigonal planar M_3O trimers are particularly significant among various cluster types in MOF chemistry, serving as key inorganic building units in several prominent MOF platforms.

Along the above lines, we report the one pot synthesis of Fe-Ni-pbpta (H_4pbpta = 4,4',4'',4'''-(1,4-phenylenbis(pyridine-4,2-6-triyl))-tetrabenzoic acid), a MM-MOF with the underlying **soc** topology.[3] EDS spectroscopy confirmed the co-incorporation of both metals, with a Fe:Ni ratio of approximately 2:1. The combination of these charge-complementary metal ions (Fe^{3+} / Ni^{2+}) results in a charge balanced framework with enhanced porosity, attributed to the absence of any counter ions within the framework's pores. The high microporosity, combined with the presence of different, potentially unsaturated, metal centers in close proximity prompted us to investigate in detail the corresponding H_2 storage properties. Important structural details and extensive gas sorption properties will be presented and discussed.



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DESIGN AND SYNTHESIS OF A STABLE POROUS PORPHYRINIC ZIRCONIUM MOF FOR APPLICATIONS IN PHOTOCATALYSIS

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Keywords: *Porphyrinic metal organic framework, cubic, size-controlled, nanoparticles*

In recent years, porphyrin-based and porphyrin-containing metal organic frameworks (PMOFs) have particularly attracted attention for their photoactivity.[1],[2] Inspired by the enhanced hydrophobicity and higher stability to oxidation and light on fluorinated MOFs,[3], [4] we have ignited an effort to explore the synthesis and functional properties of fluorinated PMOFs. Specifically, we developed the gram scale synthesis of the fluorinated analog of the tetrakis(4-carboxyphenyl)porphyrin (TCPP), named F_{16}TCPP to be used as linker.

It is established that the strong interaction between Zr(IV) and carboxylate make the resultant MOFs chemically stable, bearing this in mind, we constructed a polyfluorinated porphyrinic zirconium MOF by combining Zr precursor and F_{16}TCPP (5,10,15,20-tetrakis-(4-carboxy-2,5,6-tetrafluorophenyl)porphyrin) through adjusting the reaction conditions. By carefully choosing different metal precursors and exploring the reactivity in different solvents, a new Zr-F-PMOF could be isolated in a reproducible manner with good yield. Synchrotron diffraction data revealed that Zr-F-PMOF crystallizes in the *P*432 space group, the structure is arranged in cubes formed of eight corner-sharing $Zr_6O_4(OH)_4$ units and six face-sharing F_{16}TCPP porphyrins, leading to a cubic structure and ~19.3 Å pore size. The topology of this framework can be classified as a 3-D (4,12)-connected **ftw** net. Furthermore, achieving precise size control of Zr-F-PMOF crystals while retaining their intrinsic physicochemical properties and high uniformity represents a critical challenge in advancing their functional applications. Notably, nano-sized crystals usually show an enhanced catalytic activity than their bulk analogues, attributed to their increased exposure of active sites and reduced mass transfer limitations. In our work, through an ultrasound-assisted method, we successfully tuned the size of Zr-F-MOF crystals from 15 µm to 180 nm, to achieve nano Zr-F-PMOF with high crystallinity and uniform morphology (**Fig. 1**). In this communication, relevant structural, spectroscopic and textural properties will be discussed.

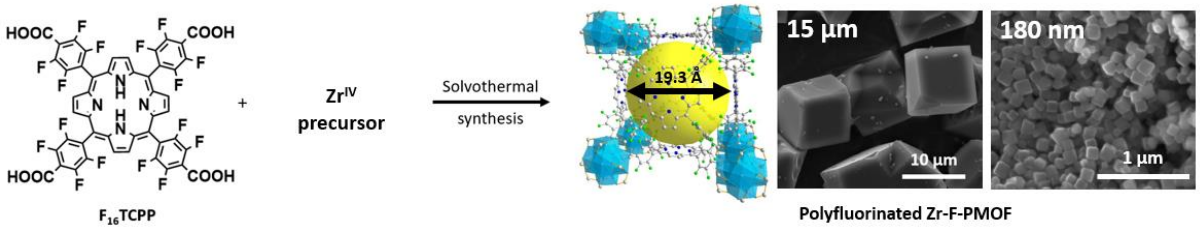


Fig. 1. Schematic Diagram of Polyfluorinated PMOF synthesis and SEM pictures illustrating the particle size tunability.

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ULTRALIGHT LITHIUM MOFS USING ALKYNYL, ARYLOXIDE, AND CARBOXYLATE BASED LIGANDS

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Keywords: *Lithium, MOF, alkynyl, aryloxide, carboxylate*

Ultralight lithium-based metal-organic frameworks (Li-MOFs) have attracted significant interest due to their potential applications in gas storage, catalysis, and energy materials [1,2]. This study explores the chemical and structural characteristics of Li-MOFs synthesized using alkynyl, aryloxide, and carboxylate-based ligands, resulting in 1D, 2D, and 3D network architectures (Fig. 1). A combination of experimental techniques, including powder X-ray diffraction (PXRD), Fourier-transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and single-crystal X-ray diffraction (SXRD), was employed to investigate the impact of ligand types and reaction conditions on network dimensionality, stability, and crystallinity. The reaction of LiOH with carboxylate-based ligands in mixed solvents led to the formation of 1D solvated structures, while 2D networks were obtained under modified solvent conditions and reaction parameters. Aryloxide-based ligands, including phenol- and quinoline-based ligands, reacted with lithium bis(trimethylsilyl)amide (LiHMDS) to produce 2D materials, while other linkers led to 3D hydrogen-bonded cubane cluster networks with solvent molecules incorporated in the networks. Additionally, a 3D lithium-based framework was synthesized using alkynyl ligands (acetylide) under Schlenk line conditions. Although gas adsorption measurements were not conducted for all materials, computational calculations suggest promising gas storage capabilities for the 3D lithium acetylide MOF. These findings provide valuable insights into the structural diversity and potential functional applications of Li-MOFs.

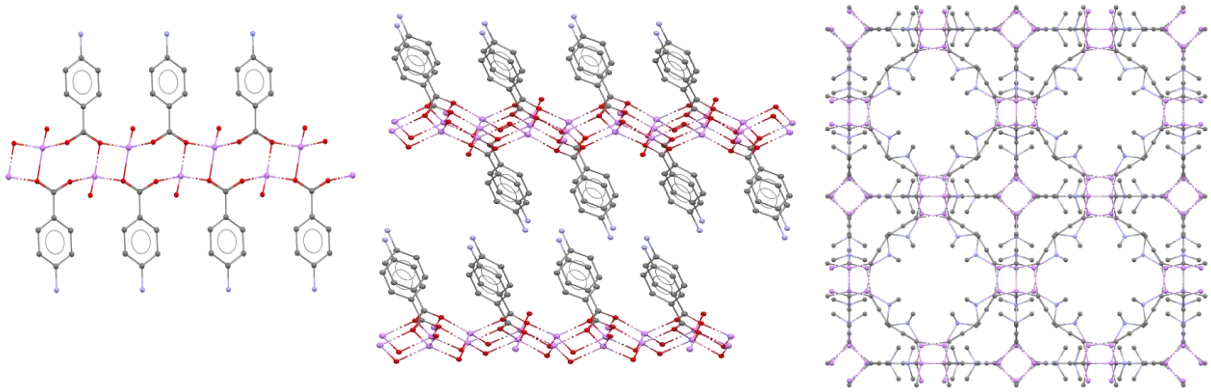


Fig. 1 1D, 2D, and 3D Lithium based MOFs (left to right). Element colours: C = grey, Li = pink, O= red N = purple

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HARNESSING FLEXIBILITY AND ORDER TO ACCESS NEW AREAS OF CHEMICAL SPACE

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Keywords: *metal-organic framework, metal-organic cage, flexible*

Development of novel, highly functional molecules and materials will be essential to tackle the challenges facing humanity over the coming century. In supramolecular chemistry, ligand geometry determines the range of metal-organic architectures accessible. Even small changes in the angle between metal-ligand coordination vectors can profoundly impact the resulting structure. This is particularly well studied in the self-assembly of Pd metal-organic cages, where ligand geometry has been exploited to selectively target,[1] and even transform between,[2] diverse structures with exquisite control.

We envisaged that, by leveraging flexible ligands in a controlled manner, we could access a wide range of unusual metal-organic architectures with a limited number of building blocks. Here we present our recent work using ligands with hinge-like or rotational flexibility to access new metallosupramolecular architectures, with particular focus on the role flexibility plays both in the materials formed, and their solid-state structures. Our findings open new avenues for designing topologically diverse and adaptable molecules and materials.

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Zr(IV) BASED METAL ORGANIC FRAMEWORKS FUNCTIONALIZATION WITH CARBON NANOSTRUCTURES FOR ENERGY RELATED APPLICATIONS

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Keywords: *Zirconium-MOFs*, *MOF-functionalization, Nanocarbon hybrids.*

Metal–organic frameworks (MOFs), due to their high porosity, tunable structures, and diverse chemical functionality, have emerged as promising platforms for the development of advanced hybrid materials. Combined with functional guest components, such as nanocarbons, MOF-based hybrids exhibit synergistic properties significantly enhancing their performance in energy-related applications (e.g., batteries, catalysis, and water splitting) through the improvement of their photoelectric properties. [1-3]

Among the plethora of reported MOFs, over the past decade, Zr (IV)-MOFs have stood out as highly promising platforms for hybrid material development [2-4]. Their wide range of porous scaffolds—arising from diverse topologies [5]—along with exceptional chemical and thermal stability, makes them ideal candidates. Additionally, the availability of coordination sites on their Zr_6O_8 cluster, resulting from its flexible coordination modes, enhances their capacity for functionalization [6].

In this context, various functionalization techniques have been explored to optimize these hybrids, including in situ encapsulation [2-4], direct growth on functionalized surfaces, impregnation, and solvent-assisted linker installation (SALI) [6]. Each of these strategies offers unique advantages tailored to the target application.

In this work, we present the development and characterization of hybrid materials based on porous Zr-MOFs, synthesized from polytopic carboxylate linkers, with selected carbon nanostructures like fullerenes and carbon nanotubes. We explore key synthesis parameters to create stable hybrids and characterize them by employing advanced techniques (Figure 1) as PXRD, N_2 Porosimetry, SEM, FT-IR, Raman, and UV-Vis spectroscopy. Their performance in energy-related applications, such as water splitting, is also evaluated.

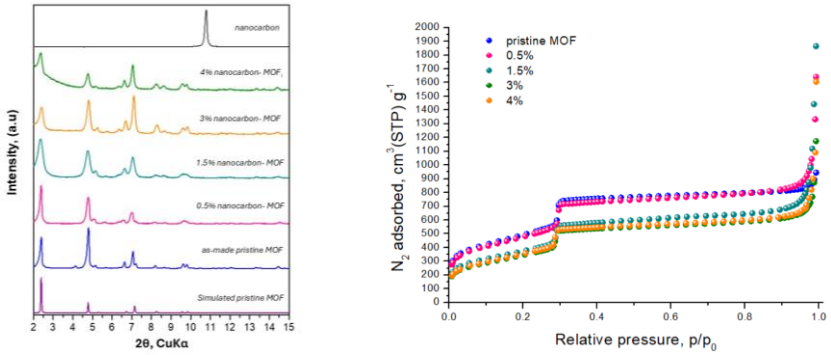


Figure 1. PXRD diagrams and N_2 sorption isotherms of the developed hybrid materials compared to the parent MOF.

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MONOVALENT ANION-PILLARED COPPER(II) FRAMEWORKS: UNCOMMON ARCHITECTURES WITH PECULIAR ADSORPTION BEHAVIOR

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Keywords: *Cu-MOFs, APMOFs, Monovalent Anion, CO_2 Adsorption*

Anion-pillared metal-organic frameworks (APMOFs) are a distinctive subclass of MOFs in which two-dimensional layers are connected by coordinated anions, often resulting in 3D ultramicroporous materials with exceptional gas adsorption and separation properties.[1] While most reported APMOFs employ divalent anionic pillars (e.g., SiF_6^{2-}, TiF_6^{2-}, $NbOF_5^{2-}$, SO_4^{2-}),[1,2] examples based on monovalent anions remain extremely rare, largely due to synthetic and structural challenges.[3]

Herein, we present a new family of isoreticular Cu(II)-based MOFs pillared by monovalent anions (BF_4^-, ClO_4^-, NO_3^-) and built from functionalized bis(imidazolyl)benzene ligands (**bibR**, with R = CF_3, CH_3, Cl, OCH_3). These materials, denoted as **UdP-X** (where *UdP* stands for *Università di Pisa*), exhibit a three-dimensional **pcu** topology where anions bridge square-grid Cu–**bibR** layers, with the second monovalent anion placed in the middle of the pores to balance the copper(II) charge (Figure 1 left). Crystallographic analysis revealed a rare non-centrosymmetric tetragonal space group and disorder on both anions and the linker. The compounds display high thermal stability and exceptional resistance to humidity and solvents, with the overall framework stability and porosity modulated by the steric and electronic nature of the ligand substituents and the anion size. Gas sorption studies show permanent microporosity, promising CO_2 uptake and high CO_2/N_2 selectivity. Notably, materials based on **bibCF$_3$** exhibit CO_2 Langmuir-type isotherms, constant adsorption enthalpy and high performance under flue gas conditions (Figure 1 centre), while **bibCl**, **bibCH$_3$** and **bibOCH$_3$**-based analogues display peculiar structural flexibility upon activation and/or CO_2 adsorption, switching between 3D and 2D structures (Figure 1 right).

These findings introduce the first family of APMOFs pillared by monovalent anions, offering a modular platform for tuning gas adsorption behaviour *via* ligand functionalization and anion selection. The observed structure–property relationships pave the way for targeted design of flexible and high-performing sorbents for gas separation.

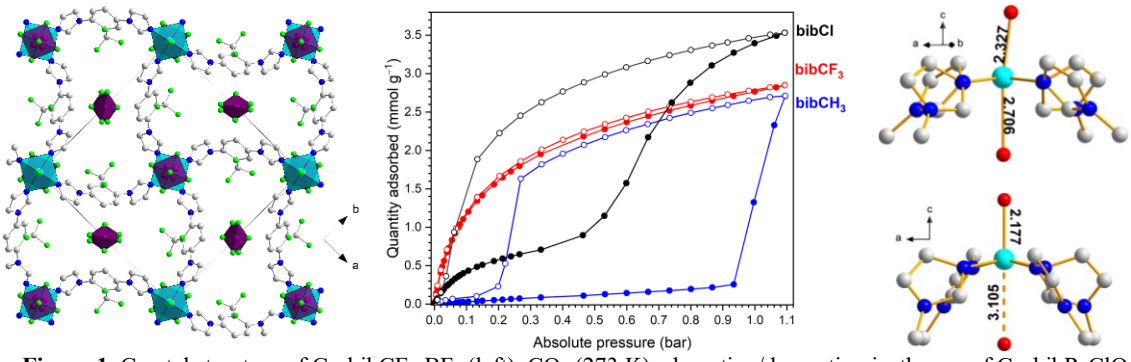


Figure 1. Crystal structure of Cu-bibCF$_3$-BF$_4$ (left), CO_2 (273 K) adsorption/desorption isotherms of Cu-bibR-ClO$_4$ (R = CF_3, Cl, CH_3) (centre) and crystal structure comparison of two Cu-bibCH$_3$-ClO$_4$ phases (right).

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SCCO2-ASSISTED CONTINUOUS FLOW SYNTHESIS OF MOF/GO NANOCOMPOSITES

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Keywords: *supercritical CO_2, continuous flow synthesis, zirconium MOFs, graphene oxides*

Metal-organic frameworks (MOFs) are highly porous crystalline structures composed of metal ions/clusters coordinated to organic ligands. Their tunable structures and high surface areas make them attractive for a wide range of applications. Graphene-based materials, with their extended conjugated carbon networks, provide excellent electrical conductivity and stability. Incorporating graphene-based materials into MOFs can result in hybrid materials with high surface area, excellent electrochemical and mechanical properties, making them promising in energy storage, catalysis, chemical sensing, and water purification.[1] Besides, surface functionalized graphene oxides can coordinate with the metal nodes of MOFs, leading to change in crystal structure, morphology and particle size.

Despite their promise, a major challenge in MOF research remains the scalable and cost-effective production. To address this, our group has developed a supercritical CO_2 ($scCO_2$)-assisted continuous synthesis method. $ScCO_2$ is a green solvent for the synthesis of nanomaterials. With a relatively low critical temperature (31.1 °C) and pressure (7.4 MPa), $scCO_2$ is particularly well-suited for energy-efficient processing of heat-sensitive materials. Our approach enables efficient synthesis of high-quality MOFs, such as HKUST-1, UiO-66, UiO-66-NH_2 and MOF-808 nanoparticles with residence time < 2.5 min.[2,3] We have identified the role of $scCO_2$ in accelerating the nucleation and growth of MOFs. Compared with batch synthesis, our method shows efficient production of typically slow-forming MOFs at production rates reaching grams per hour.

In this work, we extend this $scCO_2$-assisted continuous synthesis to the MOF/GO nanocomposites. A carboxylic acid-functionalized multilayer GO was mixed with the MOF precursors and continuously pumped into the reactor. Using MOF-808/GO as an example, we show that the GO serves as a substrate for heterogeneous nucleation of MOF-808, leading to a reduced MOF particle size. The MOF-808/GO nanocomposites show high BET surface area over 1800 m^2/g, along with enhanced electrical conductivity and thermal stability. We analyzed the effect of GO content on the physical, electrical, mechanical and chemical properties of the composites. Our method shows the potential of $scCO_2$-assisted synthesis for scalable production of MOF-based composites with tailored properties for diverse applications.

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FUNCTIONALIZED NANOCARBONS FOR MOF POST-SYNTHETIC MODIFICATION

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Keywords: *fullerene, carbon nanotube, MOF, impregnation*

The international commitment to achieve zero carbon emission has guided the research on porous materials to shift towards custom-designed photoactive metal organic frameworks (MOFs). It is widely known that molecular catalysts suffer from low surface area, fast photoinduced self-degradation and lack of recycling inhibiting large-scale applications. MOFs consisting of ordered and porous hybrid organic-inorganic scaffold with nanostructured-designed active sites come to the rescue by providing large surface area for adsorption/diffusion of reactants/products as well as increased lifetime of photogenerated charge carriers due to their unique spatial separation.[1],[2] To further exploit such systems, nanostructure engineering is possible by performing post-synthetic modifications to battle current needs application-wise. 0D and 1D nanocarbons such as fullerenes and carbon nanotubes constitute key entities functionalization-wise that can carry functional groups serving as both active sites and anchoring units. Their hybridization with photoactive MOFs offers limitless opportunities by fine-tuning the properties of the hybrid system.[2] Herein, emphasizing the tunable nature of MOFs, modified C_{60} bearing -COOH groups, oxidized single-walled carbon nanotubes and carboxylated azafullerene $(C_{59}N)_2$ were prepared to explore their post-synthetic installation and/or impregnation in several robust photoactive Ti or Cu based MOFs, aiming to create hybrid materials with enhanced performance for solar-driven hydrogen production. Full optimization protocols are presented for the post-synthetic modification of selected MOFs relying on the use of carboxylate modified C_{60}, oxidized single-walled carbon nanotubes and carboxylated aza-fullerene to prepare hybrid networks. All hybrid materials were characterized in detail using state-of-the-art spectroscopic, thermal and imaging techniques.

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SYNTHESIS OF NEW ZINC IMIDAZOLATE SOLID FORMS USING COMPUTATIONALLY ASSISTED MECHANOCHEMISTRY

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Keywords: *Zeolitic imidazolate frameworks, mechanochemistry, templation, polymorphism*

Zeolitic Imidazolate Frameworks (ZIFs) are a class of MOFs built from tetrahedral metal centers and imidazolate linkers that have great potential for applications such as separations, gas capture, and catalysis, all of which are highly dependent on their many diverse solid forms.[1] For example, the sterically unhindered zinc imidazolate (Zn**Im**$_2$), is known to exist in at least 18 topologies[2], which often appear concomitantly. Mechanochemistry has recently emerged as an excellent method for preparing MOFs, as it is fast, quantitative in yield, independent of solubility and creates little waste.[3] Importantly, it can be effectively applied to ZIF syntheses, with the ZIF solid form outcome influenced by the use of different additives, such as liquids or salts.[4]

We now explore the use of commercially available liquid templates as structure-directing agents in the mechanochemical synthesis of new solid forms of zinc imidazolate (Zn**Im**$_2$). We show that multiple Zn**Im**$_2$ forms can be prepared using LAG screening, including new forms of the **crb** topology, and use previously validated periodic DFT modeling[5] to explain the observed synthetic results.

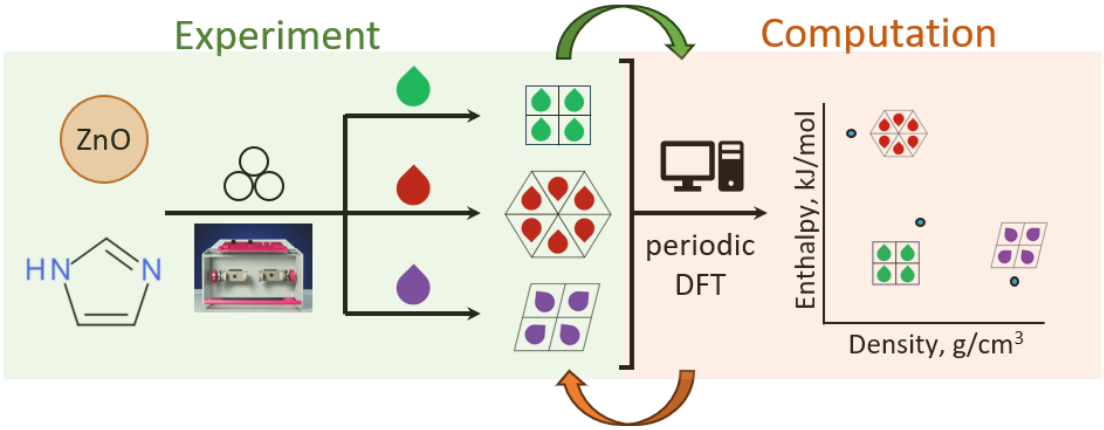


Figure 1: Schematic representation of the dependence of form outcome of the mechanochemical synthesis of Zn**Im**$_2$ on liquid additives, and the interplay of computation and experiment.

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BIOCOMPATIBLE Zn-BASED METAL-ORGANIC FRAMEWORKS FOR DRUG CAPTURE

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Keywords: *metal-organic framework (MOF), biocompatibility, amino acids, drug delivery, controlled release, foams.*

Metal-organic frameworks (MOFs) have achieved significant progress in both biological (**1**) and environmental (**2**) fields due to their biocompatibility and ability to capture pollutants. Despite these advancements, much of their potential remains untapped. This project is dedicated to developing biocompatible MOFs derived from amino acids as organic ligands, combined with metals such as Zn^{2+} and Ca^{2+} (as a secondary metal), with a particular emphasis on their application in drug delivery (**Figure 1**).

The synthesis methodology involves the direct preparation of the MOF, preceded by the synthesis of the organic ligand. Following synthesis, the materials are characterized using a variety of techniques, including Powder X-ray Diffraction (PXRD), N_2 adsorption (ADS), and microanalysis (SEM-EDX), among others.

Furthermore, future plans include conducting comprehensive scaling tests to explore the potential applications mentioned above, as well as the development of new supports, such as cellulose-derived foams (**3**), that facilitate more efficient integration of MOFs. This approach aims to enhance their drug loading capacity and controlled release properties.

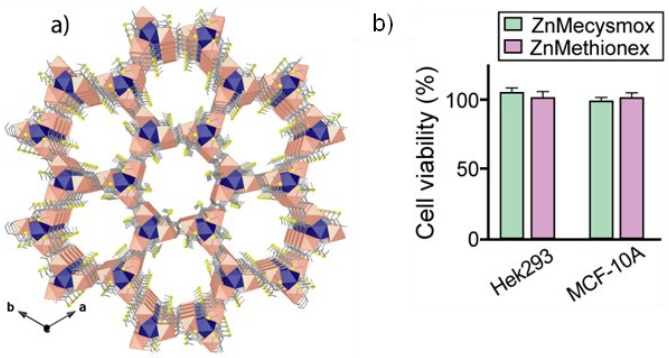


Figure 1. (**a**) Structure of $Zn_6CaMecysmox$. (**b**) Biocompatibility tests: Viability of MCF-10A and Hek293 cells after treatment with MOFs $Zn_6CaMecysmox$ and $Zn_6CaMethiomox$ (10 μM) which was assessed by MTT assay and expressed as a percentage respect to vehicle-treated cells.

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SYNTHESIS OF NEUTRAL AND IONIC METAL-ORGANIC FRAMEWORKS USING MEII IONS, TRIMESIC ACID AND IMIDAZOLE DERIVATIVES

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Keywords: *ionic metal-organic framework, imidazole, trimesic acid.*

Trimesic acid, also known as 1,3,5-benzenetricarboxylic acid (Hbtc), imidazole (mIm) and 2-methyl-imidazole (2-mIm) are well-known organic compounds frequently employed in the synthesis of metal–organic frameworks (MOFs). For example, Hbtc is employed in the production of HKUST-1 (Hong Kong University of Science and Technology – 1), while mIm and 2-mIm are used in the synthesis of Zeolitic Imidazolate Framework -4 and -8 (ZIF-4 and ZIF-8), respectively [1-2]. We have used Co^{II} ions, Hbtc and 2-mIm to synthesise a 3D ionic MOF (iMOF), named material Deutsches Elektronen Synchrotron-1 (mDESY-1) and a neutral 2D MOF named mDESY-2 [3]. Both networks are composed of linking btc linkers and mono-coordinated 2-mIm moieties as pendants throughout the framework. Since mDESY-1 is an ionic MOF, this also contains 2-methyl-1H-imidazol-3-ium ($H2\text{-}mIm^+$) as counter ions inside of the channels of the framework. Although N_2 adsorption experiments showed that the pores in both MOFs are not accessible, mDESY-1 is capable to encapsulate small molecules, such as azobenzene, during the synthesis. Recent ion exchange experiments show that mDESY-1 is also capable to exchange its $H2\text{-}mIm^+$ ions for the cationic drug Metformin, as proved by single crystal X-ray diffraction. Following the success of the first mDESY MOFs, more than 10 mixed-ligand MOFs were synthesized using Co^{II}, Cu^{II}, Zn^{II} or Ni^{II} ions as metal centres and btc and mIm or 2-mIm as ligands, including a 1D anionic MOF. This work highlights the vast potential still left in the field of MOF synthesis. Despite using conventional chemicals, the successful synthesis of mDESY-1, mDESY-2 and the new recent systems demonstrate that novel MOFs with distinct properties can still be discovered. The ongoing exploration of MOF synthesis, particularly in the ionic subclass, is likely to yield further breakthroughs, advancing the capabilities of these versatile materials.

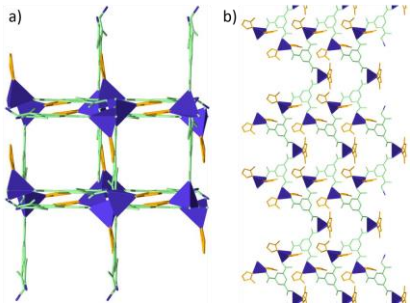


Figure 1. Packing of a) mDESY-1 and b) mDESY-2 view along the c axis.

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RAPID DEVELOPMENT OF VAST FAMILY OF ANIONIC METAL-ORGANIC FRAMEWORKS FACILITATED BY STRUCTURE-DIRECTING GUESTS AND 3D ELECTRON DIFFRACTION

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Keywords: *Electron diffraction, MOFs, Structure-directing agent, Ellagic acid*

Structure directing agents (SDAs) are widely used in the synthesis of porous oxide materials such as zeolites, but their application and role in the synthesis of metal-organic frameworks (MOFs) has been comparatively understudied. Here we report a diverse family of anionic MOFs with frameworks constructed exclusively from the same metal cation and plant-based organic linker — Zr(IV) cations and ellagate anions.[1] Applying the same 1h synthesis conditions but changing only the species or amount of SDA resulted in 20 novel zirconium ellagate MOFs (denoted SU-103 – SU-122). The short synthesis protocol combined with fast 3D electron diffraction (3D ED) for crystal structure determination contributed to the rapid discovery of these novel materials — in the case of SU-106, SU-116 and SU-119 all were synthesized and their structures were determined within the same day. 3D ED also revealed the location of the SDAs in the pores of all MOFs, enabling a detailed study of their host-guest interactions. All 20 MOFs have unique structures with varying dimensionality, topology, Zr(IV) coordination geometry, intermolecular framework interactions, and varying degrees of framework interpenetration. Despite most of the MOFs having similar framework compositions, their properties differ due their unique framework structures and chemical properties of the SDAs. The MOFs demonstrate chemical stability in aqueous media, basic conditions, and concentrated salt solutions, which is attributed to the strong Zr-catecholate chelation consolidating the frameworks. We anticipate these 20 MOFs make up only a small portion of a plethora of potential MOFs within this system. This lays the groundwork for the rapid development of many other guest-directed MOFs made with different SDAs, framework metal cations, as well as other organic linkers with polyanionic functional groups.

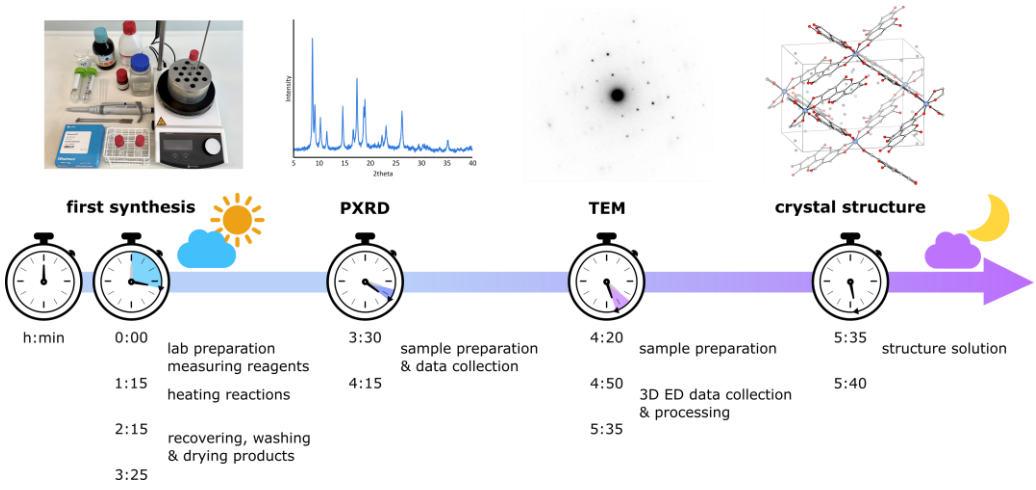


Figure. Schematic illustration of synthesis and structure solution of novel MOFs within in a single day.

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MULTICOMPONENT ULTRAPOROUS MOFs WITH HIERARCHICAL POROSITY FOR GAS/VAPOR STORAGE APPLICATIONS

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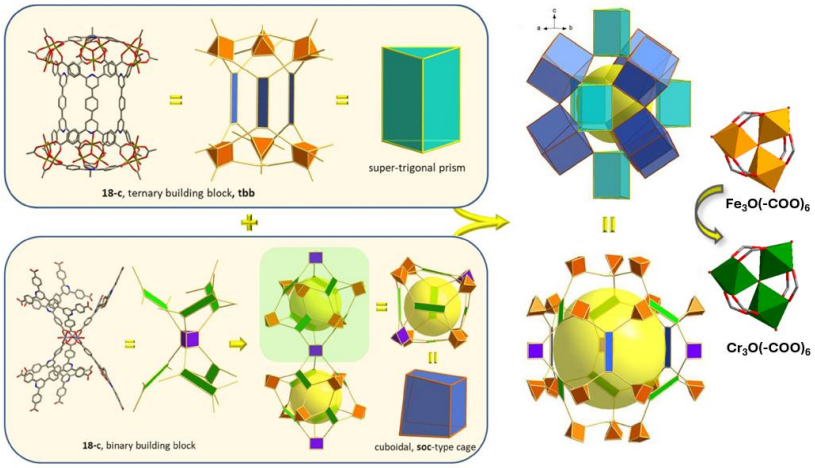
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Keywords: *Metal-Organic Frameworks, Reticular Chemistry, Supermolecular Building Blocks, Gas Storage, Water Adsorption*

Metal-Organic Frameworks (MOFs) have emerged as a distinctive class of crystalline, open-framework solids, demonstrating impressive potential to address major global challenges related to energy and environmental sustainability. Importantly, the assembly of MOFs can be rationally guided by the principles of Reticular Chemistry towards the generation of made-to-order materials. In particular, the embedded geometrical information within both the inorganic and the organic molecular building blocks serves to precisely code the desired network topology. However, the "true" design of MOFs mainly relies on the availability of highly connected building blocks because their combination has a limited number of compatible, outcome nets.

In this regard, we report the discovery of novel 18-connected, trigonal prismatic, ternary building block (tbb's), emerging from the assembly of triangular (3-c) and rectangular (4-c) carboxylate-based organic linkers and trigonal prismatic $[Fe_3(\mu_3\text{-}O)(-COO)_6]+$ clusters.[1] The tbb's are subsequently linked together by an 18-connected binary building block to form 3D MOFs, denoted as Fe-**tbb**-MOF-x (x: 1,2,3), with hierarchical micro- and mesoporosity. The ultraporous nature of Fe-**tbb**-MOF prompted us to investigate its H_2 and CH_4 storage properties, revealing well-balanced high gravimetric and volumetric deliverable capacities for cryoadsorptive H_2 storage, as well as CH_4 storage at near ambient temperatures. Post-synthetic transmetallation of Fe-**tbb**-MOF-x with Cr(III) afforded the isostructural Cr analogues (Cr-**tbb**-MOF-x), further expanding this novel family of MOFs. Cr-**tbb**-MOF-x exhibits exceptional chemical and hydrolytic stability, combined with high porosity, resulting in one of the highest reported water vapor uptake capacities.[2] Important synthesis and structural details as well as in-depth gas/vapor sorption studies will be presented and discussed.



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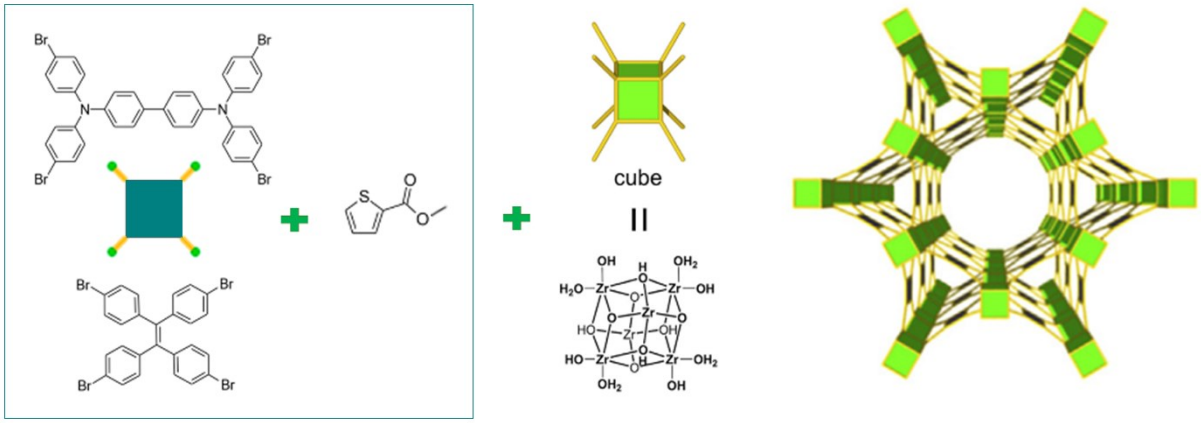
DESIGNING LINKERS, CRAFTING PORES: SHORTCUT STRATEGIES FOR SYNTHESIS OF MESOPOROUS Zr-MOFs AND ADVANCED CHARACTERIZATION

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Keywords: *Mesoporous MOFs, Modulator, Direct arylation*

The pursuit of greener routes for synthesizing MOFs has garnered significant attention, as this is a critical step toward scalable applications. This study presents an efficient methodology for the systematic design of extended tetratopic organic linkers (LE-4 and LE-5) to create shortcut pathways to mesoporous Zr-MOFs with tailored structural properties. By employing simple and cost-effective organic precursors, we demonstrate a streamlined synthetic approach that reduces the number of reaction steps while maintaining high efficiency and yield. Our strategy uses simple organic precursors to generate tetratopic cores with Br ends, the main building blocks for extended linkers. These cores are further functionalized through one-pot in situ reactions with carboxylated thiophene-based arms. In this approach, we use direct arylation for C–C coupling, which offers several advantages over traditional cross-coupling techniques, including higher yields, fewer synthetic steps, lower catalyst loadings, and elimination of organometallic intermediates[1]. We also used different modulators and investigated their influence on the synthesis of the Zr-MOFs. Comparing the synthesis products using different modulators showed that, in some cases, coordination isomers have been achieved by just changing the modulator type. The structural characterization of the synthesized MOFs is conducted using state-of-the-art techniques, including three-dimensional electron diffraction (3DED) and synchrotron X-ray diffraction. These advanced methods provide complementary insights into the crystallographic and topological features of the MOFs[2,3].



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DESIGN OF NOVEL METAL ORGANIC FRAMEWORKS BUILT FROM OXAMATE-FUNCTIONALICED AMINO ACID LIGANDS

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Keywords: MOFs, amino acids, oxamate ligands, oxamidate ligands, metalloligand.

The primary objective of this study is to advance the design and synthesis of metal-organic frameworks (MOFs) incorporating oxamate-based ligands derived from amino acids—a field that has seen remarkable growth in recent years. To achieve this, we have selected functionalized oxamate derivatives to construct extended architectures capable of exhibiting intriguing properties, such as chirality.

The synthesis process follows an indirect route for the oxamate-based compounds: first, the amino acid oxamate is synthesized as a ligand; then, the Cu^{2+} complex (metalloligand) is formed with the oxamate; and finally, the MOF is assembled using Ni(cyclam)Cl_2 as the second metal.

Characterization of the MOFs is performed using powder and single-crystal X-ray diffraction (PXRD and SCXRD), microanalysis (SEM-EDX), and N_2 or CO_2 adsorption measurements. The synthesis conditions will be further optimized to identify the most suitable ones and apply them to enantiomer separation, leveraging the chiral nature of amino acids.

Additionally, some of the oxamate-based MOFs that incorporate sulfur atoms into their structure are capable of absorbing gold (Au) through sulfur-gold interactions, enabling the recovery of this metal from solution [1].

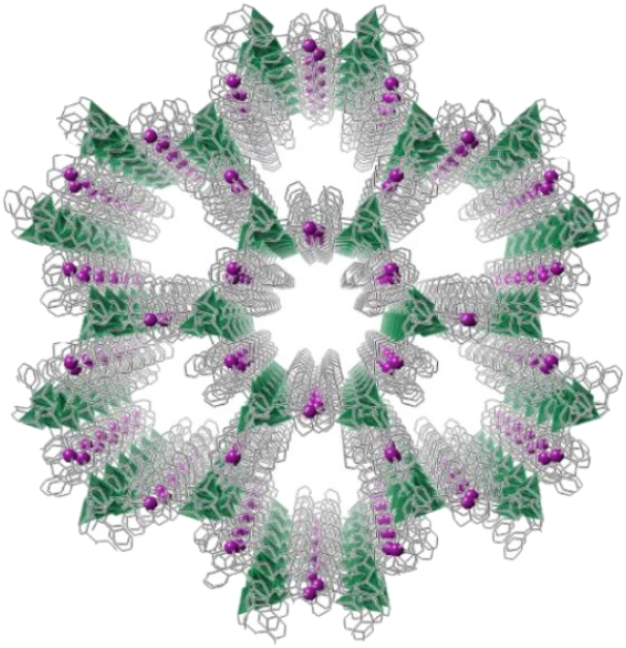


Figure 1. The copper(II) and nickel(II) atoms are represented by green polyhedra and purple spheres, respectively. The ligand backbone is depicted as grey sticks.

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MOLECULAR SHUTTLES AS LINKERS FOR THE DESIGN OF FLEXIBLE MOF ARCHITECTURES

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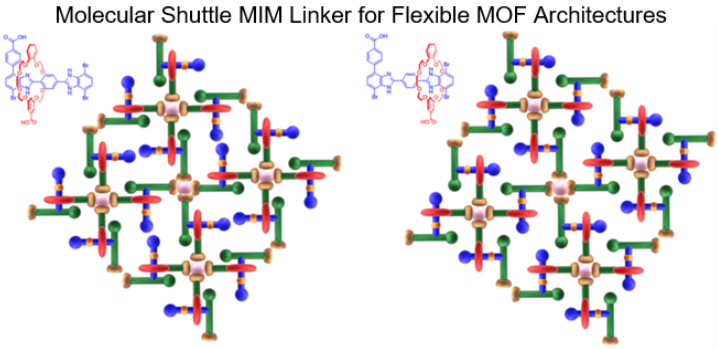
Keywords: *molecular shuttles, MIM linkers, flexible MOFs, dynamic behavior, VT-NMR*

Molecular shuttles are a subclass of Mechanically Interlocked Molecules (MIMs), alongside catenanes and rotaxanes. They feature a macrocycle that moves along a molecular axle between two or more recognition sites. The dynamic nature of MIMs has inspired their incorporation into Metal–Organic Frameworks (MOFs), leveraging the exceptional structural tunability of MOFs to incorporate motion-enabled linkers. However, achieving framework-level flexibility through the integration of dynamic MIMs remains a significant challenge. [1-6]

Our current research focuses on the design of a new class of molecular shuttle MIM linker capable of affording flexible MOF materials. In this work, we present the synthesis of a new MIM-based linker that was successfully achieved through a modular synthetic platform involving multi-step organic syntheses. This molecular shuttle MIM linker features an L-shaped axle and a macrocyclic ring with strategically positioned carboxylic acid groups to enable coordination leading to MOF architectures. Its formation was confirmed by spectroscopic analysis, including ^{1}H, ^{13}C NMR, IR, as well as mass spectrometry.

To probe the dynamics of the molecular shuttle MIM linker, we performed VT (Variable-Temperature) ^{1}H NMR experiments across its protonation states. In the neutral form, rapid shuttling was observed even at the lowest accessible temperatures, suggesting a low energy barrier between co-conformations. Upon titration, the formation of charged species led to a single dominant co-conformation. These findings support the design of our linker as a responsive MIM motif.

Current efforts are focused on crystallizing this linker into a single-crystal MOF material for structural characterization and investigation of its dynamic behaviour, with the goal of developing flexible frameworks with emergent mechanical properties and, ultimately, enabling controlled, stimuli-responsive function.



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A MILD WATER-BASED ROUTE TO SYNTHESISE UIO-66 FROM TEREPHTHALATE ESTERS

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Keywords: *UiO-66, water-based synthesis, terephthalate esters*

The Zr-terephthalate MOF UiO-66 was discovered more than a decade ago, and it has rapidly become one of the most studied MOFs, owing to its high thermal, chemical and mechanical stability.[1] UiO-66 is typically prepared by solvothermal synthesis in *N*,*N*-dimethylformamide (DMF), which is also involved in the workup stage. This is necessary because of the limited solubility of terephthalic acid in the most common organic solvents and in water. The use of DMF is one of the major drawbacks for the transfer of UiO-66 in applications since DMF is flammable, toxic and teratogenic. Furthermore, DMF has a high boiling point (153 °C), and its removal from the product requires many washes with more volatile organic solvents, like methanol, or water. Besides this, the European Commission has recently proposed to restrict the industrial use of DMF because of its toxicity.[2] Thus, the development of a DMF-free process to synthesise and purify UiO-66 is a topic of interest to enable commercial deployment of this MOF.

In this work, we propose a water-based route to synthesise UiO-66 through the reaction shown in Figure 1. The terephthalate ester bis(2-hydroxyethyl) terephthalate (BHET), which can be obtained from the glycolysis of waste polyethyleneterephthalate,[3] was used as a source of the linker. Hydrochloric acid and acetic acid were used as modulators during the synthesis to control the kinetics of ester hydrolysis and MOF crystallisation, aiming to avoid collateral precipitation of terephthalic acid. A chemometric design of experiments was employed to optimise the reaction parameters, finding that 15 molar equivalents of hydrochloric acid enable hydrolysis without inhibiting crystallisation, while acetic acid controls which phase is obtained, favouring the desired **fcu** topology at 15 molar equivalents. The optimised conditions afford UiO-66 with high crystallinity and porosity in just 2 hours at 90 °C. A crucial role in the process is played by the monoester, which is more soluble than both the diester and the diacid in the reaction environment and can be involved in the formation of secondary building units. We also developed a DMF-free workup protocol based on the use of ethanol/dimethylsulfoxide mixtures and water. 50-fold scale up (500 mL) was demonstrated using a round bottom flask, producing UiO-66 with properties comparable to the product of the small-scale synthesis and with a space-time yield > 200 kg m^{-3} d^{-1}.

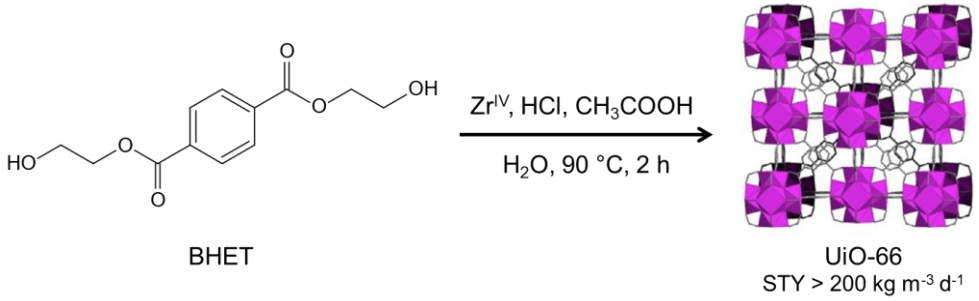


Figure 1. Water-based Synthesis of UiO-66 starting from BHET as the source of terephthalic acid.

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A SIMPLE DESIGN STRATEGY FOR HIGHLY STABLE LARGE-PORE ZIRCONIUM MOFS

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Keywords: *Zirconium MOF, piperazine, stability, precious metals recovery*

Metal-organic frameworks (MOFs) are widely studied in the field of porous materials research, owed to their remarkable structural tunability, record porosity, and versatility in potential host-guest applications[1]. Among these, zirconium carboxylate-based MOFs, as for example UiO-66[2], are of particular interest due to their chemical, mechanical and thermal stability, which derives in part from the strong bonds formed between the Zr metal cluster and the carboxylate ligands[3]. To broaden their applicability in host-guest chemistry and the tunability of their pores, emphasis has been placed at designing large, structurally diverse ligands that promote pore expansion and higher pore volumes. Unfortunately, such ligands are typically composed of multiple interconnected aromatic rings;[4] thus, their syntheses, which usually require Pd-catalyzed C-C coupling chemistry, is often cumbersome and expensive, rendering their scale-up challenging.

Given this, we recently developed a novel, simplified strategy for the synthesis of long organic ligands; by simply replacing the center aromatic ring with piperazine building units, the synthetic route is proven to be less time and resource intensive (i.e., eliminating the need for transition metal catalyst, reducing synthetic steps, etc) and scalable[5]. Moreover, this synthetic pathway makes the functionalization and tuning of the ligand straightforward, by simply selecting the adapted starting material (**Figure 1a**). Therefore, we have been working to show that these ligands can offer a simple, cost-effective, and scalable route for producing an extensive library of new highly porous (up to more than 3000 m^2/g) Zr-MOFs having large pore dimensions and simultaneously comparing their stabilities to their oligophenylene analogs. Here we present our findings on the development of new robust materials built from piperazine-based ligands (Zr-piperazine MOFs, **Figure 1b**). We will focus on our efforts to tune the ligand structure to improve the chemical stability of the resulting materials. Notably, approaches discussed include ligand rigidification via sterically hindering groups that "lock" rotations of the C-N bond[6] and the use of functionality that are intended to chemically protects the piperazine core and/or increases the hydrophobic nature MOFs pores. Moreover, in addition to being highly stable by retaining both porosity and crystallinity even in strongly acidic environments, it will be shown that selected Zr-piperazine metal-organic frameworks can present high performances in precious metal recovery.

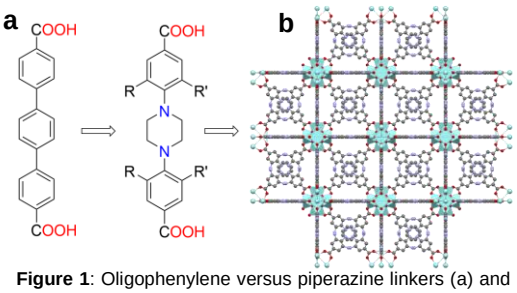


Figure 1: Oligophenylene versus piperazine linkers (a) and the resulting fcu topology of Zr-piperazine MOFs (b)

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EXPLORING THE SYNTHESIS OF HIGH NUCLEARITY CLUSTER-BASED METAL–ORGANIC FRAMEWORKS USING EARLY LANTHANOIDS

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Keywords: *cluster-based MOFs, rare-earth*

Metal–organic frameworks (MOFs) are porous materials generated by the assembly of inorganic metal nodes and multitopic organic linkers. The term rare-earth (RE) element includes yttrium, scandium and the fifteen lanthanoids. Using RE metal nodes in MOFs is interesting due to the diverse coordination chemistry of RE ions as well as their unique electronic properties arising from their 4*f* electrons. Additionally, RE elements present similar chemical behavior, such as oxidation state and accessible coordination number (CN), allowing the formation of series of RE-MOFs with the same structure save for the elemental composition of the inorganic node.

To access RE-MOFs containing high nuclearity clusters, the utilization of fluorinated modulators, most commonly α-fluorinated acids, is necessary.[1] Recent studies have shown evidence of the presence of μ_3-F groups bridging the clusters, suggesting that the C–F bond from the modulator is broken in the reaction conditions, incorporating fluoride into the MOF.[2]

While there are many reports of MOFs obtained with early lanthanoids presenting metal chain nodes, or low nuclearity clusters, there are few examples of high nuclearity clusters made from these metals. Moreover, most of the reported examples lack characterization, suggesting that the synthesis is challenging, might not be reproducible, or that the obtained phases present impurities.[3,4] There is a clear limitation when it comes to employing these larger metal ions, but there is no evidence of the cause behind it. The study of this limitation could be important, not only to access these new analogues, but also to better understand the mechanism of formation of RE cluster-based MOFs.

In this work, six new hexanuclear cluster-based MOFs containing early lanthanoids are synthesized and characterized. All the MOFs are obtained as pure phases and with high reproducibility. The parameters that need to be controlled in order to obtain these structures are identified and their effects on the formation of the desired product are studied. Additionally, the differences between the formation of these MOFs compared to the analogues obtained with the late lanthanoids are discussed.

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SUSTAINABLE AL-FUMARATE SYNTHESIS: SPRAY DRYING UPSCALING AND DEVELOPMENT OF ALTERNATIVE GREEN APPROACHES

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Keywords: *Aluminum MOF, sustainable, spray-drying, large scale, sol-gel*

Aluminium-based MOFs, are promising candidates for various applications such as water harvesting[1] or thermal heat management[2]. However, significant obstacles remain in the synthesis of these materials, including the use of toxic solvents, harmful reagents, demanding pressure and temperature conditions, and their susceptibility to degradation in humid air. These challenges hinder the scalability of their production and limit their industrial applications.

Our study introduces an efficient, upscaled synthesis of Al-fumarate via spray-drying, a process that combines synthesis and work-up into a single step. This all-in-one synthesis method produces high-quality, calibrated Al-fumarate grains without the need for further processing (Figure 1). Unlike previously reported aqueous-phase synthesis routes that require basic conditions (e.g., NaOH addition[3]), the approach presented here operates at a pH below 3. The use of aluminium isopropoxyde as a base enables a steady reaction with fumaric acid without requiring pH adjustment. Structural analysis reveals major differences in the meso- to macroporous structure depending on the drying process: the spray-dried pilot batch exhibits high-density characteristics with an absence of intergranular porosity, unlike other drying techniques. We show here a demonstration at pilot scale using an industrial sized spray-drier allowing production of 10 kg/h.

As a proof-of-concept, air dehumidification was performed in a fluidized bed, highlighting its advantages over fixed beds. The fluidized bed's superior heat transfer ensures greater isothermicity, as demonstrated by the breakthrough curve profile, which shows a longer $t_{50\%}$ and confirms improved column isothermicity.

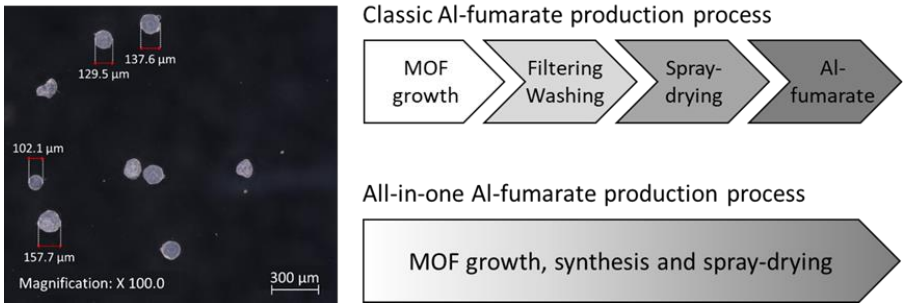


Fig. 1. Calibrated al-fumarate dense spheres obtained at the spray-drier pilot at Axel'One (left) and schematic representation of the all-in-one designed synthesis process (right).

Ultimately, we developed a comprehensive 3-in-1 process that integrates synthesis, drying, and shaping, while also demonstrating its potential for production intensification. This synthetic approach paves the way for the scalable production of other aluminium-based MOFs with promising application such as CO_2 capture. In addition to spray drying, other sustainable and efficient alkoxy sol-gel processes have been developed to expand the green production of aluminium-based MOFs.

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OPTIMIZATION OF SYNTHESIS PARAMETERS FOR PHASE-SELECTIVE, ENVIRONMENTALLY FRIENDLY AL-BTC PRODUCTION

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Keywords: *Al-BTC MOF, phase selectivity, in situ Raman*

Aluminum-based metal–organic frameworks (Al-MOFs) have attracted considerable attention due to their strong potential in key applications such as water adsorption and purification, or coating of heat exchangers. Their structural robustness in the presence of moisture makes them suitable for large-scale use. We recently developed a green synthesis route for Al-MOFs using aluminium alkoxide precursors such as aluminium isopropoxyde[1]. This method operates solely in water and eliminates the need for a filtration step (no saline co-products are formed). These features make this approach promising for simplified and sustainable large-scale production of Al-MOFs, such as Al-fumarate or MIL-160(Al).

Among Al-MOFs, Al-BTC is a well-known polymorph MOF. It is constructed from benzene-1,3,5-tricarboxylate linker (H_3BTC) and can form three distinct phases: MIL-96, MIL-100 and MIL-110[2]. This study explores how our green synthesis pathway was adapted to selectively obtain different Al-BTC phases. Interestingly, the MIL-100(Al) phase could not be achieved using our method. Instead, subtle transitions between MIL-96 et MIL-110 were observed. We systematically investigated synthesis parameters—including the molar ratio between aluminum and the linker, reaction temperature, and duration—and were able to construct a phase predominance diagram under stoichiometric conditions as a function of reaction temperature (Figure 1).

After optimizing the reaction conditions, we focused on investigating the potential phase evolution between MIL-96 and MIL-110. To this end, we employed in situ Raman spectroscopy during the synthesis of both MOFs. This technique enabled us to monitor spectral bands associated with both reactants and products over the course of the reaction. Our goal is to identify Raman features capable of distinguishing between the two phases and to determine whether a phase transition occurs during synthesis.

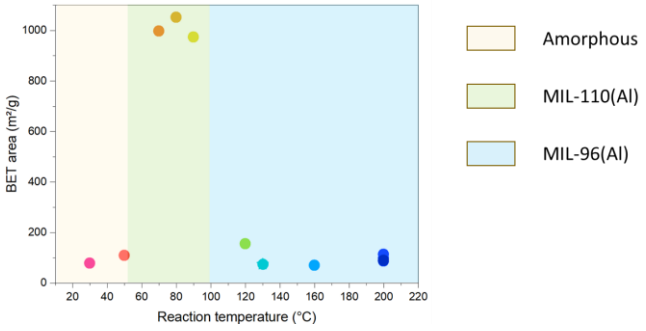


Figure.1: phase predominance diagram under stoichiometric conditions as a function of reaction temperature.

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IONIC COVALENT ORGANIC FRAMEWORK NANOSHEETS-BASED MEMBRANES WITH ENHANCED PROTON CONDUCTION THROUGH SYNERGISTIC DUAL FUNCTIONALIZATION AND MONOMER ENGINEERING

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Keywords: *covalent organic framework, fuel cell, ion exchange capacity, nanosheet, proton exchange membrane*

Achieving high proton conductivity in solid-state electrolytes under wide operating conditions remains a significant challenge for proton exchange membrane fuel cells.[1] Among crystalline porous materials, ionic covalent organic frameworks (iCOFs) have attracted extensive attention as proton exchange membranes owing to their ordered ion channels with abundant ion groups and remarkable structural tunability. Proton conductivity of iCOFs is strongly governed by their ion exchange capacity (IEC); however, the limitation of IEC arises as the ionic groups are primarily derived from monomer.[2] Post-synthetic modification (PSM) can boost the IEC by introducing additional ionic groups into pre-established iCOFs, yet PSM step itself reduces membrane processability, and the intrinsic ionic groups in iCOFs further impede the PSM efficiency.[3] Therefore, the systematic monomer engineering to enable efficient PSM is essential for fabricating post-modified COF-based membranes.

Here, we demonstrate a dual-functionalization strategy via PSM on iCOF nanosheets with intrinsic sulfonic groups to effectively overcome conventional IEC limitation of iCOFs and fabricate free-standing films with high proton conductivity. Through systematic engineering of amine and aldehyde monomers with varying reactivity and solubility, we optimized the formation of iCOF nanosheets, solution processability and PSM efficiency (Figure 1a). The β-ketoenamine-linked iCOF with sulfonic groups (COF-$(SO_3H)_2$) inherently possesses sufficient ionic groups, further enriched through PSM, yielding COF-$(SO_3H)_2$-PSM (Figure 1b). Specifically, the controlled ionization of sulfonic groups in solution through the monomer engineering modulates charge-induced electrostatic repulsion between ionic groups, promoting in-plane anisotropic growth of nanosheets (Figure 1c). The excellent solution processability of these elaborately engineered nanosheets allow efficient grafting of alkyl sulfonic groups onto enamine linkages and subsequent fabrication of free-standing films (Figure 1d). Dual-functionalization with sulfonic groups from both intrinsic frameworks and additional PSM significantly enhances surface charge density and IEC. Notably, the introduction of elongated alkyl sulfonic groups via PSM substantially expands the hydrogen-bonding networks into internal ion channels for efficient proton conduction. Furthermore, the flexible alkyl chains dynamically reorganized to form a continuous proton conduction pathway, overcoming the spatial limitation of fixed and short ionic groups typically present in the pristine iCOFs (Figure 1e). These synergistic improvements in both IEC and hydrogen-bonding networks lead to substantially enhanced proton conductivity across a wide range of operating conditions. This study provides promising guidance for the rational design and fabrication of highly conductive iCOF-based membranes for various application.

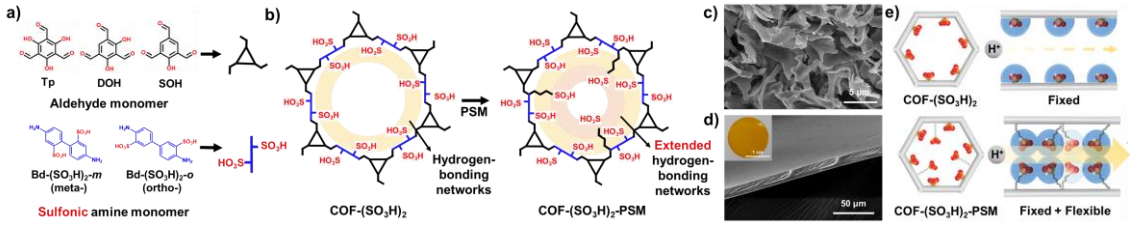


Figure 1. (a) Monomer engineering with various combinations, (b) he schematic illustration of COF-$(SO_3H)_2$-PSM,SEM images of COF-$(SO_3H)_2$-PSM (c) nanosheets and (d) free-standing films with its photo (inset), (e) The illustration of the ion channel structure of COF-$(SO_3H)_2$ and COF-$(SO_3H)_2$-PSM

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MATERIAL PREPARATION INFORMATION FILE (MPIF): A COMMUNITY-DRIVEN STANDARD FOR REPORTING MOF SYNTHESES

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Keywords: *Synthesis, reproducibility, data-management, standardization*

The synthesis of metal-organic frameworks (MOFs) typically requires the use of several chemical components including an organic linker, an inorganic salt, a solvent, and often a modulator. In many cases, the glassware and equipment used can impact the quality of the synthesized product. The reporting of successful syntheses is generally performed through free-text descriptions in scientific publications, with limited standardized guidelines. Scientists mainly rely on their professional education and training, as well as their personal writing preferences, to provide the "best-possible" description of the synthesis procedures of any materials, including MOFs. This relatively unstructured approach to reporting often results in incomplete synthetic protocols that can cause reproducibility issues, particularly in third-party laboratories. Furthermore, important details and “know-how” that can be essential for the successful synthesis of a particular MOF can sometimes be omitted. This often leads to significant efforts needed for further synthesis optimization based on the procedures written in the literature.

We propose a standardized presentation format for MOF synthesis in the form of the machine-readable, text-based ‘**Material Preparation Information File**’ (MPIF). Each MPIF contains detailed information related to the synthesis of MOFs, including synthesis scale; lab conditions; details regarding reactors, reactants and solvents; masses, moles and volumes used; energy source; reaction conditions; isolation methods; yields; stroage conditions; etc. MPIF has a modular structure and presents the relevant information in a systematic way and can be expanded to include fields related to atypical synthesis conditions. The preparation of a MPIF can be done manually or via a web-based interface. In addition, basic characterization data such as powder X-ray diffraction patterns, N_2 adsorption/desorption isotherms, and thermogravimetric profiles can be embedded into a single MPIF. We envision that MPIF files will be included as a supplementary file to a relevant publication and later be incorporated into large chemical databases such as the Electronic Laboratory Notebook (ELN) and Repository for Research Data Chemotion. Furthermore, the widespread adoption of MPIF can increase the inter-laboratory reproducibility of MOFs and is also an essential part of the scaled-up synthesis of MOFs for industrial application.

The MPIF initiative is jointly developed by several research groups through the EU4MOFs network (an Action funded by the European Cooperation in Science and Technology – COST CA22147).

ENGINEERING PILLARED-LAYERED FCU-MOFS FOR HYDROCARBON SEPARATION

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Keywords: *pillared **fcu**-MOFs, crystal engineering, hydrocarbon separation*

Throughout the evolution of the field of reticular chemistry, numerous design strategies have been developed.[1] Among which is the supermolecular building layer (SBL) approach, which permits the practice of isoreticular chemistry in one dimension, through pillaring, while preserving the integrity of the layers.[2]

Through the careful investigation of the well-known **fcu** topology, its compatibility with the SBL approach to produce mix-ligand MOFs has shown to be quite promising. Such opportunity of combining two organic MBBs of different nature (shape, length, functionality, etc.) in distinct crystallographic positions, led us to develop a series of rare-earth and Zr-based isoreticular **fcu**-MOFs. Additionally, varying the pillaring mode by the careful choice of linkers permits the modification of the layer stacking mode, either through targeting the **hex** topology or through pursuing additional possible pillaring options.

Although the tridimensional nature of the materials' porous system does not allow, a priori, the separation of gas pairs, the specific consideration of the dynamic triangular pores of the chosen SBL suggests otherwise. Through crystal engineering, we were able to control the morphology of the crystals into their respective nanosheets, and consequently orient and incorporate them successfully in a mixed-matrix membrane, showing enhanced hydrocarbon separation.

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MODULATOR-CONTROLLED EXFOLIATION OF TWO-DIMENSIONAL Zr-MOFs

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Keywords: *2D-MOF, Liquid-Phase Exfoliation, Nanosheets, HRTEM, Modulator Exchange*

Exfoliation of layered materials into nanosheets offers a route to access high surface areas, increase the accessibility of active sites and reach unique physical properties. For MOFs, strong interlayer interactions and relatively weak coordination bonds in the layer hinder efficient exfoliation, especially without compromising crystallinity.[1] Herein, we address this challenge by tuning the surface chemistry of a two-dimensional Zr-MOF to modulate interlayer interactions and control exfoliability.

DUT-84(Zr) ($[Zr_6O_8(2,6\text{-ndc})_6(CH_3COO)_2]_n$, ndc = 2,6-naphthalenedicarboxylate])[2] is a two-dimensional MOF that consists of Zr_6O_8 secondary building units (SBUs) coordinated in-plane by four and out-of-plane by two ndc ligands, forming a double-layered structure, which is capped by modulator ligands. Naphthalene linker cores of the neighboring double layers in DUT-84 are parallel displaced with an inter-layer distance of 3.86 Å, pointing on the considerable attractive forces between π-systems. The mono-carboxylate modulator ligands dictate the crystal structures inter-layer distance.

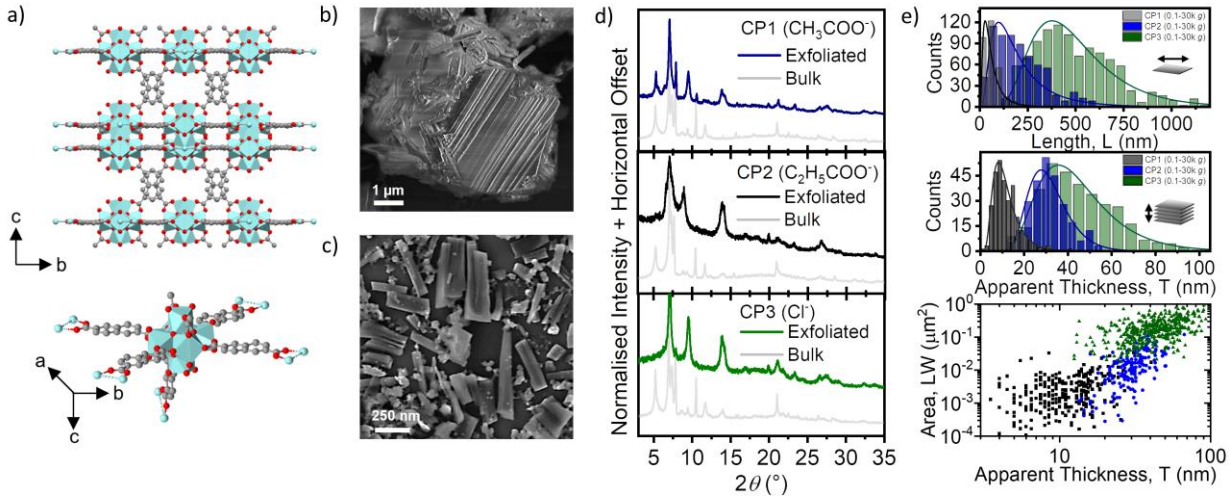


Figure 1. (a) Crystal structure of DUT-84 along the *a* axis (top) and SBU (bottom). SEM images of bulk (b) and exfoliated materials (c). (d) Experimental PXRD patterns of bulk and exfoliated MOFs with altered modulator ligands. (e) Length-/ thickness-count of exfoliated crystals with thickness-area plot.

Through the strategic use of modulator molecules - introduced either during synthesis or via post-synthetic exchange - the nature and spatial arrangement of modulator ligands that dictate interlayer forces could be altered. Replacing acetate with bulkier propionate increases the interlayer spacing, facilitating the exfoliation to thinner nanosheets upon ultrasound-assisted liquid-phase treatment. Exchanging capping groups with chloride ions reduces the interlayer distance and increases electrostatic attraction, thereby suppressing exfoliation.

Systematic structural and morphological analyses reveal a threefold variation in nanosheet thickness across the modified materials. This work establishes a framework for chemically guided exfoliation of MOFs, underlining the critical role of crystallographic design and surface termination in achieving high-quality nanosheet dispersions.

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CONTROL OF DECARBONATION REACTIVITY BY CO_3^{2-}-BASED COORDINATION POLYMERS

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Keywords: *CO_2 circulation, Carbonate ions, Decarbonation*

Materials capable of reversibly fixing and releasing CO_2 under mild conditions are key to energy-efficient CO_2 capture. Metal carbonates have been widely studied because of their high CO_2 contents and capability to capture CO_2 from the air. On the other hand, metal carbonates require high temperature above 300 ºC for decarbonation. The high decarbonation temperature (T_{de}) is due to the strong ionic bonds between metal ions and CO_3^{2-}.[1]

In this study, we focused on coordination bonds to immobilize CO_3^{2-} within a coordination polymer lattice (Figure 1). The tunable feature of coordination bonds enables control over chemical environment of CO_3^{2-}, which influences the decarbonation reactivity. While CO_3^{2-}-based coordination polymers (CO_3^{2-}-CPs) have been reported, the decarbonation reactivity remains unexplored.[2] We synthesized CO_3^{2-}-CPs by converting atmospheric CO_2 into CO_3^{2-}. The decarbonation behaviors of CO_3^{2-}-CPs were characterized by TGA equipped with a CO_2 sensor. CO_3^{2-}-CPs exhibited decarbonation temperature lower than that of metal carbonates due to the low coordination number of CO_3^{2-} with metal ions. Variable-temperature PXRD revealed structural transformation of CO_3^{2-}-CPs during decarbonation. We will discuss the correlation between the chemical environment of CO_3^{2-} within CPs and decarbonation properties.

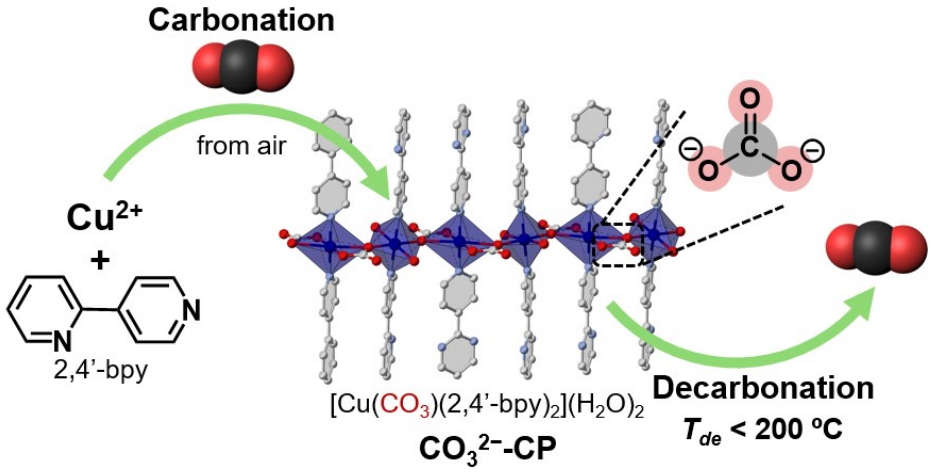


Figure 1. CO_2 capture through the carbonation and decarbonation of CO_3^{2-}-CP.

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PROBING THE CRITICAL BUILDING UNIT CONCENTRATIONS FOR UTSA-280 NUCLEATION ON GOLD SUBSTRATES

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Keywords: *MOF nucleation, cathodic deposition, building unit concentration*

Nucleation is crucial for the size, polymorphism, orientation, and many other properties of crystals.[1] Yet many unknowns and debates remain owing to the lack of experimental techniques to monitor this process. For instance, despite the prosperous development of metal-organic frameworks (MOFs), the critical concentrations of the building units for MOF nucleation on a substrate remain unknown. Here, we propose a novel electrochemical approach to addressing this issue, which relies on an in-situ surface pH measurement and an in-situ surface mass change test during a cathodic deposition process. When taking UTSA-280 as a demonstrating example, the critical metal ion/ligand concentrations for UTSA-280 nucleation on a gold substrate are determined for the first time. It is found that the required concentration of the deprotonated linker for UTSA-280 nucleation varies with the metal ion concentrations, and importantly, the products of these concentrations are similar, which can be seen as a solubility product analogue of UTSA-280. The presented method can be applied to other MOFs like ZIF-8 and HKUST-1.

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BROAD RANGE THERMAL DEFECT ENGINEERING IN MOLECULAR FRAMEWORKS WITH VOLATILE LINKERS

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Keywords: *Hofmann clathrate, defectivity, thermal vacancies.*

The controlled generation of defects in crystalline materials is recognized for their utility in tailoring various properties to optimize application performance. The same strategies are now focused on tunning metal-organic frameworks (MOFs) with controlled levels of vacancy defects [1]. We introduce a novel MOF defect engineering (MOF-DE) approach for the selective and controlled removal of linkers to create open metal vacancies. This method allows for defect generation across a broad compositional range without the need for a mixed linker strategy. We precisely control the linker removal process to achieve predetermined degrees of compositional defectivity with minimal error. Using the Hofmann-type MOF [Fe(pz){Pt(CN)4}] (pz = pyrazine) as an exemplary material [2], we perform a comprehensive characterization of the structural evolution of the defective framework and the nature of the generated open metal Fe (II) sites. This reveals their accessibility and effectiveness as Lewis acid sites in catalysing the cyanosilylation of aldehydes.

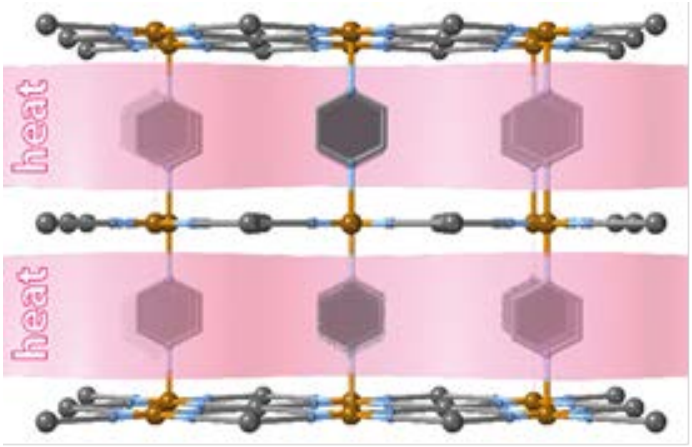


Figure 1. Thermal defect generation in [Fe(pz)x{Pt(CN) showcasing the thermal removal of the pillaring pz linkers, water molecules in the pores and pz disorder have been removed for clarity.

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THIOPHENE-ENRICHED TETRATHIENONAPHTHALENE(TTN)-BASED COVALENT ORGANIC FRAMEWORKS (COFS)

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Keywords: *tetrathienonaphthalene, donor-acceptor, photoactive, photocathodes*

Thiophene and its derivatives, known for their electron-rich characteristics and favorable light-harvesting capabilities, have been successfully incorporated into covalent organic frameworks (COFs), demonstrating significant promise in the realms of photovoltaics, water splitting, and optoelectronic functionality.[1, 2] However, the choices of thiophene-based multifunctional building blocks (nodes) are still limited, and the introduction of thiophene derivatives into COFs remains challenging, primarily due to the unique angles present in five-membered rings and the complex synthetic pathways. Therefore, it is essential to develop novel building blocks tailored for thiophene-enriched COFs.

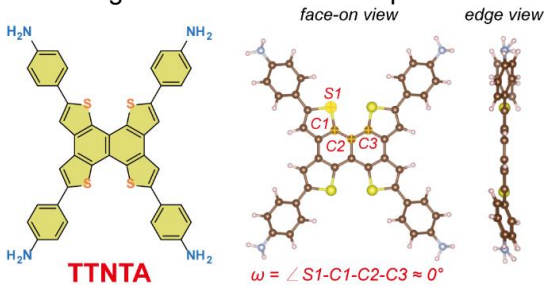


Figure 1: Chemical and DFT calculated structure of TTNTA with face-on (left) and edge (right) views.

Tetrathienonaphthalene (TTN) is of great interest in the field of organic electronics due to its electron-rich nature, its potential as a semiconductor, and the ability to enhance the performance of diverse optoelectronic devices.[3] Here, a novel thiophene-enriched TTN-based node 4,4',4'',4'''-(naphtho[1,2-b:4,3-b':5,6-b'':8,7-b''']tetrathiophene-2,5,8,11-tetrayl)tetraaniline (TTNTA) featuring *C2*-symmetry was synthesized *via* a facile and efficient synthetic routine for the construction of imine-linked COFs (Figure 1). Utilizing TTNTA, we successfully synthesized highly crystalline, thiophene-enriched donor-donor (D-D) and donor-acceptor (D-A) type COFs, denoted as TT COF and $BDT(BT)_2$ COF, respectively, by using two distinct aldehyde-functionalized linear building blocks: [2,2'-bithiophene]-5,5'-dicarbaldehyde (TT) and 7,7'-(4,8-diethoxybenzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(benzo[c][1,2,5]thiadiazole-4-carbaldehyde) ($BDT(BT)_2$).[4] The successful synthesis of highly crystalline and oriented TTNTA COF films on various substrates *via* a solvothermal method enabled further comprehensive optical and electronic characterization. Optical-pump terahertz-probe (OPTP) spectroscopy was employed to investigate the charge-carrier dynamics of the resulting COF films, revealing charge carrier mobilities of 0.34 ± 0.04 $cm^2V^{-1}s^{-1}$ for TT COF and 0.18 ± 0.02 $cm^2V^{-1}s^{-1}$ for $BDT(BT)_2$ COF. Furthermore, the TTNTA-based COFs were demonstrated to show promising potential as photocathodes in photoelectrochemical water splitting with notable photocurrent densities of 10 and 15.3 μA/cm^2, respectively. These findings highlight the potential of TTNTA-based COFs in energy-related applications and provide valuable insights into the design of thiophene-enriched COFs with high crystallinity and tunable electronic properties.

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THE INFLUENCE OF SYNTHESIS CONDITIONS ON ZEOLITIC IMIDAZOLATE FRAMEWORK-8 THIN FILMS

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Keywords: *metal-organic frameworks, ZIF-8, thin films, synthesis conditions*

The presence of toxic gases, such as CO_x and NO_x, and volatile organic compounds (VOCs) in the atmosphere presents a safety concern in indoor as well as industrial environments. Gas detection down to very low concentrations is possible with selective chemical sensors where metal-organic frameworks (MOFs) play an integral role due to the large internal surface area and a substantial amount of available adsorption sites within the structure of these nanoporous materials compared to conventional sorbents. [1] One of the more widely studied MOFs for chemical sensing applications is zeolitic imidazolate framework-8 (ZIF-8). For the purposes of sensor fabrication, the sensing material must be integrated in thin film form. Different methods of ZIF-8 thin film preparation exist; however, little is known on the influence of synthesis conditions and type of substrate on the film formation. In this systematic study we prepared ZIF-8 thin films from methanolic solutions of $Zn(NO_3)_2 \cdot 6H_2O$ and 2-methylimidazole on silica, gold, and silane-functionalised surfaces at different temperatures and varying metal-to-linker ratios. We characterised the prepared films by analysing their structure, morphology, and VOC adsorption capabilities. In addition, the films on gold surfaces were used to fabricate capacitive sensors and their performance was evaluated against a set of model VOCs.

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THIAZOLOTHIAZOLE 2D METAL-ORGANIC FRAMEWORKS BASED ON ISOPHTHALIC ACID DERIVATIVES

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Keywords: *metal-organic frameworks, isophthalic acid derivatives*

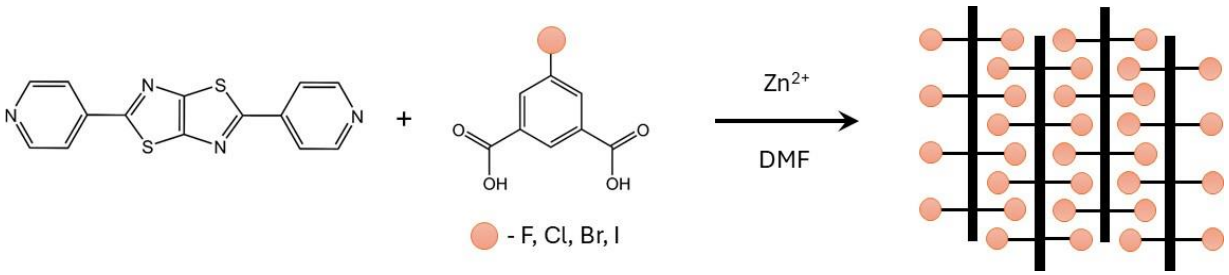
Two-dimensional metal–organic frameworks (2D MOFs) have gained significant attention across various fields, due to their exceptional physical and chemical properties—such as ultrathin layers, large specific surface area, high aspect ratio, numerous exposed unsaturated metal sites and tunable surface properties[1].

In this study, we present a series of four two-dimensional metal−organic frameworks: [Zn(iso-F)(BPTzTz)]$_n$ (1), [Zn(iso-Cl)(BPTzTz)]$_n$ (2), [Zn(iso-Br)(BPTzTz)]$_n$ (3), and [Zn(iso-I)(BPTzTz)]$_n$ (4). These were synthesized from zinc nitrate, 5-bis(4-pyridyl)thiazolo[5,4-d]thiazole (BPTzTz), and isophthalic acid derivatives (H_2iso-X; X = F, Cl, Br, I; Scheme 1) in N,N-dimethylformamide.

All materials were obtained in crystalline forms, and the crystal structures of 1, 3, and 4 were determined using single-crystal X-ray diffraction. These materials feature two-dimensional structures in which the adjacent layers are variably displaced relative to each other. Such layer shifts might be attributed to the presence of halogen groups, which can facilitate unique halogen bonding interactions.

In addition, the activated form of [Zn(iso-I)(BPTzTz)]$_n$ was evaluated for its sorption properties. The material demonstrated the capacity to adsorb four ethylene molecules per metal cluster.

Scheme 1. Synthesis scheme.



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POLYHEDRAL CRYSTAL FILMS OF COVALENT ORGANIC FRAMEWORKS

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Keywords: *porous crystals, COFs, films, thermal flexibility, membrane separation*

Porous crystal films offer great potential for tackling energy and environmental challenges[1-3]. However, despite over a decade of intensive research, covalent organic framework (COF) films exhibiting polyhedral textures reflective of their crystalline nature remain exceedingly rare. Here we present a scalable and adaptable biphasic strategy to fabricate pyrene (Py)-COF polyhedral crystal films with exceptional crystalline order under ambient conditions. This method enables precise control over polycrystal formation in solution and crystal growth on substrates, yielding Py-COF polyhedral films with tunable nanometer-scale thicknesses on a 4-inch wafer scale. Among them, a Py-1P film achieves a record-high Brunauer-Emmett-Teller surface area reported for COF films with comparable pore sizes, alongside remarkable chemical stability. Real-space electron microscopy elucidates previously undisclosed details underlying COF crystal film growth. These polyhedral crystal films show anisotropic thermal flexibility along the [001] lattice direction, with dynamically adaptive thermal expansion coefficients of 1.64-2.15 × 10^{-4} K^{-1}. Through sensor testing, we correlate polyhedral film crystallinity with device performance and longevity. Moreover, we prepare the Py-1P polyhedral crystal film on a porous substrate to produce separation membranes that demonstrate high selectivity for precise molecular separation in liquids. This research expands the boundaries of COF films and reveals tremendous possibilities to advance COF materials science and applications.

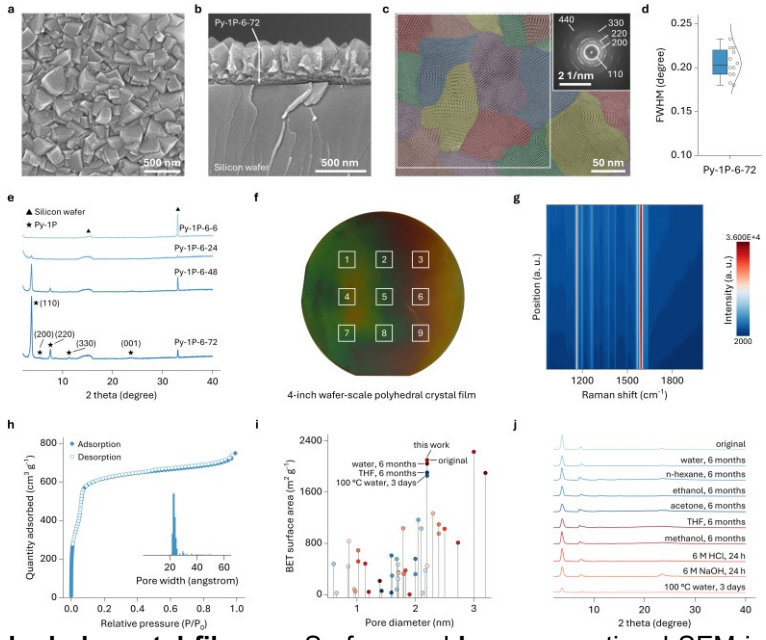


Fig. 1. Py-1P polyhedral crystal films. a, Surface and **b**, cross-sectional SEM images of the Py-1P film. **c**, False-colored HRTEM image of the Py-1P film. The inset shows FFT of the boxed region. **d**, Box-and-whisker plots of FWHM values for the Py-1P films across 12 replicates. **e**, PXRD patterns of the Py-1P films. **f**, Photograph of a 4-inch wafer-scale Py-1P-6-72 film. **g**, Raman spectral contour map of the 4-inch Py-1P film with data collected across 9 areas in (**e**). **h**, 77 K N_2 adsorption-desorption isotherms of the Py-1P film. The inset shows the pore size distribution. **i**, BET surface area comparison. **j**, PXRD patterns of the Py-1P film subjected to various treatments.

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COORDINATION-DRIVEN STRUCTURAL EVOLUTION AND PROTON TRANSPORT IN COPPER METAL-ORGANIC MATERIALS

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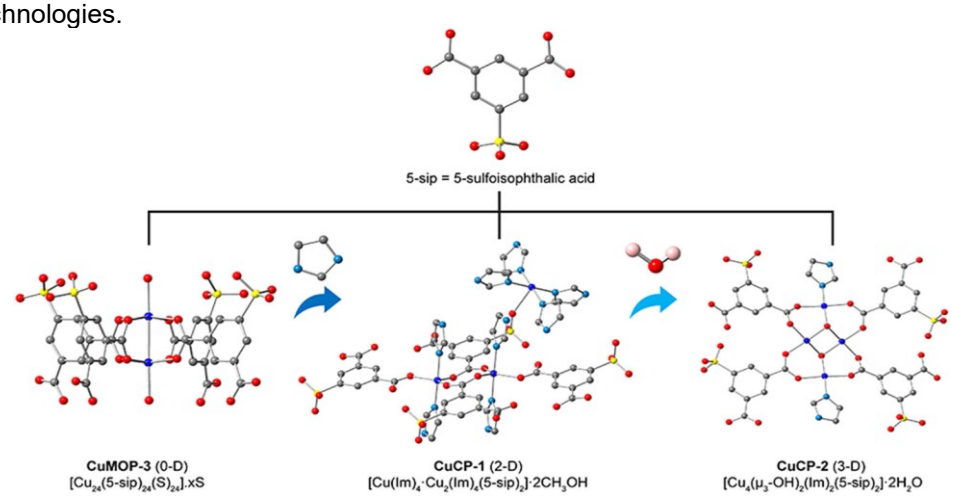
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Keywords: *metal-organic materials, structure transformation, guest insertion, proton conductivity*

Metal–organic materials (MOMs), encompassing discrete and extended coordination networks such as zero-dimensional (0D) metal–organic polyhedra (MOPs) and one-, two-, and three-dimensional (1D, 2D, and 3D) coordination polymers, have garnered significant interest due to their structural versatility and tunable functionalities. Recent advancements have demonstrated that the deliberate selection of metal nodes and organic linkers enables precise control over the structural and physical properties of MOMs, particularly for applications related to ion and electron transport.

In the present study, copper (II) ions and the hemilabile ligand, 5-sulfoisophthalic acid (5-sip), were employed to synthesize a series of MOMs via a coordinative guest insertion approach. The resulting materials include CuMOP-3 (0D; $[Cu_{24}(5\text{-sip})_{24}(S)_{24}]\cdot xS$, where S = DMF/MeOH), CuCP-1 (2D; $[Cu(Im)_4\cdot Cu_2(Im)_4(5\text{-sip})_2]\cdot 2CH_3OH$), and CuCP-2 (3D; $[Cu_4(\mu_3\text{–}OH)_2(Im)_2(5\text{-sip})_2]\cdot 2H_2O$). Single-crystal X-ray structural analyses reveal that the stepwise introduction of imidazole (Im, $C_3N_2H_4$) and water into the CuMOP-3 framework induces a transformation of the copper paddlewheel secondary building units (SBUs) from monomeric to dimeric (CuCP-1) and subsequently tetrameric (CuCP-2) motifs. These dimensional transformations are accompanied by distinct changes in the coordination modes of the sulfonate ($R\text{–}SO_3^-$) moieties of the 5-sip ligand, which serve as structural drivers for framework evolution. As a result, the derived coordination networks exhibit enhanced thermal and chemical stability, along with improved functional properties such as gas adsorption capacity and humidity-dependent proton conductivity. This work proposes a generalizable synthetic strategy for constructing structurally dynamic and functionally robust MOMs by integrating hemilabile linkers and coordinative guest insertion, thereby contributing to the rational design of next-generation materials for energy technologies.



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ENGINEERING OF COVALENT ORGANIC FRAMEWORK MEMBRANES WITH ASYMMETRIC CHANNELS VIA SEQUENTIAL POST-SYNTHETIC MODIFICATION FOR REVERSE ELECTRODIALYSIS

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Keywords: *Covalent Organic Frameworks, Ion Exchange Membrane, Asymmetric Channel, Post-Synthetic Modification*

Two-dimensional covalent organic frameworks (COFs) constructed via reticular chemistry provide outstanding ion transport properties through structurally tunable and uniformly aligned channels. These features make COFs a promising candidate for ion exchange membranes in reverse electrodialysis (RED), a clean energy generation method converting Gibbs free energy from salinity gradients into electricity. As RED performance is governed by membrane-mediated ion selectivity and transport, the membrane's role is central to energy harvesting efficiency. However, the high pore density of COFs tends to cause ion accumulation on the dilute side of the membrane, disturbing the effective salinity gradient—a phenomenon known as ion concentration polarization (ICP). Additionally, under high-salinity conditions, the electric double layer (EDL) effect, which is essential for achieving selective ion transport in nanochannels, is diminished due to the relatively large pore size of COFs. To overcome these challenges and simultaneously enhance ion selectivity and permeability, one of the compelling strategies is to develop COF-based heterogeneous structures that create asymmetric ion channels and promote preferential ion transport. While this strategy alleviates ICP and enhances ion permeability by suppressing back diffusion, it also presents several drawbacks—increased internal resistance due to longer ion transport pathways, interfacial resistance at heterogeneous junctions, and limited scalability arising from fabrication complexity—all of which impair ion transport efficiency and limit its viability in terms of membrane design.

In this study, we report a strategy to achieve asymmetric ion transport channels within a single COF membrane by precisely tuning the internal charge distribution and effective pore size without the need for multilayer integration or heterogenous interfaces. We selected an imine-linked COF with an alkyne-containing backbone for its structural robustness and compatibility with mild reaction conditions. The pristine COF film was grown on a controlled substrate via solid/liquid interfacial polymerization, yielding a long-range ordered and uniform structure. A two-step post-synthetic modification (PSM) via copper-catalyzed azide-alkyne cycloaddition (CuAAC) was then conducted in the same system to sequentially introduce two negatively charged azide moieties: bulky disulfonated azide with two azides and azidoacetic acid with a single azide group. Due to the difference in their reactivity and diffusivity, each moiety is selectively anchored on the surface and inside channel of COFs, respectively. This spatially controlled functionalization generates asymmetry in both charge density and effective pore size. Notably, the pore constriction by the disulfonated azide moiety leads to sub-1 nm-sized channels, enabling the full development of the EDL effect under high salinity conditions, thereby mitigating the trade-off between ion selectivity and permeability. This work demonstrates that directional ion transport can be realized through precise channel tuning within a single COF membrane, offering a structurally efficient platform for high-performance osmotic energy harvesting.

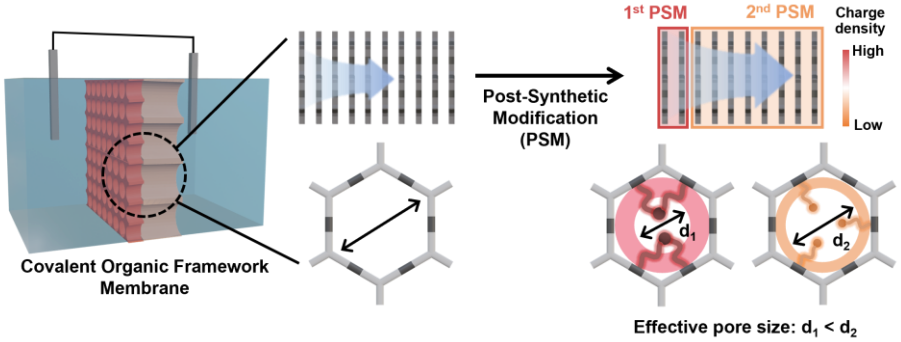


Figure 1. A schematic illustration of post-functionalized COF membrane with asymmetric channel structure.

ENHANCING OPTOELECTRONIC PROPERTIES IN PHTHALOCYANINE-BASED SURMOFS: SYNTHESIS OF ABAB LINKERS BY AVOIDING STATISTICAL CONDENSATION WITH TAILORED BUILDING BLOCKS

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Keywords: *SURMOFs, ABAB-ditopic Phthalocyanine linkers*

Phthalocyanine (PC)-based metal–organic frameworks (MOFs) are emerging as powerful materials for energy storage, sensing, and catalysis, owing to their remarkable chemical stability and superior electron transport properties. Despite their potential, the integration of PC linkers with well-defined geometries into MOFs remains a synthetic challenge, limiting the development of structurally diverse PC-based frameworks. Conventionally, research has focused on easily accessible tetratopic PC linkers; however, these restrict design versatility.

In this work, we introduce a novel strategy employing ditopic ABAB-phthalocyanine linkers, precisely engineered to avoid statistical condensation during synthesis. This approach enables the controlled formation of zinc-based surface-anchored MOF (SURMOF) thin films with tailored architectures. We comprehensively characterize the resulting materials using X-ray diffraction, scanning electron microscopy (SEM), and density functional theory (DFT) simulations. UV–Vis spectroscopy confirms enhanced electronic absorption, which directly translates to improved light-harvesting efficiency.

We demonstrate the practical utility of these materials by constructing a photodetector that exhibits strong responsivity in the near-infrared region (780 nm), positioning this system as a promising platform for advanced optoelectronic and sensing applications. This study paves the way for next-generation PC-MOFs with customized linkers, broadening the design landscape of functional framework materials.

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AMINE-GRAFTED POROUS ORGANIC POLYMER FOR IMPROVED DIRECT AIR CAPTURE OF CO2

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Keywords: Direct Air Capture (DAC), CO2 Adsorption, Porous Organic Polymers, Amine Functionalization.

Direct air capture (DAC) of CO_2 using solid sorbents presents a promising alternative to conventional amine scrubbing systems, owing to its lower energy requirements for regeneration, higher selectivity, and improved stability.[1-2] In this study, a hydroxyl-rich porous organic polymer (OPTP-8) was synthesized and subsequently functionalized with (3-aminopropyl)trimethoxysilane (APTS) to yield OPTP-APTS, a material designed for efficient low-pressure CO_2 capture.[3-4] Structural characterization confirmed successful grafting of amine functionalities via covalent bonding, while N_2 sorption revealed a significant decrease in surface area post-functionalization due to partial pore blockage.[5] Despite this reduction, OPTP-APTS exhibited enhanced CO_2 uptake at low pressure (0.98 mmol/g at 0.15 bar and 1.58 mmol/g at 1 bar, 298 K), as well as exceptional CO2/N2 selectivity, exceeding 900 at 298 K and over 2200 at 273 K under DAC conditions (400 ppm CO_2). This enhancement is attributed to strong chemisorption interactions with amine groups, as confirmed by high isosteric heat of adsorption (Q_{st} > 90 kJ/mol). Furthermore, OPTP-APTS demonstrated excellent thermal stability, cyclic durability over 32 cycles, and consistent performance under both dry and humid breakthrough tests. These findings underscore the potential of amine-functionalized POPs for high-performance CO_2 capture in DAC systems.

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SUSTAINABLE DESIGN AND MODIFICATION OF CUBTC FOR HIGH-PERFORMANCE HYDROGEN STORAGE APPLICATIONS

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Keywords: *Design of Experimental methodology, CuBTC, Bimetal CuBTC, Pellet CuBTC, Hydrogen storage*

As greenhouse gas emissions become serious, the need for sustainable and efficient hydrogen storage solutions to replace traditional fuel energy becomes increasingly urgent. This study focuses on enhancing the hydrogen storage performance of the MOF CuBTC through innovative green mechanochemical synthesis, mechanochemical modification, and pelletisation methodology, as seen in Figure 1.

The design of Experiments (DoE) methodology was applied to design the CuBTC, which systematically analysed the effects of six synthesis conditions on CuBTC properties[1]. This novel application of DoE enabled the design of an optimised CuBTC with a hydrogen uptake of 3.2 wt.% at 20 bar and 77K. This value is comparable to that of solvothermal CuBTC (3.37 wt.%) and 10% higher than previously reported values[2]. This design project, without chemical solvent, reduces CuBTC synthesis time to just minutes, consuming less than 2% of the energy required for traditional solvothermal synthesis [1].

To extend the application potential of the designed CuBTC, we proposed, for the first time, a novel post-synthesis metal node modification using mechanochemical ball milling. By introducing Ni^{2+} into the CuBTC framework, hydrogen uptake was increased to 4.2 wt.% at 20 bar and 77 K. This represents a 31% improvement over the originally designed CuBTC and highlights the potential of mechanochemical modification as a scalable and efficient strategy for enhancing MOF performance.

To mitigate the risk of dust explosions during transportation, a pelletization strategy was employed in this study. It was found that after being soaked in methanol for 60 min, the resulting pellets retained 92.2% of their original hydrogen storage capacity, achieving 3.54 wt.% H_2. Additionally, this method yielded twice the amount of product compared to the mechanochemical synthesis approach.

This study offers valuable insights into environmentally sustainable synthesis methods and pelletization strategy, which highlights the potential of CuBTC as a high-performance material for hydrogen storage. These advancements lay the foundation for future innovations in MOFs design and energy storage technologies.

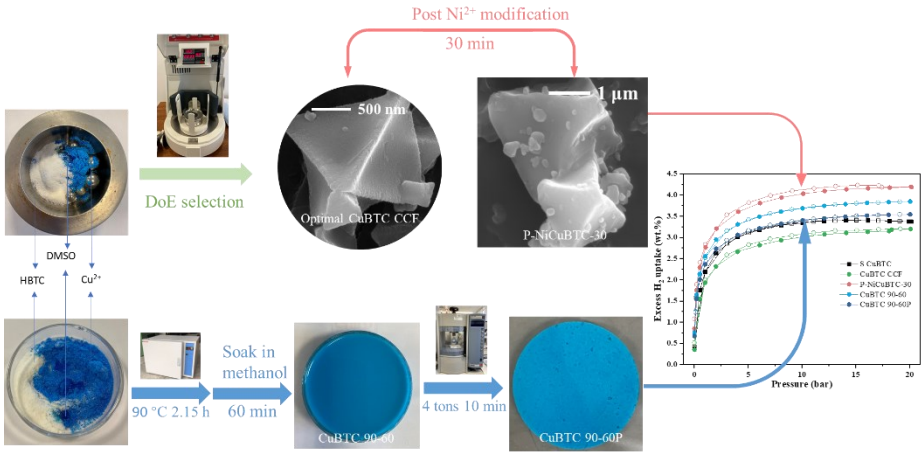


Figure 1. Sustainable design and modification of MOFs for hydrogen storage

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SCALABLE, LOW-ENERGY SYNTHESIS OF COBALT–CITRIC ACID MOFS WITH CO_2 UPTAKE POTENTIAL

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Keywords: *cobalt MOF, citric acid, room-temperature synthesis, CO_2 adsorption, porous materials*

Metal–organic frameworks (MOFs) are promising porous materials for CO_2 capture, but scalable, low-energy syntheses remain a challenge. In this study, we report the room-temperature aqueous synthesis of a cobalt–citric acid MOF (Co-CA-MOF) prepared by simply mixing $Co(NO_3)_2 \cdot 6H_2O$ and citric acid under ambient conditions. The obtained material was characterized by powder X-ray diffraction (PXRD), Fourier-transform infrared spectroscopy (FT-IR), and thermogravimetric analysis (TGA), confirming framework formation, ligand coordination, and stability up to ~300 °C. Nitrogen adsorption–desorption experiments revealed a permanent porous structure with a moderate surface area, while CO_2 adsorption studies demonstrated a measurable uptake, indicating the material's potential for selective CO_2 capture. These preliminary results show that a simple, environmentally friendly route can yield functional cobalt–citric acid MOFs without the need for solvothermal methods or organic solvents. Ongoing work is directed at optimizing synthesis conditions and improving textural properties to enhance CO_2 adsorption performance.

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ADVANCED MULTIFUNCTIONAL SANDWICH STRUCTURE ZR AND ZN-BASED MOFS FOR ACTIVE O_2/N_2 AND H_2/O_2 GAS SEPARATION

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Keywords: *MOF, Multifunction, Gas separation, Hydrogen*

Abstract:

Efficient gas separation technologies are critical for industrial applications such as air separation and hydrogen production []. This study explores a novel sandwich-structured metal-organic framework (MOF) composed of ZIF-8 (Zn-based) and UiO-66-NH_2 (Zr-based) layers, grafted onto a carbon nanotube (CNT) chain to achieve high-performance O_2/N_2 and H_2/O_2 separation. The integration of these MOFs layers within a CNT framework using molecular-level engineering [2] enhances selectivity, stability, and permeability, leveraging the distinct properties of each MOF component.
ZIF-8, with its well-defined pore size (~3.4 Å) and hydrophobicity, selectively allows smaller gas molecules such as O_2 and H_2 to pass while restricting larger gases like N_2. UiO-66, known for its exceptional thermal and chemical stability, provides additional molecular sieving and adsorptive properties, contributing to enhanced separation performance. The CNT backbone ensures a continuous transport pathway, reducing resistance and improving mechanical robustness.

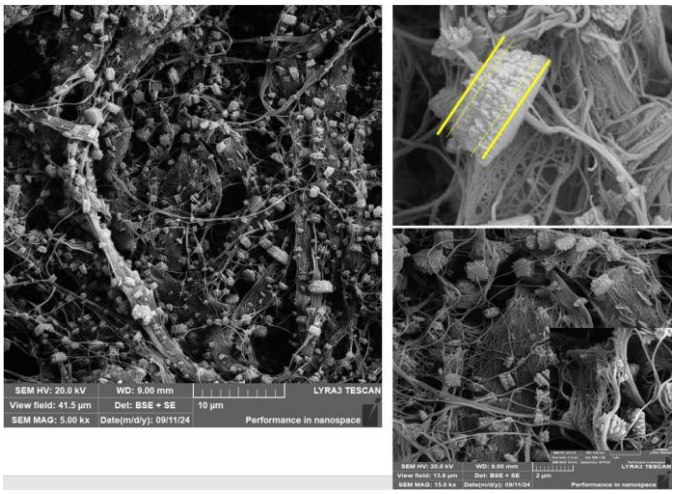


Figure1. SEM images of multi-layer structures of the Zif-8 and UiO-66-NH_2 which grafted on the CNT.

The hierarchical structure offers synergistic advantages: (1) Size-sieving and kinetic selectivity from ZIF-8, (2) Adsorptive and electrostatic interactions from UiO-66-NH_2, and (3) Fast gas diffusion and structural integrity from CNTs. The resulting hybrid material is expected to demonstrate high selectivity (>8 for O_2/N_2 and >80 for H_2/O_2), fast permeation to surpass the Robeson upper bound diagram, and long-term stability. This work provides a new direction for designing multifunctional MOF-based membranes and adsorbents for efficient mixture gas separations based on target gas molecules and accordingly target MOF assembly, with potential applications in air separation, hydrogen purification, and energy-related processes.

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HIERARCHICAL DESIGN OF CO/CO-NI MOF-DERIVED CATALYSTS TOWARD ENHANCED HYDROGEN EVOLUTION

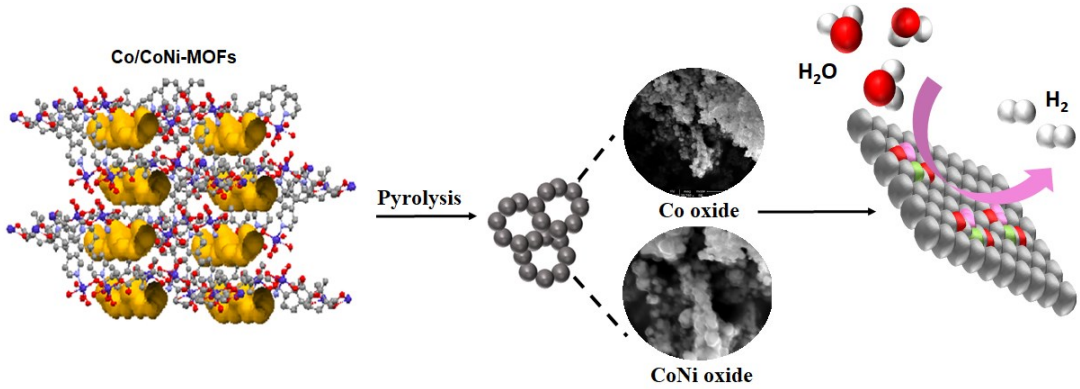
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Keywords: *Water splitting, metal-organic frameworks, hydrogen evolution reaction, dual-doped carbon, hydrogen production.*

Abstract: Sustainable hydrogen production via electrocatalytic water splitting demands highly efficient, and cost-effective catalysts. We present a strategic approach converting novel metal-organic frameworks (MOFs)[1] into hierarchically porous carbon-based electrocatalysts. In this work, we synthesized mixed-ligand Co and CoNi MOFs, featuring a unique 3D framework with left- and right-handed helical motifs and intrinsic porosity (11.6% void, ~12.4 Å pores). Upon controlled pyrolysis, these MOF precursors yield a robust, hierarchically structured Co/Co-Ni dual-doped carbon materials, acting as a superior electrocatalysts for the hydrogen evolution reaction (HER) in alkaline media. The optimized bimetallic CoNi-MOF@850°C catalyst demonstrates remarkable HER performance with 190 mV overpotential at 10 mA cm^{-2} and a competitive 86 mV dec^{-1} Tafel slope. This enhanced activity and excellent long-term stability are attributed to the dual synergistic effect between Co and Ni, that facilitates efficient charge transfer and enhances active site availability. These findings highlight the immense potential of bimetallic MOF-derived catalysts as cost-effective, sustainable alternative for large-scale green hydrogen production. [2]



Scheme: Schematic illustration for the preparation of mono- and bimetallic Co/CoNi-derived MOF catalysts.

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POST-SYNTHETIC BIOFUNCTIONALIZATION OF ZIRCONIUM MOFs VIA ALKYNE CLICK REACTIONS AND THEIR RADIOMODIFICATION BEHAVIOR

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Keywords: *zirconium MOFs, post-synthetic modification, alkyne click chemistry, inosine ligands, radiomodification, biocompatibility, green synthesis*

Zirconium-based metal-organic frameworks (Zr-MOFs) represent a class of porous hybrid materials characterized by high thermal and chemical stability, large surface area, and versatile structural tenability[1]. Their robustness under physiological and harsh conditions makes them particularly attractive for biomedical applications including drug delivery, biosensing, and radiotherapy. However, achieving controlled biological interaction and responsiveness remains a key challenge.

In this study, we present the synthesis and detailed characterization of Zr-MOFs functionalized via atom-economic alkyne click reactions followed by post-synthetic modification with inosine, a biologically relevant nucleoside. The project implements a green and catalyst-free [2+2] cycloaddition–retro-electrocyclization (CA-RE) cascade to introduce high-density bioactive ligands into both terminal and internal alkyne-functionalized Zr-MOFs. The resulting frameworks were analyzed via XRD, FTIR, UV-Vis, SEM/TEM, and cyclic voltammetry to assess their crystallinity, chemical structure, and optoelectronic properties.

Inosine grafting not only enhanced the frameworks' bioaffinity but also contributed to selective molecular recognition, opening avenues for responsive biosensing. Gamma irradiation studies demonstrated structural rearrangements in the frameworks, suggesting a radiomodification effect that may be leveraged for controlled drug release or radioprotective applications. In vitro assays confirmed moderate antibacterial activity, high antioxidant response, and biocompatibility with mammalian cell lines.

This work introduces a sustainable and scalable route for the development of nucleoside-functional Zr-MOFs using environmentally friendly chemical transformations. By combining green synthetic strategies with biological functionalization and radiation response, the project proposes a new class of smart materials suitable for targeted therapy and controlled delivery. The originality lies in the integration of inosine as a functional ligand via click-based post-synthetic modification of MOFs, which has not been previously reported for biomedical MOF platforms.

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SELECTIVE PROTEIN HYDROLYSIS BY SOL-GEL SYNTHESIZED Zr-UiO-66 NANOZYME

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Keywords: *Sol-gel method, heterogenous nanozyme, Metal-organic Framework, zirconium, hydrolysis, proteins*

Protein hydrolysis plays a crucial role in proteomics research, particularly in studies of disease mechanisms, biomarker discovery, and drug target screening[1]. However, existing natural enzymes still face challenges that prompt the development of more robust and tunable materials, such as metal-organic frameworks (MOFs), that mimic enzymatic hydrolysis reactions[2-3]. In this work, we explore the modulation of the interaction between MOFs and proteins through surface modifications to achieve selective protein hydrolysis. We selected Zr-UiO-66 as an artificial nanozyme for myoglobin (Mb) hydrolysis, as this MOF possesses excellent structural chemistry and catalytic activity, making it an ideal model system for studying MOF-mediated protein hydrolysis. Aerogels synthesized by low-temperature sol-gel methods have been enriched with surface hydroxyl groups, which further enhance hydrolysis efficiency and protein adsorption specificity. We found that hydroxyl groups modulate the electrostatic adsorption of proteins on MOFs, leading to the selective hydrolysis of Mb at peptide bonds containing positively charged residues. This study provides new insights into the development of efficient artificial proteases for the selective hydrolysis of proteins.

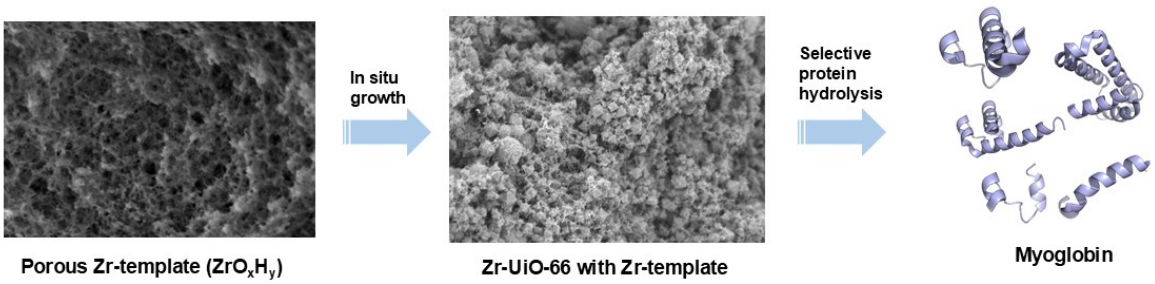


Figure 1. Schematic illustration of the growth process of Zr-UiO-66 using a Zr-based template, and its application in the selective hydrolysis of myoglobin (Mb).

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SYNTHESIS OF PROTON CONDUCTING COVALENT ORGANIC FRAMEWORKS

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Keywords: *covalent organic frameworks, irreversible linkages, proton conduction, fuel cells*

The shift towards a fossil fuel free society comes with the need for a multitude of new, clean technologies. One alternative energy carrier, in the spotlight of many current research projects and industrial programs, is hydrogen, based on which fuel cells and electrolysers are already starting to find their place in stationary and transport applications. Despite their tremendous promise, these devices face some issues, one of which is the limited operation temperature due to water loss when a proton conducting (polymer) membrane dehydrates. Covalent organic frameworks (COFs) show promising properties and have been highlighted for use as proton exchange membrane (PEM) in fuel cells, revealing a high proton conduction even at low relative humidity.[1] Furthermore, by tuning their building blocks, COFs offer the opportunity for incorporating both intrinsic and extrinsic proton conduction.[2]

In this contribution, I aim to present my ongoing work on achieving new, robust COF structures for proton conduction at temperatures between 80 and 120 °C. Although reversible reactions have repeatedly been shown to be the most reliable way to obtain highly crystalline COFs, they make the resulting COF vulnerable to harsh conditions, such as the highly acidic environment of a PEM fuel cell. Therefore, my research strives to make irreversible bonds more accessible, using different routes to grant access to these more resilient structures. More precisely, I am exploring ways to obtain heterocyclic linkages, namely imidazole, through different synthetic strategies such as linker exchange and the use of modulators, whereby I characterise the COFs produced by methods such as TEM, FT-IR, and PXRD. An example of my recent results is given in the figure below.

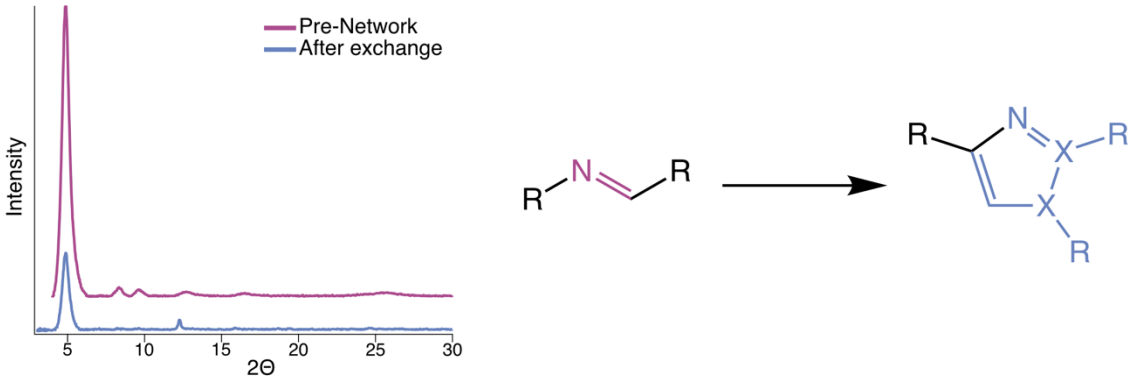


Figure: PXRD spectra of an imine linked pre-network as well as the thiazole linked product after exchange (left), and an imine linkage (purple) which we explore how to replace with heterocycles (blue).

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VINYL-FUNCTIONALIZED IONIC COVALENT ORGANIC FRAMEWORKS FOR LITHIUM BATTERY APPLICATIONS

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Keywords: *Ionic Covalent Organic Framework (iCOF), Vinyl-functionalization, Lithium-ion battery, Ion transport, Electrolyte interface, Composite materials*

Covalent organic frameworks (COFs) are crystalline, porous polymers constructed from light elements (e.g., C, H, B, N, and O) via robust covalent bonds. Their high surface area, ordered nanochannels, and structural tunability make them highly promising for applications involving ion transport and electrolyte accessibility. To further enhance ionic conductivity and stabilize electrode–electrolyte interfaces, ionic covalent organic frameworks (iCOFs) have emerged as a novel platform. These materials retain the structural advantages of conventional COFs while incorporating ionic functionalities, rendering them suitable for advanced electrochemical systems, including lithium-ion batteries.

In this study, we report the rational design and synthesis of a vinyl-functionalized iCOF aimed at improving lithium-ion battery performance. The introduction of vinyl groups facilitates extended π-conjugation throughout the framework, thereby promoting charge transport and significantly enhancing ionic conductivity. The functionalized iCOFs were incorporated into composite systems, where their ionic nature and porous architecture synergistically modulate ion mobility and interfacial properties. The resulting composites exhibit uniform morphology, robust structural integrity, and enhanced compatibility with electrochemical environments, underscoring their versatility across a range of device configurations.

Comprehensive characterization—including X-ray scattering, thermogravimetric analysis, nitrogen adsorption–desorption isotherms, X-ray photoelectron spectroscopy, and scanning electron microscopy—confirmed their ordered architecture, thermal stability, high porosity, and chemical functionality. These findings demonstrate that vinyl-functionalized iCOFs offer a versatile strategy for developing next-generation battery components. While the specific integration pathway is currently under exploration, their tunable framework and intrinsic ionic character suggest broad applicability across electrolytes, separators, and interfacial layers depending on system design and processing conditions. Detailed insights into their structural properties and electrochemical performance will be presented.

CHEMICAL DESIGN OF REDOX COVALENT ORGANIC FRAMEWORKS AS HIGH VOLTAGE CATHODES FOR LI-ION BATTERIES

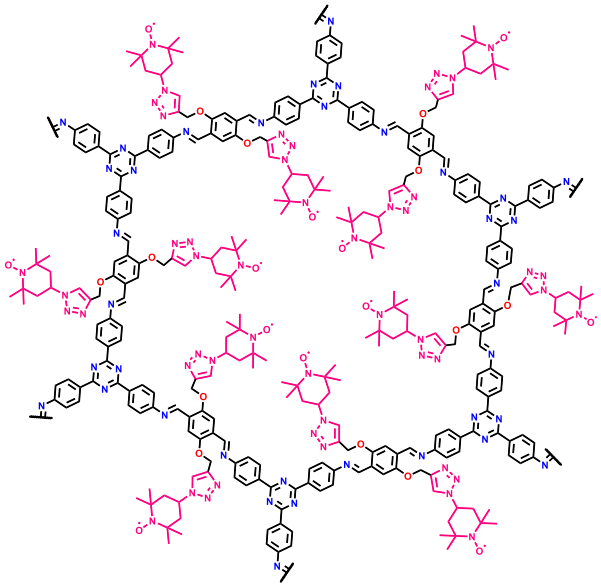
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Keywords: *Redox-active covalent organic frameworks, post-synthetic modification, organic cathodes, Li-ion battery*

The development of sustainable rechargeable batteries with high energy density is one of the main current challenges to efficiently store energy from renewable sources. Among them, lithium-ion batteries (LIBs) are the most promising due to their superior performance. While conventional inorganic LIBs present limited energy density and problems associated with the availability of critical raw materials, electroactive organic materials are an attractive alternative due to their tunable electrochemical properties and resource availability. In particular, covalent organic frameworks (COFs) have emerged as promising electrode materials due to their insolubility in electrolyte, porosity to facilitate ion diffusion and huge chemical and structural versatility.[1] In general, (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) is a well-studied organic radical as electrode material because of its high voltage and electrochemical stability. Covalently attaching TEMPO units within a COF is a good strategy to improve the insolubility of the radical moieties in electrolyte.[2,3] Thus, new design strategies to increase simultaneously the energy density and stability of the organic electrode materials are required. Herein, we present a new redox-active triazine-based TAPT-BPTA COF in which the TEMPO radicals are incorporated into the framework which has been explored as a cathode in LIBs.



Scheme 1: Schematic representation of TAPT-BPTA TEMPO-COF.

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TAILORED DESIGN OF AN OXYGEN-RICH STABLE CO-MOF INTEGRATED WITH MXENE NANOFIBERS AS ADVANCED HETEROSTRUCTURES FOR HIGH-PERFORMANCE AMMONIUM-ION SUPERCAPACITORS

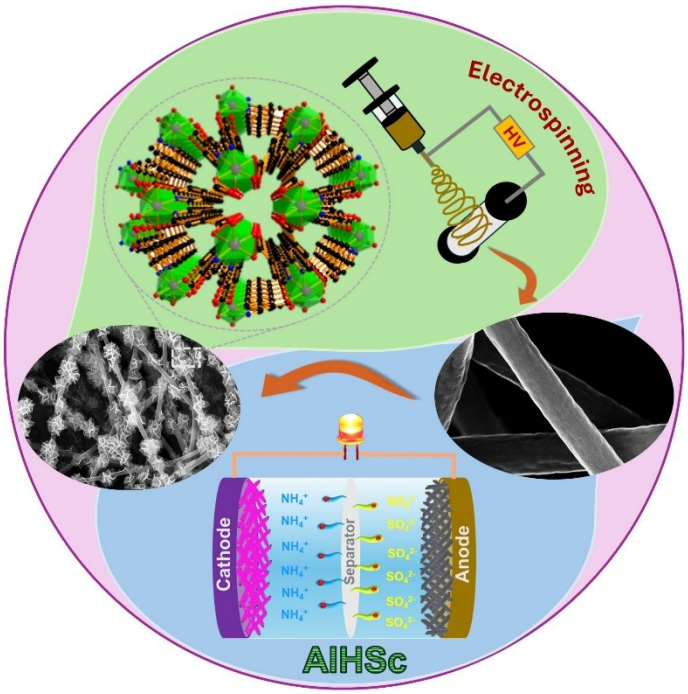
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Keywords: *Oxygen-rich Co-MOF, Electrospinning, MXene nanofibers, Ammonium ion hybrid supercapacitor*

Ammonium ions (NH_4^+) are promising non-metallic charge carriers for sustainable and cost-effective advanced electrochemical energy storage. However, the development of electrode materials with well-defined structural features to facilitate rapid NH_4^+ diffusion kinetics remains a significant challenge. In this study, we demonstrate the design of a novel oxygen-rich cobalt-based metal-organic framework (Co-MOF) showcasing unique (O_4-Co-N_2) coordination geometry. This distinctive structure of Co-MOF contributes to high stability, abundant active sites, and enhanced electrochemical performance. To further boost performance, Co-MOF nanoflowers were uniformly integrated with $Ti_3C_2T_x$ MXene carbonized nanofibers (MXCNF), forming advanced Co-MOF@MXCNF heterostructures. These heterostructures exhibit a highly porous, nanofibrous morphology, delivering a notable specific capacitance of 980 F g^{-1} at a current density of 1 A g^{-1} and excellent cycling stability, retaining 91.1% capacitance after 16,000 cycles. When paired with porous MXCNF anode, the ammonium-ion hybrid supercapacitors (AIHSCs) delivered an impressive energy density of 41.5 mWh kg^{-1} with the corresponding power density of 800 mW kg^{-1}, retaining 87% of their capacitance after 16,000 cycles. This study highlights the synergistic advantages of integrating stable MOFs with MXene nanofibers for remarkable ammonium-ion storage. It establishes a framework for designing high-performance energy storage materials, paving the way for next-generation sustainable energy storage devices.



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MOF SCALE-UP SYNTHESIS BY SPRAY-DRYING

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Keywords: *MOF scale-up, spray-drying synthesis*

Axel'One is a French collaborative innovation platform in the Chemistry and Environment sector created in 2011 and dedicated to smart processes and innovative materials. Located in Lyon, Auvergne-Rhône-Alpes Region, Axel'One is an independent non-profit association (French law 1901, private and public partnership) whose main missions are to provide shared facilities, tools and services for collaborative research and development projects. In 2023, Axel'One hosts around 20 SMEs and provides its services to 30 collaborative projects representing more than 250 people located on the platform (around 6 M€ turn over).

The platform offers access to 45 M€ shared tools from fundamental research to pre-industrial stage (from TRL 3 to 7) in the field of advanced materials and polymers, smart processes, on-line analysis, digital solutions and industrial catalysis. Its activities support industrial companies from the chemical, textile & composite, recycling, water treatment and energy sectors, among others.

Axel'One has a huge expertise in materials development and up-scaling, in particular catalysts and solids. Axel'One has access to operate on a complete set of shared tools for catalysts and solids up-scaling (extrapolation, synthesis, shaping, thermal treatment, impregnation) with production of independent and competitive batches of catalysts / solids at kg scale (for homogeneous and heterogeneous catalytic processes), extrapolation and validation of new catalyst / solid preparation methods, up-scaling facilities allowing to operate in ATEX conditions.

Following an introduction of Axel'One activities, the presentation will be focused on spray-drying principle and its relevance in MOFs production scale-up. The completed European project PRODIA and its success story on HKUST-1 spray-drying production as well as two ongoing projects, a European one called SHEETS and a French one called DEFIMOF will be presented.

The objective of the SHEETS project is to develop cheap and scalable sheet-shaped sorbent modules for CO2 capture processes while DEFIMOF project focus on the development of a French value chain for MOF industrialization.

Mechanical Behaviour of ZIF-71 Monoliths and Polymer@ZIF-71 Composites

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Keywords: *MOF-polymer composite, Nanoindentation, MOF mechanics, nanoFTIR, MOF monoliths*

This study demonstrated a facile approach to synthesize ZIF-71 [$Zn(dcIM)_2$; dcIM = 4,5-dichloroimidazole] monoliths with a polymer binder, namely employing poly-methyl methacrylate (PMMA) through a sol-gel process [1-3]. Previous studies have reported several examplars of pure MOF monoliths which are relatively brittle and generally smaller than 5 mm [4, 5]. In this study, we show that the addition of a slight polymer binder to the sol-gel mixture would improve the mechanical properties and enhance the size of the resultant polymer@MOF monoliths. The mechanical properties of the composite monoliths such as the elastic modulus, hardness, fracture toughness, strain hardening, and creep behaviour were studied and compared with the pure ZIF-71 monolith. Nitrogen sorption measurements showed that the composite monoliths have a high surface area (~370 m^2/g) although it was reduced from ~500 m^2/g due to pore blockage by the polymer. Composite monoliths are found to exhibit less surface cracks and are relatively stiffer but notably tougher than the pure ZIF-71 monoliths as the fracture toughness tripled from around 0.15 $MPa.m^{0.5}$ to around 0.45 $MPa.m^{0.5}$. The content of polymer binder in the monolith was estimated to be ~10 wt% through thermogravimetric analysis (TGA). Despite the incorporation of a small quantity of polymer in the monolith this has a significant impact on increasing the mechanical stiffness, hardness and fracture resistance of the resulting monoliths. A low creep response under a constant load in the composite monolith is the only indication from the mechanical tests that it contains a small amount of PMMA. Nearfield infrared (IR) nanospectroscopy *via* nanoFTIR and pseudoheterodyne (PsHet) imaging [6] on plastically deformed and indented surfaces revealed local chemical structure-mechanical interactions. Furthermore, synchrotron far-IR spectra revealed that the addition of PMMA does not alter the Zn-N interaction, but the vibrational mode of PMMA was shifted in the composite monolith suggesting strains in the binder. Our findings suggest that the polymer chains are trapped inside the ZIF-71 pores, thereby improving the mechanical resilience that might pave the way to future scaling up of MOF monoliths for industrial gas sorption applications and robust sensors.

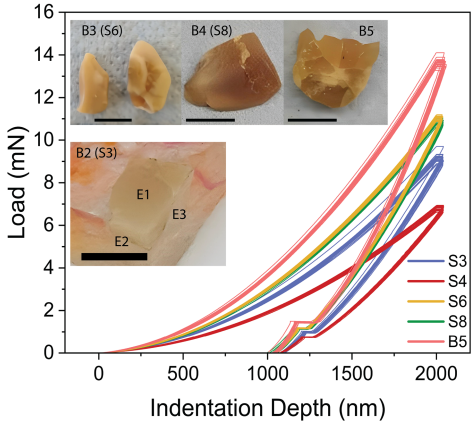


Figure 1. Load-depth indentation curves for different ZIF-71 monoliths and PMMA@ZIF-71 polymer composites. The scalebar represents 5 mm, (B) represents the batch number, (S) represents the Sample number, and (E) represents the reduced modulus at different sides of the monolith. Unpublished results [7].

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SUPERCRITICAL CO_2 CONTINUOUS FLOW SYNTHESIS OF METAL ORGANIC FRAMEWORKS

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Keywords: *supercritical CO_2, continuous flow synthesis, HKUST-1, zirconium MOFs*

The use of supercritical CO_2 ($scCO_2$) as a solvent in chemical synthesis has attracted increasing attention, driven by the growing demand to transition conventional synthesis to greener and more sustainable processes. While $scCO_2$ has demonstrated effectiveness in the preparation and functionalization of nanomaterials, further investigation into its role in the synthesis of a broader range of materials remains highly valuable. Metal-organic frameworks (MOFs) are especially of interest given their broad tunability and variety in applications. However, the challenges in large scale synthesis of MOFs hinder the advancement of these technologies and restrict their widespread implementation in real-world applications.

Our work developed continuous flow synthesis methods using $scCO_2$ for scalable production of both kinetically fast and slow-forming MOFs.[1,2] $ScCO_2$ is considered a promising solvent for MOF synthesis for its mild critical point (31.1°C and 7.4 MPa), which makes it ideal for low-energy processing of thermally sensitive materials. Its zero-surface tension also allows for the removal of unreacted precursor materials and solvents without causing pore collapse. Our synthesis achieved the continuous production of high-quality HKUST-1[3] and zirconium MOFs (UiO-66, UiO-66-NH_2, MOF-808) nanoparticles with residence times of approximately 10 seconds and 2 minutes, respectively. The low solubility issue, which has been a major concern in MOF synthesis, was addressed by using a co-solvent. The use of $scCO_2$ reduces the need for toxic solvents and provides an energy efficient route for the fast MOF particle growth at high production rates.

The roles of $scCO_2$ in continuous flow synthesis are demonstrated through the analysis of HKUST-1 product morphology, size distribution, and adsorption capacities: (1) $scCO_2$-induced turbulence accelerates nanoparticle collisions; (2) its low dielectric constant reduces particle repulsion, promoting coagulation and ripening; (3) $scCO_2$ removes solvents and impurities from micropores, yielding high surface areas without additional MOF activation. A non-classical crystal growth mechanism observed with HKUST-1 nanoparticles in $scCO_2$ shows that $scCO_2$ accelerates particle growth through aggregation and vapor deposition. Nascent particles aerosolize in a mixture of $scCO_2$ and unreacted precursors. With limited unreacted precursors, products form via particle aggregation; with excess precursors, vapor deposition occurs on particle aggregates, altering product morphology.

Understanding the role of $scCO_2$ offers insights for designing scalable synthesis routes for various MOFs. For MOFs with slow formation kinetics (such as the zirconium MOFs), particle aggregation in the $scCO_2$/co-solvent mixture was controlled by adding an acid modulator to adjust the nucleation rate of nanoparticles, enabling the formation of high-quality products with morphologies ranging from aggregated structures to well-faceted octahedrals, both with high crystallinity and specific surface areas.

Our work demonstrated highly efficient syntheses of MOFs, an important class of porous materials, using $scCO_2$. We investigated the role of $scCO_2$ and explored methods to control the particle size and morphology of the products, offering insights for scaling up synthesis from laboratory to large-scale production.

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A UNIQUE POST-SYNTHETIC TREATMENT USED TO PREPARE ORDERED DEFECTS IN THE UIO-66 SYSTEM

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Keywords: *MOFs, ordered defect, post-synthetic treatment …*

As a common porous material, the defect engineering of MOF is of great significance in improving gas adsorption and separation, heterogeneous catalysis, etc.[1-2] However, the disordered distribution of defects makes the internal composition of the MOF framework complex, which is not conducive to clarifying the mechanism by which defects play a role in improving performance. Therefore, achieving the ordered distribution of defects in MOF is a challenging task, it beneficial to harness the advantages of both defects and well-defined structures. Among the methods for introducing defects through de novo synthesis, both the common modulation method and the mixed linker method have difficulty in controlling the ordered distribution of defects. Therefore, choosing a mild and effective post-synthetic treatment method is a feasible approach. Selected the *fcu* topological MOF, synthesized by Rosseinsky et al., formed by the ordered arrangement of terephthalic acid and fumaric acid.[3] Then selectively removing fumaric acid which is more sensitive to heat and ozone, the MOF with ordered linker defects was obtained. This work finds that it is difficult to achieve completely ordered defects in a 1:1 ratio dual-linker MOF through the post-synthetic treatment. There is an upper limit to the number of defects; otherwise, certain structural stability needs to be sacrificed. It is necessary to balance the relationship between the number of defects that the MOF framework can tolerate and the stability of the MOF structure. This work provides a new path for extending multivariate (MTV) MOF to obtain ordered defects.



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CONSTRUCTION OF A THREE- DIMENSIONAL PORPHYRIN ORGANIC FRAMEWORK FROM POROUS ORGANIC CAGE BLOCKS

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Keywords: Covalent organic Frameworks, *Porphyrin, Porous Organic Cage, Photophysics, Reactive Oxygen Species*.

Covalent Organic Frameworks (COFs) are highly ordered, crystalline, and porous materials constructed through covalent bonds between organic building blocks. Notably, three-dimensional (3D) COFs have garnered significant attention due to their modularity, tunable pore structures, and enhanced photophysical properties resulting from reduced π-π stacking.

In this study, we designed, synthesized, and characterized a 3D COF constructed from a porous organic cage and porphyrin. Organic cages have emerged as versatile building blocks for 3D COF assembly due to their preorganized geometry, multiple reactive sites, and intrinsic structural flexibility. Their polyhedral structures facilitate directional covalent bonding in three dimensions, enabling the formation of crystalline 3D networks. Furthermore, the conformational adaptability of cage units allows precise tuning of the framework's topology and porosity. Additionally, we incorporated a porphyrin ligand, known for its excellent optical activity, and further enhanced its photoactivity by introducing a radioactive isotope at the porphyrin core. This modification enables internal Cherenkov radiation to amplify optical activation within the framework. The synthesized cage-based, optically active COF was comprehensively characterized using infrared spectroscopy, wide-angle X-ray scattering, and dynamic light scattering. Furthermore, its biomedical potential was extensively evaluated [1], [2].

In conclusion, we successfully demonstrated the synthesis and characterization of cage-based 3D COFs and validated their potential for biomedical applications. Detailed results will be discussed in this presentation.

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Diamondiyne: A 3D carbon allotrope with mixed valence hybridization

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Keywords: *carbon allotrope, covalent organic framework*

Carbon allotropes is a kind of material made only of carbon, such as fullerene, nanotubes and graphene. Diamond is the only naturally occurring 3D structure of carbon, and it is formed with sp^3 hybridized carbon atoms. If sp hybridized carbons are introduced to the diamond structure, a new family of carbon allotropes is formed. Diamondiyne (Fig. 1a) is one in this family with sp^3 hybridized carbons connected by four sp hybridized carbons. The diyne linker allows it to keep a diamond topology, but expends the structure, making it similar to a covalent organic framework.

The first documented trial of making diamondiyne was made by Feldman about 30 years ago[1] and recently we have successfully made it using a bottom-up strategy.[2] Diamondiyne films are formed at a liquid-liquid interface through an interfacial reaction, where a basic building block binds one by one to the growing film. Furthermore, we show that the synthesized diamondiyne film is in a good uniformity and continuity (Fig. 1b) with a scalable thickness (Fig.1c). The obtained films are polycrystalline, and the crystalline structure with well-defined lattices has been found under high resolution transmission electron microscopy (Fig. 1d). We also simulated the electron diffraction of the crystallographic information that confirms a two-interpenetration structure of diamondiyne (Fig. 1e).

Our work not only marks the finish for a 30-years quest but also provides the starting point for research on a new class of carbon allotrope.

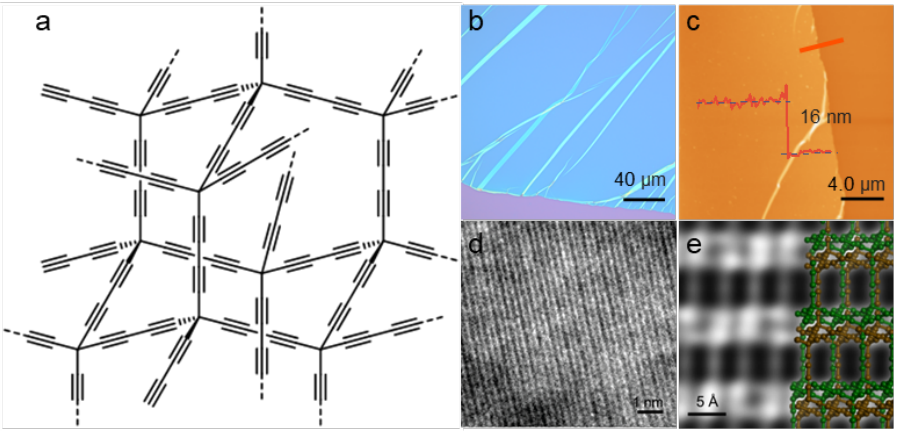


Figure 1 Structure, morphology and crystallinity of diamondiyne films. b) Optical microscopic image of a film on a silicon substrate. c) AFM height image of a film with a thickness of 16 nm. d) HRTEM image of a thin film. e) Simulated iDPC-STEM image with the structure of the asymmetric two-fold interpenetrated diamondiyne shown overlayed.

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ELECTROCLEAVAGE SYNTHESIS OF MOLECULAR-LEVEL HYBRID COF/SINGLE-LAYER MOF-DERIVATIVE MOOH CATALYSTS WITH INTERFACE-HETEROJUNCTION FOR BIOMASS ELECTROOXIDATION REACTION

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Keywords: *Covalent Organic Framework (COF), Electrochemical Thin Film, MOF-Derived MOOH, Hierarchical Interface-Heterojunction (IHJ), Biomass Electrooxidation Reaction (BEOR)*

A molecular-level hierarchical interface-heterojunction (IHJ) electrode of hybrid COF/single-layer MOF-derivative MOOH catalysis will be introduced. This system utilizes the complementary properties of COFs, which provide a porous scaffold with tunable chemistry, and MOF-derived MOOH, which offers abundant redox-active sites.[1] The hierarchical IHJ architecture promotes efficient charge separation and enhances electron/proton transport, significantly improving catalytic performance.[2] This will realize a synergistic multi-component design of biomass electrooxidation reaction (BEOR) catalysts from single to multi-scale, and will reveal the structure-component-performance relationships of hierarchical IHJ electrodes at multiple components.

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ENHANCED UPCONVERSION EMISSION OF LANTHANIDE METAL-ORGANIC FRAMEWORKS

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Keywords: *lanthanides, MOF, metal cluster, luminescence, upconversion,*

Metal organic frameworks (MOFs) are exceptionally versatile, unlocking a vast and unprecedented treasure trove of chemical possibilities, seamlessly combining inorganic and organic building blocks.[1] Apart from monometal MOFs, multimetal MOFs offer enhanced functionality by combining the unique properties of different metals, enabling applications like catalysis, sensing, and luminescence. Unlike monometal MOFs, they leverage synergistic effects between metals, such as improved energy transfer or cooperative catalysis. The inclusion of multiple metals allows fine-tuning of pore environments and electronic properties, making them highly versatile.[2] Incorporation of lanthanides additionally offers predictable optical signals that are beneficial for designing MOFs for desired optical properties.[3] In this context, the formation of the lanthanide-based multi-metal cluster for the upconversion emission process could be promising in developing ultrasensitive optical materials. Towards this, we synthesized a multi-metal cluster using carboxylic acid-based conjugated aromatic ligand and three metal ions (Yb3+, Er3+, and Y3+) through a conventional solvothermal process. Different doping ratio for the metal ions was utilized to synthesize the multi-metal cluster, and the structure was confirmed using the PXRD technique. The chemical composition and doping ratios were confirmed through Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) analysis (Figure 1), which was further supported by the ICP-OES analysis. Upon confirmation of cluster formation, the optical spectroscopic study was carried out to verify the UC emission of the synthesized cluster. Enhanced UC emission was observed for the cluster material compared to the non-cluster based MOF upon excitation with a 980 nm laser. This work depicted the synthesis of multi-metal clusters to develop UC emissive materials, which can be utilized for various optical applications.

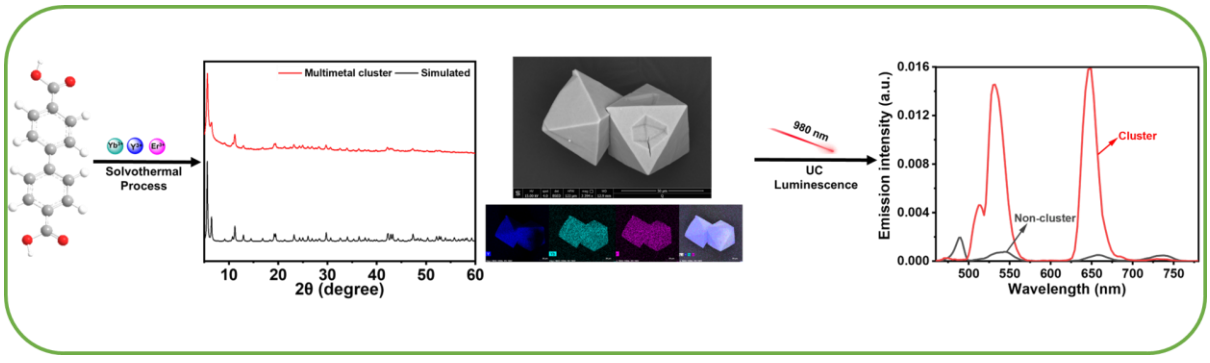


Figure 1: Depiction of multi-metal cluster synthesis and its UC luminescence property.

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INVESTIGATING CHARGE FLOW IN MULTIVARIATE REDOX-CONDUCTIVE MOFS

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Keywords: *Redox-Conductive Metal Organic Frameworks (RC-MOFs), Electron Transport, Electron Transfer, Apparent Electron Diffusion Coefficients (D_e^{app})*

Over the past three decades, metal–organic frameworks have experienced remarkable advancement and have been widely studied for potential applications in environmental and energy research. In the context of electrochemical applications, the development of redox-conductive metal–organic frameworks (RC-MOFs) and a thorough understanding of the mechanisms governing charge transport within their porous architectures are appealing research targets.

In this study, we investigate hopping-like electron transport in multivariate MOFs by employing mixed redox-active linkers with distinct redox potentials. The crystalline MOF films are grown on fluorine doped tin oxide, and charge propagation through the thin film proceeds through a linker-to-linker hopping mechanism that is charge-balanced by counterion transport from the electrolyte. Consequently, cyclic voltammograms of the thin films display features typical of a diffusion-controlled process[1] where different redox events can be accessed simply by varying the applied potential. Pulsed step-potential spectrochronoamperometry gives insight into various modes of electron propagation and well-separated spectroscopic signatures of the associated oxidation states, which provide an excellent platform to probe electron-transfer processes between linkers of different redox properties.[2] Under transient conditions, apparent electron diffusion coefficients, D_e^{app}, are determined, offering microscopic insights into charge propagation through diffusional electron transport coupled with thermodynamically driven electron transfer processes.

Moreover, we explore the role of counterions and the influence of various contributing factors such as solvents, framework architecture, distance between hopping sites, ligand functionality, ion pairing, and external potentials to provide an in-depth understanding of charge transfer processes. These studies can be essential in electrocatalysis to evaluate the structure-transport property relationship and improve the performance of electric devices and energy storage materials.

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TAILORING COFS: TRANSFORMING NONCONDUCTING 2D LAYERED COF INTO A CONDUCTING QUASI-3D ARCHITECTURE VIA INTERLAYER KNITTING WITH POLYPYRROLE

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Keywords: *Covalent organic frameworks (COFs), conjugation bridge, conductivity.*

Improving the electronic conductivity and structural robustness of covalent organic frameworks (COFs) is crucial for expanding their application in energy storage and electronic devices[1]. In this work, we introduce a novel strategy to transform 2D COFs into quasi-3D structures by covalently cross-linking them with polypyrrole (Ppy) chains[2]. This cross-linking enhances the electronic conductivity of the COF from 10^{-9} to 10^{-2} S m^{-1}, representing a significant advancement. The resulting 3D COF exhibits well-defined reflections in selected area electron diffraction (SAED) patterns, which correspond closely to the modeled crystal structure, confirming the retention of long-range order.

The enhanced conductivity is attributed to the presence of a density of states near the Fermi level, which elevates the valence band maximum by 0.52 eV compared to the parent 2D pyrrole-functionalized COF. This electronic shift aligns with the observed optoelectronic band gaps, underscoring the influence of the conjugated polypyrrole cross-links. Notably, electron paramagnetic resonance (EPR) measurements reveal a strong signal indicative of polaron formation, suggesting the predominant existence of radical cations sourced from the cross-linked Ppy chains.

A supercapacitor fabricated using this 3D COF (COF20-Ppy) achieves a high areal capacitance of 377.6 mF cm^{-2}, surpassing the performance of COFs loaded with non-covalently linked Ppy. The polypyrrole chains act as conjugated bridges across COF layers, providing additional conduction pathways and polarons that further reduce the band gap and enhance charge transport.

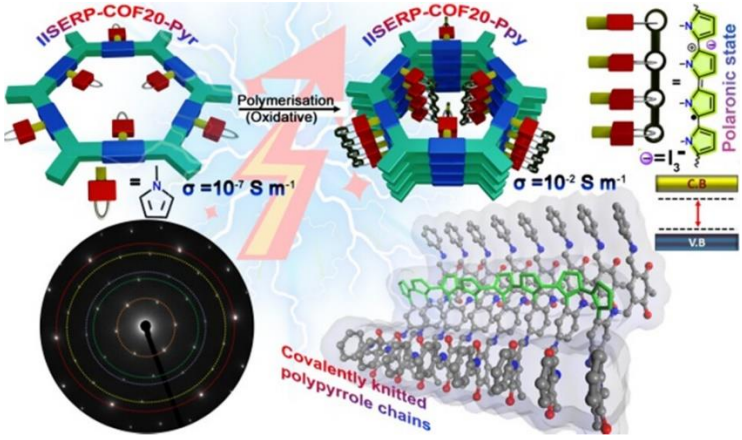


Fig. 1: Schematic representation of Transforming Non-Conducting 2D COFs into Conducting Quasi-3D Structures through Polypyrrole Interlayer Knitting

This study highlights a transformative approach to converting 2D COFs into highly ordered and conductive 3D materials, offering a promising platform for next-generation energy storage systems and electronic applications.

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ENGINEERING 3D FULLY CONJUGATED COFs: BUILDING HETEROCYCLIC FRAMEWORKS AND EXPLORING CHARGE CARRIER DYNAMICS

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Keywords: 3D-Fully Conjugated COFs, Thin Films, GIWAXS, Photoconductivity, Electron Mobility

In the realm of covalent organic frameworks (COFs), it is an intriguing but challenging goal to achieve fully conjugated three-dimensional frameworks (3D-COFs). Such systems would offer extended electron delocalization throughout the entire framework, a key feature for optoelectronic applications. In this work, we introduce, for the first time, donor-acceptor heterojunctions in fully conjugated 3D COFs. To achieve this challenging goal, three novel moieties were synthesized. These non-planar linkers are based on a saddle-shaped annulene skeleton with 8 π-electrons [1], where the functional groups required for framework formation are directly attached to various heterocycles, such as thiophenes (CO-Th), furans (CO-Tf), or a combination of both within the same linker (CO-TfTh). By employing a modulation approach, we successfully synthesized a family of distinct 3D fully conjugated COFs with high crystallinity as a bulk and thin film materials and permanent porosity.

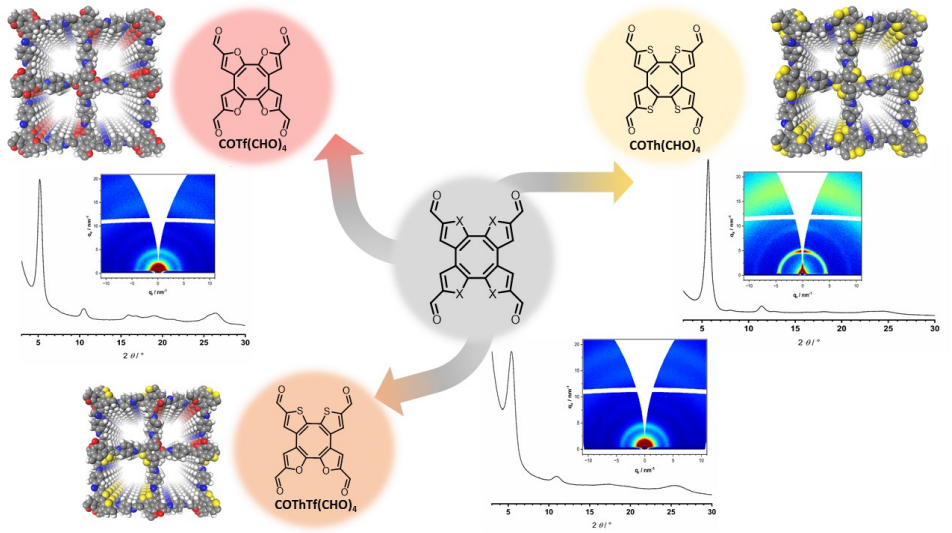


Figure 1: Schematic representation of the different building blocks and their corresponding PXRD and GIWAXs data showing crystalline 3D fully conjugated COFs.

The ability to create crystalline and oriented films of fully π-conjugated 3D COTh-based COFs on non-modified substrates is expected to open the way for integration of such frameworks into diverse optoelectronic applications. Optical pump terahertz probe studies provide insights into the excited state and charge carrier dynamics of these unique 3D organic frameworks. [2]

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THE EFFECT OF HYDROSTATIC AND NON-HYDROSTATIC PRESSURE ON PCN-250

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Keywords: *PCN-250, Diamond-Anvil cell, Pressure-Transmitting Medium, Hydrostatic Pressure, Non-hydrostatic Pressure*

Pressure is the most pertinent external stimulus to study the mechanical properties of the hard and soft matter.[1] Being an important thermodynamic variable, pressure can substantially change the atomic structure, as well as the microstructure of materials. Materials compressed at high pressure may reveal unexpected and intriguing functional properties such as piezochromism, spin crossover, orbital re-ordering, etc. Metal-organic frameworks (MOFs) having open pore frameworks with structural flexibility[2] are ideal candidates to study the effect of pressure on it. This framework flexibility can be triggered readily in response to pressure. MOFs can undergo different dynamic structural behavior under pressure such as change of bond length and angels, possible phase transition and inclusion of guest molecules inside the pores.[3]

For the experimental analysis of the MOFs under high pressure, a Diamond-Anvil Cell (DAC) is the standard experimental equipment typical for diffraction and spectroscopic measurements. Along with a MOF single crystal, a Pressure-Transmitting Medium (PTM) liquid are loaded inside a hole drilled in a metal gasket, put under the two anvils of the DAC to apply a uniform hydrostatic pressure on the crystal. On the other hand, application of uniaxial mechanical stress on the MOF crystal is the way to measure the structural changes produced by non-hydrostatic compression. These two different pressurization methods may in fact induce distinct structural transformations within the crystals. A recent report by Zhou and co-workers reveals the sequential phase transformation phenomenon of PCN-250 MOF (Formula= C_{48} H_{20} Fe_6 N_6 O_{32}, space group= *P-43n*, at ambient pressure) crystals by the application of non-hydrostatic pressure up to 300 MPa. [4] However, so far there is no report on the behavior of PCN-250 crystals upon hydrostatic pressurization.

In our study, we have determined the structural compression of PCN-250 crystals upon a hydrostatic pressurization inside the DAC. Further, we also have investigated the effect of both penetrating and non-penetrating pressure-transmitting medium. Moreover, we have explored the non-hydrostatic regime up to a higher pressure.

In this poster, we report the results of a comparative study of the effect of hydrostatic and non-hydrostatic compression up to 1 GPa on PCN-250, showing how the non-hydrostatic conditions induce a more severe modification of the channels inside the MOF.

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A MICROPOROUS BIMETALLIC ALUMINUM-COPPER-CARBOXYLATE-PYRAZOLATE MOF FOR CO_2 CAPTURE

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Keywords: CO_2 capture, adsorption, metal-organic frameworks (MOFs), bimetallic MOF

Achieving net-zero CO_2 emissions by 2050, as targeted by the IPCC, requires urgent improvements in carbon capture technologies. In 2024, global emissions are projected at 37.4 billion metric tons, while current CCS efforts capture only 0.13% of this total. [1] Amine-based absorption, though widely used, suffers from high energy demands and poor thermal stability. Adsorption based technology offers a cleaner, more energy-efficient alternative, but its scalability depends on developing solid adsorbents with high CO_2 capacity, selectivity, and fast kinetics. Advancing such materials is key to enabling efficient, large-scale carbon capture. [2]

In this regard, MOFs are highly promising for CO_2 capture due to their tunable porous structures, enabling high uptake, selectivity in the presence of impurities (including moisture), and good thermal and chemical stability. [3] CALF-20 has emerged as a benchmark MOF for post-combustion CO_2 physisorption, maintaining high performance even at 25–30% relative humidity and demonstrating scalability at the industrial level. [4] However, further development of MOF-based sorbents is needed to meet diverse process requirements and reduce energy costs.

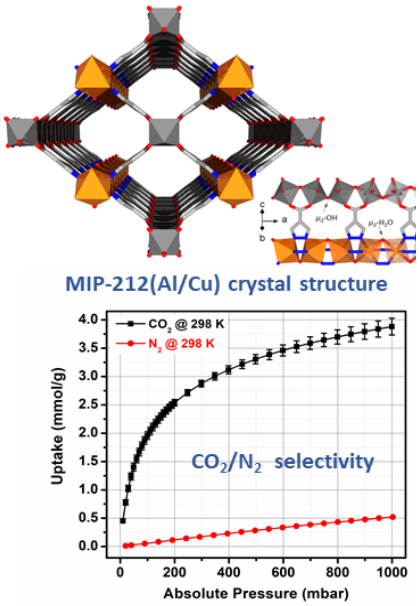


Figure showing the MIP-212(Al/Cu) crystal structure, AlO_6 – grey polyhedron; CuN_4 $(H_2O)_2$ – orange polyhedron and corresponding CO_2 and N_2 isotherms measured at 298K.

This study presents MIP-212(Al/Cu), a novel bimetallic MOF built from the shortest carboxylate–pyrazolate linker, 1H-pyrazole-4-carboxylic acid. Combining Al carboxylate and Cu pyrazolate chemistries based on the HSAB principle, it features two types of narrow pores with distinct functional sites (μ_2-OH groups and Cu open metal sites). Upon high-temperature activation, MIP-212(Al/Cu) exhibits high CO_2/N_2 IAST selectivity (~30 at 1 bar) and notable CO_2 uptake (2.5 mmol/g at 200 mbar; 3.9 mmol/g at 1000 mbar). Breakthrough experiments under CO_2:N_2:H_2O mixtures highlight its potential for post-combustion CO_2 capture. In this communication, more details on the synthesis, the crystal structure and characterization of MIP-212(Al/Cu), together with a highlight on the performances towards the CO_2 capture from point source. Future directions towards improving the performances in presence of impurities (e.g., moisture) and/or by tuning the chemical composition of this MOF will be also discussed.

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PHOTOCATALYTIC POTENTIAL OF CERIUM MOFs: EXPLORING LIGAND EFFECTS IN POLLUTANT DEGRADATION

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Keywords: MOFs, Photodegradation, pollutants, cerium, methylene blue, organic ligands

Lanthanide-organic frameworks (LnOFs) have gained significant attention as advanced photocatalytic materials for addressing persistent environmental pollutants. In this study, we developed and evaluated three cerium-based MOFs, Ce-HMT (hexamethylenetetramine), Ce-TPA (terephthalic acid), and Ce-PDC (pyridine-2,6-dicarboxylic acid), synthesized via a hydrothermal method at 160 °C. These materials were tested for their photocatalytic activity in degrading methylene blue (MB), a common industrial dye pollutant, under 15 W UV-A light (λ_max = 350 nm). All three MOFs exhibited distinct photocatalytic performances, with degradation efficiencies of 86% for Ce-HMT, 66% for Ce-PDC, and 6% for Ce-TPA after 120 minutes of exposure. These results clearly demonstrate the crucial influence of ligand structure on the photocatalytic behavior of cerium-based MOFs.

The use of different ligands not only affects the MOF morphology and light absorption properties but also directly impacts the efficiency of charge separation and reactive species generation. The superior performance of Ce-HMT is attributed to enhanced interaction between the ligand environment and cerium centers, leading to better photocatalytic dynamics. This work highlights the importance of ligand engineering in optimizing MOFs for environmental applications.

Building upon these findings, our ongoing research is focused on expanding the application of lanthanide-based MOFs and their TiO_2-based composites for the degradation of more challenging contaminants, including pharmaceutical dyes (caffeine, paracetamol, Sulfamethoxazole) and PFAS (per- and polyfluoroalkyl substances). Additionally, we are exploring their potential in photocatalytic hydrogen production as part of a broader strategy for sustainable energy and environmental remediation. This study not only contributes to the fundamental understanding of MOF-based photocatalysts but also aligns with our long-term goal of developing multifunctional materials for clean water and clean energy technologies.

CONSTRUCTION OF LDH-DERIVED BIMETALLIC METAL-ORGANIC FRAMEWORK (BMOF) FOR ENERGY CONVERSION AND STORAGE APPLICATION

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Keywords: Metal-organic framework, oxygen evolution reaction, urea oxidation reaction, and supercapattery.

The 2D metal-organic framework (MOF) has emerged as a promising material for advanced energy conversion and storage technologies. In our research, we have developed a facile strategy for growing ultrathin NiMn-MOF nanosheet arrays on Ni foam (NS/NF) via in situ transformation from NiMn-layered double hydroxide (LDH) arrays.[1] The as-synthesized LDH-D NiMn-MOF exhibited an overpotential of 350 mV to drive a current density of 100 mA/cm^2 for the oxygen evolution reaction. However, because of its sluggish kinetics, the oxygen evolution reaction (OER) is not exquisite for efficient hydrogen generation at significant potential. Electrochemical urea oxidation reaction (UOR) appears to be a more thermodynamically feasible process than water electrolysis because of the lower theoretical overall urea electrolysis potential (0.37 V) compared to water electrolysis (1.23 V). Impressively, LDH-D NiMn-MOF required a potential of 1.39 V at 100 mA/cm^2 towards UOR, showcasing its superior catalytic performance. Interestingly, beyond catalysis, the LDH-D NiMn-MOF was also explored as high-performance energy-storage material for supercapattery with a specific capacity value of 2613.9 mC cm^{-2} at 1 mA cm^{-2} which is 1.5 times higher than NiMn-LDH (1724.3 mC cm^{-2}). An aqueous asymmetric supercapattery device LDH-D NiMn-MOF// Fe_2O_3/Fe_3O_4/CNF was fabricated [2], which provided a maximum energy density of 64.1 Wh kg^{-1} and a power density of 14.82 KW kg^{-1} with 77.8 percent of capacitance retention after a continuous run of 8000 cycles at a current density of 10 mA cm^{-2}. Moreover, structural modifications to the system resulted in the development of a new MOF with the introduction of defects along with surface reconstruction, resulting in improved electrochemical performance as an energy-storage material (supercapattery).[3] The defect-engineered MOF provided the energy storage capacity of 532 C/g, which outperformed both the NiMn-LDH (423 C/g) and Direct NiMn MOF (258 C/g). Similarly, an aqueous asymmetric supercapattery fabricated device delivered a maximum energy density of 55.99 Wh kg^{-1} and power density of 6.83 KW kg^{-1}, with excellent cyclic stability (94.4% of its original capacitance after 6000 continuous cycles at 10 mA cm^{-2}). Therefore, the development of the LDH-derived bimetallic metal-organic framework underscores its potential for future sustainable energy conversion and storage applications.

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A NOVEL MECHANO-SYNTHESIZED ZEOLITIC TETRAZOLATE FRAMEWORK FOR HIGH-PERFORMANCE TRIBOELECTRIC NANOGENERATOR AND SELF-POWERED SELECTIVE NEUROCHEMICAL DETECTION

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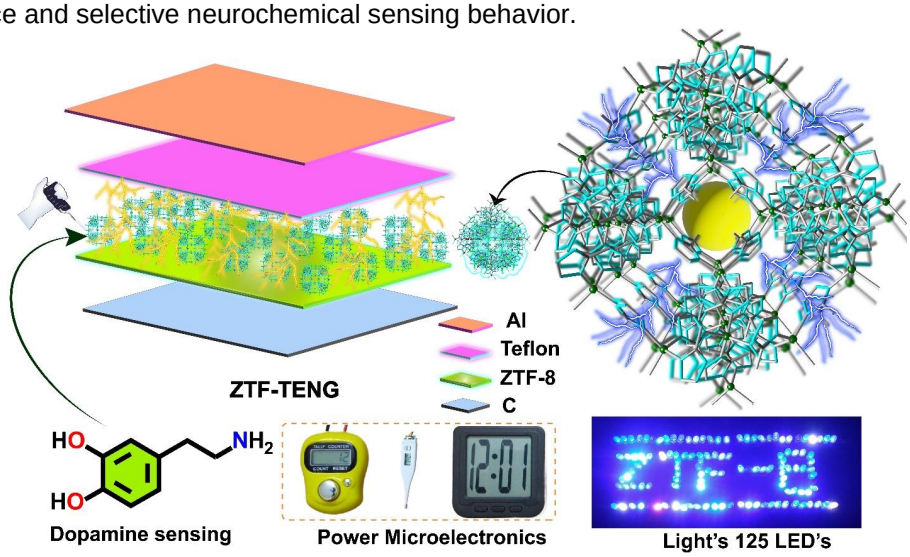
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Keywords: *metal−organic framework, zeolitic tetrazole framework, mechanochemistry, triboelectric nanogenerator, energy harvesting,additive manufacturing, dopamine, self-powered sensors*

Designing a high-performing triboelectric novel material with eco-friendly, rapid, cost-effective synthesis is the future of material research in triboelectric nanogenerators (TENG). We report a mechanochemical ball mill synthesis of a Zeolitic Tetrazolate Framework (ZTF-8) which is isostructural with the well-known zeolitic imidazolate framework ZIF-8 [1]. ZTF-8 is extremely stable in water, 0.1 M aqueous acid and base solutions for 75 days at 25 °C and boiling water (100 °C) for 7 days [2,3]. Kelvin probe force microscopy and Molecular Electrostatic Surface Potential computational analysis showed that ZTF-8 has very high positive surface potential. Three-Dimensional Digital Microscopy Analysis and Atomic Force Microscopy studies reveals the high roughness profile in the ZTF-8 film. The unique structure, exceptional acid/base stability, good dielectric property, high roughness profile combined with extreme electropositive nature of ZTF-8 makes it as a suitable candidate as a polymer free triboelectric positive material in TENG with outstanding performance (power density of 720 mW /m^2). This high triboelectric output was further validated using COMSOL Multiphysics simulation tool. Simple mechanical hand tapping of the ZTF based TENG (ZTF-TENG) device generates high electric output, which was practically used to power numerous low-powered devices like tally counter, clinical thermometer, digital clock and also illuminates 125 numbers of Light Emitting Diodes. In addition, the efficiency of ZTF-TENG was utilized as a self-powered device for selective dopamine (DA) sensor with good sensitivity (377.76 mV/µM/cm^2), wide range linearity (5-120 µM), and excellent limit of detection (0.42 µM). This report is extremely distinct and stand-out due to the fact that the developed TENG device's positive layer contains no polymer participation (low cost, scalable and eco-friendly approach) but still provides excellent performance and selective neurochemical sensing behavior.



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MECHANOCHEMICALLY SYNTHESIZED COVALENT ORGANIC FRAMEWORK EFFECTIVELY CAPTURES PFAS CONTAMINANTS

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Keywords: *COF • Mechanochemistry • in situ study • PFAS • Adsorption*

Per- and polyfluoroalkyl substances (PFAS) are highly stable, bioaccumulative environmental contaminants that pose significant health risks. Effective removal of these “forever chemicals” from water sources remains an urgent challenge.[1] Recently, covalent organic frameworks (COFs) have emerged as a promising alternative for PFAS adsorption.[2] In this study, we report the mechanochemical synthesis[3] of a highly crystalline COF constructed from 1,3,5-tris(4-aminophenyl)benzene (TAPB) and 1,3,5-triformylbenzene (TFB). The formation process was tracked in real time using time-resolved *in situ* synchrotron X-ray diffraction, revealing rapid framework development under solvent-free conditions.

The resulting TAPB-TFB COF exhibited excellent adsorption performance, efficiently removing two common PFAS such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) from water within minutes, over 80% of uptake occurring in the first 10 minutes. Molecular-level interactions between PFAS and the COF framework were further elucidated through X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy (FTIR). Our results highlight the potential of mechanochemically synthesized, metal-free COFs as robust, scalable, and environmentally friendly materials for water purification and PFAS remediation.

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ULTRAFAST BIMOLCULAR PROCESSES IN ENGINEERED SCINTILLATING METAL ORGANIC FRAMEWORKS

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Keywords: fluorescent MOFs, bimolecular processes, ultrafast emitters, scintillation, Stokes shift

Metal-Organic Frameworks (MOF) are nanoporous and luminescent hybrid materials consisting in a crystalline framework of conjugated fluorescent ligands linked to metal-oxide clusters nodes. High efficiency and large Stokes shift ultrafast scintillation is observed for the first time in engineered hetero-ligand MOFs containing heavy hafnium atoms in the linking nodes. Two fluorescent conjugated polyacene ligands of equal molecular length and connectivity, yet complementary photophysical properties, are co-assembled by hafnium oxy-hydroxy clusters, generating highly crystalline MOF. The presence of heavy elements enhances the scintillation yield by promoting ultrafast recombination of the ionized free charges generate upon interaction with high energy photons. [1] [2] [3] Moreover, the fast diffusion of singlet molecular excitons in the framework enabled by the fine tuning of the ligand molecular orbitals properties permits the activation of the low energy emitting ligands by ultrafast non-radiative energy transfer in the ps time scale. [4] [5] Hetero-ligand MOFs show therefore an excellent scintillation yield of 12000 ph MeV^{-1}, with an actual Stokes shift of 1.3 eV and emission lifetime ~ 750 ps. Photoluminescence and scintillation spectroscopy experiments ascribe the observed sub-nanosecond kinetics to a partial quenching of the excited states through singlet-singlet annihilation (SSA), a loss channel made competitive by the fast diffusion of singlets created in the framework at high concentration upon interaction between high energy photons and hafnium ions. The extremely efficient SSA is therefore exploited to realize UV emitting scintillating homo-ligand MOF showing an unprecedented 150 ps scintillation pulse and yield as high as 13000 ph MeV^{-1}. These values surpass most of commercially available fasts scintillators and alternative nanomaterials recently proposed, thus opening the way to breakthrough advances in the radiation detection technology for high energy physics and medical imaging.

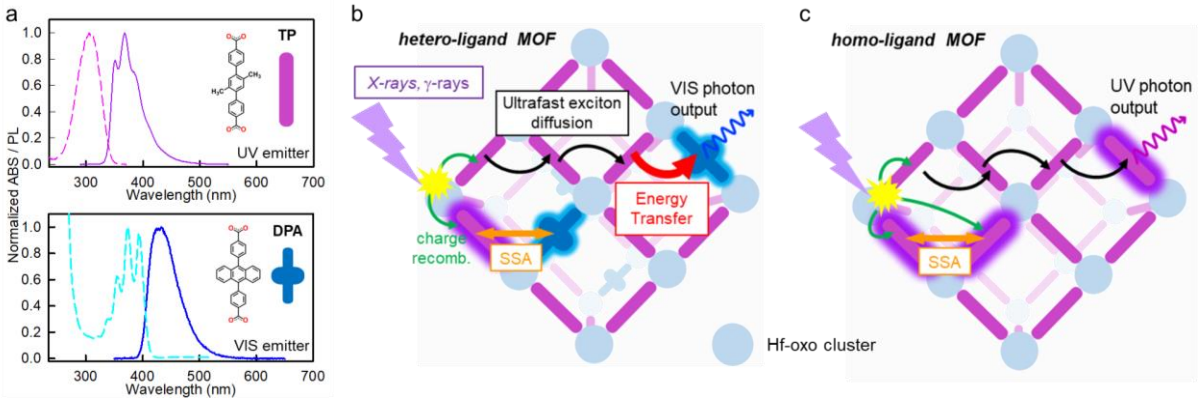


Figure 1. a) Molecular structure of the MOF building blocks, namely the TP and DPA fuorescent ligands. b,c) Energy flux in the MOF structure after generation of a TP singlet exciton upon absorption of a UV photon. In the homo-ligand MOF, the singlet exciton diffuses within the framework until radiative recombination or experience singlet-singlet annihilation (SSA). In the hetero-ligand MOF, the singlet exciton diffuses until it reaches the co-ligand DPA, which is excited by non-radiative energy transfer and then after heteromolecular SSA it emits a blue photon with zero re-absorption of its luminescence.

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LEAVING THE DARK SIDE: TRANSFORMING IMINE-COFS INTO HIGHLY EMISSIVE MATERIALS

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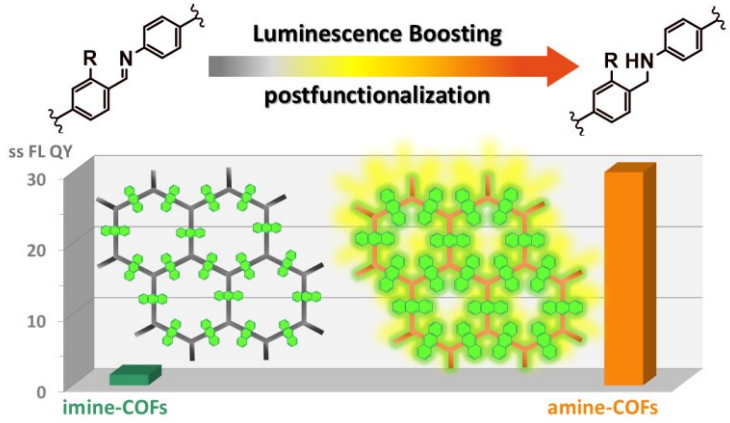
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Keywords: *covalent organic frameworks, imines, amines, emission, chromophores*

Covalent organic frameworks (COFs)[1] are readily synthesized, highly ordered, and porous materials. Their structural modularity make them appealing for diverse applications, including optoelectronics.[2,3] However, intrinsic interactions in imine-based COFs—such as π–π stacking, extended conjugation, and interlayer coupling—can significantly alter the emission behavior of the monomeric structural units, leading to fluorescence quenching in these materials.



To address this issue, we report a simple post-synthetic strategy to convert non-emissive, anthracene-based imine COFs into **highly emissive amine-based COFs** via imine bond reduction using $NaBH_3CN$:BzOH. This transformation gives structurally modified COFs with solid-state fluorescence quantum yields (ss FL QY) reaching up to 33%. To investigate excited-state energy dissipation, we synthesized molecular reference compounds with imine or amine groups. Photophysical characterization, supported by DFT calculations, shows that in both cases emission exhibit weak charge transfer (CT) character. Comparative analysis reveals that COFs emission is attributed to the suppression of nonradiative decay pathways caused by post-synthetic modification of polymer matrix. These findings provide a clearer understanding of COFs photophysics and offer a practical route toward designing emissive porous materials for advanced optoelectronic applications.

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SYSTEMATIC BAND-GAP ENGINEERING IN COVALENT ORGANIC FRAMEWORKS THROUGH ISOMERIC ALLOYING

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Keywords: *covalent organic frameworks, optical properties, band-gap engineering, thin films, isomers*

Covalent organic frameworks (COFs) represent a class of crystalline porous polymers that are emerging as promising active materials in catalysis, energy storage, chemical sensing and optoelectronics. Typically, the functionalities of the resulting COF structures are pre-determined by the design and synthesis of functionalized monomers.[1,2] Since molecular pre-design of the building blocks offers only limited control over the characteristics of the resulting COFs, a way to predict and systematically tune the optical properties of COFs by rational design is of high interest. In the case of inorganic materials, band-gap engineering is a powerful tool for tailoring the optical and electronic properties through methods such as crystal downsizing or elemental doping, yet in the context of organic solids, systematic band-gap tuning remains a significant challenge.

Here, we present a novel approach towards controlling the optical properties of COFs by utilizing isomeric thienothiophene-based (TT) building blocks.[3] The combination of these isomeric building blocks with three different tetratopic amines i.e., *Wurster*, *Etta* and *Pyrene*, resulted in three exceptionally crystalline pairs of isomeric COF bulk materials termed WTT, EttaTT and PyTT, where each pair possesses almost identical ordered structure. Furthermore, highly oriented, crystalline thin films of all isomeric COFs were successfully grown on different substrates. Interestingly, all isomeric COF pair films exhibit light absorption within a 300-700 nm spectral range, wherein the respective absorption onsets as well as photoluminescence (PL) emission profiles are significantly affected by the respective isomeric TT structure implemented. By chemically doping a pure isomeric TT COF with its corresponding isomer, the PL emission maxima as well as the respective absorption onset of the COF-blended framework can be continuously and precisely tuned. The extent of π-conjugation within the framework, as revealed by density functional theory (DFT) calculations, is thereby crucial for tuning the optical properties. This concept has been further expanded to isomeric benzodithiophene (BDT-)containing WBDT COFs.[4] Establishing band-gap engineering by altering the isomer blending ratios in the COF synthesis expands the scope of COF modulation concepts, allowing for precisely adjusting the COF properties for an efficient use in future organic (opto-)electronic devices.

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ENHANCING COF EMISSION: FROM PHOTOPHYSICAL INSIGHTS TO UPCONVERSION APPLICATIONS

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Keywords: *emission, imine, amine, aminal, upconversion*

The well-defined structure of crystalline Covalent Organic Frameworks (COFs) makes them ideal candidates for studying energy dissipation processes in condensed organic materials, especially when incorporating photoactive building blocks. While the photoactivity of COFs has been extensively explored, mainly focusing on non-radiative deactivation relevant to catalysis,[1–3] strategies to enhance radiative deactivation (i.e., fluorescence) remain largely underexplored.[4] Notably, imine-linked COFs, one of the most widely studied COF classes, are often considered intrinsically non-emissive[5–8]; however, the underlying quenching mechanisms have not been thoroughly investigated.

To convert a weakly emissive imine-COF (EQY ~0.1%) based on anthracene units into a strongly fluorescent material, we employed a simple post-synthetic modification: the reduction of imine bonds to amines. This transformation led to a significant increase in solid-state emission quantum yield, reaching up to 30%. To gain deeper insight into the excited-state energy dissipation mechanisms in both imine- and amine-COFs, we synthesized and studied molecular references. Spectroscopic analysis, supported by DFT calculations, revealed a weak charge-transfer process as the origin of fluorescence in both references and COFs, and identified C=N bond twisting as a likely non-radiative deactivation pathway.

These findings inspired the *de novo* design and synthesis of aminal-linked COFs[9] incorporating anthracene emitters. These materials exhibited fluorescence behavior similar to their molecular analogs and were not influenced by the radiative and non-radiative processes that affect imine- and amine-COFs.

Finally, we demonstrated the application of the aminal-linked COF in energy upconversion, representing—to our knowledge—the first example of a COF used to convert low-energy into high-energy radiation.

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TOPOLOGY ENGINEERING VIA POLYMORPHISM IN PURE AND MIXED-PHASE NI(II)-BASED METAL–ORGANIC FRAMEWORKS

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Keywords: *Metal-Organic Framework, Topology, Polymorphism,*

Polymorphism describes the ability of a single chemical compound to crystallize into two or more distinct structural forms, each exhibiting unique physical properties despite having the same molecular composition.[1] In porous materials, this phenomenon results in variations such as different pore geometries and surface characteristics, all originating from the same chemical building blocks. In recent years, polymorphism has drawn significant attention in the field of metal–organic frameworks (MOFs).[2] However, most studies have concentrated on pure-phase polymorphs, while intermediate and mixed-phase structures remain underexplored—primarily due to their structural complexity and the difficulty in controlling their formation.

In this work, we revisit the polymorphism of the Ni-BDC-DABCO MOF system. Alongside the well-established pure-phase polymorphs featuring square (sql) and Kagome (kgm) topologies,[3] we explore mixed-phase MOFs using a combination of structural characterization and gas adsorption analyses to probe structure–property relationships. Additionally, a systematic investigation of synthesis conditions reveals key parameters governing phase composition in these mixed-phase materials

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ZIF-8 THIN FILM-BASED SENSORS FOR THE OPTICAL DETECTION OF VOLATILE ORGANIC COMPOUNDS

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Keywords: *ZIF-8, thin films, gas sensing, ethanol, acetaldehyde, formaldehyde.*

Ethanol, acetaldehyde, and formaldehyde in their gaseous forms present notable health and environmental concerns. Although ethanol is relatively less harmful, it is highly flammable and can be dangerous at elevated concentrations. Acetaldehyde is more toxic and is typically released from combustion processes such as vehicle emissions and tobacco smoke. It also plays a role in the formation of ground-level ozone, a harmful air pollutant. Formaldehyde is the most hazardous among the three, recognized as a human carcinogen, and is commonly emitted from materials like treated textiles, building products, and furniture. Even at low concentrations, formaldehyde exposure can lead to respiratory issues. Given their toxicity, volatility, and especially their presence in indoor air, there is a clear need for detection systems that are not only highly sensitive and selective but also energy-efficient. In light of this, the present study focuses on the development of a gas detection system based on metal–organic frameworks (MOFs). MOFs are considered highly promising materials for gas sensing due to their unique set of properties. They offer a large surface area, providing numerous sites for gas adsorption, as well as high porosity, which enhances gas diffusion. Their chemical tunability allows precise structural adjustments to target specific gases. Additionally, the possibility of functionalization further improves both sensitivity and selectivity for various analytes.

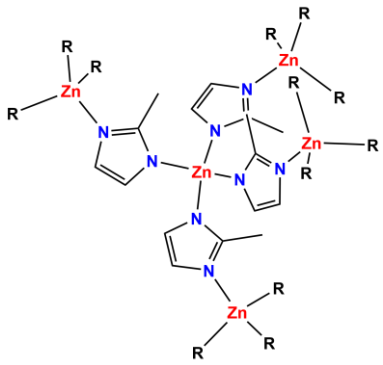


Figure 1: zeolite 2-methylimidazole

A particular subclass of MOFs, known as zeolitic imidazolate frameworks (ZIFs), is composed of zinc ions and imidazole-based ligands.[1] ZIFs are widely explored for various applications such as gas storage, [2] separation, [3] catalysis, [4] and chemical sensing, [5] owing to their uniformly sized micropores and excellent structural stability. Among them, ZIF-8, which is the one we can see on the picture on the left, stands out as one of the most extensively studied types. It consists of zinc and 2-methylimidazole (Hmim), forming a sodalite-type framework. While ZIF-8 has commonly been applied in powder form for sorption and catalysis, it also shows promise as a gas sensor when deposited as a thin film on a substrate. This is due to the fact that its refractive index changes upon gas adsorption, making it suitable for optical sensing techniques [6].

In this work, various synthesis conditions were explored to coat silica substrates with ZIF-8 for their use to detect low concentrations ethanol, acetaldehyde, and formaldehyde diluted in air. The obtained materials were characterized using Powder X-ray Diffraction (PXRD), Scanning Electron Microscopy (SEM), and profilometry to assess their structure, morphology, and film thickness. The change of the optical parameters of these materials when exposed to these fases will be reported and will be discussed as function of the synthesis conditions.

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DEFECT ENGINEERING IN A ROBUST TWOFOLD-INTERPENETRATED BISMUTH MOF: UNRAVELING THE STRUCTURE-PROPERTY PARADIGM

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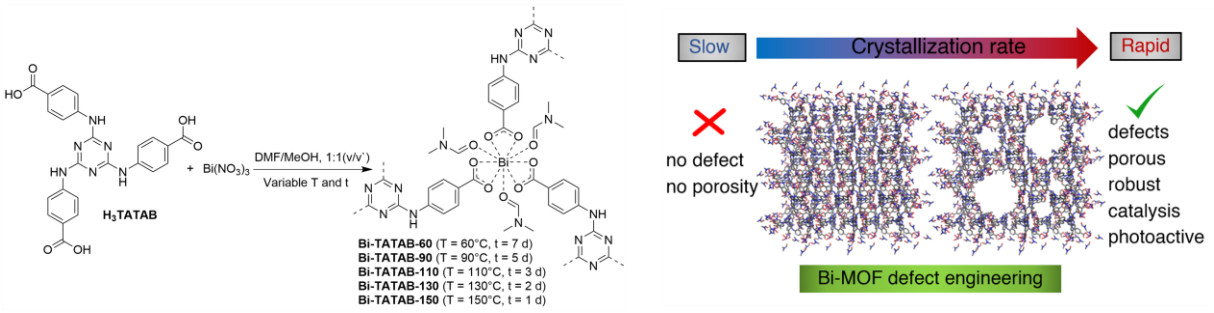
Keywords: *Bismuth, MOFs, Defects, Interpenetration, Porosity.*

Bismuth-based MOFs (Bi-MOFs) remain underexplored despite their immense application potential. In this first-of-its-kind study, we investigate defect chemistry in a novel flexible ligand-based, nonporous, 2-fold interpenetrated Bi-MOF, donated as Bi-TATAB.[1] Instead of strong reagents or post-treatments, we opted for a simple "temperature and reaction span-guided crystallization approach" to generate missing linker defects (up to ~68% of linker absence per Bi node). This approach allowed us to observe that clustering of numerous point defects results in a high degree of large-scale mesoporous defects (LSMD).

This procedure gradually augments micro- and mesoporosity in the originally dense and non-porous network while retaining its intrinsic robustness. Moreover, the defects generate uncoordinated Bi-sites functioning as Lewis acidic centers. The materials show an improved CO_2 and water sorption capacity and augmented catalytic epoxide ring-opening activity. In addition, the photophysical properties (light capture, charge transfer, emitted light color) are highly tunable by careful control of defect density.

Our findings revealed, for the first time, an unexpected solvent-based effect, where DMF acts as a competitive co-ligand/modulator during the defect engineering process. This emphasizes the necessity of systematically exploring diverse MOF systems for advancing the defect engineering studies.

This study has shown that even highly interpenetrated MOFs with no apparent porosity may still find applicability akin to porous structures via defect engineering. Accordingly, research on new MOF structures should not be restricted to porous structures in predictive computational models.



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DESIGN AND CHARACTERIZATION OF COPPER–ORGANIC FRAMEWORKS WITH CHROMOPHORIC LIGANDS

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Keywords: metal organic framework, *chromophoric ligand*

Metal–organic frameworks (MOFs) are a versatile class of crystalline materials composed of metal ions or clusters coordinated to organic ligands. Recent advances have highlighted the potential of mixed-ligand MOFs—structures incorporating more than one type of organic linker—to achieve enhanced structural complexity and tunable functionality [1,2]. In this work, we explore MOFs incorporating both structural and chromophoric ligands, the latter serving as photoactive or optoelectronically responsive components. The inclusion of chromophoric ligands opens new pathways for applications in light harvesting, chemical sensing, and photocatalysis.

We present a systematic investigation of mixed-ligand MOFs based on copper(II) centers, selected for their favorable coordination flexibility and catalytic activity. Our proposed framework integrates a rigid dicarboxylate linker, biphenyl-4,4′-dicarboxylic acid, for structural integrity, and a π-conjugated chromophoric ligand, 1,1,2,2-tetrakis(4-(1H-imidazol-1-yl)phenyl)ethene, to impart light-responsive behavior. Rational design and preliminary modeling suggest that this architecture supports efficient ligand-to-metal charge transfer (LMCT), enabling potential photoactivity within the framework. The thermal stability of the Cu-MOF was assessed via thermogravimetric analysis (TG), while its chemical robustness was evaluated across various solvent environments. Comprehensive characterization included morphological analysis (SEM, TEM), optical properties (UV-vis absorption and photoluminescence), sorption capacity, and specific surface area determination (BET analysis).

This study proposes a novel dual-ligand MOF design, offering insights into the development of multifunctional materials. The targeted applications of this structure include visible-light-driven photocatalysis and chemical sensing, where the interplay between porosity, structural stability, and light responsiveness is crucial. Ongoing synthesis and detailed physicochemical characterization will further elucidate the properties and potential applications of the designed MOF.

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WHEN GOLD MEETS Zr-MOFs: OVERCOMING SYNTHETIC INCOMPATIBILITY IN CORE-SHELL NANOSTRUCTURES

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Keywords: *Zr-MOFs, AuNPs, nanocomposites, Zr-alkoxides, reshaping.*

The fabrication of core-shell nanocomposites combining plasmonic nanoparticles with Zr-based Metal-Organic Frameworks (MOFs) is a promising yet challenging task. [1] Zr-MOFs such as those in the UiO-66 family, PCN-224, and NU-1000 require synthetic conditions like high temperatures, long reaction times, and halide-based Zr precursors, [2] that can severely compromise the structural and optical integrity of gold nanoparticles. This is especially critical for anisotropic plasmonic systems like gold bipyramids (AuBipy), which are highly sensitive to halide-induced etching and thermal reshaping.

In this study, we develop synthetic methodologies that overcome these limitations by employing Zr-alkoxide precursors which are not widely use in MOF's synthesis, [3] and preformed Zr_6-oxo clusters. The use of alkoxides enables the formation of UiO-type MOFs under significantly milder conditions, yielding well-defined core-shell AuBipy@UiO structures in as little as 30 minutes which are far shorter than conventional overnight solvothermal reactions at 120 °C. These conditions result in higher yields, enhanced control over shell growth, and preservation of the Au core's localized surface plasmon resonance (LSPR), particularly in the near-infrared (~800 nm) region.

Furthermore, these approaches enable the synthesis of hybrid nanocomposites with more complex Zr-MOFs, such as PCN-224 [4] and NU-1000 [5], by tailoring reaction parameters to prevent the degradation of the plasmonic core. The resulting nanostructures are colloidally stable, optically active, and well-suited for a broad range of applications, including photothermal therapy and light-triggered cargo release from their porous structure.

Our work provides a practical and generalizable strategy to overcome the synthetic incompatibilities between Zr-MOFs and plasmonic nanoparticles, opening new avenues for the development of advanced multifunctional nanomaterials. These hybrid systems combine the optical and photothermal properties of plasmonic nanoparticles with the high surface area and cargo-loading capacity of MOFs, making them highly promising for bioapplications. [6]

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FACILE SYNTHESIS OF FLUORINATED METAL-ORGANIC FRAMEWORKS: POTENTIAL CANDIDATES FOR GAS ADSORPTION

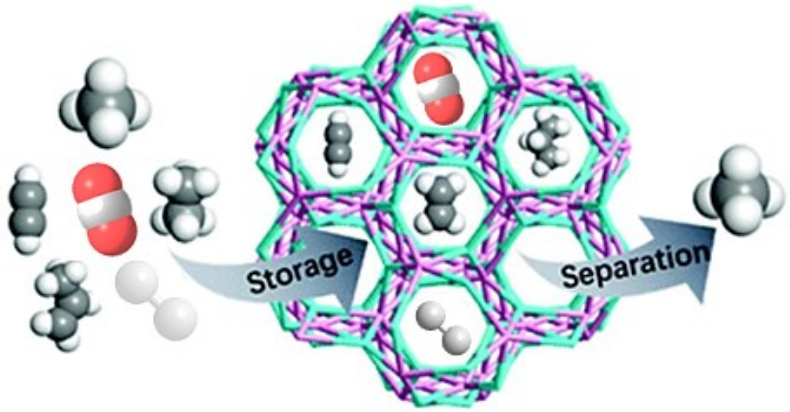
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Keywords: Fluorinated Metal-Organic Frameworks, Mechanochemical Synthesis, Gas Adsorption, Porous Materials, Sustainable Energy

Metal-organic frameworks (MOFs) are a diverse class of porous crystalline materials formed by the self-assembly of metal ions or clusters with organic linkers. Due to their exceptional tunability, high surface area, and structural diversity, MOFs are attractive for selective gas separation and energy storage. However, many MOFs suffer from limited structural stability and competitive adsorption of gases, which can hinder their practical uses. The incorporation of fluorine atoms—owing to their high electronegativity, low polarizability and strong C–F bonds—imparts outstanding chemical and thermal stability to the framework. This modification also creates a unique electronic environment that improves gas adsorption properties for molecules such as H_2, CO_2 and CH_4, making fluorinated MOFs (F-MOFs) excellent candidate for advanced gas storage and energy applications.

In this study, we report a facile, rapid and scalable synthesis of novel F-MOFs using partially fluorinated organic ligands, like 4,4'-(hexaflouroisopropylene)bis(benzoic acid) combined with various heterocyclic *N*-donor ligands coordinated to transition metal centers like Zn(II) or Co(II). This solvent-free, ambient-condition approach circumvents the need for solvothermal processes, offering an environmentally friendly and reproducible route to robust 3D frameworks. Single-crystal X-ray diffraction (SCXRD) analysis confirms the formation of well-defined porous structures. The synthesized F-MOFs demonstrate superhydrophobic nature with exceptional stability in both aqueous and organic environments, along with tunable porosity. These materials highlight their significant potential for gas storage, particularly hydrogen and carbon dioxide capture, supporting future sustainable energy and environmental solutions.



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CONTROLLING THE DEGREE OF INTERPENETRATION IN 3D COVALENT ORGANIC FRAMEWORKS FOR TAILORED POROSITY

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Keywords: *3D COFs, Interpenetration, Porosity, Gas adsorption, Structural modulation*

Three-dimensional covalent organic frameworks (3D COFs), composed of lightweight organic building blocks linked by strong covalent bonds, extend porosity into all spatial dimensions - unlocking high surface areas, interconnected channels, and mechanical robustness. These properties position 3D COFs as promising platforms for gas storage, catalysis, and separations.[1] However, their performance is fundamentally influenced by interpenetration - the intertwining of multiple frameworks within a single crystal lattice. While interpenetration enhances structural stability, it often reduces pore accessibility (Figure 1, top center), necessitating precise control to balance rigidity with functionality.[2]
Here, we present a conceptual and synthetic strategy to dynamically modulate interpenetration through steric tuning. By incorporating sterically bulky, silyl-protected aldehyde groups - specifically 2,5-bis((tert-butyldimethylsilyl)oxy)terephthaldehyde with tetra(4-anilyl)methane under solvothermal conditions, we direct the formation of a silyl protected COF (Figure 1, bottom center) with modulated interpenetration. Subsequent silyl deprotection yields a second framework (Figure 1, bottom right) with a reduced interpenetration number compared to COF-301, enhancing porosity while preserving long-range order and covalent connectivity. Structural (PXRD, TEM) and spectroscopic (FTIR, elemental analysis) analyses confirm framework integrity, while N_2 adsorption measurements and modeling show increased surface area and pore volume after deprotection. This work establishes a versatile strategy to enhance COF porosity by controlling interpenetration, offering insights for designing advanced materials for energy and environmental applications.

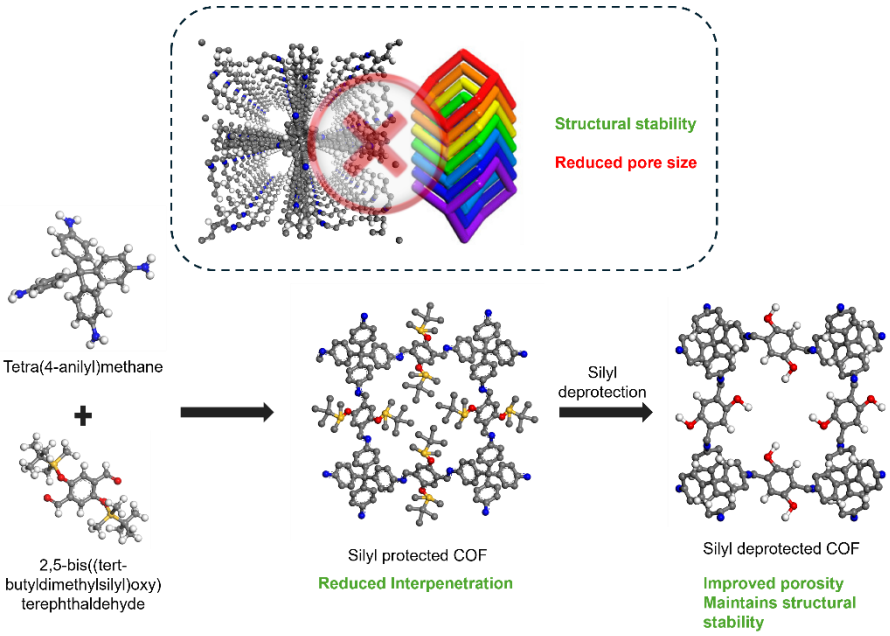


Figure 1: Schematic representation of a strategy to reduce interpenetration in COFs using bulky silyl-protected linkers. Incorporation of bulky groups limits interpenetration, and subsequent deprotection enhances porosity while maintaining structural integrity.

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SERS-ACTIVE HYBRID MATERIALS DERIVED FROM COVALENT ORGANIC POLYMERS AND GOLD NANOSTARS FOR SAXITOXIN DETECTION

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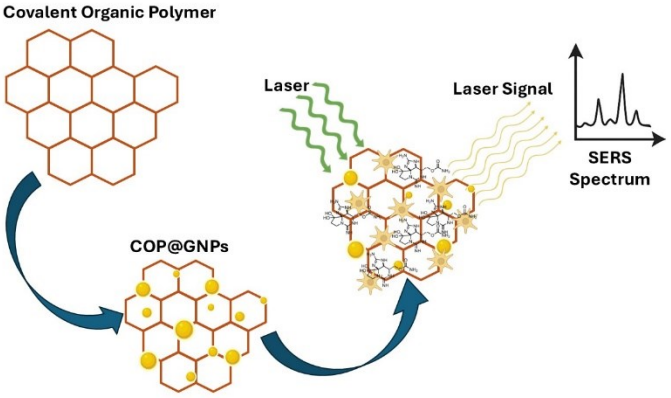
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Keywords: *Covalent organic polymer*, *COP, Saxitoxin, SERS, Gold Nanoparticles*

Marine toxins are a serious safety concern since they can intoxicate people and cause significant financial losses in areas that produce seafood. Therefore, it is essential to create quick, economical, effective, and trustworthy methods to identify and contain these compounds to lessen the adverse effects of marine toxins. Saxitoxin (STX), a widespread neurotoxin in aquatic environments and an emerging cyanotoxin in freshwater, is the primary cause of paralytic shellfish poisoning in humans through the consumption of contaminated shellfish.[1] This growing threat highlights the urgent need for rapid in situ detection technologies for STX in water.

Surface-enhanced Raman scattering (SERS) presents a promising solution for STX monitoring. It offers rapid, specific, and ultrasensitive toxin detection with almost no sample preparation.[2] However, its effectiveness relies on developing optimal plasmonic substrates with a higher SERS effect due to water's extremely low STX concentrations and low Raman cross-section of this toxin. In this study, our group reports on the design and fabrication of plasmonic organic hybrid nanostructures based on a covalent organic polymer (COP) and anisotropic gold nanoparticles (AuNPs).TpPa-COOH-COP was selected for its ability to adsorb STX from natural freshwater efficiently.[1] AuNPs were grown on the COP surface using an in situ seed-mediated method to create the hybrid composite.

This plasmonic hybrid nanostructure was fully characterized. UV-Vis-NIR analysis indicated that the composites' localised surface plasmon resonance (LSPR) band was in resonance with the selected excitation laser line, 785 nm, for the SERS-based detection. Electron microscopy techniques revealed the star-like morphology of the AuNPs on the COP surface. Adsorption experiments confirmed that AuNPs did not compromise the COP's adsorption capacity for SXT. SERS experiments using different Raman reporters with physicochemical properties like STX demonstrated the composites' suitability as SERS substrates. The limit of detections obtained went from 5 nM for parasoniline (the highest Raman cross-section) to 1 µM Adenine-9-β-D-Arabinofuranoside (the lowest Raman cross-section). The detection of oxidized STX by SERS using these COP/AuNPs composites was successful at an initial concentration of SXT of 1 µM. These results position the newly developed plasmonic organic hybrid composites as promising materials for STX detection in natural water systems.



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AN ULTRA-MICROPOROUS ZINC-DIAMINOTRIAZOLATE OXALATE METAL ORGANIC FRAMEWORK WITH NONLAYERED-PILLARED STRUCTURE SHOWING HIGH CARBON DIOXIDE UPTAKES AT LOW PARTIAL-PRESSURES

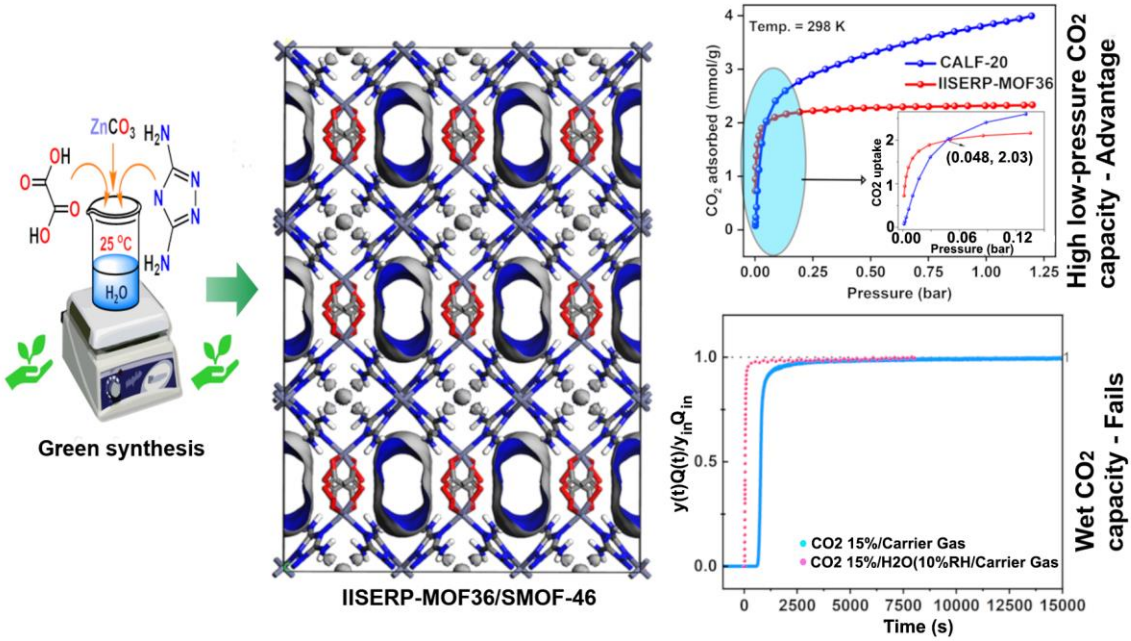
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Abstract:
We report a zinc-diaminotriazolato-oxalate Metal-Organic Framework, **IISERP-MOF36 (1)**, inspired by the remarkable CO_2 selectivity of its triazolate analog, CALF-20. Unlike the layered structure of the CALF-20 family, **1** adopts a distinct non-layered, pillared framework despite its similar composition. The presence of 1D ultramicroporous channels in this MOF facilitates strong CO_2-framework interactions, while the T-shaped orientation of CO_2 molecules within the pores promotes cooperative CO_2-CO_2 interactions. These features result in significantly enhanced low-pressure CO_2 uptake compared to CALF-20, positioning **1** as a promising sorbent for applications such as Natural Gas Combined Cycle (NGCC) and Direct Air Capture (DAC). However, despite its structural and compositional resemblance to CALF-20, **1** exhibit reduced hydrophobicity due to subtle differences in the pore environment. These findings highlight a new approach to designing next-generation sorbents that integrate the advantageous properties of both these MOFs.



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BIMETALLIC MOF-DERIVED CARBONS AS BIFUNCTIONAL ORR/OER ELECTROCATALYSTS FOR ZINC-AIR BATTERIES

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Keywords: *MOF, ORR, OER, Zinc-air battery, Metal-air battery, Electrocatalyst*

Metal-organic frameworks (MOFs) have gained significant attention due to their high surface area, tunable properties and structural versatility, making them ideal precursors for functional materials in gas separation, drug delivery and catalysis [1, 2]. Through controlled pyrolysis, MOFs can be transformed into conductive carbon matrices embedded with metal or metal oxide nanoparticles, serving as efficient electrocatalytic sites.

Zinc-air batteries (ZABs) are emerging as promising energy storage systems attributed to their high energy density and safety. However, the development of efficient bifunctional oxygen catalysts remains a key challenge [3-5]. Here, a nitrogen-doped porous carbon catalyst with embedded cobalt nanoparticles (labelled as mCo_xZn_y@CN(T)) was synthesized through the pyrolysis of a Co-Zn bimetallic zeolitic imidazolate framework (ZIF) [6] modified with melamine. The optimized material, mCo_3Zn_1@CN(800), giving outstanding bifunctional electrocatalytic with a low potential gap (ΔE) of 1.77 V, a Tafel slope of 79.95 $mV \cdot dec^{-1}$, an ORR onset potential of 0.98 V and an OER overpotential of 0.34 V at10 mA cm^{-2}. When applied as an air cathode in a ZAB, the catalyst delivered a high open-circuit potential of 1.430 V and excellent cycling stability over 250 hours (1250 cycles). The superior performance could be attributed to the high surface area, well-dispersed, Co-N active sites, and conductive graphitic carbon/CNT framework, collectively enhancing both OER and ORR. These findings highlight the potential of MOF-derived materials as high-performance bifunctional electrocatalysts for next-generation ZABs.

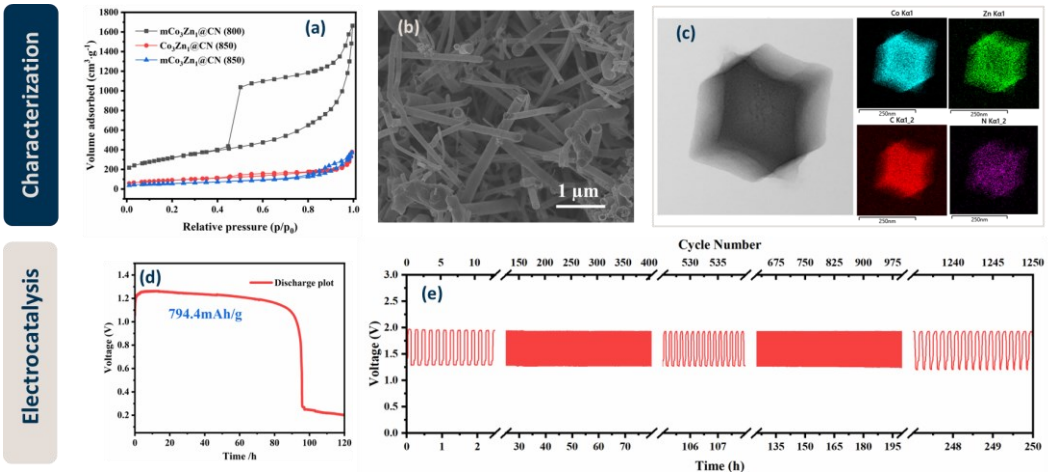


Figure 1. (a) BET tests. (b) SEM of mCo_3Zn_1@CN(800). (c) STEM of Co-ZIF-8. (d) Discharge plot and the corresponding specific capacity of the ZABs normalized by the mass consumption of the Zn plate. (e) Charge/discharge cycling curve of ZABs using mCo_3Zn_1@CN(800) as air electrode catalysts.

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IN SITU ENCAPSULATION OF CATIONIC [2]CATENANE IN A STABLE ZIRCONIUM METAL-ORGANIC FRAMEWORK

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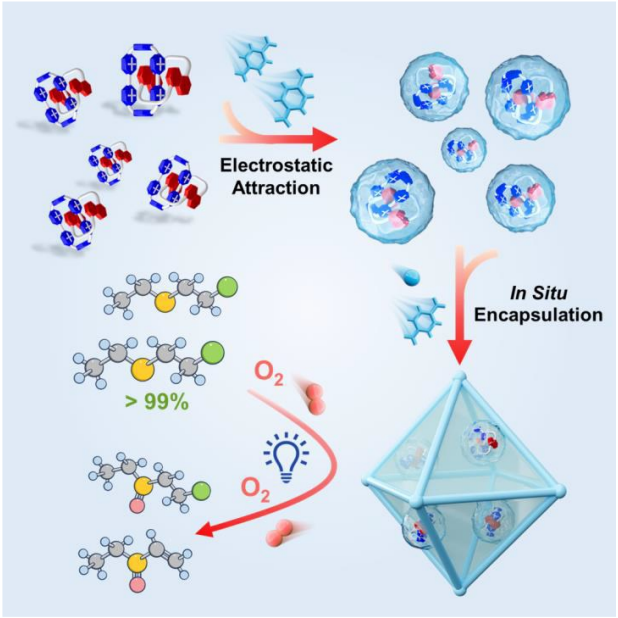
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Keywords: *catenane, metal-organic frameworks, In situ encapsulation, heterogeneous catalysis*

As an emerged class of porous support, metal-organic frameworks can host multifarious guests to realize diverse applications. Among the guest-introducing approaches, *in situ* encapsulation method is unique in its ability to incorporate a diverse range of guests, from small organic molecules, metal clusters to proteins and even more complicated guests. Previous investigations have focused on guests that are either neutral or negatively charged. The realization of *in situ* encapsulation of cationic catenanes in metal-organic frameworks under mild conditions, however, has rarely been investigated. Herein, we have accomplished *in situ* encapsulation of a cationic catenane (DA[2]C) within UiO-66-F_4 - a metal-organic framework consisting of Zr_6 nodes and tetrafluoroterephthalic acid ligands at room temperature using H_2O as a green solvent. Theoretical calculations elaborated that tetrafluoroterephthalic acid ligands interact strongly with the cationic DA[2]C. This observation is a result of electrostatic interactions between carboxylate anions and DA[2]C cations, as well as the attraction of electronegative F atoms in tetrafluoroterephthalic acid to the cations. As a proof-of-concept application, DA[2]C•4Cl/UiO-66-F_4 composite demonstrated heterogeneous catalytic detoxification of 2-chloroethyl ethyl sulfide to the sulfoxide with complete conversion rate (> 99%) and high selectivity (> 97%). This method could also be extended to other organic cationic molecules including dibenzyl benzoimidazoloimidazole chloride and a pyrene-functionalized cyclobis(paraquat-*p*-phenylene), rendering it as a universal platform for constructing host-guest MOF systems with various applications.



METAL-ORGANIC FRAMEWORK FOR HYDROGEN PRODUCTION BY PHOTOCATALYTIC OVERALL WATER SPLITTING

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Keywords: *metal-organic frameworks (MOF), photocatalysis, overall water splitting*

Non-sustainable, fossil fuel-dependent processes still account for most of the worldwide hydrogen (H_2) production.[1] Among alternatives, photocatalyzed water dissociation into H_2 and O_2 is particularly appealing owing to its intrinsic sustainable nature.[2] However, up till now reported catalysts for light-driven water splitting still do not meet the techno-economical requirements for industrial implementation as they suffer from either a lack of solar-to-hydrogen conversion (STH) efficiency and/or stability under operation, require complex synthesis processes and are in most cases inactive under visible light irradiation.[3]

Over the last few years, metal-organic frameworks (MOF) have drawn increasing interest as candidate catalysts, but most reported studies deal with either of the half reactions, i.e., the hydrogen and oxygen evolution reactions (HER and OER, respectively), thus requiring the use of sacrificial agents.[4] In this regard, the MOF2H2 project [5] is ambitious to be a game changer in producing hydrogen from water through a more sustainable process, the photocatalytic overall water splitting (OWS), using non-noble MOF-based catalysts.

This project relies, so far, on two main families of MOFs. Inspired by nature, a MOF made of a multicopper-based metalloligand reminiscent of the active site of certain reductive enzymes was first selected and found to be an efficient catalyst for photo-induced water splitting reactions. Besides, the specific $Ti_{12}O_{15}$-based MOFs[6] are also being explored. While the first studies demonstrated the high potential of these MOFs for HER and OWS,[7,8] deeper photophysical and photocatalytic investigations are on-going and driving the chemical modifications/optimization to reach higher performances.

In this communication, we will present the MOF2H2 project concept as a whole. A specific highlight will be shed on the most recent advances leading to ground-breaking results in terms of H_2 photo-induced production. Finally, our ongoing work directed at improving the MOF-based catalysts' performances will also be discussed.

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POST-SYNTHETIC MICROENVIRONMENT TUNING OF COVALENT ORGANIC FRAMEWORKS FOR SELECTIVE CO_2 REDUCTION

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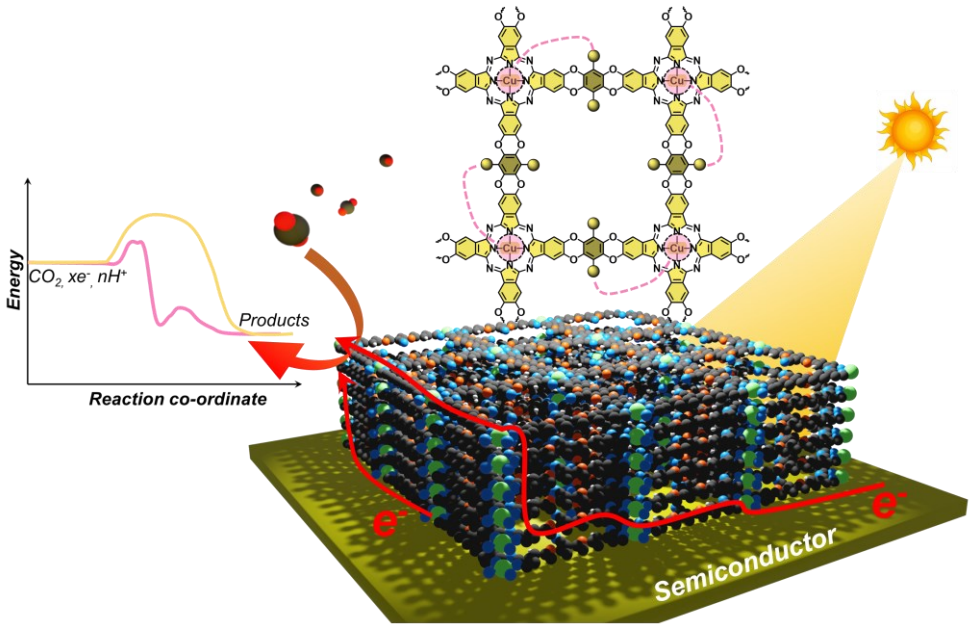
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Keywords: *CO_2 reduction, COFs, post-synthetic modification, microenvironment tuning*

Microenvironment tuning in covalent organic frameworks (COFs) for photo/electrochemical CO_2 reduction draws direct inspiration from natural systems, such as CO deshydrogenase, which optimizes electron transfer and catalytic efficiency through precisely positioned peripheral functional groups. In this biological system, peripheral moieties modulate the local electronic environment, enhancing reactivity by influencing electron density and stabilizing reaction intermediates. Mimicking this approach, COFs can be post-synthetically modified with electron-donating ($–CH_2NH_2$) or electron-withdrawing (–CN, –COOH) groups to fine-tune the work function and the adsorption energies of key intermediates (e.g., *COOH, *CO), thereby improving CO_2 reduction performance.[1] As a validation of previous reports,[2] we observed that a CuPc-TFPN COF exhibits a two-electron Faradaic efficiency of 82.8% under electrochemical conditions at an applied potential of -1.5 V *versus* SCE. To further optimize selectivity and efficiency, we are implementing post-synthetic strategies to systematically introduce functional groups such as sulfonic acids ($–SO_3H$) for enhanced proton transfer, quaternary ammonium ($–NMe_3^+$) and imidazolium for ionic conductivity and CO_2 affinity, and metalated porphyrins for tunable catalytic centers. These modifications aim to precisely control the local electronic structure, proton-coupled electron transfer mechanisms, and secondary coordination sphere effects, with the goal of achieving efficient (photo)electrochemical CO_2 conversion at lower overpotentials. Results and detailed mechanistic insights will be presented at the conference.



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POST-SYNTHETIC MODIFICATION OF ZIRCONIUM MOFs THROUGH ATOM-ECONOMIC ALKYNE CLICK REACTIONS

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Keywords: *Metal-organic frameworks, click chemistry, coupling, fluorescent sensing, porous materials,* retro-electrocyclisation

Metal-organic frameworks (MOFs) are crystalline porous materials with tunable cavities, allowing for advanced applications in gas storage[1], separation[2], catalysis[3], sensing[4], and drug delivery[5]. However, the direct incorporation of reactive functional groups such as alkynes or nitriles into MOFs is often limited due to their instability during MOF synthesis. To overcome these challenges, we propose a post-synthetic strategy for functionalizing alkyne-tagged zirconium-based MOFs via atom-economic click reactions, focusing on catalyst-free [2+2] cycloaddition and cascade retro-electrocyclisation (CA-RE) [5]. The project begins with the synthesis of orthogonal linkers via Sonogashira and Suzuki couplings to afford bis-terminal alkyne-containing ligands coordinated to Zr4+ clusters, forming stable porous frameworks.

Post-synthetic modifications are performed by introducing electron-accepting tetracyanoethylene and related species, yielding electroactive and non-emissive MOFs. These materials can function as fluorescent turn-on sensors, selectively detecting amine analytes in aqueous environments. This method avoids the need for metal catalysis, enhancing environmental compatibility. The work involves advanced spectroscopic and structural techniques such as single-crystal XRD, solid-state NMR, FTIR, and gas sorption analysis. The approach offers a pathway to novel MOF materials with precise functionality and expands the potential of click chemistry in confined nano-environments.

This approach expands the functional diversity of MOFs without compromising their porosity or stability. By tailoring the pore environment using orthogonal and electron-rich alkynes, specific guest-host interactions can be designed, enabling improved selectivity in molecular recognition. The use of cascade retro-electrocyclisation (CA-RE) further allows efficient transformation of internal alkynes into push-pull systems with defined donor-acceptor architectures, suitable for photophysical modulation[6].

In addition to structural innovation, this project also integrates training in advanced characterization techniques. The researcher will be trained in Schlenk line techniques, single-crystal X-ray diffraction, powder XRD, solid-state ^{13}C NMR, FTIR, SEM, thermogravimetry, and gas sorption analysis. Fluorescence properties of the modified MOFs will be studied using analytes such as dimethylamine and diisopropylamine to establish their performance as sensors in food safety and environmental monitoring.

Overall, this study contributes to the growing body of knowledge on click-modified MOFs and offers a pathway toward multifunctional porous materials with application in environmental sensing, catalysis, and photonic devices.

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FUNCTIONALITY MODULATION TOWARD THAINTHRENE-BASED METAL-FREE ELECTROCATALYSTS FOR WATER SPLITTING

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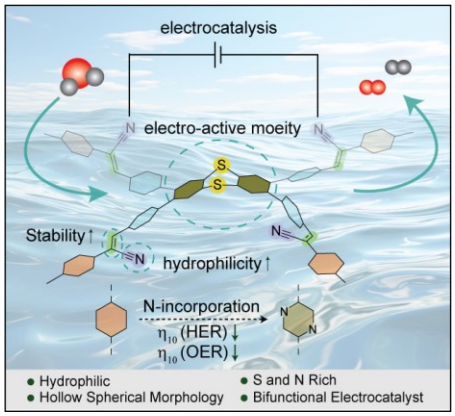
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Keywords: *Water Splitting, Bifunctional Electrocatalyst, Overpotential, Thianthrene, Porous Organic Polymers*

Abstract: The development of metal-free bifunctional electrocatalysts for hydrogen and oxygen evolution reactions (HER and OER) is significant but rarely demonstrated.[1] Porous organic polymers (POPs) with well-defined electroactive functionalities show superior performance in hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).[2] Precise control of the active sites' local environment requires careful modulation of linkers through the judicious selection of building units.[3] Here, a systematic strategy is introduced for modulating functionality to design and synthesize a series of thianthrene-based bifunctional sp^2 C═C bonded POPs with hollow spherical morphologies exhibiting superior electrocatalytic activity.[4] This precise structural tuning allowed to gain insight into the effects of heteroatom incorporation, hydrophilicity, and variations in linker length on electrocatalytic activity. The most efficient bifunctional electrocatalyst THT-PyDAN achieves a current density of 10 mA cm^{-2} at an overpotential (η_{10}) of ≈65 mV (in 0.5 m H_2SO_4) and ≈283 mV (in 1 m KOH) for HER and OER, respectively. THT-PyDAN exhibits superior activity to all previously reported metal-free bifunctional electrocatalysts in the literature. Furthermore, these investigations demonstrate that THT-PyDAN maintains its performance even after 36 h of chronoamperometry and 1000 CV cycling. Post-catalytic characterization using FT-IR, XPS, and microscopic imaging techniques underscores the long-term durability of THT-PyDAN.



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THEORETICAL AND EXPERIMENTAL INSIGHTS INTO THE SPATIAL DISTRIBUTION OF FUNCTIONAL GROUPS IN MULTIVARIATE FLEXIBLE METAL-ORGANIC FRAMEWORK

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Keywords: flexMOFs*, spatial distribution, flexibility*

Erwin Schrödinger in his ingenious series of lectures[1] collected in the book "What is Life?", emphasized the fundamental differences in complexity between structures of interest to chemists and those found in living organisms. He noted, "The arrangements of atoms in the most vital parts of an organism and the interplay of these arrangements differ fundamentally from all those arrangements of atoms which physicists and chemists have hitherto made the object of their experimental and theoretical research." Combining the concepts of flexibility and multivariate properties into one material may bring scientists closer to realizing the dream of aperiodic crystals that can conduct sophisticated reactions or store and retrieve information. The flexible backbone allows for structural adjustments, while many functional groups attached to it can encode information or provide anisotropic environment.[2]

Inspired by this concept and former understanding of JUK-8 chemistry[3-5] we prepared a series of flexible multivariate JUK-8$(NO_2)_x(Br)_{1-x}$ ($0 < x < 1$) compounds (MTV-MOFs) and introduced experimental and theoretical methodologies for their investigation **(Figure 1**). 1H-NMR was employed to determine the molar fraction of the linker in the bulk sample, whereas single crystal X-ray diffraction verified this value for single crystals. CO_2 adsorption studies at 195 K revealed that the monosubstituted JUK-8(NO_2) transitioned from a less porous to a porous phase at p/p0 ~ 0.20, while for JUK-8(Br), this process occurred at p/p_0 ~ 0.58. For the MTV-MOFs, in contrast to the anticipated steady increase in transformation pressure with the molar fraction of Br-pip, x_{Br}, we observed a constant gate opening pressure, p/p_0 ~ 0.33, across a broad range of x_{Br}, 0.27-0.63, and then its gradual increase up to p/p_0 ~ 0.48 for x_{Br} up to 0.96. Resolving the crystal structure of the closed phases of JUK-8(Br) and JUK-8(NO_2) allowed us to identify the crucial interactions governing this phenomenon. Finally, by constructing theoretical models of a multivariate structure and employing solid-state NMR crystallography supported by DFT simulation, we shed light on the possible spatial arrangement of functional groups in JUK-8$(NO_2)_{0.50}(Br)_{0.50}$. Overall, we introduce a methodology that could potentially be utilized for investigating multicomponent flexible MOFs.[6]

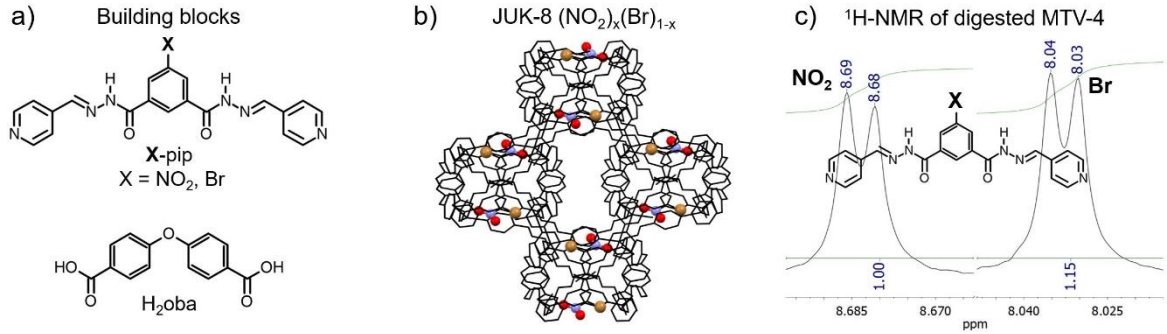


Figure 1 a) Organic building blocks used for the preparation of **b**) multivariate flexible series of JUK-8$(NO_2)_x(Br)_{1-x}$. **c**) ^{1}H-NMR-spectra of digested JUK-8$(NO_2)_{0.50}(Br)_{0.50}$.

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SPATIALLY RESOLVED SELECTIVE ADSORPTION PROFILES

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Keywords: *adsorption, selectivity*

Selective adsorption plays a crucial role in gas separation,[1] environmental remediation,[2] and water purification,[3] making it fundamentally important for various industrial applications.[4] However, current methods typically provide only a single selectivity value under specific temperature and pressure conditions for a mixture of adsorbates,[5, 6] lacking the capability to reveal spatial variations in adsorption selectivity within porous materials. Here we present a novel method to calculate spatially resolved selectivity profiles in porous framework materials. This approach enables understanding of selective adsorption sites in porous materials, providing critical design principles for developing next-generation materials with tailored selective adsorption and separation properties.

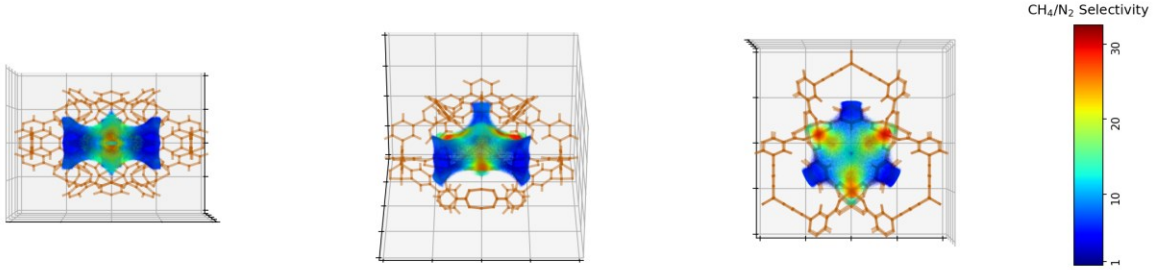


Figure. Spatially resolved CH_4/N_2 selectivity profile in a cage of Victoria University Framework-1.

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OVERCOMING SIZE LIMITATIONS IN MOF RESEARCH: STRUCTURAL ELUCIDATION BY ELECTRON DIFFRACTION

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Keywords: *Electron Diffraction, 3D ED, microED, phase transition*

Since its launch in 2021, the XtaLAB Synergy-ED[1] has produced many structures, with over 600 unique structures from Rigaku labs alone. The majority of those structures have been conducted at ambient temperature, lately with low temperature, particularly cryo-transfer, showing considerable usefulness for preservation of sensitive samples both those sensitive to vacuum and those sensitive to electron beam damage.

Thanks to its compatibility with the existing ecosystem of holders available for TEM instruments, the XtaLAB Synergy-ED is able to provide structural scientists with access to several experiment types already used in X-ray crystallography.

Cryo-transfer specimen holders such as the Gatan ELSA enable the protection of samples before introduction to the vacuum, allowing the study of solvates and other vacuum-sensitive species, [2] in addition to allowing exploration of phase behaviour. Some results from samples for which cryo-transfer proved essential are discussed.

In addition, the Hummingbird Scientific MEMS biasing/heating holder offers the possibility to increase temperature, allowing for exploration of the phase behaviour of materials such as porous materials. Our recent results using single-crystal data from 3D ED/microED electron diffraction on a MOF system, $Cu(ta)_2$ (Hta = 1H-1,2,3-triazole), at room temperature and at 200 °C were compared to a previous study by Grzywa *et al.*[3] of the same material from 2012 done using SC-XRD and PXRD.

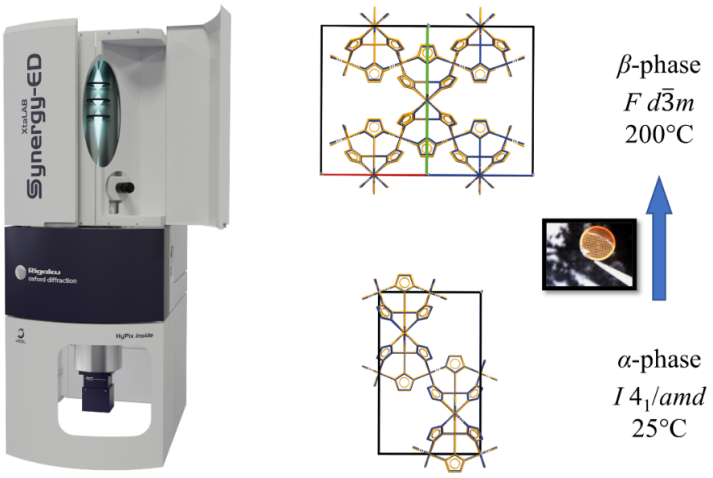


Figure 1 Overlays of the ambient and high temperature phases of $Cu(ta)_2$ from the XtaLAB Synergy-ED (blue) and the X-ray structures by Grzywa *et al.* (orange).

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NMN STABILIZATION THROUGH DUAL ENCAPSULATION OF γ-CD MOF AND LIPOSOMES

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Keywords: *Encapsulation, Nicotinamide mononucleotide* (*NMN), γ-CD MOF*

Metal-organic frameworks (MOFs) have a large surface area with porous characteristics. They are known to be able to form guest-host molecules as hosts because they have a hydrophilic surface and a hydrophobic space. γ-Cyclodextrin (γ-CD) is a cyclic oligosaccharide that has symmetry and has been studied for a long time as a drug carrier so that it can be safely applied in the cosmetics field. γ-Cyclodextrin Metal-Organic Frameworks (γ-CD MOFs) made using this are one of the types of MOFs made of biocompatible materials and are actively being applied and researched in various fields such as catalysts and drug delivery. Liposomes are bilayer vesicles that have both hydrophilic and hydrophobic properties and are formed through the self-assembly of phospholipids in an aqueous solvent. It is similar to the components of skin cell membranes and can improve skin absorption. In addition, it has the advantage of improving stability and helping maintain functionality by protecting the active material from external environmental factors such as light, pH, and temperature through encapsulation. Nicotinamide mononucleotide (NMN) is a precursor of NAD+ and is known to contribute to the production of NAD+ in the body, which can help reduce anti-aging effects and melanin production. There is growing interest not only in food but also in cosmetics, but research is needed to improve its stability as it is vulnerable to heat and moisture. In this study, to increase the stability of NMN, γ-CD MOF and liposomes were used for encapsulation. γ-CD MOF was first synthesized using the Vapor Diffusion Method and then NMN was primarily encapsulated. Then, the γ-CD MOF encapsulating NMN (γ-CD MOF (NMN)) was secondarily encapsulated through liposomeization. Subsequently, SEM and Cryo-TEM analysis confirmed that the crystal structure of γ-CD MOF (NMN) was maintained and the formation of Lipid-CD MOF (NMN) (L-CD MOF (NMN)) was confirmed. Successful encapsulation of NMN and liposome characteristics was confirmed through UV-Vis, DLS, and Turbiscan. HPLC analysis showed that the content of NMN was maintained stably for months. Through this, it appears that stability can be increased by double encapsulating not only NMN but also materials that are unstable to external environmental factors. It is expected to be applicable to various fields such as cosmetics, food, and pharmaceuticals.

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MODULAR POLYHEDRAL SILVER-PHOSPHINIDENIDE CLUSTERS AS VERSATILE PRECURSORS FOR POLYDIMENSIONAL METAL-ORGANIC ARCHITECTURES

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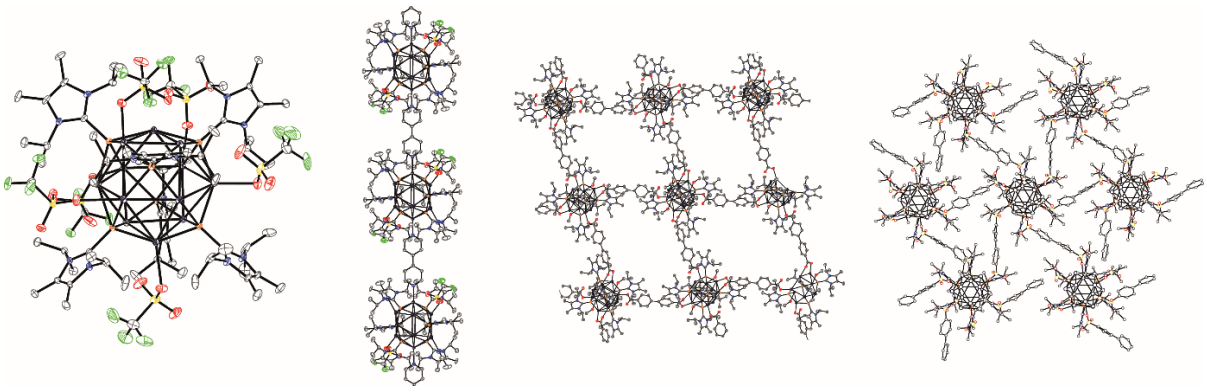
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Keywords: *silver clusters, phosphinidenides, supramolecular building blocks, metal–organic frameworks*

The supramolecular building block (SBB) approach enables the formation of metal-organic frameworks (MOFs) through the rational linkage of pre-organized metal-organic polyhedra (MOPs)[1]. While the design of tailored MOPs and organic linkers has yielded topologically diverse and highly connected frameworks[2], this strategy also enables the integration of functional nanoclusters into extended networks, allowing for fine-tuning of their properties.[3] Coinage-metal nanoclusters, particularly those based on silver, exhibit exceptional structural variability and tunable properties, making them promising candidates for applications in catalysis, sensing, and optoelectronics[4,5]. However, their broader integration into higher-dimensional frameworks has been hampered by synthetic challenges, including poor selectivity and scalability.



In this contribution, we report a new class of isolable, highly stable polyhedral silver-phosphinidenide complexes that exhibit anion-controlled architectures. These compounds are synthesized in a modular and scalable fashion, affording multigram yields with excellent reproducibility. Owing to their well-defined structures and accessible Ag coordination sites, these complexes serve as versatile SBBs for the construction of one-, two-, and three-dimensional MOF architectures. Assembly can be further directed via anion exchange using polytopic organic linkers. The synthesis, structural features, and connectivity-driven framework formation will be presented, along with selected inclusion properties of these promising materials.

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REAL-TIME OBSERVATION OF BILAYER GROWTH IN IMINE-LINKED 2D COFs

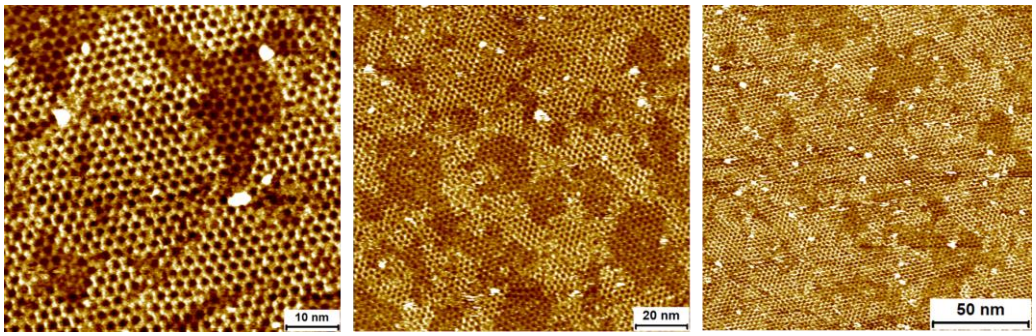
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Keywords: *covalent organic frameworks, on-surface synthesis, scanning tunneling microscopy, dynamic process*

A comprehensive understanding of both in-plane and interlayer growth mechanisms of two-dimensional covalent organic frameworks (2D COFs) is critical for advancing their structural control and synthetic strategies. While recent achievements, such as the direct observation of monolayer boroxine-linked COFs on graphite by scanning tunneling microscopy (STM), have unveiled in-plane dynamics, experimental evidence of interlayer growth at the molecular level scale remains scarce, particularly for imine-linked 2D COFs.[1-2] This limitation is likely due to the rapid kinetics of imine condensation, which hinders direct molecular-scale visualization. Here, we present a controllable on-surface synthesis strategy for bilayer imine-linked 2D COFs. A pre-formed monolayer serves as a buffer layer, significantly slowing the growth rate of the second layer and enabling real-time STM monitoring of its nucleation and elongation under ambient conditions. This approach not only reveals the dynamic growth behavior of the upper layer but also demonstrates that its growth rate and coverage can be finely tuned by the linker concentration. Our findings provide pioneering molecular-level insights into the interlayer formation of imine-linked COFs and offer perspectives for the synthesis of multilayered COFs.



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POTENTIAL OF METAL-ORGANIC FRAMEWORKS IN HYDROGEN STORAGE: SCALE-UP AND STABILITY ASSESSMENT OF FE-SOC-MOF UNDER HUMID CONDITIONS

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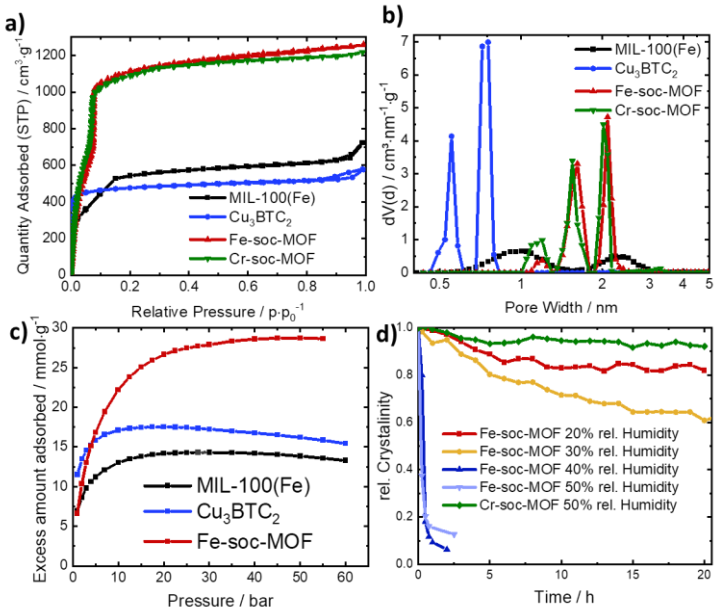
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Keywords: *soc-MOF, Hydrogen Storage, Hydrolytic Stability,*

To tackle the challenge of global warming the effective utilization of green energy technologies, such as the physisorption-based storage of hydrogen in porous materials is explored [1]. Metal-organic frameworks (MOFs), renowned for their crystalline and highly porous characteristics are excellent candidates for hydrogen storage applications, if high H_2-sorption capacity is coupled with good chemical and thermal stability [2]. However, the synthesis of MOFs with soc topology is typically confined to milligram-scale lab experiments, and their stability in atmospheric conditions is insufficiently explored. This study presents synthesis protocol for a scale-up of the previously identified Fe-soc-MOF [3], along with a comprehensive investigation of its degradation under humid conditions.

Scale up Fe-soc-MOF synthesis: Into 90 mL of a 0.1 M $Fe(NO_3)_3$•9H2O solution a H_4pbpta ligand solution was added (2.0 g ; 150 mL DMF) and stirred for 5 min. 30 mL of acetic acid were added under stirring into the solution and placed in a preheated oven at 135°C for 3 days. The MOF was recovered by centrifugation and subsequently dried with a N_2 gas flow and stored under inert conditions.



In Figures 1 a-c) the synthesized soc-MOF is compared with standard MOFs such as Cu_3BTC_2 and the MIL-100. Fig. 1 a and b) shows the textural characterization using argon adsorption at 87 K combined with non-local density functional theory (NLDFT) pore size analysis. High pressure hydrogen adsorption isotherms (Figure 1 c) were measured at 77 K to investigate the influence of pore size, geometry, and network connectivity on H_2 uptake behavior. Additionally, the hydrolytic stability of the high sorption capacity soc-MOF material was assessed in a H_2O/N_2-stream via situ powder XRD measurements (Fig. 1d). However, significant improvement of the materials hydrolytic stability was realized through ion exchange with chromium [4,5]. The systematic investigation elucidates crucial structure-property interrelations that are pivotal for identifying optimal thermodynamic parameters conducive to hydrogen storage applications.

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IS BIGGER ALWAYS BETTER? POROSITY AND ADSORPTION IN FRAMEWORK MATERIALS

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Keywords: *covalent organic frameworks, gas adsorption, porosity*

Covalent Organic Frameworks (COFs), introduced in 2005, represent a class of crystalline nanoporous materials synthesised through reticular chemistry, a discipline pioneered by Yaghi and colleagues.[1] These materials are characterised by their low density, high specific surface area, permanent and tuneable porosity, and a broad spectrum of possible chemical functionalisation. Many applications of porous materials rely on their ability to host small molecules inside their pores. Geometric properties of these pores, most prominently their diameter and volume, are often the focus of material design. At the same time, specific non-covalent interactions between the pore interior and guest molecules are the driving forces behind encapsulation, countering the unfavourable entropic effects. The interplay between pore size and uptake capacity is multifaceted: larger pores provide greater surface areas for interactions, but also larger inner volumes, within which many guest molecules are effectively shielded from the pore walls at high loadings. This raises a fundamental question of whether an optimal pore size exists for thermodynamically favoured adsorption and maximum uptake capacity. COFs with different pore sizes often differ in topology, linker chemistry, functionalisation, and node structure, making it difficult to isolate the direct impact of pore size alone. To address this challenge, we design a series of COFs with identical linkers, nodes, and functional groups, where the pore size is systematically increased by linearly extending the linker units.

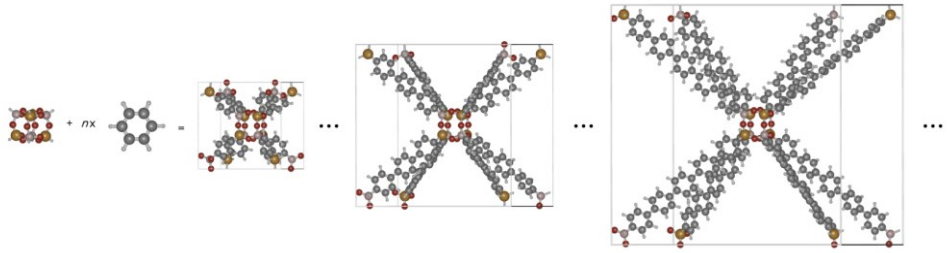


Figure 1: *Example COF series constructed from one node–linker combination, retaining identical chemistry and topology, with pore size tuned by linear linker extension.*

This ceteris paribus approach allows us to directly assess the impact of pore size on gas adsorption while eliminating other structural variations. The study provides new insights into rational COF design strategies and highlights the importance of balancing pore geometry with host–guest interactions.[2]

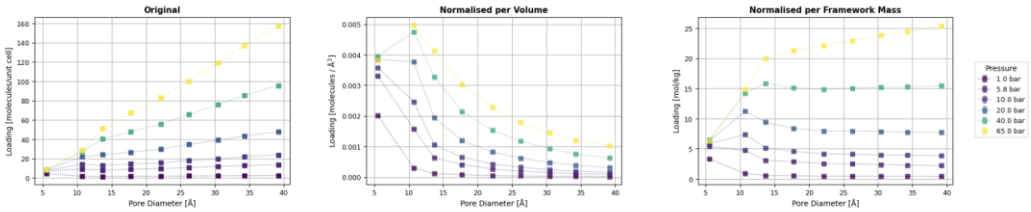


Figure 2: *Excess CH_4 adsorption versus pore size for the exemplary COF series (same as Figure 1): shown as adsorption per unit cell (left), normalized per pore volume in molecules/Å³ (middle), and normalized per framework weight in mol/kg (right), across different pressures.*

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DYNAMIC BREATHING BEHAVIOUR OF THE TITANIUM-BASED METAL-ORGANIC FRAMEWORK NTU-9 UPON ADSORPTION OF WATER AND ORGANIC SOLVENTS

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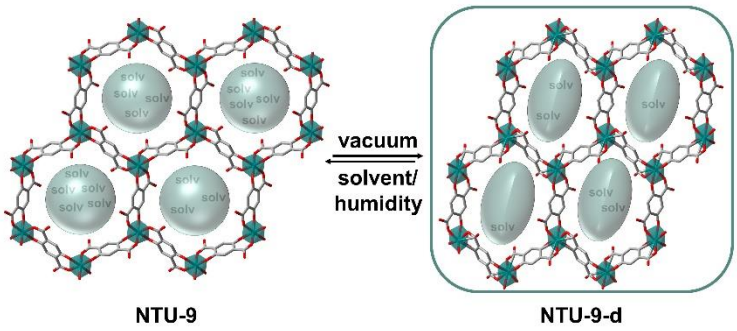
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Keywords: *titanium MOF, flexible MOF, stimuli-responsive MOF, breathing behaviour, in situ PXRD*

Understanding the structural response of framework materials to stimuli has been of great interest since the first report of the breathing/swelling behaviour in MIL-53 in 2002.[1] However, little is known about the stimuli responsiveness of titanium-based metal-organic frameworks (MOFs).

We investigate the reproducibility of synthesising the two-dimensional MOF NTU-9 (NTU = Nanyang Technological University) composed of Ti^{4+} cations and 2,5-dihydroxyterephtalate as the organic linker.[2, 3] We optimised the synthesis parameters and evaluated for reproducibility towards large single crystals and microcrystalline bulk powders.

While investigating the influence of different activation procedures, we discovered a dynamic behaviour of NTU-9 triggered by guest adsorption and desorption. Pure heat treatment under ambient conditions removes a significant amount of the incorporated guest solvent molecules without alteration of the framework's structure. After applying additional stimuli (i.e., vacuum), the material exhibits a pore distortion by compression in the lateral dimension, forming the new metastable form NTU-9-d (d stands for distorted). We investigated the structural transitions by *in situ* powder X-ray diffraction and THz Raman spectroscopy. Our work establishes a reproducible synthesis procedure and a detailed mechanism of the previously unknown framework dynamics.[4]



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ELUDICATING THE IMPACT OF THE SYNTHESIS METHODE ON THE STRUCTURAL FLEXIBILITY OF MIL-88 A (FE) DURING WATER HARVESTING

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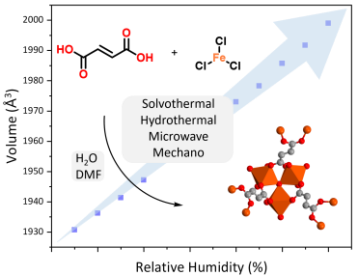
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Keywords: *flexible MOF, swelling, water harvesting, adsorption, in situ PXRD*

Flexibility and dynamics in framework materials have aroused interest in recent years.[1] The flexibility of the metal-organic framework MIL-88 A has been known since 2005.[2] Its flexibility can lead to a change in unit cell volume of up to 85%. This behavior depends on the pore loading and the temperature.

MIL-88 A was first described in 2004[3] and consists of a trinuclear iron cluster and fumaric acid as linker, forming a porous structure. MIL-88 A crystals have a hexagonal bipyramidal shape, also described as diamond-shaped, spindle-like, or rod-like, depending on the length. Various routes are known for the synthesis of MIL-88 A: MIL-88 A is usually synthesized solvothermally with *N,N*-dimethylformamide (DMF), but syntheses in a microwave or with the help of ultrasound are also established.[4]



Even though the system has been known for two decades, many questions remain unanswered about its dynamic behavior. One of these open questions is investigating whether different synthesis approaches influence the flexibility. For such an investigation of the swelling behavior of MIL-88 A, we chose a variety of synthesis strategies. We performed sorption experiments and *in situ* powder X-ray diffraction (PXRD) under variable humidity conditions to probe the swelling behavior of the synthesized MOFs. The changes in the PXRD-patterns indicate additional phases between the open and closed states of MIL-88 A. Similar conclusions can be drawn from the sorption data demonstrating multistep and high-level water adsorption properties that could be interesting for water harvesting. The uptake steps are in similar ranges to the changes in the PXRD, allowing us to correlate adsorption and structural flexibility. We also observe that this dynamic behavior strongly depends on the synthesis procedure and, for the first time, correlate these aspects.

Additionally, we suggest two structures for the intermediate crystal phase of MIL-88 A observed during the swelling process. The discussed structure models explain the changes in the collected PXRD patterns during ad- and desorption of water in the material.

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LIGHTWEIGHT INORGANIC HYDRIDES CONFINED WITHIN ZIRCONIUM AND BERYLLIUM METAL-ORGANIC FRAMEWORKS AS HYDROGEN STORAGE MATERIALS

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Keywords: *MOF, zirconium, beryllium, BN inorganic hydrides, hydrogen storage*

Hydrogen is widely recognized as a clean and renewable energy carrier. One of the main hurdles to its widespread adoption lies in ensuring its safe and efficient storage and transport. Chemical hydrogen storage, in which H_2 is incorporated into stable, non-toxic compounds that can release it controllably under mild temperature and pressure conditions is a promising approach. Lightweight BN hydrides like ammonia borane (AB, 19.5 wt.% H) and hydrazine bis(borane) (HBB, 16.7 wt.% H) stand out for their favorable gravimetric (wt.%) and volumetric (g/L) hydrogen densities. MOFs have emerged as excellent platforms for hosting such hydrides.[1] Their ability to confine hydride species within their nanoscopic pores leads to the formation of [hydride@MOF] composite materials. Two zirconium-based MOFs, $[Zr_6O_4(OH)_4(TzTz)_6]$ (**Zr_TzTz**) and $[Zr_6O_4(OH)_4(PyPy)_6]$ (**Zr_PyPy**), both featuring a UiO-67-type framework and derived, respectively, from 2,2'-bithiazole-5,5'- and 2,2'-bipyridine-5,5'-dicarboxylic acids were employed as hosts for AB and HBB.[2] In order to increase the gravimetric density of the loaded substrate, a new beryllium-based MOF built with the 2-aminoterephthalate linker $[Be_4O(BDC\text{-}NH_2)_3]$ (**Be_BDC-NH$_2$**) sharing the same topology as that of MOF-5(Be)[3] was synthesized and explored for chemical and physical hydrogen storage. The resulting composites were fully characterized in the solid state through high-resolution powder X-ray diffraction, temperature-programmed decomposition, surface area and pore size distribution analysis and multinuclear (^{1}H, ^{15}N, ^{11}B) solid-state NMR spectroscopy. The results will be presented.

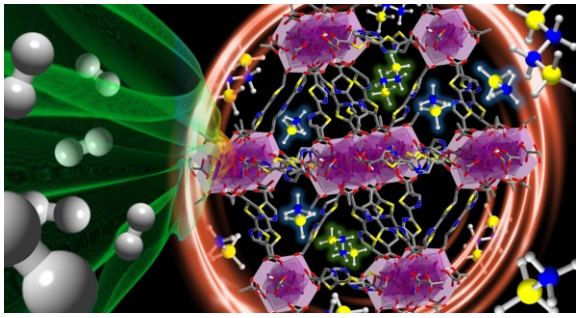


Figure 1. *AB and HBB in* ***Zr_TzTz*** *as chemical hydrogen storage material. From reference [2].*

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MOF-SUPPORTED METAL COMPLEXES FOR CO_2 CONVERSION IN E-FUELS

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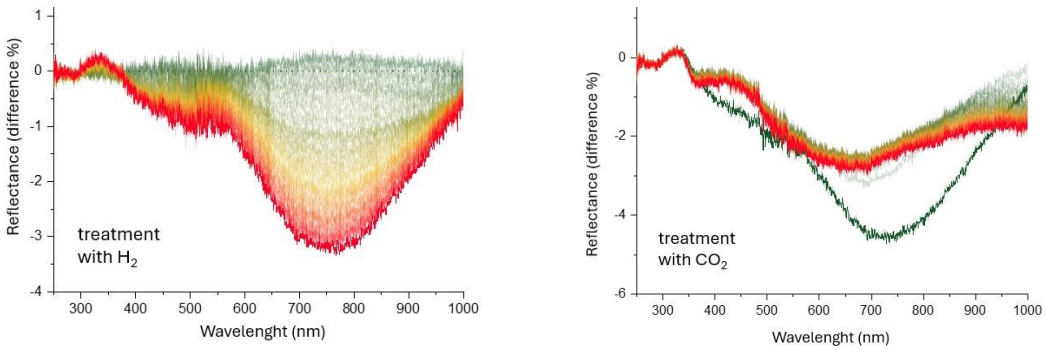
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Keywords: *Heterogeneous Catalysis, Metal Complexes, CO_2 Conversion, E-fuels.*

E-fuels are a class of liquid fuels obtained via direct reduction of CO_2 captured from the atmosphere or recovered from industrial processes with H_2 derived from water electrolysis powered by renewable energy. These fuels are of particular interest for vehicles which are difficult to electrify, such as airplanes.[1] Since several industrial processes are already available for converting light alcohols to heavier hydrocarbons, the main focus of this research is to produce methanol from CO_2 and H_2.

To tackle this objective, a modified version of the Hf-based UiO-67 MOF has been synthesized to include functional groups able to bond active metal complexes into the MOF's structure. A mixed linker Hf-UiO-67 MOF with a 90% of the usual linker 4,4'-biphenyldicarboxylic acid and a 10% of 2,2'-bipyridyl-4,4'-dicarboxilic acid, was made in large amounts in a one-pot reaction, showing high crystallinity and the expected surface area.[2] The obtained material was then functionalized with Ru^{2+} or Ir^{3+}, by stirring the MOF in a methanolic solution of a stoichiometric amount of the complexes $[Ru^{II}(\eta^6\text{-}C_6Me_6)(H_2O)_3][SO_4]$ and $[Ir^{III}(\eta^5\text{-}Cp^*)(H_2O)_3][SO_4]$. FT-IR studies have been conducted using CO as a molecular probe to verify the availability of the metal centers (Ru^{2+}, Ir^{3+}). Both materials showed the rapid formation of an intense signal attributable to the stretching frequency of the C≡O coordinated to the metal centers. Both materials preserve crystallinity and porosity even if treated up to 170 °C and at 10 bars of H_2 and show the formation of hydrides already at 120° C with 0.1 bar of H_2 (detected by *in situ* IR). The reactivity towards H_2 and CO_2 has been studied by *in situ* DRS-UV-Visible spectroscopy

heating the materials at 120° C in a flux of 5 mL/min of H_2 and subsequently in CO_2 5 mL/min; some results for Ru^{II}@UiO-67 are illustrated in the figures below (evolution of spectra goes from green to red).



Hydrides formation (left panel) is testified by the erosion of the band at 750 nm (spectra are reported in difference) while, the successive treatment with CO_2 (right panel) causes the formation of a broader band with a maximum at 650 nm. Ir^{III}@UiO-67 shows a similar behavior. The hydrogenation of CO_2 to CH_3OH has been studied by means of a flow reactor equipped with a MS. Simultaneous effect of f pressure, temperature and composition of the gas mixture have been explored, to obtain high CO_2 conversion and good selectivity towards CH_3OH.

The authors acknowledge MOST (National Sustainable Mobility Center), supported under the National Recovery and Resilience Plan (NRRP) financed by the European Union – NextGenerationEU.

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SUPPORTED PD SINGLE-ATOM CATALYSTS ON UIO-66 FOR CO_2 HYDROGENATION TO METHANOL

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Keywords: *UiO-66, single atom catalysts, Pd, CO_2 hydrogenation*

In this work, single atoms of Pd have been immobilized on a functionalized UiO-66-NH_2 and UiO-66-I metal-organic framework. A combined experimental and theoretical approach has been undertaken to ascertain the nature and speciation of the well-defined Pd moieties. The study revealed that for the UiO-66-NH_2 framework, a mixture of single atoms and Pd_{17} nanoclusters have been embedded in the pores, whilst for the iodo-functionalized framework, only neutral single atoms of Pd were stabilized. Catalytic testing of the Pd-laden MOFs further revealed that Pd speciation plays an intrinsic role in the performance of the material, as only the supported Pd nanoparticles embedded in Pd-UiO-66-NH_2 demonstrated activity for the selective hydrogenation of CO_2 to methanol.

Functionalized terephthalic acid-based linkers have been synthesized and integrated into the UiO-66 topology following a previously reported procedure.[1] Metalation of the functionalized MOF was then carried out, involving the incorporation and *in-situ* reduction of the Pd precursor.[2] This results in the embedment of neutral Pd atoms within the MOF pores. It was found that tuning the number of linker defects in the framework influenced Pd incorporation, with a more defective framework displaying a higher Pd loading when quantified with microwave plasma atomic emission spectroscopy (MP-AES), compared with a less linker defective framework. A higher Pd loading is indicative of aggregations of the metal, while a strong metal-support interaction promotes the stabilization of single neutral atoms of Pd and consequently leads to lower metal loadings.

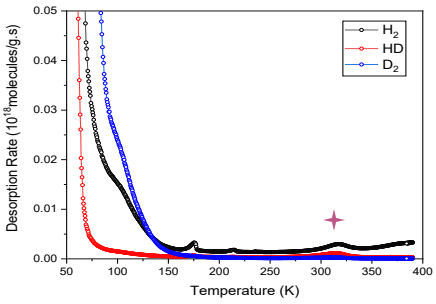
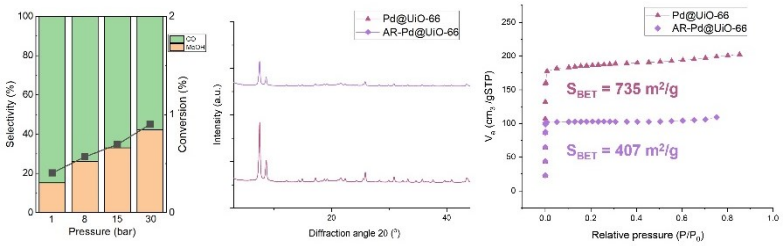


Figure 1: TDS spectrum of Pd@UiO-66 showing a desorption peak at 315 K caused by the formation of an interstitial hydride.

Structural elucidation of the material using a combination of advanced characterization methods, including X-ray absorption spectroscopy (XAS), inelastic neutron scattering (INS), thermal desorption spectroscopy (TDS) and transition electron microscopy (TEM) revealed the nature and speciation of the Pd-laden MOFs. By studying the interactions between H_2 with the supported Pd MOFs, it was revealed that single atoms of Pd were embedded within the pores of Pd-UiO-66-I, demonstrated by the formation of an interstitial hydride species detected in both the INS and TDS spectrum (**Figure 1**). The desorption peak observed at > 300 K is caused by the interaction between H_2 and single atoms of Pd immobilized within the pores of the framework, and not present when there are only nanoclusters of Pd.

Structural characterization of the spent catalyst revealed that a change in Pd-UiO-66-NH_2 has occurred, as the material displayed a substantial decrease in BET surface area, and SEM imaging revealed the presence of Pd on the MOF surface. The overall crystallinity of the framework remains intact (**Figure 2**).

Figure 2: (left) Product selectivity distribution and CO_2 conversion for Pd@UiO-66 under varying pressures and at 170 ºC (CO_2/H_2/inert = 1/6/2). (middle) Measured powder X-ray diffractograms and (right) N_2 adsorption isotherms of Pd@UiO-66 and spent Pd@UiO-66 (AR-Pd@UiO-66).



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OPTIMIZING MOF MORPHOLOGY FOR ENZYME ENCAPSULATION: INSIGHTS FROM NANOSCALE CHARACTERIZATION

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Keywords: *modulator ligand, enzyme encapsulation, enzyme activity, nanoscale characterization*

Imagine enzymes - nature's catalysts - revolutionize biocatalysis by operating efficiently under extreme conditions such as high pressure, high temperature, high salt concentration. Enzymes are highly efficient catalysts, playing a vital role in biocatalysis, biosensors, and biomedical applications. Despite their efficiency, enzymes often suffer from instability, loss of activity under harsh conditions, and limited reusability, hampering their wider application. These limitations require the development of advanced support materials that improve enzyme stability, maintain long-term catalytic efficiency, and enable easy recovery and reuse [1].

In this context, metal–organic frameworks (MOFs) have proven to be highly adaptable hierarchical materials with exceptional chemical and thermal stability, making them well-suited for enzyme immobilization and encapsulation. Their synthesis process allows for precise control over structural properties, including composition, size, morphology, and crystallinity. With their high porosity and structural adaptability, MOFs provide a protective yet accessible environment for enzymes, enhancing their stability and catalytic performance for various applications [2].

The aim of this study is to improve enzyme stability and catalytic efficiency through precise control of the MOF structure such as morphology and particle size. By systematically tuning synthesis parameters, e.g., by using modulating ligands, we aim to understand how these parameters influence the enzyme encapsulation, structural integrity and catalytic properties of enzyme-MOF nanocomposites. Different enzyme concentrations were introduced during encapsulation to further explore the loading capacity of the modified MOF structure as well as the corresponding enzyme-MOF interactions. Encapsulation efficiency and activity retention were measured using UV-Vis spectroscopy and enzymatic activity assays. Advanced (electron) microscopic and spectroscopic techniques confirmed the successful encapsulation of enzymes into the MOF structure and elucidated the enzyme/MOF interactions at the nano scale.

Our results demonstrate that controlling the MOF properties significantly influences enzyme stability, while optimal enzyme concentration ensures a balance between catalytic efficiency and structural integrity. High-resolution scanning/transmission electron microscopy (HR-S/TEM) and energy dispersive X-ray spectroscopy (STEM-EDS) mapping reveal uniform distribution of enzymes inside the MOF.

By addressing the critical challenges in enzyme encapsulation within the MOF, this study lays the foundation for the rational development of MOF-based biocatalytic systems and paves the way towards more sustainable and efficient biocatalysis applications.

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HOW POWERFUL IS LIGAND ENGINEERING IN ENHANCING MOF PERFORMANCE?

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Keywords: *Ligand engineering strategy, Open metal sites, Electrocatalysis, Water purification.*

In this conference, I plan to report on three research works I led [1-3], focusing on ligand engineering strategies and their effects on modifying MOFs/ZIFs. These strategies include the mixed-ligand and the selective ligand removal (SeLiRe), applied in energy and environmental fields.

First, I introduce the mixed-ligand strategy to enhance the activity and stability of (photo)electrocatalytically active MOFs [1]. Four mixed-ligand variants of zeolitic imidazolate framework-67 (ZIF-67) were synthesized, enabling a detailed analysis of the influence of secondary ligands on the reconstruction of ZIF frameworks during the electrocatalytic oxygen evolution reaction (OER). Some secondary ligands preserved the fundamental framework while inducing surface reconstruction to form an in-situ cobalt (oxy)hydroxide layer. This contrasts sharply with the complete reconstruction observed in single-ligand ZIFs. The cobalt (oxy)hydroxide layer, along with its interfacial synergistic effects, enhanced conductivity and catalytic performance while also improving (photo)electrochemical stability.

Further, I continue to introduce how the SeLiRe strategy to design hierarchically porous ZIFs [2]. This novel method involves synthesizing mixed-ligand ZIFs with varying ratios of two ligands, followed by controlled thermal treatments to selectively remove the thermolabile secondary ligand. This process resulted in a dual-pore structure comprising micropores and newly introduced mesopores. In terms of applications, the hierarchically porous ZIF exhibited a 40-fold enhancement in adsorption capacity for various organic dyes in aqueous solutions. Additionally, by incorporating open metal sites (OMS) — specifically high-valence HO−Zn−N_2 active sites in the ZIF-8 — I achieved an exceptionally low overpotential of 0.41 V, enabling a sustained current density of 1.0 A cm^{-2} with 120-hour stability [3]. Theoretical simulations further demonstrated that these high-valence HO−Zn−N_2 active sites significantly improved water molecule activation kinetics, enhancing the efficiency of the Volmer step.

These successful cases clearly demonstrate that ligand engineering has a powerful effect for designing advanced functional frameworks with enhanced activity, selectivity, and durability for environmental and energy applications.

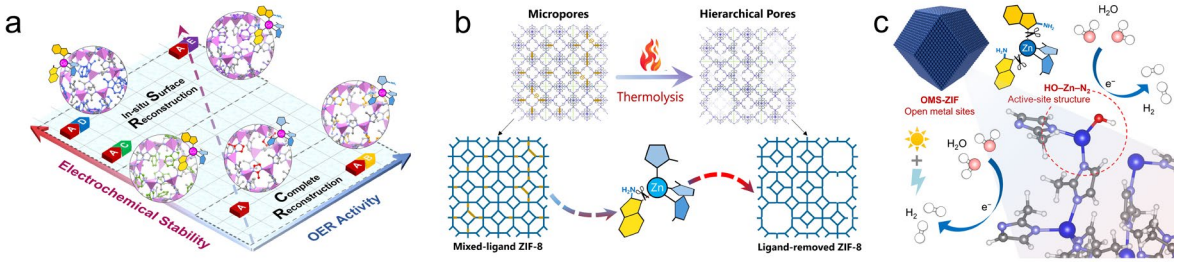


Figure: Schematic diagram of the mixed-ligand strategy (a) [1], selective ligand removal strategy (b) [2] and open metal sites (c) [3] for the ZIF frameworks.

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ENGINEERING PHOTOSWITCHING DYNAMICS IN 3D PHOTOCHROMIC METAL-ORGANIC FRAMEWORKS THROUGH METAL-ORGANIC POLYHEDRON DESIGN

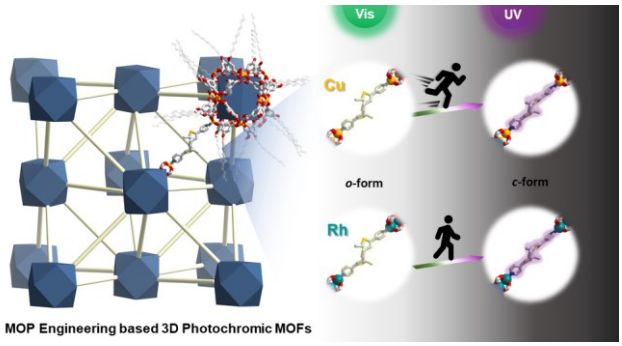
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Keywords: *Photochromic MOFs, Metal-organic polyhedrons, Photoisomerization, Kinetics*

Four-dimensional (4D) metal-organic frameworks (MOFs) represent a transformative advancement over conventional 3D MOFs by incorporating time-resolved structural adaptability in response to external stimuli such as light, temperature, and pressure. These dynamic features position 4D MOFs as highly promising platforms for sensing, catalysis, and energy storage.[1,2] However, realizing efficient photoresponsivity in 3D MOFs remains a major challenge, primarily due to the limited micromechanical compliance of organic ligands and the consequent restriction in controlling photoisomerization kinetics. Herein, we report the rational design and synthesis of two novel 3D photochromic MOFs, DUT-210(Cu) and DUT-210(Rh), based on the supramolecular assembly of photochromic diarylethene (DTE) based *N*-donor ligands with lipophilic functionalized metal-organic polyhedra (MOPs).[3] The lipophilic surface engineering facilitates MOP solubility and promotes crystallization in aliphatic solvents. The resulting frameworks feature multiaxially aligned DTE moieties capable of reversible photochromic switching between open and closed configurations. Comprehensive characterization including *in situ* powder X-ray diffraction and diffuse reflectance spectroscopy, and density functional theory simulations demonstrates that modulation of metal–ligand bond strength enables control over photoswitching kinetics. The structural rigidity conferred by MOP-based architectures further supports operational stability under variable UV irradiation intensities, emphasizing their utility in robust light-responsive systems. These findings not only underscore the potential of MOPs as modular, dynamic scaffolds for advanced functional materials but also offer a pathway toward the development of photon-driven molecular machines, actuators, and programmable release platforms.



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CONVERSION OF CO_2 INTO POROUS METAL-ORGANIC FRAMEWORK MONOLITHS

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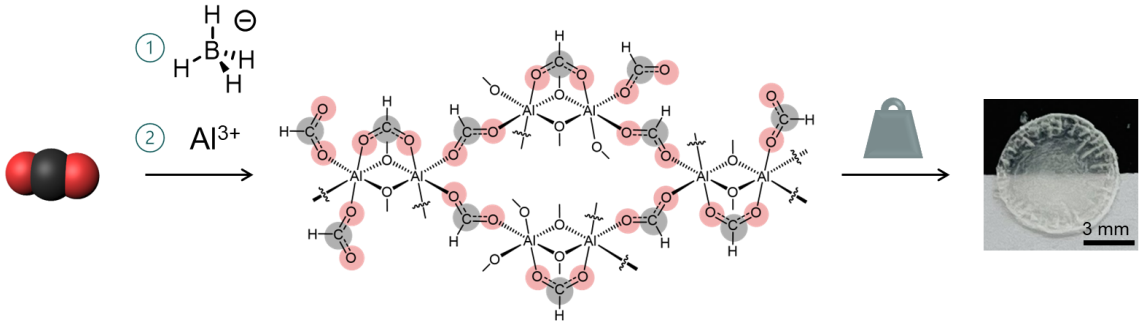
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Keywords: *CO_2 conversion, Porous monoliths, Amorphous*

Conversion of CO_2 into functional materials remains a significant synthetic challenge. Recently, the synthesis of metal-organic frameworks (MOFs) from CO_2 has gained attention.[1, 2] These studies have focused on crystalline CO_2-derived MOFs; on the other hand, amorphous phases of CO_2-derived MOFs remain unexplored. Amorphous MOFs provide unique features such as the formability of grain-boundary-free porous monoliths. This work aimed to synthesize amorphous, moldable MOFs from CO_2 by using formate ($OCHO^-$) with small steric hindrance to form isotropic amorphous coordination networks.

Al^{3+}-based MOF, $[Al_2(OCHO)_3(OMe)_3]$ (**Al-CO_2**) was synthesized from CO_2 by converting CO_2 into $OCHO^-$ through hydride transfer of borohydride (Fig. 1).[3] Solid-state NMR and synchrotron total X-ray scattering analysis revealed the local coordination geometries of the metal centers. **Al-CO_2** exhibited a gravimetric CO_2 content of 47 wt% and BET surface area of 363 $m^2\ g^{-1}$. A transparent, grain-boundary-free microporous **Al-CO_2** monolith was prepared by hot-pressing. This method improved the H_2 adsorption selectivity of **Al-CO_2** monolith over N_2 by mechanically reducing its pore size. Both the strength of metal-oxygen bond and the coordinating flexibility of $OHCO^-$ were key factors in the formation of the porous monolith.



$[Al_2(OCHO)_3(OMe)_3]$
Al-CO_2

Figure 1. Schematic illustration of the formation of **Al-CO_2** via conversion of CO_2 into $OCHO^-$ and its transformation to transparent MOF monolith by hot-pressing.

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BINARY PHASE DIAGRAM OF COORDINATION POLYMER WITH EUTECTIC MELTING BEHAVIORS

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Keywords: *Phase diagram, Coordination polymers, Melting, Crystallization*

Binary compounds of metals and ceramics have unique thermal and mechanical properties. Creating binary systems of coordination polymers (CPs) / metal-organic frameworks (MOFs) is a significant challenge to discovering new functional binary compounds. In this work, we attempted for the first time to construct binary phase diagrams of CP/MOFs.[1] Mechanical mixing is a general technique to obtain binary compounds in metallurgy. We define the mechanical mixing products of two CP crystals as binary compounds. We used CPs composed of Ag^+, counter anions, and dicyanide ligands as shown in Figure 1, *i.e.*, $Ag(GN)_2(BF_4)$ (**1**, GN : glutaronitrile), $Ag(PN)_2(BF_4)$ (**2**, PN : pimelonitrile), $Ag(AN)_2(BF_4)$ (**3**, AN : adiponitrile), Ag(AN)(OTf) (**4**, OTf : trifluoromethanesulfonate), and $Ag(AN)_2(PF_6)$ (**5**), because they show reversible melting and crystallization without forming metastable states such as glass.[2]

We prepared and constructed three types of binary phase diagrams using the five CPs.[2] Three phase diagrams have all eutectic points where two constituents simultaneously melt. For example, the binary compounds $\mathbf{1}_x\mathbf{2}_{(1-x)}$ have lower melting temperatures (T_m, 100°C) than **1** (147°C) and **2** (120°C). Especially, $\mathbf{1}_{0.46}\mathbf{2}_{0.54}$ is in the eutectic ratio with only one T_m at 100°C, where **1** and **2** simultaneously melt (Figure 1). $\mathbf{1}_{0.46}\mathbf{2}_{0.54}$ represents the heat storage capacity of 97 kJ kg^{-1} at 100°C and releases the heat at 80 °C with an energy recovery efficiency of 0.99, indicating that $\mathbf{1}_{0.46}\mathbf{2}_{0.54}$ is a representative latent heat storage material.

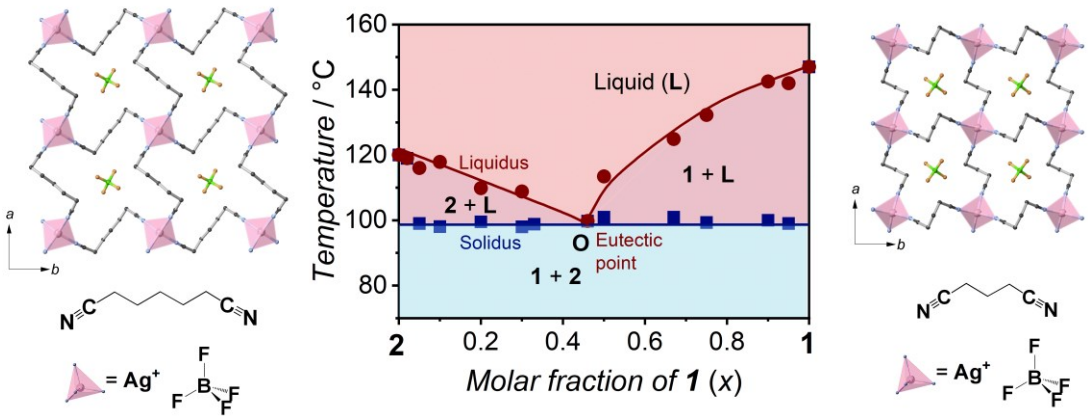


Figure 1 Crystal structures of $Ag(GN)_2(BF_4)$ (**1**, right) and $Ag(PN)_2(BF_4)$ (**2**, left) and the binary phase diagram of **1** and **2**. C, N, Ag, B, and F atoms are black, blue, pink, green, and orange, respectively. The red lines and blue line are liquidus and solidus lines, respectively. O represents the eutectic point.

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TOWARDS CONDUCTIVE RU-BASED COORDINATION POLYMERS

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Keywords: *Mixed-metal MOF, Magnetic ordering, Conductivity, Coordination polymers*

Metal-organic frameworks (MOFs) and coordination polymers (CPs) have garnered significant interest for their tunable structural, electronic, and magnetic properties. Among these, mixed-metal MOFs with different unpaired electrons offer a promising avenue for developing materials with enhanced conductivity and magnetic ordering. Ru-based coordination polymers exhibit strong metal–ligand interactions, extended conjugation, and redox activity, making them ideal candidates for applications in molecular electronics, spintronics, and energy storage.[1] The incorporation of secondary metals alongside Ru in these frameworks introduces synergistic effects that modulate electron transport and magnetic ordering, leading to improved conductivity and switchable magnetic behaviour. Transition metal complexes with well-defined coordination geometries, such as cis-protected Pd(II) and Pt(II) square-planar units, have been widely used in constructing macromolecular frameworks, including polyhedral cages for molecular recognition. Inspired by the reported mixed-metal Ru–Ag coordination networks utilizing the trans-[$RuCl_2(pyz)_4$] (pyz = pyrazine) building block,[2] we aim to develop a series of Ru-based coordination polymers incorporating multiple metal centers with varying unpaired d-electrons. These unpaired electrons facilitate diverse exchange interactions, potentially enhancing both magnetic ordering and charge transport properties in MOF architectures, which exploit redox-active centers, strong spin-orbit coupling, and ligand-mediated electronic interactions to realize quantum coherence and emergent magnetic states.

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OPTIMIZATION OF SOD-TYPE ZIF THIN-FILMS FOR OPTICAL APPLICATIONS THROUGH TARGETED LAYER FORMATION AND ADSORPTION CONTROL

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Keywords: Zeolitic imidazolate frameworks (*ZIFs), thin films, adsorption behavior, optical applications*

Zeolitic imidazolate frameworks (ZIFs), a subclass of metal-organic frameworks, crystallize in zeolite-like structures and are noteworthy for their high porosity and remarkable chemical and thermal stability. These features make them highly promising for novel applications in optics, where precise shaping and film formation are crucial.

Our research focuses on growing ZIFs as crystalline thin films with optical quality. Using a seeding layer method, we produced layers of five different sod-type ZIF derivatives in a defined sequence, which differ in linker molecules and metal ions to control polarity and adsorption behavior. The crystallinity of all films was verified via X-ray diffraction, confirming their sod topology, while their thickness and intergrowth were observed with SEM. Distinct growth of the layers was validated by SEM/EDX and XPS analyses.

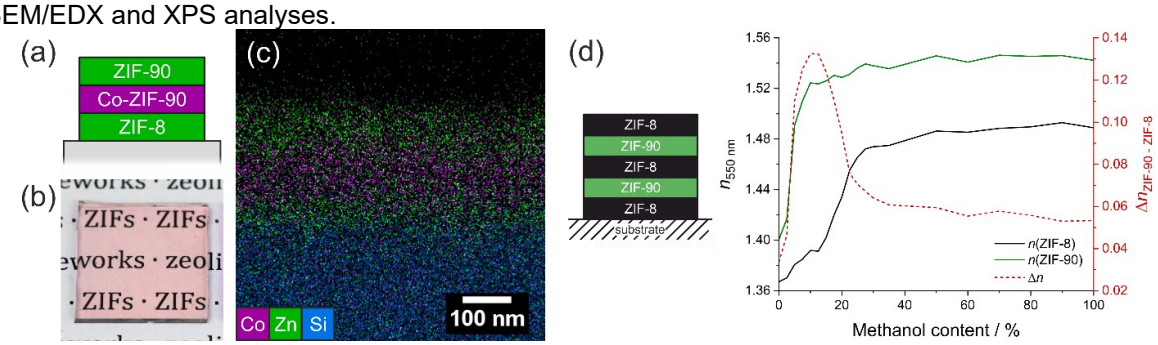


Fig. 1: (a) scheme of the mixed ZIF stack, (b) photograph of the stack fabricated on glass, (c) EDX mapping of a cross-section. (d) Scheme of the alternating ZIF-8/ZIF-90 layers and the resulting refractive index switch with differing methanol vapor content.

Vapor sorption experiments evaluated ZIFs' vapor affinity in powdered form. These differing affinities were utilized to tune the optical properties of the thin films, including refractive index, reflectance, and transmittance. Changes in these properties were assessed through ellipsometry and UV/vis spectroscopy. We specifically studied alternating ZIF-8/ZIF-90 layers, revealing adsorption behaviors linked to polarity. These film stacks are being developed for optical applications such as sensors and switchable reflective coatings like Bragg mirrors. Additionally, we explored thin film growth on multimode optical fibers for sensor applications. Our work underlines the versatility and promise of ZIF thin films for advanced optics, demonstrating their potential for adaptive optical devices.

Acknowledgements:

We would like to thank Prof. Dr. Peter Behrens, former group leader and initiator of this project, for his invaluable contributions. Unfortunately, he passed away in early 2023. We also gratefully acknowledge the fruitful discussions with Prof. Dr. Michael Fröba from the University of Hamburg.

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EXPLORING THE WORLD OF DYNAMIC LN AND MN MOFS AND THE ROLE OF THE METAL SBU IN THE GATE-OPENING EFFECT

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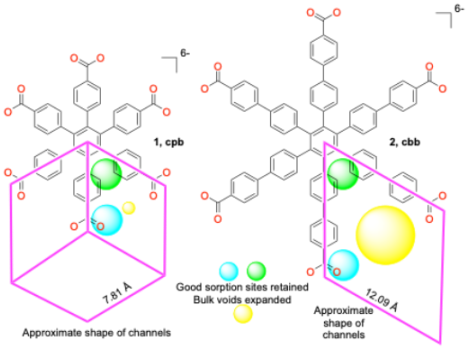
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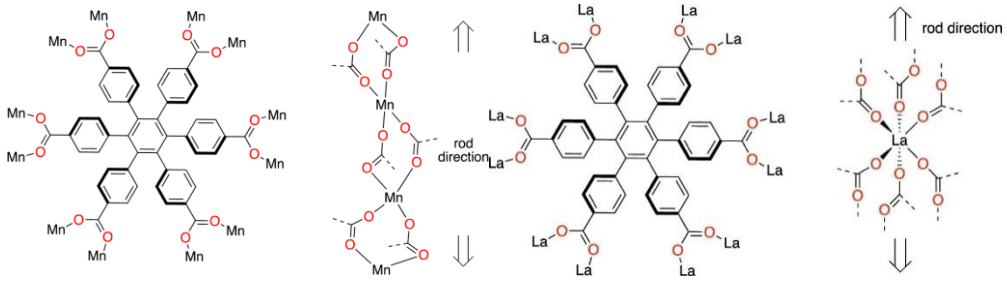
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Keywords: *Gate Opening, Metal-organic framework, Lanthanoids, Manganese, Hexatopic Linker, Dynamic MOF*



Metal Organic Frameworks (MOFs) are a subcategory of coordination polymers and belong to the field of reticular chemistry. In general, similar metal ions perform similar coordination chemistry. As such, the idea that the lanthanoids (Ln) making similar frameworks is not considered a shock. However, whereas the Ln ions are known for their similarities, there are differences between them. Cerium (Ce) as an example is commonly occurring in 3+ and 4+ oxidation states whereas europium (Eu) can be encountered as 2+ and 3+. Similarly, manganese (Mn) is well known for its many different oxidation states and thus provide a broad canvas from which we can design our MOFs. Herein, we report MOFs made with the hexatopic linkers 1,2,3,4,5,6-hexakis(4-carboxyphenyl) benzene **1**, H_6cpb[1,2,3], and hexakis(4-(4-carboxylphenyl)phenyl)benzene, H_6cbb **2**. Different $Ln^{3+/4+}$ and $Mn^{2+/3+}$ were combined and compared in terms of structure[2,3], dynamic behaviour[2], and how these properties impact the properties of the MOFs[1,2,3]. As such, we can gauge the utility of these hexatopic linkers, and figure out how they can provide us with fundamental knowledge about the hexatopic nature, ligand size within these constraints, and broaden our understanding of the "gate-opening effect"[2].



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DIMENSIONAL ENGINEERING OF PORPHYRIN-BASED COVALENT ORGANIC FRAMEWORKS FOR TUNABLE PHOTOPHYSICAL PROPERTIES

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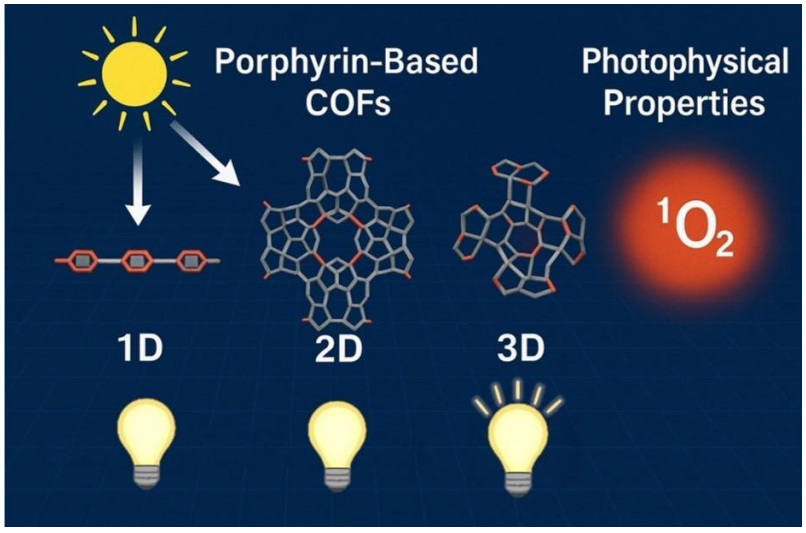
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Keywords: *Covalent Organic Framework, Porphyrin, Structural dimensionality, Photophysical properties, Reactive oxygen generation*

Covalent Organic Frameworks (COFs) are crystalline, porous materials constructed via strong covalent bonds, offering high stability and tunable architectures for diverse applications, including catalysis, sensing, and optoelectronics. Among them, porphyrin-based COFs have garnered significant interest due to their applications in light-mediated processes, including photocatalysis and photodynamic therapy. The structural dimensionality of COFs clearly affects their photophysical characteristics. Despite their potential, a systematic investigation into the correlation between porphyrin-based COF structures and their photophysical characteristics remains limited.

In this study, we demonstrate a precise synthetic strategy to control the dimensionality of porphyrin COFs across 1D[1], 2D[2], and 3D[3] frameworks. By employing sensible molecular design and tailored synthetic approaches, we successfully tuned the framework architecture, thereby enabling customizable functionality. Structural characterization using X-ray diffraction, electron microscopy, and spectroscopic techniques including low-temperature phosphorescence measurements, confirms the well-defined crystallinity and porosity of the obtained COFs. These findings are further supported by phosphorescence data, which provide insights into the relationship between structural dimensionality and singlet oxygen generation efficiency.

Furthermore, we evaluated the impact of COF dimensionality on catalytic performance by conducting a light-driven oxidation reaction. The results highlight a direct correlation between porphyrin-based COF dimensionality and their photophysical properties, demonstrating their potential for advanced photocatalytic applications. Additionally, the generation of reactive oxygen species in these COFs was examined, providing deeper insights into their reactivity under light exposure. These findings offer valuable perspectives for the rational design of next-generation light-harvesting materials and contribute to the broader development of photoactive systems.



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FLUORESCENT MOF EMISSION TUNING AND APPLICATION TOWARD RADIOACTIVE GAS DETECTION.

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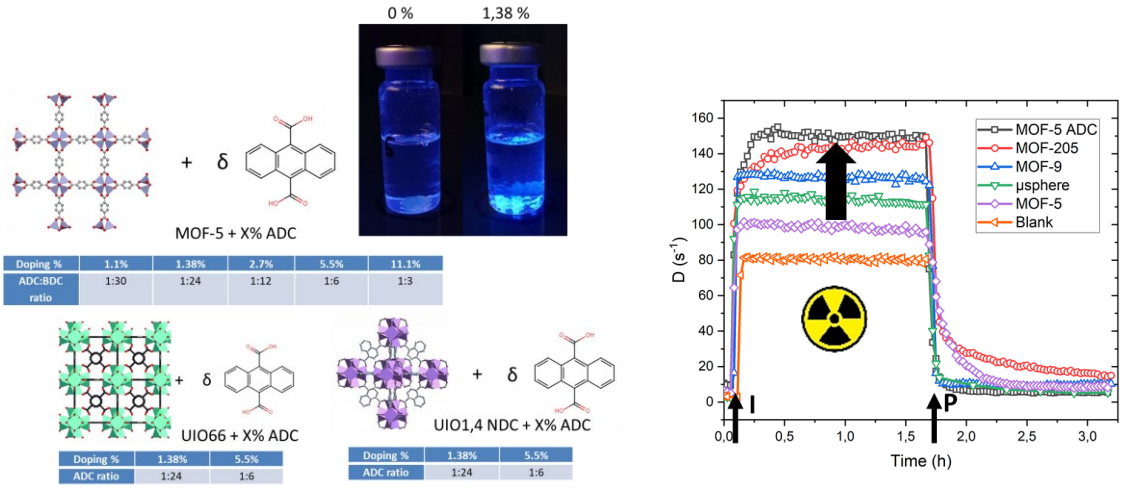
Keywords: Scintillation, Radioactive gas detection, partial ligand doping

Radioactive gases are the hardest type of contamination to contain, evaluate and quantify. Fortunately, only a handful of isotopes have real societal impact: ^{85}Kr, ^{3}H and ^{222}Rn. They are beta or alpha emitters, hence weakly penetrating and consequently strongly sensitive to self-shielding. This makes traditional planar detectors unsuitable, which reflect in the state of the art, though each traditional technics do detect radioactive gas have impractical drawbacks. The most common one are offline or long measurements timing (1h to 24h) and bulkiness (> 10 kg).

In order to answer this limitation, we developed a family of porous scintillators in order to have a large contact area between the gases and the scintillating medium. Hybrid organic-inorganic scaffold such as Metal Organic Frameworks (MOF) are ideal porous candidates for this application. This choice was motivated by the recent effort of the community to developed fluorescent MOF[1], and report of affinity for noble gas [2], which ^{85}Kr and ^{222}Rn are members of.

We present here a comprehensive summary of our research on Zr and Zn scillating MOFs [3] design as well as a study of their response towards ^{85}Kr, ^{222}Rn and ^{3}H. Some MOF present interesting gas affinity but low scintillation yields. This was optimized with the use of principle close to classical organic scintillation: fluorophore doping. Our study showed that insertion of same length photoactive ligand have a beneficial impact on the detection efficiency of radioactive gas. We also demonstrate that MOF can act as a radioactive gas sponges that concentrate 85Kr in its pores, hence giving us access to a higher local concentration of radioactive species.

This new field of application for MOF is very promising as the overall system have performances comparable to the industry requirements but have a shorter response time and is more practical than commercially available radioactive gas detection methods.



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CHEMIRESISTIVE SENSORS FOR ETHYLENE DETERMINATION BASED ON SILVER(I) BIPYRAZOLATES

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Keywords: *chemiresistive, sensor, silver, bipyrazolates, ethylene*

The agri-food industry faces substantial losses due to the over-ripening and spoilage of climacteric fruits, which continue to ripen post-harvest due to ethylene, a key phytohormone.[1] Accurate detection of ethylene is thus essential for effective storage and transportation management. Most chemiresistive sensors for ethylene detection are based on wide band gap n-type metal oxide semiconductors (MOS).[2]

In this study, a novel series of chemiresistive ethylene sensors based on silver(I) bipyrazolates (Ag(I)-BPZs) was developed.[3] The bipyrazolate ligands were functionalized with different substituents (methyl, ethyl, phenyl) and their structural, photochemical, and electrical properties were systematically characterized. These coordination polymers were embedded in a poly(vinylidene fluoride) matrix with 1-ethyl-3-methylimidazolium tetrafluoroborate and deposited as thin films on printed plastic slides containing silver electrodes (Fig). Sensor performance was evaluated by measuring resistance changes under exposure to ethylene and other gases (ethanol, methanol, ethyl acetate, acetaldehyde, CO_2) at concentrations up to 300 ppm. The sensor response increases linearly with the adsorbate concentration, and is influenced by the amount of substituents on the bipyrazolate skeleton. The practical applicability was demonstrated by monitoring ethylene levels during plum ripening in a controlled environment, highlighting the sensor's selectivity, rapid response, and potential to prevent over-ripening by enabling real-time ripening stage assessment.

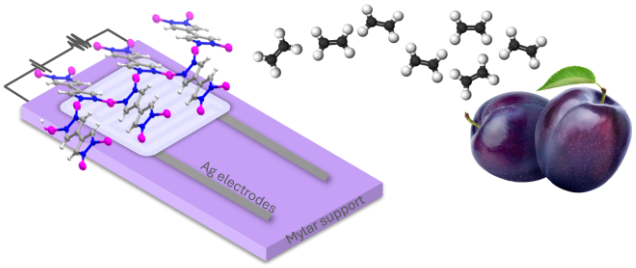


Figure. Schematic illustration of chemiresistive ethylene sensor architect.

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EXAMINING THE IMPACT OF SYNTHESIS METHOD ON THE ADSORPTION OF ETHANOL IN ZIF-71 & ZIF-93

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Keywords: *ZIFs, Green Synthesis, Sorption studies, Ethanol adsorption.*

The growing demand for heating and cooling energy is becoming increasingly important due to the continual rise in global population. As heating and cooling account for up to 50% of the world's final energy consumption, there is growing interest in environmentally friendly methods to optimise thermal energy use. One such solution is thermal energy storage (TES), which relies on reversible chemical reactions and/or gas sorption processes in solids or liquids, offering minimal heat loss and significantly higher energy storage densities. Sorption-based TES can utilise traditional adsorbents like zeolites or more advanced materials such as metal-organic frameworks (MOFs). A notable subgroup of MOFs is Zeolitic Imidazolate Frameworks (ZIFs), which consist of transition metal ions (e.g. Zn, Co) and imidazolate linkers. Structurally similar to zeolites—with metal ions replacing Si/Al and imidazolate linkers replacing oxygen—ZIFs are known for their high stability. Their ordered porous structures and ability to be formed into glass-like monoliths also make them promising candidates for adsorptive separation.

Despite their potential, research into optimising ZIFs for heat storage and allocation remains limited, with most studies focusing on water as the working fluid. However, ethanol has shown advantages in this context, particularly at lower operating temperatures, as demonstrated in a study by De Lange et al. (2015) and confirmed more recently by Byrne et al. (2025).[1-2] Yet, the use of ethanol as an adsorbate remains underexplored.

Large-scale adoption of ZIFs is also hindered by the lack of low-cost, sustainable production methods. Most stable ZIFs are synthesised via solvothermal methods, which typically require high temperatures and long reaction times—often up to 72 hours. These processes also still heavily rely on N,N-dimethylformamide (DMF), a toxic and potentially carcinogenic solvent. In response to increasing environmental concerns and EU restrictions on DMF since 2023, efforts have intensified to develop greener synthesis methods using alternative solvents.

ZIF-71 and ZIF-93 were selected for this study based on their large pore sizes and capacities, both exhibiting a RHO topology. DMF was successfully replaced with methanol in their synthesis. However, to our knowledge, these ZIFs have not yet been successfully synthesised via mechanochemical methods, which represent a greener approach by eliminating the need for solvents altogether. In this study, ZIF-71 and ZIF-93 frameworks were synthesised at room temperature using greener solvents (water, methanol, and ethanol) and via mechanochemical methods. Structural and textural analyses showed that the selected ZIFs largely retained their properties, though mechanochemically produced samples displayed slightly lower crystallinity and microporosity compared to conventional solvothermal synthesis. Ethanol sorption tests revealed that the ZIF-93 series exhibited ethanol uptake comparable to reference samples from the literature. This was also true for the ZIF-71 series, apart from one sample made via liquid-assisted ball milling, which showed reduced uptake due to partial structural degradation during the sorption test. The ethanol arrangement in the pores of both materials has also been evaluated. A stability assessment of the four best-performing samples over 20 sorption/desorption cycles indicated that materials prepared by ball milling and precipitation maintained their original capacity, suggesting good long-term stability.

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DEFEROXAMINE NANOCOMPOSITES FOR METAL BINDING

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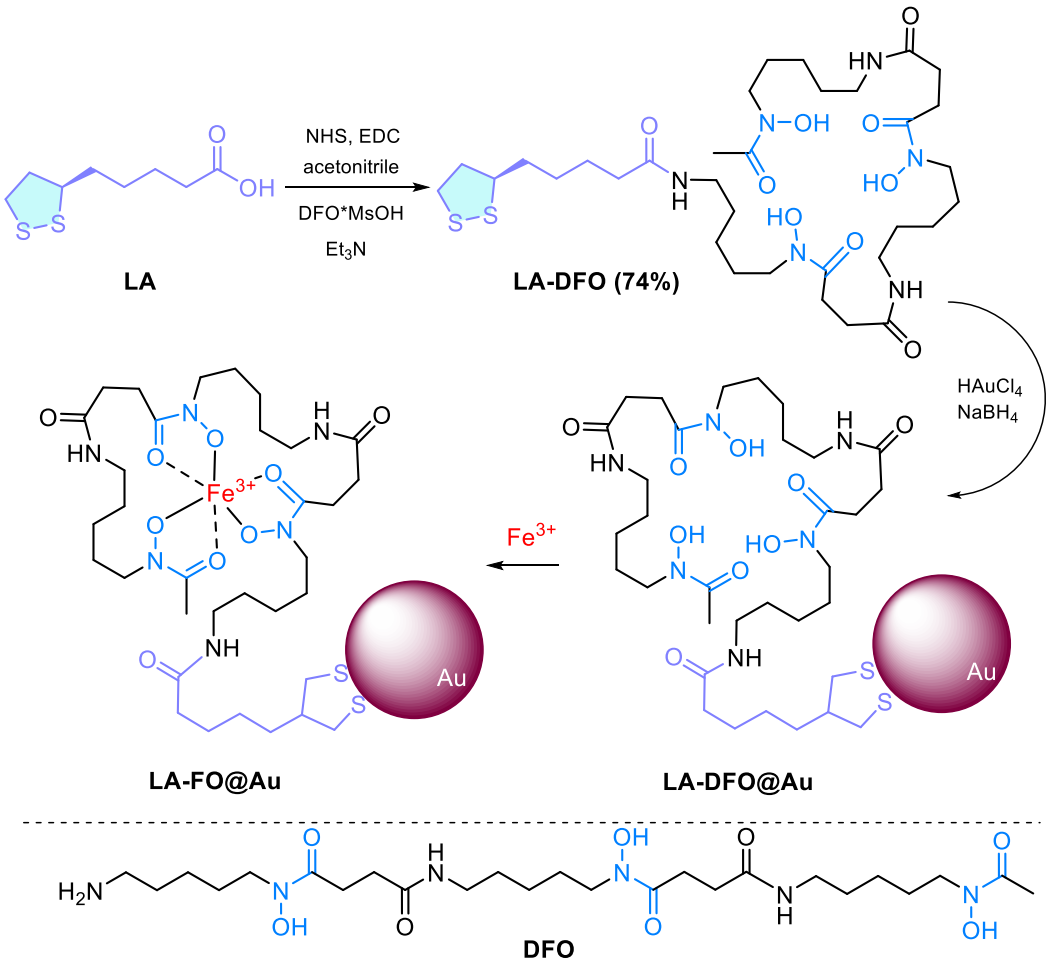
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Keywords: *deferoxamine, lipoic acid, gold nanoparticles, adsorption, metals*

Deferoxamine (DFO) is a natural siderophore that can interact with metal cations through its three hydroxamic groups (highlighted in blue). Recently raised concerns about DFO toxicity [1] have led to the development of new iron chelators, including DFO nanoparticles (NPs), which have improved biocompatibility.[2] Here, gold NP-core-based novel DFO nanocomposites were synthesized. For this approach, lipoic acid (LA) (highlighted in purple) was used as a linker because it is a naturally occurring compound that has carboxylic and disulfide groups. The carboxylic group can interact with the amino group of DFO to form the amide **LA-DFO** with 74% yield, and the disulfide groups have a high affinity to gold to facilitate stable Au NP-based composite formation. Thus, the **LA-DFO@Au NPs** were obtained by combining **LA-DFO** and $HAuCl_4$ as gold NPs precursor, and $NaBH_4$ as a reductant. **LA-DFO@Au NPs** are strong Fe^{3+} adsorbents and have a biocompatible profile enabling them for potential biomedical applications.



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SUSTAINABLE DYNAMIC SOLVENT SYSTEM (DSS) UNRAVELING FLEXIBILITY OF PYRAZOLATE MOFS WITH WINERACK TOPOLOGY

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Keywords: *MOF synthesis, Flexibility, Green Chemistry*

Pyrazolate metal-organic frameworks (PzMOFs) are a very promising, but, in our opinion very much undervalued MOF class with distinct properties. First reported after 2006, although potentially known for over a century, as the first pyrazolate transition metal salts were reported by E. Buchner in 1889,[1] the PzMOFs demonstrate great properties for tackling modern day problems. In contrast to the transition metal carboxylates, PzMOFs are more robust towards high pH conditions akin to imidazolates when formed with Lewis “soft” transition metal cations. Thus, the possibility to form functional PzMOFs from earth abundant and inexpensive transition metals, which are stable in a wide range of conditions, is one of their major advantages. Until recently the toolkit to influence the size and shape of pyrazolate MOFs was very limited as compared to the classic carboxylate materials. Not only is a sufficient crystal size crucial for certain analytical techniques (e.g. single crystal X-ray diffraction, SCXRD), it plays a major role for some unique MOF properties, such as flexibility.[2]

Recently the dynamic solvent system (DSS) concept was developed in our group, which rendered synthesis of large single crystals of two prominent PzMOFs [Ni(bdp)]n and [Zn(bdp)]n (H_2bdp = 1,4-bis(4-pyrazolyl)benzene) possible, while also making their synthesis more sustainable.[3] The DSS is an inherently reactive solvent mixture, which reacts with itself on the same time scale as the MOF formation, thus gradually changing the crystallization conditions. Our proposed model DSS is the 1-butanol (BuOH) and acetic acid (AA) mixture, which undergoes esterification to form 1-butylacetate (BuOAc) and water. The high concentration of the modulating AA during the nucleation phase of the MOFs, which declines over time to allow more rapid crystal growth, results in large crystal formation (Fig. 1b). Importantly, the mixture is non toxic and undergoes a valorization during synthesis, in contrast to DMF, which is toxic, highly regulated, and decomposes under solvothermal conditions to less valuable compounds (Fig. 1a).

The [Ni(bdp)]n and [Zn(bdp)]n obtained from the DSS synthesis demonstrate superior size, crystallinity, and flexibility, with pronounced multistep breathing and multi-step gate-opening behaviors respectively, as compared to the same materials obtained from the traditional reflux synthesis. The flexibility of these improved materials was investigated through application of versatile stimuli (solvent, gas, temperature), which revealed a very flat energy landscape between the different phase transitions.

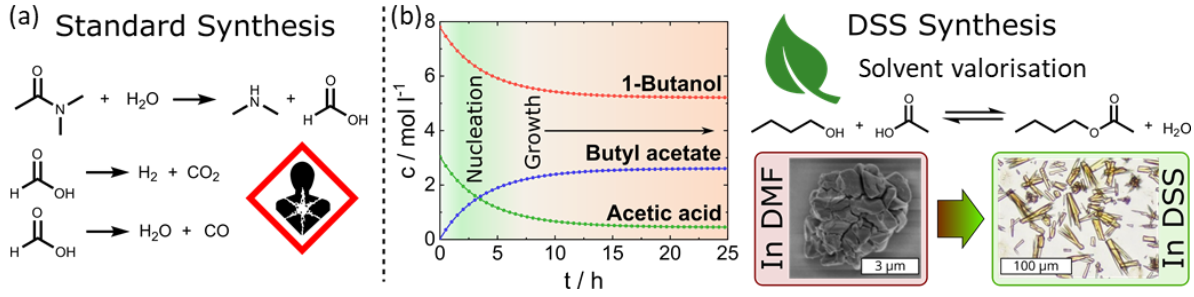


Figure 1. Comparison of standard DMF and DSS synthesis of [Ni(bdp)]n.

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SYNTHESIS AND ADVANCED CHARACTERIZATION OF Zr BASED METAL-ORGANIC FRAMEWORKS FOR CO_2 SEPARATION IN MIXED MATRIX MEMBRANES.

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Keywords: *Zirconium MOFs, Synthesis, CO_2 adsorption, Characterization*

Zirconium based MOFs have been extensively studied over the past decades due to their unique properties, making them promising candidates for a wide variety of applications such as gas storage and separation, heterogenous catalysis, drug delivery and as fillers for Mixed Matrix Membranes (MMMs) [1] Zr-MOFs are well-known for their excellent structural and thermal stability, which makes them very promising for a wide range of applications.[1] In addition, Zr-MOFs possess high surfaces area and permanent porosity, features that are particularly attractive for CO_2 capture and separation processes.[1] Importantly, Zirconium (IV) is classified as a non-critical raw material, offering an advantage in terms of sustainability. This study also employs short-chain C4 dicarboxylic acids – specifically fumaric acid, succinic acid and mesaconic acid- as organic linkers. Fumaric acids and succinic acids are key intermediate in the Krebs cycle, naturally occurring and readily biodegradable, which enhances the environmental compatibility. These linkers are also commercially available and low-cost, contributing to the economic viability of the materials.[2–4]
In this contribution, we present the synthesis and characterization of Zr-MOF-801 based on C4 dicarboxylic linkers, synthesized employing green, biomass-derived solvents such as γ-valerolactone (GVL). A multi-technique characterization approach was adopted to gain a comprehensive understanding of the material properties. Fundamental structural and thermal analysis were conducted via Powder X-Ray diffraction (PXRD), Variable Temperature PXRD (VT-PXRD), Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM), while advanced techniques including solid-state NMR spectroscopy, Infrared Spectroscopy and volumetric gas adsorption measurements provided a deeper insight into the material framework and textural properties.

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STUDY OF TITANIUM SILICATE 1 (TS-1) FOR TREATMENT OF DIFFERENT DYES IN WASTEWATER

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Keywords: *Wastewater treatment; titanium silicate 1 (TS-1); Photocatalytic degradation; Organic dyes removal*

This study investigates the effectiveness of titanium silicate 1 (TS-1) as a catalytic material for the photodegradation of various dyes present in wastewater. Photodegradation, is one of the used technologies due to its relatively simple design and cost effectiveness. Photodegradation involves the breakdown or decomposition of different organic contaminants, various dyes using UV or visible light solar spectrum. Titanium silicates are considered promising candidates for photodegradation owing to their low cost, thermal and structural stability, catalytic efficiency, simple fabricating methods and yields and environment friendliness for photocatalytic applications. Due to its unique structural and catalytic properties, TS-1 was evaluated for its ability to degrade a range of synthetic dyes commonly found in industrial effluents. The research analyses the adsorption capacity, catalytic photodegradation performance and overall efficiency of TS-1 in breaking down dye molecules under different conditions. Results demonstrate that TS-1 offers promising potential for use in advanced wastewater treatment technologies aimed at reducing environmental pollution caused by dye contaminants. The typical data of the processes of degradation are shown on (Figure 1).

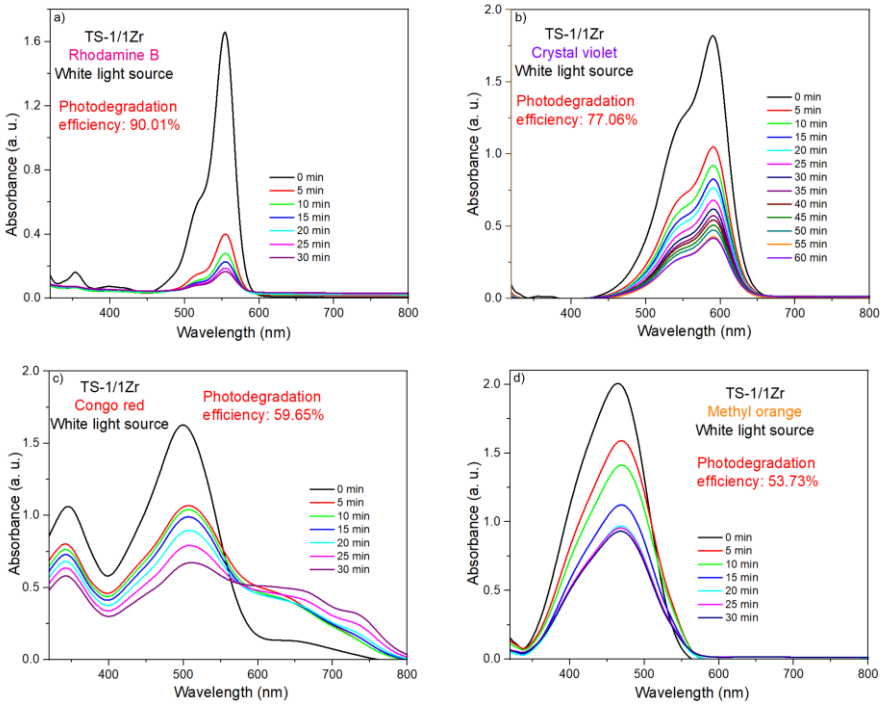


Figure 1. UV-Vis monitoring of the photodegradation processes of a) Rhodamine B, b) Crystal violet, c) Congo red and d) Methyl orange promoted by TS-1/1Zr and white light irradiation.

Acknowledgement: This work was financially supported by the Bulgarian National Science Fund, contract KP-06-COST/28

STRUCTURAL CHARACTERIZATION, ADSORPTION BEHAVIOR, AND PHOTOCATALYTIC PERFORMANCE OF A ZINC-BASED MOF INCORPORATING 2,4,6-TRIS-(4-CARBOXYPHENOXY)-1,3,5-TRIAZINE

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Keywords: *2,4,6-tris-(4-carboxyphenoxy)-1,3,5-triazine; wastewater treatment; photodegradation; single crystal; MOF*

This study presents the design, synthesis, and characterization of MOF-S1, a novel zinc-based metal–organic framework (MOF) constructed from the rigid tritopic ligand 2,4,6-tris-(4-carboxyphenoxy)-1,3,5-triazine (TCPT) and zinc nitrate [1]. Prepared via solvothermal methods, MOF-S1 crystallizes in a trigonal system with a two-fold interpenetrated 3D network featuring zinc paddle-wheel nodes (Figure 1). Structural analysis using single-crystal and powder X-ray diffraction confirmed its high crystallinity and robustness. The framework exhibits ultramicroporosity, a median pore width of 6.5 Å, and a specific surface area of 711 m^2/g. Gas sorption studies further demonstrated its notable uptake of CO_2 and H_2. Thermal and spectroscopic analyses confirmed excellent thermal stability and a wide band gap of 4.24 eV, indicating UV light responsiveness.

The adsorption behavior of MOF-S1 was evaluated using four dye molecules—Congo Red, Methylene Blue, Methyl Orange, and Rhodamine B—revealing high removal efficiency and fast adsorption kinetics, predominantly following pseudo-second-order models and Langmuir isotherms. Photocatalytic degradation studies under UV irradiation showed MOF-S1 to be highly effective, achieving ~93% degradation of Methyl Orange and ~74% of Rhodamine B. These results position MOF-S1 as a promising candidate for water purification and photocatalytic applications in UV-active environments.

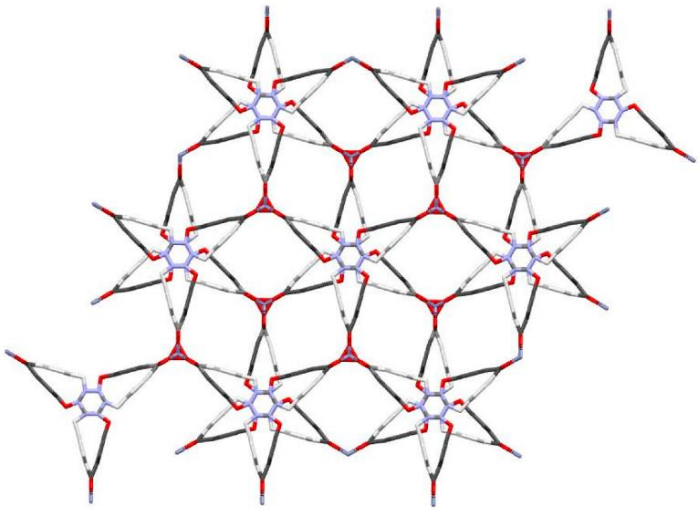


Figure 1. Single-crystal X-ray diffraction (SCXRD) analysis of MOF-S1, showing the three-dimensional interpenetrating networks.

Funding: This research was funded by the Bulgarian National Science Fund (BNSF), grant number KP-06-COST/3.

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IMPROVED PREPARATION OF THIN-FILM MOF-COATED BLADES

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Keywords: *Metal-organic frameworks, thin-film, blades, synthesis, characterization*

Metal-organic frameworks (MOFs) have shown impressive applicability within analytical chemistry, particularly in miniaturized sample preparation strategies, given their permanent porosity and high surface area, together with versatility, and acceptable chemical and thermal stability, thus allowing their use as sorbents for the extraction of a wide variety of compounds from complex samples. A progressive sophistication has been observed in this field, from initially powder-based applications to their last incorporation in different devices and geometries, with the purpose of enhancing properties such as reusability and automation. From the different analytical geometries available to incorporate sorbents within microextraction, thin film coatings onto metallic blades are of interest as permitting the uniform deposition of a sorbent, thus ensuring high areas of exposure available for the microextraction, together with thin films that ensure short kinetic times.

Nevertheless, current approaches for the preparation of these MOF-based devices include the need of mixtures of glues and/or polymers which, occasionally, end up producing device irreproducibility and even the clogging of the pores of the MOF. Besides, leaching of such additional polymer is possible when used in the analytical field, in turn altering the signals expected from the target compounds. Several attempts have been made to achieve a direct linking of the MOF to the support without the requirement of third materials, being the *in-situ* growth approach the most successful strategy. In this strategy, the pre-functionalized support is submerged into the MOF-precursor solution, forming a coating by *in situ* growing of the crystalline structure on it. This functionalization plays a key role in the posterior linkage of either the metal or the organic linker, directly related to the further MOF-coating formation. While this approach seems feasible, it is time-consuming, usually requiring several strategies, or the incorporation of hard-to-handle reagents, among others.

This work presents a novel approach for the preparation of MOF-coated blades, following a milder, quick, and easy strategy based on thiol-chemistry. This approach has been used for the preparation of different Al and Zr-based MOF thin film devices, which have been completely characterized, proving the correct formation of the analytical devices.

Acknowledgements

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DIAMINOTRIAZOLE-BASED MOF FOR CO_2 ADSORPTION AT LOW CONCENTRATIONS

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Keywords: *microporous MOF, CO_2 capture, amine-functionalization, post-synthesis modification.*

Metal–Organic Frameworks (MOFs) have found broad application across various fields, primarily due to their well-regulated structural arrangement, high surface areas, and exceptional tunability[1]. Their unique properties have positioned MOFs as promising materials for selective CO_2 capture and separation[1,2]. Specifically, the chemistry of MOFs has been developed to the point that one can rationally and systematically modulate the interplay between the MOF structure and the desired properties.

One effective strategy to improve CO_2 capture involves functionalizing the framework by introducing additional functional groups to the structure[3]. This enhances the number of active sites within the MOF, enabling stronger interactions with CO_2 molecules. A notable example demonstrating that the incorporation of additional functional groups can enchance CO_2 adsorption is CALF-15[4] – a framework derived from CALF-20[5], featuring an extra amino group on the triazolate linker. Building on this concept, we aimed to incorporate an additional amino functional group into the framework, resulting in a new MOF structure named NICS-24[6] (fig. 1). The introduction of an additional amine group in NICS-24 led to improved CO_2 capture performance to CALF-15, with both materials outperforming CALF-20 at low CO_2 concentrations.

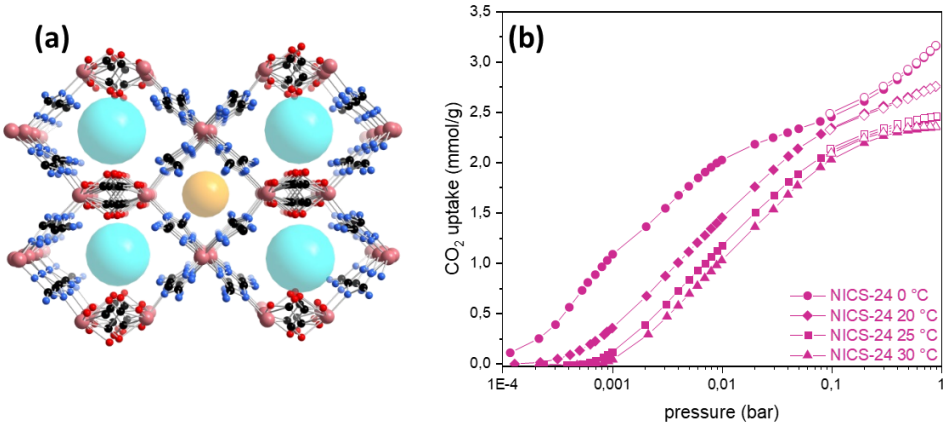


Fig.1. (**a**) Visualization of NICS-24 structure, (**b**) equilibrium adsorption isotherms for CO_2 up to 1 bar for NICS-24 at different temperatures.

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EXPLORING RENEWABLE REGENERATION TECHNIQUES FOR EFFICIENT CO_2 DESORPTION

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Keywords: *MOF, DAC, Magnetic Heat Induction, Magnetic particles*

Rising CO_2 levels are a major driver of global warming, reaching approximately 412 ppm in 2020[1]. While technologies like Integrated Gasification Combined Cycle and Pulverized Coal power plants help reduce emissions, they remain insufficient to meet Paris Agreement targets[2]. Negative Emission Technologies (NETs) are therefore essential. Among them, Direct Air Capture (DAC), using either liquid solvents or solid sorbents, is gaining attention due to the land use and food security concerns associated with alternatives such as Bioenergy with Carbon Capture and Storage (BECCS) and afforestation[1]. Metal-organic frameworks (MOFs), composed of metal nodes and organic linkers forming porous structures, are particularly promising due to their tunable properties. However, identifying suitable MOFs remains challenging, requiring materials with high CO_2 uptake at low pressures, strong stability, low toxicity, and feasible synthesis routes[3]. A particularly important part of the DAC process that we consider is regeneration of the sorbent material. Solid sorbents, which capture CO_2 via physisorption or chemisorption, regenerate at low temperatures (80–150 °C), making them more energy-efficient and scalable[4]. While MOFs offer easier regeneration, the two main methods, temperature swing adsorption (TSA) and pressure swing adsorption (PSA), still demand significant energy. One solution is to use Magnetic Induction Swing Adsorption (MISA) which aims to incorporate magnetic particles (MPs) that generate heat under alternating magnetic field[5].

Until now, we synthesis and studied 200nm MPs with different ligands which are able to achieve temperatures high enough to regenerate but not destroy the MOF. We report that we have already observed the importance of the ligand in influencing the initial MOF growth on MPs, as our results clearly demonstrate the formation of different sizes and morphologies depending on the ligand used. Additionally, we observed that the ligand can influence the heat dissipation capacity of the MPs, resulting in different temperatures and heating rates depending on the ligand used. Moreover, it was observed that depending on the MPs response to the alternating magnetic field, modulated by changing the power, we can tune both the heating rate and the maximum temperature that can be reached. Thus, by finding a suitable ligand, we expect to obtain MPs coated with a thin nano-MOF layer on top, which would ensure efficient heat distribution and complete MOF regeneration. We also report that after a few attempts, a support was coated with the MPs. The MPs appeared to be well anchored to the support as we were able to move it using a magnet without the MPs detaching. However, due to the strong adhesion of the MPs, a weaker response to the magnetic field was observed. The next step of this project is to grow the MOF on the MPs-coated support and evaluate the adsorption and desorption behavior of the formed system, to determine whether the adsorption is modified by the presence of the MPs, and to verify if our magnetic heating approach is more effective than conventional regeneration methods.

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RESOURCE RECOVERY USING POROUS COMPOSITE MATERIALS

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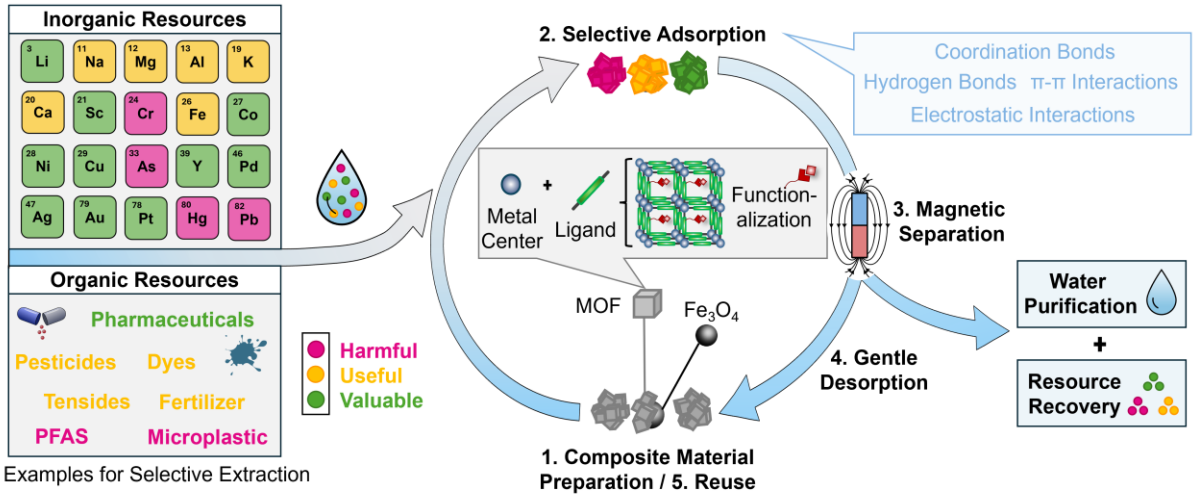
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Keywords: *Metal-organic frameworks, Fe_3O_4 composites, resource recovery from water*

Rising water scarcity driven by climate change demands new solutions for sustainable water use and management, as underscored by the 6th Sustainable Development Goal of the United Nations.[1] Yet water is not only a medium that needs to be cleaned of harmful substances – it also contains valuable resources that can potentially be recovered and reused.[2] Therefore, a targeted and selective recovery of resources from (waste) water would enable both the purification of the water (environmental benefit) and the reuse of the extracted resources (circular economy and sustainability).

The hybrid materials class of metal-organic frameworks (MOFs) offers great potential for such selective resource recovery. Their chemical architecture can be fine-tuned in numerous ways (*e.g. via* modification of metal nodes or linkers, defect engineering, or functionalization) and their highly porous structures and large surface areas allow for the adsorption of ions and molecules.[2] This versatility has already been exploited in several studies for the selective extraction of resources by MOFs or MOF composites.[3] However, the applicability of such materials, as well as their reuse, are still insufficient. To facilitate their recovery, we investigate the combination of promising MOF structures for the selective recovery of inorganic or organic resources with superparamagnetic Fe_3O_4, *e.g.* in form of core-shell particles, allowing simple material separation *via* an external magnetic field (**Scheme 1**). To further ensure the reusability of the magnetic MOF composites, gentle material regeneration protocols will be established.[4] Our innovative approach could revolutionize the current extraction of resources from water.



Scheme 1: Selective resource recovery with superparamagnetic Fe_3O_4-MOF composites from water sources.

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TRANSITION METAL-SILOXANE CLUSTER-BASED METAL-ORGANIC FRAMEWORKS FOR GREENHOUSE GAS CAPTURE

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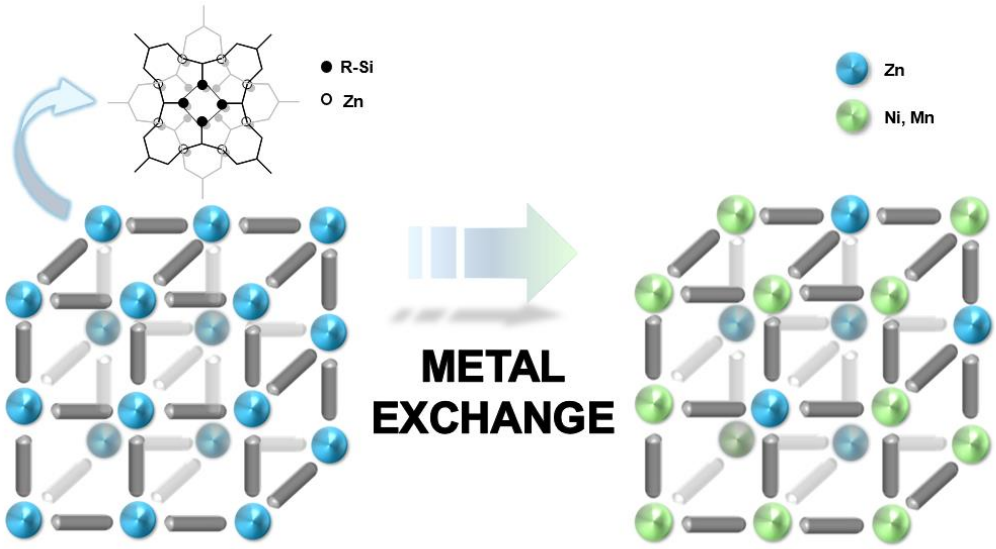
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Keywords: *Metal-organic framework, Metal-siloxane cluster, Post-synthetic metal exchange, Composition control, Structural and chemical properties, Property variations*

Metal-organic frameworks (MOFs) are a class of crystalline materials composed of metal ions or clusters coordinated to organic ligands, forming extended porous networks. They have attracted significant attention due to their high porosity and tunable structures, enabling diverse applications. While conventional MOFs are primarily constructed using metal-oxygen or metal-carboxylate linkages, metal-siloxane-based MOFs remain relatively underexplored despite their exceptional structural and thermal stability.

In this study, we successfully synthesized metal-siloxane MOFs via post-synthetic metal exchange (PSME) using transition metals, with SiMOF-11[1] as a structural platform. Comprehensive characterization confirmed that the atomic composition of the MOFs could be precisely tuned while preserving the original framework. This compositional tuning was achieved by varying synthesis parameters such as temperature, reaction time, and metal precursor equivalents. X-ray photoelectron spectroscopy (XPS) and X-ray powder diffraction (XRPD) analyses verified the successful incorporation of exchanged metals into the framework. Thermogravimetric analysis (TGA) demonstrated the frameworks retained high thermal stability following metal exchange, further confirming structural preservation. Additionally, sorption measurements revealed enhanced gas separation and storage capabilities. Following successful characterization, the synthesized MOFs were employed for the capture of greenhouse gases.

In conclusion, transition metal-siloxane MOFs offer a promising strategy for designing tunable frameworks distinct from conventional MOFs. The successful application of PSME in these systems highlights their potential for precise compositional control, paving the way for advanced applications in gas storage and separation technologies. Detailed results will be discussed in this presentation.



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UNRAVELING THE RELATIONSHIP BETWEEN DEFECT TYPE AND CATALYSIS IN UIO-66

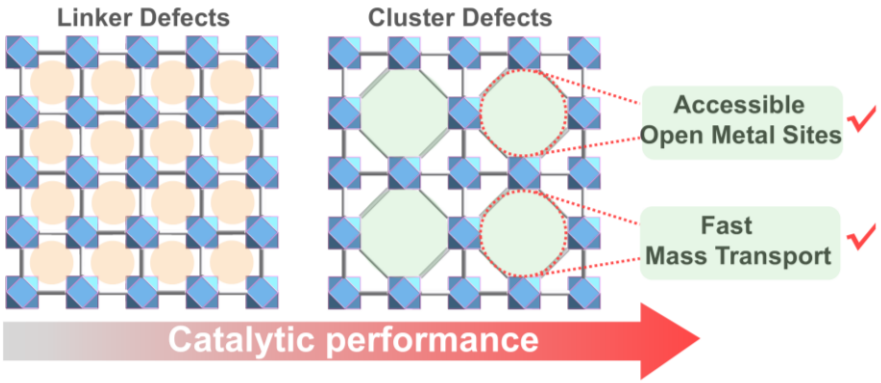
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Keywords: *Catalysis, Cluster defects, Defect types, Linker defects, MOFs …*

Defects are inherently present in solid crystalline materials and play a crucial role in determining and influencing their properties.[1] As a subclass of crystalline porous materials, metal-organic frameworks (MOFs) are similarly affected by the presence of defects.[2-4] However, the coexistence of various types of defects in MOFs, combined with the challenges associated with their quantitative characterization, complicates the establishment of clear structure–activity relationships in catalysis.[5] In this study, we employed a controlled defect-engineering strategy to synthesize UiO-66 with distinct and exclusive defect types: linker defects and cluster defects. Through a series of organic catalytic tests, we found that cluster defects predominantly enhance catalytic activity. These defects promote the formation of accessible open metal sites and larger pores, which alleviate mass transfer limitations and thereby improve catalytic performance. In contrast, although linker defects also increase the number of open metal sites, the accompanying rise in mass transfer resistance limits their catalytic benefits. This work delineates the distinct catalytic roles of different defect types and highlights the critical importance of both the accessibility of active sites and efficient mass transport in MOF-based catalysis. These findings offer valuable insights for the rational design of MOFs with targeted functionalities.



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CATALYTIC TANDEM REACTIONS IN MESOPOROUS METAL-ORGANIC FRAMEWORKS

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Keywords: *MIL-100, MIL-101, photocatalysis, post-synthetic modification*

Hydrogen from water splitting can be a key technology for the transition to a decarbonized energy system. However, the oxygen evolution reaction (OER) requires a four-electron transfer leading to high overpotentials and sluggish reaction rates. A good alternative would be to replace it with thermodynamically more favorable organic oxidation reactions like in the oxidation of alcohols to aldehydes or amines to amides in order to obtain high-value added chemicals.[1] In tandem reactions these aldehydes or amides can be further converted for example into chiral compounds. A sustainable possibility to increase the efficiency of oxidation reactions is photocatalysis or photoelectrocatalysis which is a combination of photocatalytic and electrolytic processes.[2] Metal-organic frameworks (MOFs) have been widely studied as flexible catalytic platforms in photocatalysis and photoelectrocatalysis of several reactions including oxidation reactions.[3] If more than one catalytic active site is incorporated into the MOF tandem reactions are possible.[4]

The present work investigates the integration of a chiral proline catalyst into the backbone of MIL-101 through post-synthetic modification (PSM) via Steglich reaction and click reaction. This enables a tandem reaction where photocatalytic oxidation is performed at the coordinatively unsaturated sites (CUS) of the MOF, and a chiral product is obtained through the following reaction at the proline catalyst connected to the terephthalic acid linker.

The used MOFs have been thoroughly investigated using PXRD, Ar physisorption and diffuse reflectance UV-VIS spectroscopy as well as UPS to investigate the band gap. After PSM the resulting MOFs were tested for crystallinity, yield of PSM using liquid-state NMR spectroscopy and influence of modifications on bandgap width. The suitability of different (mixed-metal) MIL-100 and MIL-101 species as photocatalysts for the anaerobic photocatalytic oxidation of alcohols to aldehydes using varying sacrificial agents in different organic solvents was examined. MIL-100 was introduced as a second photocatalyst to study the photocatalytic oxidation process. Mixed-metal MOFs were introduced due to enhanced stability and the possibility of bandgap tuning. The catalysis reaction was performed in a self-constructed apparatus consisting out of a quartz-glass slurry reactor and a 300 W Xe arc lamp with infrared filter for illumination. Further, a daylight filter was used in the photocatalytic experiments. The products were quantified using ethanol as a secondary standard in ^{1}H-liquid-state NMR spectroscopy. In addition, solid-state NMR spectroscopic experiments were conducted to examine the adsorption behavior of reagents to the CUS of the MOFs and get insights into the photocatalytic mechanism.

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MODULATED SYNTHESIS OF A NEW TITANIUM-BASED METAL-ORGANIC FRAMEWORK WITH PHOTOCATALYTIC ACTIVITY UNDER RED LIGHT

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Keywords: *modulator, titanium, layered structure, 1D-micropores, visible irradiation*

Titanium-based metal-organic frameworks (MOFs) are particularly interesting due to their redox-active behavior under light illumination and high hydrolytic stability.[1] The strong Ti-O bonds that commend them stable, however, also present a significant challenge for the controlled synthesis of crystalline materials, accompanied by the rapid hydrolysis of Ti-precursors and often resulting in amorphous materials. Hence, various strategies have been employed to decelerate reaction kinetics, such as the implementation of less reactive Ti-precursors, pre-formed Ti-oxo clusters or highly complexing modulators.[2-4]

Herein, we demonstrate how a previously unexplored modulator enables the formation of a new crystalline MOF phase, composed of titanium and a naturally occurring, strongly coordinating linker. Its structure is determined by 3D electron diffraction and further studied in depth by iDPC-STEM, high-resolution synchrotron XRD and EXAFS, revealing a layered honeycomb-like arrangement with 1D micropores. The material's adsorption properties correlate well with the expected structural model, showing high N_2, H_2O and CO_2 uptakes. Furthermore, its opto-electronic properties enable the use of red light (600 ± 40 nm) for exciton generation. Finally, we show that this material exhibits potential as a photocatalyst for the degradation of organic dye molecules, owing to its high porosity and extended visible light absorption. We also provide mechanistic insights into the charge transfer process, supported by electrochemical, in-situ EPR and theoretical calculations.

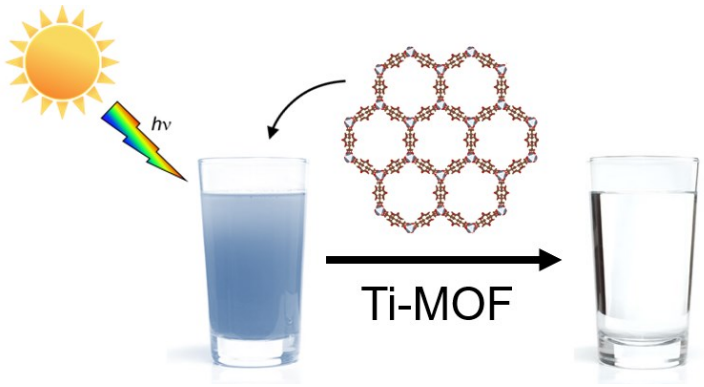


Figure 1 | The new layered, honeycomb-like titanium-based MOF shows efficient methylene blue adsorption and degradation under extended visible light irradiation (600 ± 40 nm).

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H^+-CONDUCTIVE COORDINATION POLYMER GLASS AS A MATERIAL FOR MEMBRANE ELECTRODE ASSEMBLY FOR CO_2 REDUCTION

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Keywords: Heterogeneous catalyst, Electrocatalysis, Carbon dioxide, Vitrification

CP/MOF glasses have been of interest as a new class of amorphous materials. They are promising for applications due to their unique properties, such as wide mechanical properties and high formability. $[Zn(HPO_4)(H_2PO_4)_2](H_2Im)_2$ (**Zn-1**, H_2Im = imidazolium cation) exhibits higher proton (H^+)-conductivity in the glass state (**Zn-1g**) than in the crystalline state above 100°C. This is because of low internal resistance due to the molecular dynamics and grain-boundary-free structure. **Zn-1g** is also available as a heterogeneous catalyst when metal complexes or nanoparticles are immobilized in the melt-quench vitrification process.[1]

CO_2 reduction reaction above 100°C has an advantage for the kinetic and thermodynamic viewpoints, but the design of H^+-conductive membranes working above 100°C is a challenge. Herein, we used **Zn-1g** to construct a membrane electrode assembly (MEA) for gaseous CO_2 reduction. The catalyst layer of the MEA facilitates the CO_2 reduction reaction with H^+ supplied from the conductive membrane. CO_2 and electrons (e^-) are supplied from the gas-diffusion electrode, which consists of porous carbon. We fabricated the MEA consisting of conductive membrane, catalyst layer, and gas-diffusion electrode with good compatibility by hand-pressing and annealing on the hot plate (Figure 1A).

We fabricated the **Zn-1g** conductive membrane by melting **Zn-1** followed by cooling it to room temperature.[2] We then prepared the catalyst layer by combining **Zn-1g**, carbon black, and gold nanoparticles (AuNPs). The MEA shows CO_2 reduction ability by applying negative potential. High activity was observed by heating the MEA at 120°C, where the MEA, consisting of a conventional H^+-conductive polymer membrane, decomposed (Figure 1B). Experiments with $^{13}CO_2$ indicated that CO formed in the electrocatalytic reduction is originated from CO_2 gas.

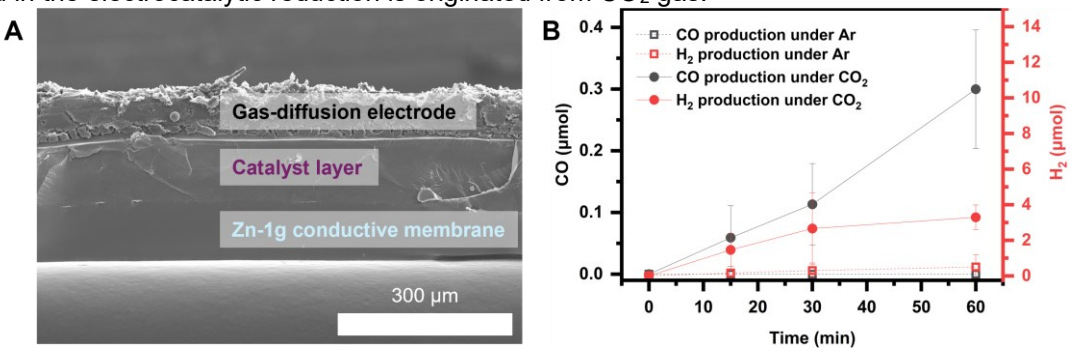


Figure 1. (A) Cross-section SEM image of MEA consisting of **Zn-1g** conductive membrane, catalyst layer, and gas diffusion electrode. (B) Yield of CO and H_2 in the electrocatalytic reduction of gaseous CO_2 using MEA at 120°C. The control experiment was carried out under Ar.

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CE-MOFS - FAST SYNTHESIS AND CHARACTERIZATION

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Keywords: Cerium, MOF-808, Ce-MOF-808, porous materials, coordination polymers, shaking, stirring, room temperature, RT, reagent sequence, trimesic acid

Enormous efforts have been devoted to the development of effective photocatalytic materials, especially visible-light responsive photocatalysts, for CO_2 reduction. In this respect, metal−organic frameworks (MOFs) are newly emerged but promising photocatalysts for CO2 photoreduction, mainly owing to their structural amenability to be designed with specific functionality [1]. Cerium-based MOFs have attracted much growing research attention due to their unique and attractive properties, such as Lewis acidity, structural and isoreticular chemistry [2], chemical stability in aqueous environments [3], and redox activity. Room temperature (RT) synthesis seems promising, and at the same time, further challenging. Compared with solvothermal and hydrothermal synthesis, the stirring and shaking route is low-cost and environmentally friendly. Hence, we successfully synthesized cerium benzene tricarboxylate (Ce-MOF-808) MOF using a simple, cost-effective, and green strategy for further application as a catalyst. Ce-MOF-808 is thermally stable up to 400˚C under air flow, and 650˚C under nitrogen flow. Significant pore width and volume are 1.410 - 2.272 nm, and 0.165 - 0.428 cm^3g^{-1}, respectively. The PXRD patterns of the synthesized materials confirmed the formation of highly crystalline MOFs. The diffraction peak was assigned to the (111), (311), and (222) planes. Moreover, Ce-MOF-808 exhibits octahedral morphology with a size is about 400 nm. MP-AES quantified the concentration of cerium in a sample around 43,3%. Besides, this work provides the order of reagent sequences during the synthesis that leads to the direct influence on the formation of Ce-MOF-808.

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WEAKLY COORDINATING ANIONIC NETWORKS AS A PLATFORM FOR CATALYSIS

Yasmin Okhassova,[a] Veit Dippold[a] and Arne Thomas[a]

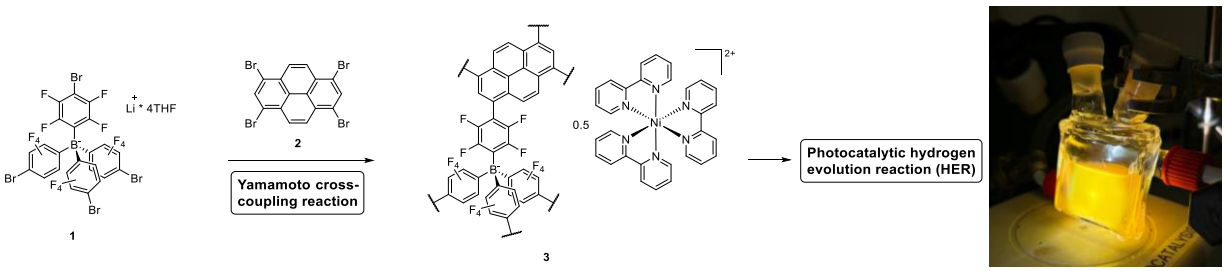
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Keywords: *borate network, weakly coordinating anions, heterogeneous catalysis, photocatalysis*

Microporous polymers networks (MPNs) are an emerging class of materials with promising applications in energy conversion, catalysis, gas storage, and gas separation.[1] In general, such networks are of an amorphous nature and exhibit high permanent surface areas from several hundred up to thousands of m^2 g^{-1}.[2] MPNs are composed of covalently connected purely organic building blocks enabling different coupling reactions and functionalization to obtain desired physical and chemical properties. If carbon atoms (group 14) are replaced by boron (group 13), an anionic charge is formed, which creates building blocks also called “weakly coordinating anions” (WCA). As an example, the polymerization of functionalized tetraphenylborate derivatives into an organic polymer network yields a WCA microporous network. Cationic molecular complexes can be embedded in such anionic network by simple ion exchange, making them viable for catalytic reactions. As a proof of concept, the cationic complex of the Crabtree’s catalyst was introduced to prepare a solid material for the gas phase hydrogenation of ethylene to ethane at room temperature.[3]

Another example of a WCA application is photocatalytic water splitting to hydrogen. By replacing the co-monomer to a light-absorbing species, for example, pyrene derivative **2**, the obtained polymer is currently being investigated for photocatalytic hydrogen evolution (HER), which showed up to 250 µmol h^{-1} g^{-1} of hydrogen production after 5 hours without any additional co-catalyst.



Scheme 1. Representation of a Yamamoto cross-coupling reaction of borate **1** and pyrene derivative **2**, and consequent test of the obtained material for the hydrogen evolution reaction (HER).

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CRUDE ENZYME EXTRACTS FOR BIOCATALYST ENTRAPMENT IN METAL-ORGANIC FRAMEWORKS

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Keywords: *MOFs, crude enzyme extract, entrapment, biocomposites, biocatalysis.*

To bolster the applicability of enzymes as catalysts, it is imperative not only to address their inherent fragility, particularly when used under harsh organic-synthetic reaction conditions, but also to mitigate deactivation during purification and enable applicability in a broad range of organic-synthetic transformations.[1] Currently, the process of purification of crude enzyme extracts and subsequent heterogenization to obtain immobilized biocatalysts often leads to partial enzyme deactivation and represents, at least in part, a resource-intensive process, which is driving up the overall production efforts. To tackle both the enzyme fragility and deactivation during purification and immobilization, we propose the direct use of crude enzyme extracts obtained from cell lysis instead of pure enzymes and their entrapment in metal-organic framework (MOF) structures. We focus on three enzyme types with varying sensitivities: aldoxime dehydratase, imine reductase and lipase. Besides, the current research on enzyme entrapment in MOFs has not systematically considered the influence of different metal ions on enzyme activity when selecting MOF types for entrapment. Therefore, we evaluate the effects of different metal sources (Al, Fe, Co, Ni, Cu, Zn), their oxidation state and counterions, as well as MOF synthesis parameters on enzyme stability and activity during their entrapment in the MOF structures. Based on this, we optimize protocols for enzyme entrapment in Fe-MIL-88A, Fe-MIL-100, Zn-MOF-74, Zn-ZIF-8 and develop a fast-aqueous room temperature synthesis of Al-MIL-53 (Figure 1).[2] Investigation of the biocatalytic performance of the enzyme@MOF biocomposites suggests that enzyme entrapment in MOFs using crude enzyme extracts can effectively maintain enzyme activity and stability in various catalytic reactions, offering a perspective for an efficient pathway for industrial applications.

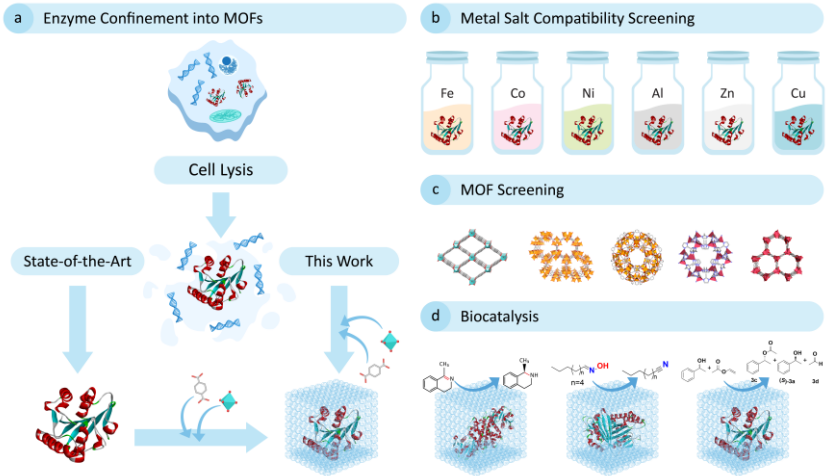


Figure 1. State-of-the-art and overview of the work.

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ACCELERATED DEVELOPMENT OF Cat@MOF CATALYST FOR INDUSTRIALLY RELEVANT HYDROGENATIONS

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Keywords: *MOF, hydrogenation, catalysis, high-throughput*

Homogeneous catalysts are renowned for their high activity and accessible active sites but are often limited by difficult separation and poor recyclability. In contrast, heterogeneous catalysts offer excellent stability and reusability but typically suffer from lower activity, limited mass transfer, and the need for harsher reaction conditions. To address these limitations, a promising strategy involves the immobilization of homogeneous species—such as organometallic complexes—within porous supports. This "heterogenization" approach seeks to integrate the strengths of both catalytic regimes. The resulting hybrid catalysts demonstrate enhanced activity, improved recyclability, and reduced deactivation, offering a compelling pathway toward more efficient and sustainable catalytic systems.

Metal-Organic Frameworks (MOFs), constructed from metal clusters and organic linkers, are highly porous materials that have emerged as attractive solid supports for catalysis. Their large surface area, well-defined porosity, and exceptional tunability make them ideal platforms for hybrid catalyst design. Traditional methods for incorporating catalytic species into MOFs often rely on covalent attachment. This can involve multiple synthetic steps as well as adjustment of the local coordination site of the metal catalyst which may be detrimental to its overall catalytic properties.[1] In this work, we present a simple, one-step approach to immobilize cationic homogeneous catalysts (Cat) into anionic MOFs via cation exchange. The positively charged catalysts are effectively confined within the MOF pores through electrostatic interactions, ensuring uniform dispersion and minimal leaching. This modular "Cat@MOF" strategy allows independent variation of both MOF scaffolds and catalyst species, facilitating high-throughput generation of diverse catalytic systems for rapid screening and optimization. [1]

Our initial study explores encapsulating cationic Ni(II), Cu(I)(II), Co(II), Fe(II), Pd(II), and Rh(I) complexes with weakly coordinated anions into sulfonated UiO-66 and MIL-101. The resulting Cat@MOFs were thoroughly characterized using Powder X-ray diffraction (PXRD), inductively coupled plasma mass spectrometry (ICP-MS) and gas uptake measurements. Recent work has focused on screening their catalytic performance in the transfer hydrogenation of methyl levulinate (ML) and Levulinic acid (LA) to Gamma valerolactone (GVL) [2,3] and other lignocellulosic biomass transformations. Later into the project, the hydrogenation of CO_2 to methanol will be explored, in mitigating the impact of fossil fuel consumption.

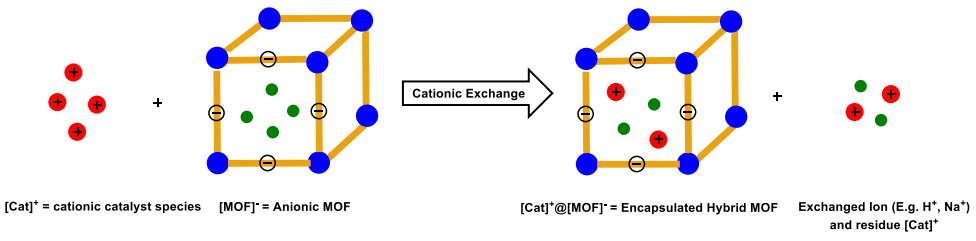


Figure 1 Encapsulation of [Cat] in MOF through one-step cation exchange

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STRUCTURAL RECONSTRUCTION OF A COBALT-BASED METAL−ORGANIC FRAMEWORK DURING THE ELECTROCHEMICAL HYDROGEN EVOLUTION REACTION

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Keyword- Metal organic framework (MOF), Hydrogen evolution, reaction (HER),

Carbon-based fossil fuels have long been essential for human survival and remain the primary source of energy worldwide. However, with the rapid industrialization and population growth, we are facing an energy crisis and adverse environmental pollution due to the escalating use of these fossil fuels.[1–3] To address this pressing challenge, it is crucial to transition from a fossil-fuel-based energy system to sustainable alternatives.[4,5] Herein we report the synthesis, characterization, and the fate of a newly designed cobalt-based MOF (**CoL1-MOF**) for the hydrogen evolution reaction (HER) in 1 M aqueous KOH. The **CoL1-MOF** exhibited a significant overpotential of 538 mV to reach a current density of 10 mA/cm², while the bare GCE showed negligible activity. Tafel analysis revealed that the HER using this **CoL1-MOF** follows the Volmer–Heyrovsky mechanism. Post-electrolysis PXRD analysis confirmed the formation of metal oxide and hydroxide phases, accompanied by morphological changes. Remarkably, the post-electrolysis **CoL1-MOF** demonstrated enhanced HER performance with a reduction in overpotential (440 mV). Overall, this study demonstrates the cost-effective synthesis of 1D transition metal-based MOFs and their potential for sustainable hydrogen production, offering a promising solution to the energy crisis. Salient features of this study will be presented.

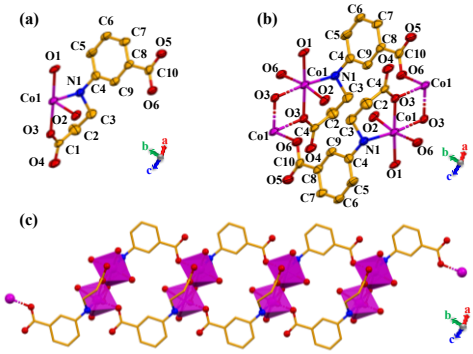


Figure 1: (a) Coordination geometry of **CoL1-MOF**, and **(b)** crystal packing diagram of **CoL1-MOF**. H atoms are excluded for clarity.

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STRUCTURAL ELUCIDATION OF A NEW POLYMORPH OF Cd(II) MOF FEATURING HEXAKIS (4-CARBOXYLATOPHENOXY) CYCLOTRIPHOSPHAZENE: TOWARD MULTIFUNCTIONAL ENVIRONMENTAL APPLICATIONS

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Keywords: *Metal–Organic Framework, NACs Sensing, Photocatalytic Dye Degradation.*

The ongoing pursuit of advanced multifunctional materials has brought metal–organic frameworks (MOFs) to the forefront of materials science research. Thanks to their inherent structural tunability, exceptionally high surface areas, and diverse chemical functionalities, MOFs have emerged as promising platforms for a broad spectrum of applications, including catalysis, sensing, and gas separation.[1] Recently, growing interest has been directed toward their implementation in environmental technologies, where their capabilities in chemical sensing, photocatalysis, and pollutant removal have been intensively explored.[2]

We report the synthesis of a new polymorph of a Cd(II)-based MOF constructed from a cyclotriphosphazene-derived hexacarboxylate linker, representing the fourth known structural variant alongside the previously reported VEYSAW[3], LENGES[4], and LENGAO[4] frameworks. The crystallographic structure of the newly obtained MOF was determined via single crystal X-ray diffraction, and its phase purity and composition were further validated by PXRD, FT-IR, TGA, and SEM. This work focuses on evaluating the dual-functional performance of the MOF in two key areas: (i) the selective luminescent sensing of nitroaromatic compounds, and (ii) the photocatalytic degradation of organic dyes under light irradiation. These studies aim to underscore the framework's potential in environmental remediation, thereby linking its unique structural characteristics to its practical functional applications.

CRYSTAL PARAMETERS	VEYSAW	LENGAO	LENGES	A New Cd(II) MOF
Chemical formula	$C_{42}H_{34}Cd_3N_3O_{23}P_3$	$C_{42}H_{38}O_{26}P_3N_3Cd_3$	$C_{42}H_{28}O_{26}P_3N_3Cd_2$	$C_{42}H_{32}Cd_3N_3O_{23}P_3$
Formula mass	1378.86	1414.92	1212.43	1376.81
Crystal system	Orthorhombic	Monoclinic	Trigonal	Monoclinic
a/Å	13.501(3)	16.783(18)	17.367(3)	17.9017(16)
b/Å	11.130(2)	43.410(5)	17.367(3)	7.4875(7)
c/Å	34.928(7)	12.158(13)	11.346(2)	18.0224(16)
α/°	90	90	90	90
β/°	90	93.688(2)	90	107.862(3)
γ/°	90	90	120	90
Unit cell volume/Å^3	5248.5(18)	8839.6(16)	2970.2(9)	2299.3(4)
Space group	*Pna*2$_1$	*P*2$_1$*c*	*P*-3*c*1	*Pc*
Z	4	4	2	2
Final R$_1$ values (I > 2σ(I))	0.0723	0.1117	0.0800	0.0639
Final R$_1$ values (all data)	0.0779	0.1425	0.1204	0.0850

Figure 1. Crystallographic data for the polymorphic forms of Cd(II)-MOFs.

This work was supported by Gebze Technical University Scientific Research Project under 2024-A-113-05 project code.

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MULTIFUNCTIONAL Zn(II) MOF BASED ON A ROBUST CYCLOPHOSPHAZENE LINKER: SENSING AND PHOTOCATALYTIC APPLICATIONS

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Keywords: *Metal–Organic Framework, Nitroaromatic Sensing, Photocatalytic Dye Degradation.*

The growing demand for multifunctional materials to address environmental pollution has spurred the development of porous structures that integrate both sensing and photocatalytic capabilities.[1] Among these, metal–organic frameworks (MOFs) stand out as highly promising candidates owing to their tunable architectures, large surface areas, and adaptable coordination environments. These features empower MOFs to function effectively as both sensors and photocatalysts, enabling the detection of hazardous substances and the degradation of pollutants under light irradiation.[2]

In this study, we report a novel anionic Zn(II) MOF that integrates both sensing and photocatalytic functionalities within a single material. MOF was synthesized via a spontaneous self-assembly process employing a cyclotriphosphazene-derived hexacarboxylate ligand in combination with a flexible imidazole-based linker. The resulting framework was thoroughly characterized using FT-IR, UV-Vis diffuse reflectance spectroscopy, single and powder X-ray diffraction, scanning electron microscopy, and thermogravimetric analysis. Structural analysis reveals that the MOF consists of corner-sharing trinuclear Zn_3 clusters, which function simultaneously as secondary building units (SBUs) and inorganic building units (IBUs), resulting in a robust 3D network. The multifunctional performance of the Zn(II) MOF was assessed through (i) its selective and sensitive detection of nitroaromatic compounds—particularly hydroxy-substituted derivatives—and (ii) its photocatalytic degradation of organic dyes under light irradiation. The anionic nature of the framework is expected to enhance electrostatic interactions with cationic pollutants, while its porous architecture facilitates guest molecule diffusion and accessibility to active sites. Taken together, these features position the Zn(II) MOF as a rare and efficient dual-function material with significant potential for environmental sensing and pollutant remediation applications.

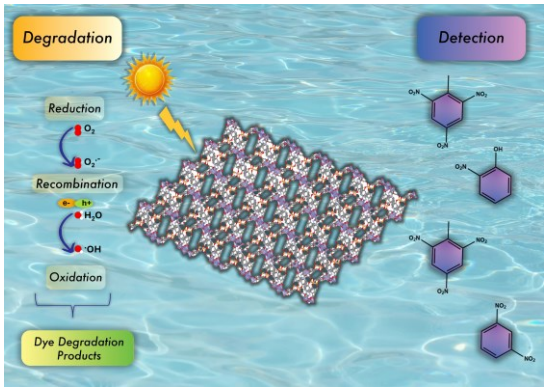


Figure 1. Zn(II) MOF for dye degradation and nitroaromatic sensing.

This work was supported by Gebze Technical University Scientific Research Project under 2024-A 113-05 project code.

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DEFECT ENGINEERING IN UiO-66-NH_2 FRAMEWORKS VIA GREEN SOLVENTS: ENHANCED PHOTOCATALYTIC DEGRADATION OF ORGANIC POLLUTANTS

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Keywords: *Defect engineering MOFs, Green solvent synthesis, Photocatalysis, Organic pollutant degradation*

Metal-organic frameworks (MOFs) have emerged as promising materials for environmental remediation due to their tunable structural and electronic properties, particularly in photocatalytic degradation of persistent organic pollutants[1,2]. Defect engineering has proven to be a powerful approach to enhance the catalytic performance of MOFs[3]. This study systematically investigates defect formation in UiO-66-NH_2 synthesized using environmentally friendly solvents, aiming at optimizing photocatalytic performance. UiO-66-NH_2 was initially synthesized using conventional solvothermal methods in dimethylformamide, both with and without formic acid as a modulator. Subsequently, greener solvents such as water and ethanol were employed under various reaction temperatures to explore their influence on defect generation.

Structural characterization, including powder X-ray diffraction, thermogravimetric analysis, nuclear magnetic resonance, and Brunauer–Emmett–Teller surface area measurements, revealed significant modulation of defect concentrations driven by solvent type and reaction temperature. Photocatalytic performance evaluation focused on diclofenac degradation under visible-light irradiation, demonstrated that defect-rich UiO-66-NH_2 exhibited markedly superior activity. Enhanced performance is attributed to defects acting as reactive sites that facilitate improved charge carrier dynamics and extend light absorption, promoting efficient charge separation and transfer.

This work highlights the critical role of controlled defect engineering through green synthetic routes, presenting a sustainable pathway to enhance photocatalytic efficiency for organic pollutant degradation and offering promising applications in environmental remediation.

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A 3D Cu(II) METAL–ORGANIC FRAMEWORK FEATURING A CYCLOPHOSPHAZENE LIGAND FOR VISIBLE-LIGHT-DRIVEN DYE DEGRADATION AND SELECTIVE CO_2 CAPTURE

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Keywords: *Metal-organic framework, Cyclophosphazene, Visible light photocatalysis, CO_2 separation*

The growing contamination of water resources by industrial dyes and organic pollutants, coupled with the rising atmospheric concentration of CO_2, has highlighted the critical need for integrated, efficient, and sustainable remediation strategies. Metal–organic frameworks (MOFs) possess distinct advantages such as high surface areas, tunable pore architectures, and remarkable chemical stability. These attributes render MOFs highly promising candidates for simultaneous applications in photocatalytic degradation of organic contaminants and selective gas adsorption and separation processes.[1,2]

In this study, we present a novel 3D Cu(II)-based MOF (**PCP-7**), constructed from a cyclotriphosphazene-derived tetracarboxylate ligand. The resulting framework features a 3D architecture composed of $\{Cu_2(COO)_4\}$ paddlewheel-type SBUs and exhibits semiconductive behavior with an optical band gap of 1.60 eV. Under visible-light irradiation, **PCP-7** achieves degradation efficiencies exceeding 90% for MB, RhB, and MO, while maintaining high recyclability. Mechanistic investigations identify $O_2^{\bullet-}$ as the predominant reactive species responsible for photocatalysis. Ideal Adsorbed Solution Theory calculations indicate that **PCP-7** exhibits excellent gas separation performance, with CO_2/N_2 selectivity reaching 41.9 at 298 K and approaching infinity at 323 K. Additionally, a CO_2/CH_4 selectivity of 29.4 was observed at 273 K, emphasizing the framework's strong potential for energy-efficient and selective CO_2 capture.

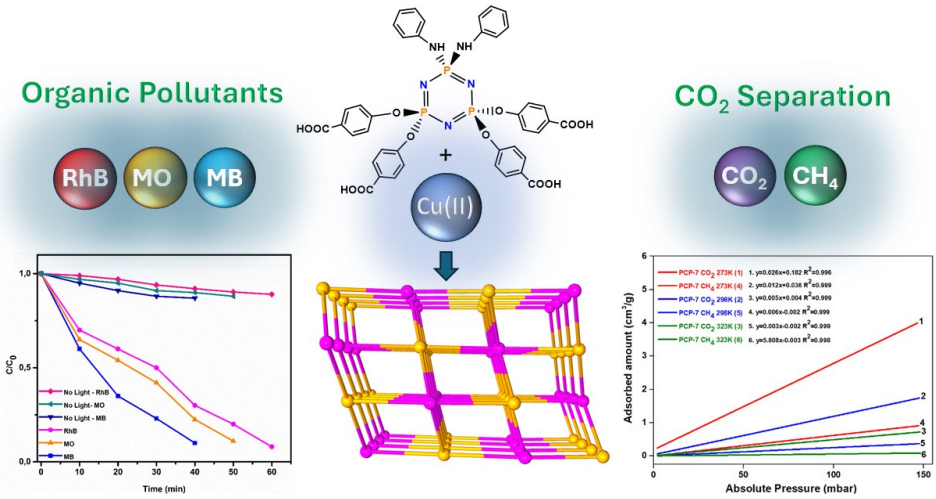


Figure 1. Structure and dual functionality of **PCP-7**: visible-light-driven dye degradation and selective CO_2 adsorption through its 3D porous Cu(II)-based MOF.

Y.Z. acknowledges a support from Turkish Academy of Sciences, Outstanding Young Scientists Awards (TÜBA-GEBİP 2021).

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THE USE OF HALF-SALEN METALLO COMPLEXES IN MIL-125(TI)-NH_2 FOR HYDROGEN EVOLUTION REACTIONS (HER)

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Keywords: *Synthesis, Titanium, Metal-Organic Frameworks, modification, photocatalysis, hydrogen evolution*

The growing demand for hydrogen gas as a sustainable energy carrier has positioned it as a focal point in the global transition toward renewable energy, particularly within the industrial sector. Currently, the predominant methods of hydrogen production rely heavily on fossil fuels—approximately 48% from natural gas, 30% from oil, with the remainder derived from coal and electrolysis.[1] In pursuit of greener alternatives, metal-organic frameworks (MOFs) have garnered significant attention due to their tuneable porosity and photocatalytic potential. However, despite promising advances, MOF-based systems face critical challenges, including low photon utilization efficiency and high electron–hole recombination rates, which limit their competitiveness with conventional hydrogen production technologies.[2-4]

In this work, four different half-salen ligands were incorporated into the organic linker of MIL-125(Ti)-NH_2 MOF by post-synthetic modification. This was followed by metalation with transition metal ions including iron (Fe), nickel (Ni), and bismuth (Bi) onto these MOFs. We examined the morphological characteristics of the obtained MOFs and showed a way to control the morphology of these MOFs. The modified MOFs showed preferential greenhouse gas sorption and separation properties, demonstrated by the high uptake of SF_6 over N_2, with SF_6 capacity of over 3.5 mmol/g at 298 K (1 bar). Their photocatalytic performance reactions such as CO_2 reduction and hydrogen evolution reactions were also evaluated.

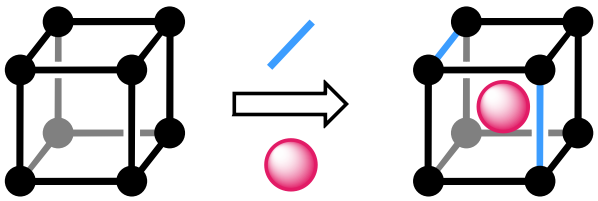


Figure 1. Schematic representation of post-synthetic modification and metal incorporation.

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COVALENT ORGANIC FRAMEWORKS AS NANO-RESERVOIR FOR ROOM TEMPERATURE RNA STORAGE

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Keywords: *Covalent organic framework, Biomolecule Storage, RNA, RNA Protection*

The emerging role of Ribonucleic acids (RNAs) for therapeutic and diagnostic application is fascinating.[1] However, RNAs are extremely labile under ambient conditions and typically need to be stored in cryogenic conditions (-20 °C to -80 °C). Hence, storage, stabilization, and transportation of RNA under ambient conditions have been an arduous task and remain an unsolved problem.[2] In this work, a guanidinium-based ionic covalent organic framework (COF), TTG_{Cl} with nanotubular morphology, was synthesized and used as nano-reservoirs for room-temperature storage of RNA for up to seven weeks.[3] To understand the role of the nanotubular morphology and chemical nature of TTG_{Cl} in stabilizing the RNA structure and for comparison purposes, a neutral COF, TMT-TT, is synthesized and studied. Further, density functional theory (DFT) studies confirmed non-covalent interaction between the COFs and the RNA nucleobases, facilitating reversible storage of RNA. RNA loaded in COFs was found to be resistant to enzymatic degradation when treated with RNase. Gel electrophoresis and sequencing confirmed the structural integrity of the recovered RNAs and their further processibility.

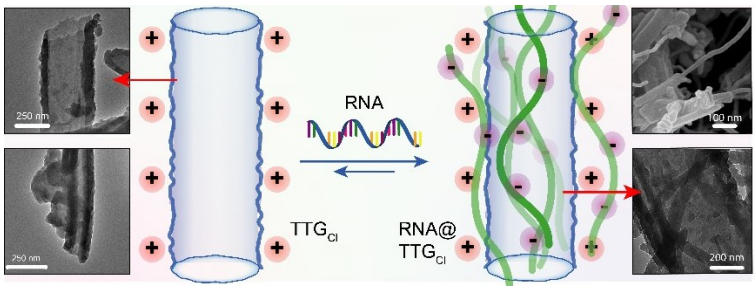


Figure 1: Schematic representation of RNA loading in ionic TTG_{Cl} COF.

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RATIONAL FUNCTIONALIZATION OF A Zr-BASED MOF WITH THE SUGAR MANNOSE FOR ENHANCED STABILITY AND TARGETED DELIVERY

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Keywords: *PCN-222, metal-organic frameworks, drug delivery, ligand functionalization, targeted release.*

Zirconium-based MOFs, particularly porphyrin-based MOFs such as PCN-222, have attracted significant attention for biomedical applications due to their regular porosity, tuneable pore size, versatile structures, and exceptional thermal stability. However, several limitations still hinder their transition to clinical use. These include unpredictable in vivo behavior, scale-up challenges, such as poor reproducibility and the use of large amounts of toxic solvents such as DMF, limited stability in physiological fluids (e.g., PBS), and the lack of rational design strategies for particle functionalization-especially when incorporating carbohydrates. According to current literature, most MOFs are functionalized with carbohydrates using basic, non-strategic approaches. Polysaccharides generally exhibit limited targeting capabilities, while monosaccharides are typically not chemically modified in a way that rationally enhances their affinity for biological targets, beyond minimal changes required for attachment to the MOF. Furthermore, specific spacers are rarely employed between the monosaccharide and the MOF, which further compromises targeting efficiency.[1]

In this work, as shown in *Figure 1*, we investigated the preparation of PCN-222 functionalized with a monosaccharide using a natural and abundant ligand. Building on our previous methodology, we successfully synthesized nano-sized PCN-222 functionalized with D-mannose, employing natural lecithin as the functionalizing ligand and DMSO as "greener" solvent. Specifically, we exploited the phosphate group of lecithin as an anchoring moiety to coordinate with the Zr(IV) of PCN-222. Cysteine was then conjugated to lecithin via a thiol–ene reaction, providing a free amino group, which was subsequently used to attach D-mannose.[2] To enable targeted and biocompatible drug delivery, the mannose-functionalized MOF was loaded with a combination of hydrophobic agents, including Nile Red (as a fluorescent model compound) and Docetaxel. We evaluated the encapsulation efficiency and loading capacity of both compounds, along with their release profiles under physiological conditions (pH 7.4, 37 °C in PBS). Furthermore, preliminary in vitro studies were conducted to assess the biocompatibility and cytotoxicity of the formulated system.

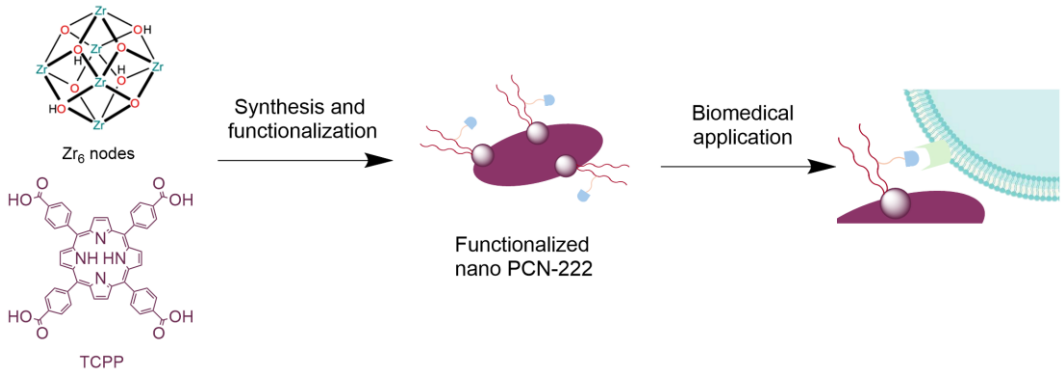


Figure 1. Schematic summary of the work aim.

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Structure-Guided Design of Smart Hybrid GlycoMOF Nanoplatforms *via* Scalable Multigram Synthesis for Biomedical Applications

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Keywords: *GlycoMOFs (Carbohydrate-functionalized Metal–Organic Frameworks); Targeted Drug Delivery; Multivalent Nanoplatforms; Process Intensification; Green Chemistry*

Glycoclusters—synthetic architectures displaying multiple carbohydrate moieties on a central scaffold—are promising therapeutic tools for cancer and infectious diseases. Among the most advanced platforms are carbohydrate-functionalized metal–organic frameworks (Carb-MOFs), which synergistically integrate the chemical versatility of MOFs with the biological specificity of carbohydrates.[1] These hybrid nanomaterials offer enhanced bioavailability, targeted uptake, controlled drug release, and improved pharmacokinetics. However, their clinical translation is hindered by challenges such as limited scalability, poor control over particle morphology, the use of toxic solvents, and an incomplete understanding of GlycoMOF interactions.[2]

Existing strategies, including post-synthetic modification (PSM), encapsulation, and sugar-based framework assembly, provide variable outcomes in terms of stability and functionality. Most rely on unmodified commercial saccharides and lack rational design, with steric hindrance often limiting receptor engagement due to absent or poorly designed spacers.

To overcome these limitations and building on our interest in glycoclusters, we developed a structure-guided strategy for next-generation Carb-MOFs. Specifically, we engineered Zr-based frameworks (*e.g.*, the PCN series) functionalized with modular carbohydrate ligands comprising: (I) an anchoring group (sulfate or phosphate), (II) a well-defined spacer (PEG or lecithin), and (III) a targeting carbohydrate motif (*e.g.*, GalNAc or mannose).[3–5] This design promotes receptor-mediated endocytosis while enabling surface tunability and multivalent display. We further expanded this platform to smart, multivalent GlycoMOFs capable of simultaneously targeting multiple receptors—an approach addressing drug resistance and supporting personalized therapeutic strategies.

We also demonstrated multigram-scale synthesis of nano-sized MOFs, such as functionalized PCN-222, using continuous flow. To resolve scalability bottlenecks, we introduced a centrifugation-free purification method based on bio-derived ligands, significantly improving reproducibility and sustainability.

This integrated approach—combining rational ligand design, innovative synthesis, and green processing—positions GlycoMOFs as a versatile and scalable nanoplatform for advanced biomedical applications

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CLICK-ENABLED RECOGNITION OF CHIRAL DRUGS IN RETICULAR FRAMEWORKS

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Keywords: *chiral separations, click chemistry, post-synthetic modifications, molecular frameworks.*

Post-synthetic modifications (PSM) are one of the most versatile tools to adapt the physicochemical properties of Metal-Organic Frameworks (MOFs) to the specific requirements of a given application.[1] In this regard, tetrazine-based linkers have emerged as a powerful weapon for intrinsically tagging the desired residues into the organic backbone of MOFs through click chemistry.[2,3] This is enabled via an inverse electron-demand Diels-Alder (iEDDA) reaction, which works under very mild conditions that allow preserving the system's structural integrity while achieving a high degree of homogeneous modifications throughout the material, among many other advantages.[4]

This work is focused on the generation of confined chiral environments utilizing click reactions between novel synthetic dienophiles and tetrazine moieties within UiO-68-TZDC's structure.[5] The dienophiles' core is based on enantiopure amino acids, which enables access to the rich chemistry provided by their side chains for facilitating the active encapsulation of guests (Figure 1). This is exemplified by studying the capture of commercial racemic drugs within the pores of the modified materials. The enantioselectivity in the process is controlled by selecting the appropriate amino acid, which can be rationalized at the molecular level thanks to the specificity of the host-guest interactions. This demonstrates the potential to engineer unique adsorbents for a myriad of pharmacological applications using reticular chemistry.



Figure 1. Schematic representation of the click modification with synthetic dienophiles in reticular materials and their subsequent application on the chiral separation of drugs.

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IMPACT OF PROCESSING CONDITIONS ON METAL-ORGANIC FRAMEWORKS FOR CHEMIRESISTIVE GAS SENSORS

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Keywords: *morphology, electronic properties, chemiresistive gas sensing.*

Two-dimensional conductive metal-organic frameworks (2D MOFs) represent a promising class of materials for technological applications. The electrical conductivity arises from the delocalization of intralayer conjugation and interlayer charge transport. These materials are particularly promising for use as chemiresistive gas sensors as they offer a unique combination of advantages including high surface area, significant porosity, tunable electronic properties, and structural flexibility.[1,2]

The impact of varying synthesis and processing conditions of 2D MOFs on morphology, electronic structure and gas sensing behavior has to date not been thoroughly investigated. Herein, different synthesis environments have been conducted in this study, three morphologies (particle, rod and silk) of $Cu_3(HHTP)_2$ (where HHTP stands for 2,3,6,7,10,11-hexahydroxytriphenylene) have been fabricated in different liquids (**Figure 1**). A mixture of water, ethanol and dimethyl formamide (DMF) was utilized to fabricate particle morphology, while water and DMF were used for the synthesis of a rod morphology. Notably, sodium dodecyl sulfate was selected as a surfactant to electrostatically interact with metal ions, which can effectively suppress the vertical growth of $Cu_3(HHTP)_2$, thus facilitating the formation of silk-shaped MOF sheets. An interesting discovery regarding the transition from p-type semiconductor behavior to n-type semiconductor behavior verified by Hall effect experiments has been observed as the synthesis condition is varied. This result is consistent with NH_3 sensing tests as different changes in resistance are observed. In addition, increased surface area has been proved to be effective in lowering the lowest detection limit (LOD) in gas sensing, especially the silk-morphology of $Cu_3(HHTP)_2$ with the highest specific surface area of 145 $m^2\ g^{-1}$ delivered a minimal LOD of 0.34 ± 0.03 ppm. This work represents insights in revealing potential impacts of processing conditions on fundamental properties and sensing performance of conductive 2D MOFs.

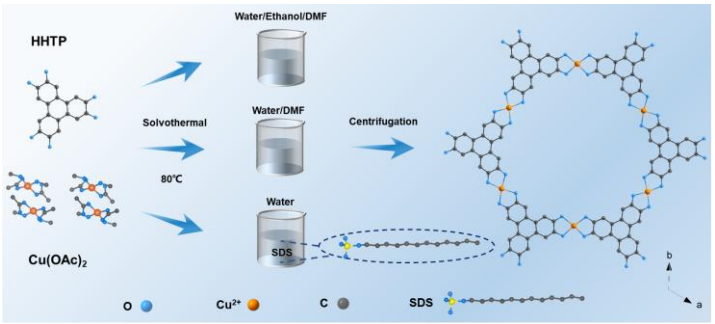


Figure 1. Schematic illustration of various synthetic conditions of 2D MOFs.

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METAL-ORGANIC FRAMEWORKS IN SUSTAINABLE APPLICATIONS

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Keywords: *Metal-organic frameworks, agrochemicals, controlled release*

The use of agrochemicals is crucial in modern agriculture to meet the growing food demand. However, due to inefficient application practices, a significant portion of these chemicals fails to reach their targets, leading to an abusive use and the ecosystem degradation.[1] Consequently, it is imperative to create novel functional materials which enable the effective application of agrochemicals while preserving productivity and profitability.

Metal-organic frameworks (MOFs) are promising materials among the novel technologies proposed in agriculture due to their interesting properties (versatile composition, enabling a broad range of combinations; large specific surface areas and pore volumes, associated with great sorption capacities; easily functionalizable cavities; scalability of synthesis; and adequate stability profiles).[2] In the past decade, MOFs have been studied as agrochemical release systems to enhance efficiency while reducing the leaching of toxic molecules to the environment. In this work, we take a further step and use organic agrochemicals as building blocks to construct agrochemical-based MOFs, what we have call as AgroMOFs. Specifically, different herbicides (glyphosine-H_5Gly, L-mimosine-H_2MI and glufosinate-H_2Glu) are employed as linkers, and combined with active metals (Cu and Zn) known for their antibacterial and fungicidal properties, led to the formation of AgroMOFs. Thus, we successfully synthetized and characterized three novel compounds: (1) $[Cu_3(H_2Gly)_2(4,4'\text{-Bipy})_2]$, (2) $[Zn_2(MI)_2]$, and (3) $[Cu_3(Glu)_2(OH)_2(4\text{-PT})(H_2O)_4]$ (4,4-Bipy = 4,4'-Bipyridine, 4-PT = 4,4'-(1,4-phenylene)bis(4H-1,2,4-triazole). The stability of the prepared compounds and their bioactivity against herbs and different bacteria have been tested, showing promising results as multifunctional agrochemicals. For example, aqueous solutions (450 $mg \cdot L^{-1}$) of GR-MOF-20, based on H_5Gly, demonstrated a better inhibition effect (21.7 ± 2.9%) in the germination of seeds of the invasive weed *Lolium multiflorum* than the free H_5Gly (13.3 ± 2.9%) after 7 days. Further, GR-MOF-20 showed an important antibacterial activity against *Escherichia coli* and *Pseudomonas syringae*, achieving the results obtained with Cu^{2+} solutions.[3]

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SYNTHESIS, MODIFICATIONS AND SENSING APPLICATIONS OF RARE EARTH METAL-ORGANIC FRAMEWORKS BASED ON $[RE_6(M_3\text{-}OH)_8]^{10+}$ SECONDARY BUILDING UNITS AND ANGULAR DICARBOXYLATES

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Keywords: *rare earth ions, secondary building units*, *metal-organic frameworks, post synthetic modification, sensing*

Metal-organic frameworks (MOFs) based on polynuclear secondary building units (SBUs) with rare earth (RE^{3+}) ions, have attracted attention because of their vast structural variability, increased thermal/chemical/hydrolytic stability and their interesting magnetic and photoluminescence (PL) properties. Post synthesis modification (PSM) includes the modification of the structure of a MOF after it has been synthesized. Generally, it is preferable for PSM to proceed in a single-crystal-to-single-crystal (SCSC) fashion, where direct structural information can be obtained. Through the combination of their porous structures, PSM, and PL properties, the materials can host analytes that lead to an alteration of the PL response enabling the detection of various pollutants.

This presentation will focus on the synthesis and characterization of RE^{3+}-MOFs based on the $[RE_6(\mu_3\text{-}OH)_8]^{10+}$-SBU and angular dicarboxylates bearing different functional groups, focusing on three families of RE^{3+}-MOFs where PSM led to superior sensors. Specifically, a family of 3-D 12-connected anionic MOFs with the general formula $\{((CH_3)_2NH_2)_2[RE_6(\mu_3\text{-}OH)_8(OBA)_6]\}_n$ (H_2OBA: 4,4′-oxybisbenzoic acid) was post-synthetically modified to improve Cd^{2+} detection capability. Another family of 2D 8-connected MOFs with the general formula $[RE_6(\mu_3\text{-}OH/F)_8(SDBA)_4(NO_3)_2(H_2O)_6]_n$ (H_2SDBA: 4,4′-sulfonyldibenzoic acid) was synthesized and characterized. Thin films of the monometallic analogues (Y^{3+}, Eu^{3+} and Tb^{3+}) displayed different responses upon exposure to various nitroaromatic and volatile organic compounds in the gas phase. Furthermore, a trimetallic analogue of this MOF, embedded in thin films, displayed a combined response of the individual components for the selected analytes leading to the fabrication of a selective and sensitive sensor. Finally, a third family of 2-D 8-connected RE^{3+}-MOFs with the general formula $[RE_6(\mu_3\text{-}OH^-/F^-)_8(BCPM)_4(NO_3)_2(H_2O)_4]_n$ (H_2BCPM: 4,4′-(hydroxymethylene)dibenzoic acid) was post synthetically modified utilizing SCSC ligand installation reactions which led to the increase of the dimensionality of the framework and turn-on of the temperature sensing capability.

This work highlights the potential displayed by RE^{3+}-MOFs based on the $[RE_6(\mu_3\text{-}OH)_8]^{10+}$-SBU to undergo structural modifications that lead to superior sensors for a variety of analytes.

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DESIGN OF BIMETALLIC MIL-53(FE,NI) MOFS FOR ENHANCED ELECTROCHEMICAL ENERGY STORAGE WITH INSIGHTS INTO CHARG STORAGE MECHANISM

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Keywords: *MOFs; energy storage; asymmetric supercapacitors; MIL-53(Fe)*

The Bimetallic metal-organic frameworks (MOFs) are considered promising electrode materials for electrochemical energy storage application due to their unique structural and component advantages[1]. Using a simple one-step solvothermal technique, nickel ion was integrated into the MIL-53(Fe) framework to design nickel-doped iron-based MOF (MIL-53(Fe)-Ni), which was eventually used as an efficient electrode to improve supercapacitor performance. Owing to its distinct hexagonal pyramid-like structure and the synergistic effect of bimetallic ions, the MIL-53(Fe)-Ni-2 electrode material demonstrates high specific capacity of 408.1 Cg−1 at 1 A g−1 and remarkable cycling stability (80.9% capacity retention over 5000 cycles at 10 A g−1) in a half-cell system configuration. For practical application, a full cell comprising a capacitive-type AC and a battery-type MIL-53(Fe)-Ni-2 were assembled to form an asymmetric supercapacitor device (ASC). The MIL-53(Fe)-Ni-2//AC ASC device delivered a specific energy of 32.63 Wh/kg at 1142 W/kg and capacity retention and coulombic efficiency of 72.5 and 99.3% respectively, which further led credence to the good stability of MIL-53(Fe)-Ni-2. This work gives insight into the effect of metal doping in modifying the properties of MOFs, demonstrating its great potential in energy storage applications.

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ELECTROCHEMICAL DEPOSITION OF HKUST-1 POLYCRYSTALLINE FILMS AS TRIBO-POSITIVE MATERIAL FOR ROBUST TRIBOELECTRIC ENERGY HARVESTERS

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Keywords: *Metal-organic framework, Electrochemical deposition, Triboelectric nanogenerator, HKUST-1 crystalline film*

The triboelectric nanogenerator (TENG) offers a promising solution for powering microdevices but metal-organic framework (MOF)-based TENGs are underrepresented in the triboelectric series[1-2]. Expanding this series and investigating the triboelectric properties of MOFs are therefore critical steps for advancing TENG technology. A key challenge in MOF-based TENG development, however, is achieving stable attachment of stable MOF films and coatings to substrates[3-5]. In this study, we show electrochemical deposition as a facile approach to tackle this challenge, enabling the effective integration of a tribo-positive HKUST-1 MOF films onto a copper substrate. HKUST-1 is grown for varying durations (0.25, 0.5, 1, 2, and 3 hour) and paired with a Kapton counter-electrode to form a functional TENG device. Among the samples, the 2-hour growth of HKUST-1 (2 h-HKUST-1) demonstrated optimal performance, producing a 5-fold increase in output voltage compared to a neat copper substrate, achieving 98 ± 5 V and a power output density of 771.8 ± 0.3 mW/m^2. The device also exhibits high stability, with negligible voltage decay over a 2-day continuous testing under contact-separation mode. Importantly, this study is the first to investigate the effect of humidity on intrinsic MOF film in the TENG. Despite the hydrophilic nature of HKUST-1, the 2 h-HKUST-1 device maintained stable output as relative humidity (RH) decreased from 70% to 10% (Fig.1a), suggesting the formation of an adsorption-desorption equilibrium surface layer. This equilibrium minimizes the impact of humidity on charge transport and surface charge accumulation, resulting in a saturation effect as illustrated in Fig.1(b). Overall, this work presents a new strategy for fabricating hydrophilic MOF-based TENGs with stable voltage output across a wide range of practically relevant humidity conditions.

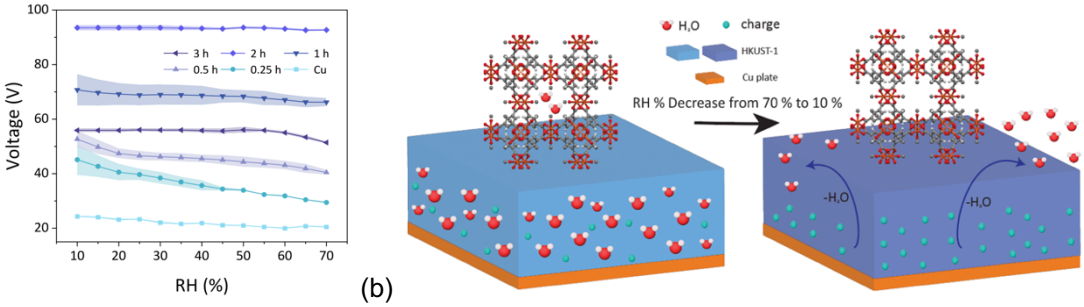


Figure 1: Humidity test across levels from 70% to 10%: a) Output Voltage, b) Proposed Mechanism – [ref.X]. Unpublished data.

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FUNCTIONALIZED COVALENT ORGANIC FRAMEWORKS FOR MODULATING THE DEPOSITION BEHAVIOR OF ZINC ANODES

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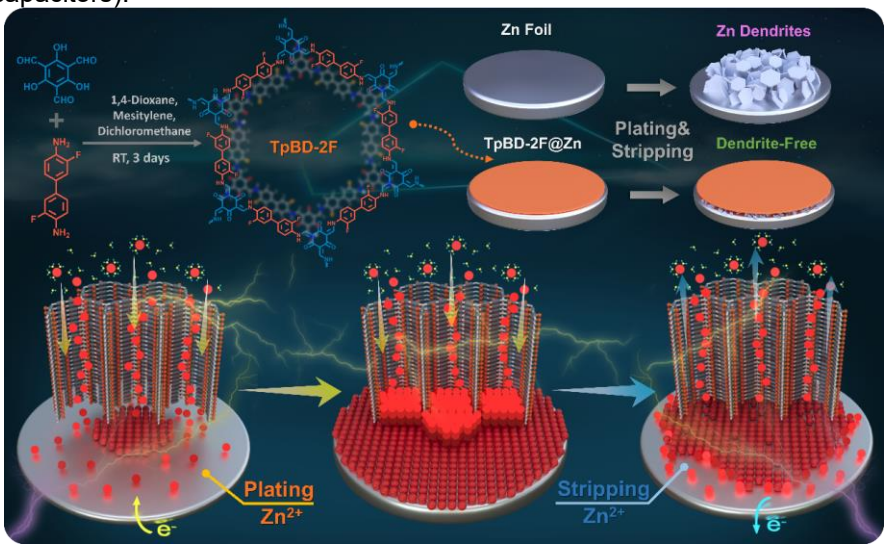
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Keywords: *covalent organic framework, Zn metal anode, dendrite-free, Zn-ion capacitors*

Zinc (Zn) emerges as an ideal anode for aqueous-based energy storage devices because of its safety, non-toxicity, and cost-effectiveness. However, the reversibility of zinc anodes has been constrained by unchecked dendrite proliferation and parasitic side reactions.[1] In particular, unchecked dendrite proliferation leads to uneven electric fields and ion distribution, prompting protons (H^+) in the aqueous electrolyte to accept electrons from thermodynamically unstable metallic zinc, resulting in the release of H_2 and the accumulation of OH^-.[2] This process inevitably leads to the formation of a passivation layer and the depletion of the electrolyte. The formation of these byproducts exacerbates the uneven electric field, further promoting irregular zinc deposition. This vicious cycle may lead to increased internal pressure, rapid electrolyte depletion, and potential short circuits in the sealed battery.[3] To minimize these adverse effects, we utilize two-dimensional (2D) β-ketoenamine-based COFs as a versatile platform to *in-situ* synthesize a highly oriented, porous, and mechanically robust fluorine-functionalized COF (TpBD-2F) thin film at room temperature, aiming at regulating zinc deposition and stabilizing interfaces. This unique, meticulously designed TpBD-2F protective film possesses the following advantages: 1) The TpBD-2F film is continuous and dense, with uniform and well-defined ion channels, facilitating the rapid and even transmission of Zn^{2+} ions; 2) the ultrathin yet mechanically robust TpBD-2F film shortens the ion transport path and provides long-lasting protection; 3) the incorporation of fluorine functional groups creates numerous zincophilic sites, precisely directing Zn^{2+} to hop/migrate swiftly along 1D fluorinated nanochannels at the nanoscale; 4) the hydrophobic F functional group helps to de-solvate hydrated Zn^{2+}, preventing hydrogen evolution and corrosion caused by direct contact between H_2O and the anode interface. As a result, the Zn anode based on TpBD-2F film shows enhanced reversibility and ultra-long cycle stability in both symmetric and full cells (Zn-ion capacitors).



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EXPERIMENTAL EVIDENCE OF "LOW-TEMPERATURE" SUPERCRITICAL TRANSITION OF NANOCONFINED WATER USING ZIF-8

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Keywords: *Metal-Organic Frameworks, Supercritical Water, Nanoconfinement, Phase Transition, Thermal Energy Storage.*

Supercritical water (SCW) is highly relevant for thermal energy storage (TES) due to its high energy density, superior heat transfer properties, and compact storage potential [1]. It enables efficient heat storage and rapid discharge without phase change losses, making it an ideal candidate for applications in nuclear reactors [2] and waste heat recovery [3]. However, when confined at the nanoscale, water's hydrogen bonding network, density, and phase transition behavior undergo significant modifications, leading to a drastic reduction in its supercritical transition temperature [4]. Despite prior studies on confined water, direct experimental evidence of a low-temperature supercritical transition in nanoconfined water remain scarce.

In this work, we employ MOFs, specifically Zeolitic Imidazolate Framework-8 (ZIF-8), a widely studied hydrophobic crystalline material, to investigate the phase behavior of nanoconfined water. Using pressure-volume (PV) isothermal measurements at temperatures up to 130°C, we provide the direct experimental confirmation of a reduction in the supercritical transition temperature for water of ~260°C.

The analysis of these isotherms revealed clear signatures of a nanoconfined supercritical state. The first key indication was the sudden reduction in intrusion volume, which is directly proportional to the difference between the liquid-like and the vapor-like densities [5]. As these densities converge, signaling the onset of the supercritical state, the discontinuity in the PV isotherms, corresponding to the intrusion volume, disappears. A second confirmation was obtained by analyzing the slope of the intrusion branch of the isotherms, a well-established method for detecting supercritical transitions. A sudden reduction in slope was observed above 105°C, further corroborating the presence of supercritical nanoconfined water. This sharp decline reflects the loss of a distinct phase boundary, reinforcing the evidence of a supercritical state with the ZIF-8 micropores.

These findings provide groundbreaking insights into the phase behavior of nanoconfined fluids, with broad implications for low-temperature supercritical fluid applications. This study also paves the way for the design of engineered nanoporous materials optimized for controlling supercritical phase transition at significantly lower temperatures.

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TRIOXOAZATRIANGULENE-BASED COVALENT ORGANIC FRAMEWORKS AS ORGANIC CATHODES FOR LITHIUM-ION BATTERIES

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Keywords: *Covalent Organic Frameworks (COFs), Lithium-ion batteries, Trioxoazatriangulenes.*

The development of next-generation rechargeable batteries is crucial in our increasingly electricity-driven society. Batteries power portable electronics, drive the electric vehicle revolution and help address critical challenges in renewable energy storage. To overcome the limitations of current technologies and improve performance while ensuring more ethical and sustainable storage systems, it is essential to explore alternative and more sustainable electrode materials, such as redox-active Covalent Organic Frameworks (COFs). COFs are crystalline porous organic polymers linked by strong covalent bonds that can be tailored – through molecular design – to meet the specific requirements of various metal-ion battery systems.[1] Trioxoazatriangulene (TOAT) is an emerging building block for the design of COFs that offers a versatile π-conjugated core with multiple redox-active sites. Recently, a TOAT-based COF has been investigated as an anode for sodium-ion battery showing high discharge capacity and long-term cycling stability (Figure 1).[2] Herein, we present the comparison of the electrochemical performance of two TOAT-COFs comprising different building blocks when used as cathodes for lithium-ion batteries.

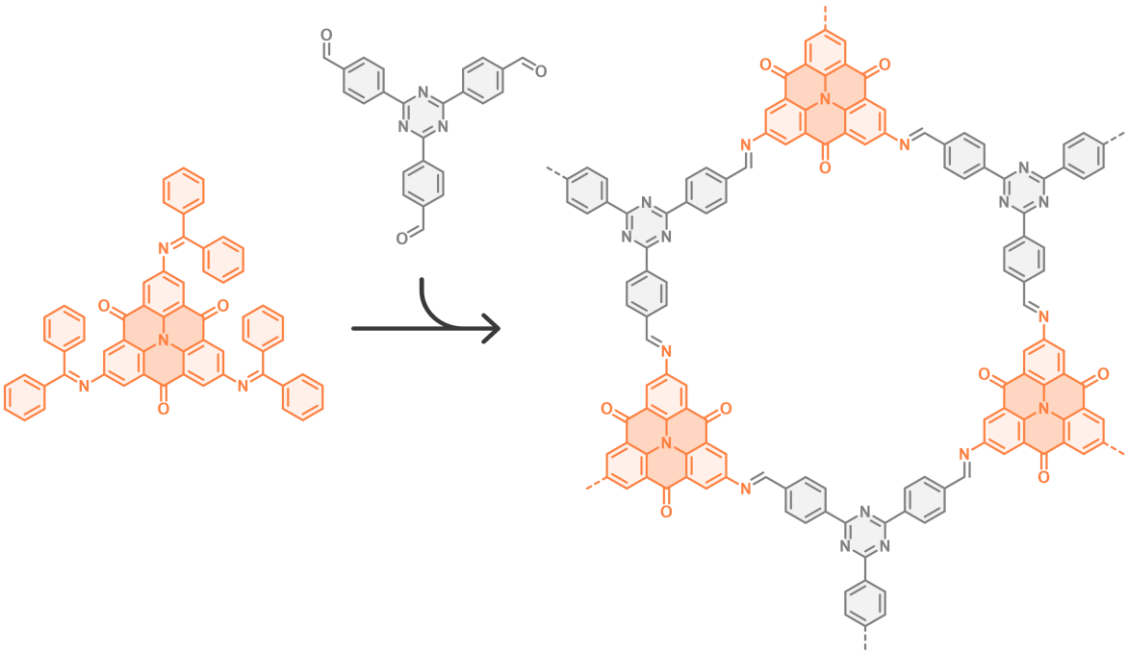


Figure 1: Schematic representation of the CityU-33 COF and its building blocks.

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DEVELOPMENT OF DEFECT-FREE METAL-ORGANIC FRAMEWORK (MOF) MEMBRANES FOR ENHANCED GAS SEPARATION PERFORMANCE

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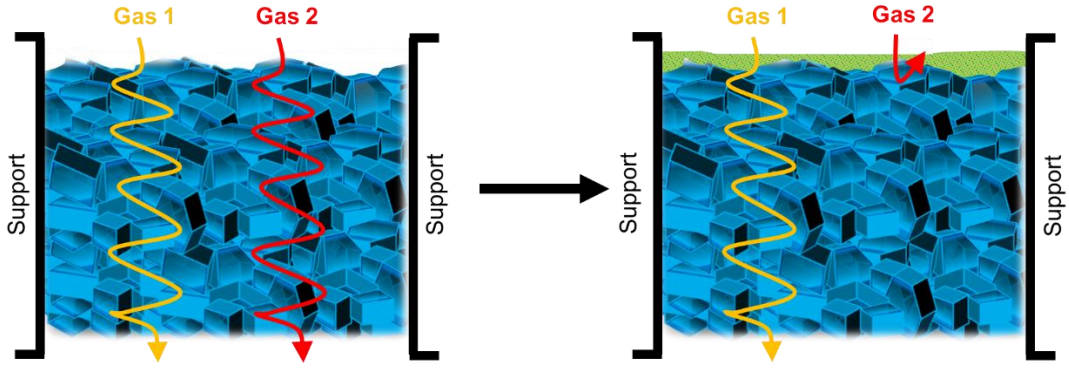
Keywords: Metal Organic Frameworks, Membranes, Gas separation

This work introduces a generalizable method for fabricating defect-free MOF membranes and advances the large-scale application of MOF membranes to industrial gas separation processes.

The well-defined, tailored pore structures of metal-organic frameworks (MOFs) have gained significant interest in the field of gas separation. However, fabricating mechanically stable, defect-free MOF membrane layers is still a challenge because of 1) The crystalline nature of MOFs resulting in non-selective grain boundaries at crystal-crystal interfaces. [1], [2] 2) The absence of methods to grow thin, defect-free layers of MOF over sufficient areas.[3]

This study introduces a novel, generalizable method for fabricating mechanically robust, high-performance, defect-free MOF membranes confined within the pores of tubular ceramic supports suitable for application in gas separation processes. We demonstrate the scientific principles behind this approach and apply it to the example of hydrogen separation from hydrogen/carbon dioxide mixtures.

Detailed characterisation of the as-fabricated membranes using scanning electron microscopy (SEM) reveals that intercrystalline boundary defects are successfully filled under specific conditions. Subsequent gas testing results confirm a marked improvement in separation performance post-treatment.



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UNVEILING THE SYNERGISTIC EFFECT OF $Co(OH)_2$-$CdIn_2S_4$ NANOHETERO-STRUCTURES FOR ENHANCED ELECTROCHEMICAL WATER OXIDATION

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Keywords: Electrocatalysis, water splitting, thiospinels, cobalt hydroxide, p-n heterojunction.

Hydrogen is integral to the future of clean energy, owing to its high energy density and its zero carbon emissions when employed as a fuel. The sustainable production of hydrogen through electrocatalytic water splitting, driven by renewable electricity, is essential for realizing carbon-neutral energy systems. However, the oxygen evolution reaction (OER), a kinetically sluggish process, necessitates the development of efficient and durable electrocatalysts to reduce energy losses and enhance reaction rates. Consequently, the rational design of highly active and robust OER electrocatalysts is critical for advancing alkaline water electrolysis.

In this presentation, we report a novel nanostructured catalyst comprising cobalt hydroxide (β-$Co(OH)_2$) nanosheets grown on the surface $CdIn_2S_4$ (CIS) thiospinel nanoparticles. This hybrid structure (Co@CIS) was fabricated through a combined hydrothermal and photochemical deposition process. The formation of a well-defined p–n heterojunction between CIS and $Co(OH)_2$ facilitates efficient separation and directional transport of charge carriers, simultaneously reducing interfacial resistance and enhancing the OER kinetics. Comprehensive characterization studies, including high-energy X-ray diffuse scattering (HE-XRDS), electron microscopy (SEM/TEM), X-ray photoelectron spectroscopy (XPS) and *in-situ* Raman spectroscopy, were performed to monitor morphological, structural and electronic changes under OER working conditions. Additionally, the interfacial charge-transfer dynamics and intrinsic electrocatalytic activity were assessed using electrochemical impedance spectroscopy (EIS). The results demonstrate the *in-situ* irreversibly transformation of $Co(OH)_2$ into the catalytically active CoOOH phase under anodic polarization, which is closely correlated with enhanced OER kinetics. The activated catalyst benefits from its high surface area, high redox activity of Co-oxo species and favorable band-edge alignment of the CIS and CoOOH semiconductors that facilitates rapid interfacial charge transfer. As a result, the optimized Co@CIS electrocatalyst exhibits a low overpotential of 294 mV at 10 mA cm^{-2} current density with 61.2 mV dec^{-1} Tafel slope, while maintaining stable OER activity over a 40-hour operation period in 1.0 M KOH. When, integrated into a two-electrode alkaline electrolyzer (with Pt/C as cathode electrode), water electrolysis required a cell voltage of 1.60 V to generate a current density of 10 mA cm^{-2}, corresponding to an electrical-to-fuel efficiency of 77%.

These results underscore the effectiveness of rationally engineering the interface between semiconductor-based materials to simultaneously enhance the intrinsic catalytic activity and long-term stability of electrocatalysts for alkaline OER.

ROOM TEMPERATURE AND GREEN SYNTHESIS OF A NOVEL K-BASED METAL-ORGANIC FRAMEWORK WITH HIGH PROTON CONDUCTIVITY

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Keywords: Metal-Organic Frameworks, proton conductivity, energy, green synthesis

Since the commercial Nafion® used as electrolyte in Fuel Cells (FCs) suffers from stability issues related to the humidification activation process during the FC operation, the search of stable proton conductive materials has attracted the attention of the scientific community. Among the possible materials (*e.g.* organic conducting polymers, ceramics, zeolites), Metal-Organic Frameworks (MOFs) appeared as an excellent alternative due to the richness of their chemistry and structural variety. However, the most promising materials (with proton conductivities > 10^{-2} $S{\cdot}cm^{-1}$)[1] are in general based rather on toxic cations (*e.g.* Co^{2+}, Cr^{3+}, Eu^{3+})[2,3,4] or in expensive lab-made ligands. Thus, the development of non-toxic low-price materials is still a requirement. In this contribution, a novel MOFs label as GR-MOF-28 based on the non-toxic high abundant K^+ cation and the commercial naphthalene tetracarboxylic acid anhydride ligand is reported. GR-MOF-28 exhibited free labile protons and water molecules along 1D channels in its structure, that combined with its stability under working conditions (90 °C and 90% relative humidity) results in very promising features for a proton conductor. Molecular simulations revealed an optimal proton transport pathway along the H-bond network of the material, and its proton conductivity was evaluated by electrochemical impedance spectroscopy reaching values up to $4{\cdot}10^{-2}$ S cm^{-1}. Remarkably, GR-MOF-28 kept its structural integrity and its proton conduction properties during at least 3 cycles. The proton conduction pathways were studied by Monte Carlo simulations, that in good agreement with the crystallographic data showed a proton transport pathway along the [100] direction of the structure thanks to a Grotthuss mechanism. Furthermore, a composite containing a high load of MOF (90% wt.) was prepared by adding a proton conductive sulfonated polysulfone, resulting in the increase of the proton conduction of the solid up to $5.5{\cdot}10^{-2}$ $S{\cdot}cm^{-1}$

Acknowledgements

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A TRIOXOTRIANGULENE NEUTRAL RADICAL-BASED COVALENT ORGANIC FRAMEWORK

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Keywords: *Covalent Organic Frameworks (COFs), Trioxotriangulene (TOT), Redox-active materials*

The global transition toward renewable energy sources has highlighted the urgent need for sustainable, safe, and efficient energy storage technologies. Organic batteries offer a low-impact, tunable solution but still face challenges in performance and long-term stability, particularly in developing stable redox-active materials.[1] Trioxotriangulene (TOT) neutral radical is recognized for its role in organic batteries, owing to its multi-stage redox ability and the capacity to form air-stable neutral radicals.[2] In this study, a novel TOT-based (TOT-TFPT) covalent organic framework (COF) has been designed and synthesized. The resulting COF exhibits a highly ordered, porous framework (BET = 1260 m^2/g) with an extended π-conjugated network, promoting efficient charge transport and offering multiple redox-active sites (C=O, C=N). Furthermore, its robust chemical structure enables post-synthetic modification to introduce stable radical species within the framework. The resulting radical COF (r-TOT-TFPT) shows remarkable air stability (an uncommon property among organic radicals) enhancing its potential for long-term energy storage.[3] These features make TOT-TFPT a promising candidate for organic batteries, where both high capacity, high conductivity and cycling stability are essential.

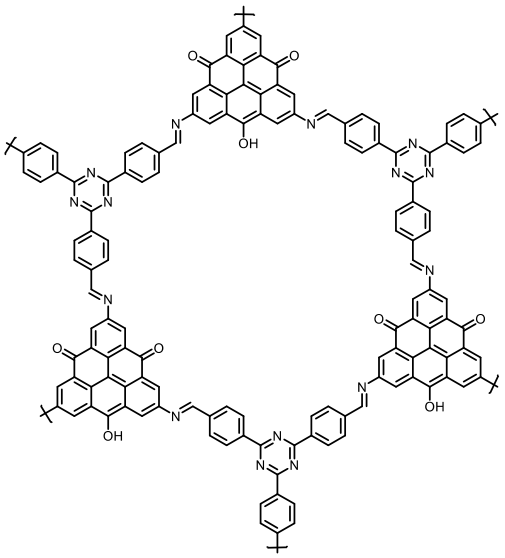


Figure 1. Structure of TOT-TFPT COF.

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3D STEREOLITHOGRAPHY-PRINTED MICRO-LATTICES FOR MOF-DERIVED ARCHITECTURES AS HIGH-PERFORMANCE SELF-STANDING PSEUDOCAPACITIVE AND SUPERCAPATTERY ELECTRODES

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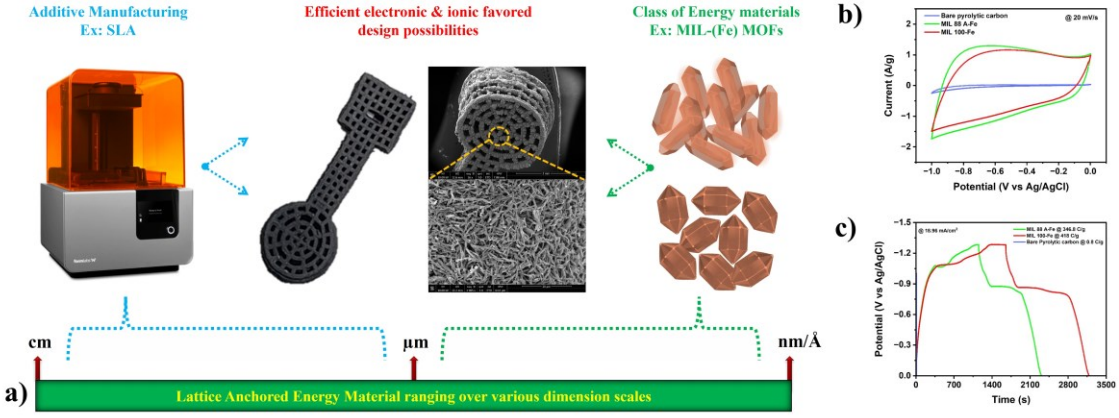
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Keywords: *Stereolithography (SLA), MIL 88 A, MIL 100, Supercapacitor, Supercapattery, Self-Standing Electrode*

The traditional drop-casting method for preparing electrodes involved binders, conductive carbons, and solvents, which adds dead mass, reduces electrical conductivity, impacts rate capability and stability, while underutilizing mesoporous redox sites. Despite optimizing the properties of energy storage materials, reliance on current collectors such as metal foams further raised concerns about commercial viability. To address these issues without impairing transport kinetics, engineering at the electrode level was crucial for creating high-performance self-standing electrodes that serve as both active materials and current collectors.[1,2,3] In this study, we addressed these challenges by using 3D SLA printed high-temperature resin-based micro-lattices and surface-dispersed Fe-MOFs (MIL 88A & MIL 100) (Fig. a). To simplify and scale the synthesis process, we 3D printed green bodies of the electrodes and surface-coated them with pre-synthesized Fe-MOFs, followed by pyrolysis and post-oxidation. The surface-coated MOFs and the 3D printed structures become mechanically well integrated due to the Kirkendall effect, forming a conductive carbon core and MOF-derived Fe_xO_y shell. This pyrolytic carbon Fe_xO_y composite functioned as an optimal self-standing 3D electrode for dual applications in supercapacitors (0 to -1V vs Ag/AgCl) (Fig. b) and supercapatteries (0 to -1.3V vs Ag/AgCl) (Fig. c). The electrochemical analysis, including CV, GCD, and EIS of bare pyrolytic carbon vs MOF-coated pyrolyzed structures, showed a remarkable increase in performance of 86.6 times in specific capacitance for MIL 88A and >520 times in specific capacity for MIL 100 in 6M KOH solution. Integrating Fe-MOFs with 3D-printed resin-derived pyrolytic composites enhances electron transport through the micro-strut architecture and optimizes ion transport via the hierarchical porosity of MOF derivatives, resulting in exceptional electrochemical performance. This approach, in the future, allows for greater design flexibility for struts and MOFs, increasing the specific surface area, refining hierarchical porosity, and improving gravimetric/volumetric pseudocapacitive and redox performance.



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A TETRATHIAFULVALENE-BASED BIMETAL-ORGANIC FRAMEWORK FOR A HYBRID LITHIUM-ION CAPACITOR: THE ROLE OF BIMETALLIC CENTERS IN CHARGE STORAGE AND STABILITY

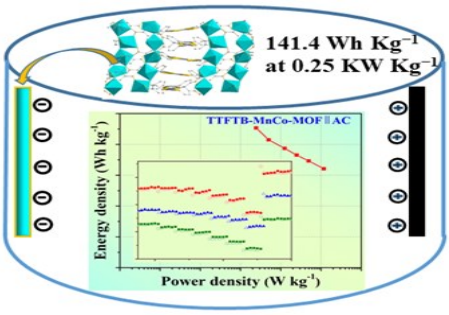
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Keywords: *bimetal, MOF,hybrid lithium-ion capacitor*

Metal–organic frameworks (MOFs) are a highly attractive class of porous crystalline inorganic–organic hybrid materials constructed from metal ion nodes and organic linkers. MOFs have been proposed as attractive pseudocapacitive electrode materials for hybrid lithium-ion capacitors (HLICs) owing to their large ion diffusion tunnels and abundant redox active sites. However, the reported pristine MOF-based electrode materials are still insufficient because of their low capacity, poor rate capability, and instability during the charge–discharge processes. To meet the challenge, many studies have focused on developing new MOF-based electrode materials containing binary transition metal ions owing to their enriched active sites. Synergistic effects are usually used to explain the enhanced performance of bimetallic MOFs. However, as far as we know, studies on a deep understanding of the role of transition metal ions in bimetallic MOFs in electrochemical performances have not been explored, which is important to design advanced MOF-based electrodes. To address this need, a first tetrathiafulvalene (TTF)-based bimetallic MOF formulated as [MnCo(TTFTB)(H_2O)$_2$]·2DMF·EtOH (**1**) (TTFTB = tetrabenzoate TTF) was synthesized and crystallographically characterized. Two isomorphic monometallic MOFs, [M_2(TTFTB)(H_2O)$_2$]·2DMF·EtOH (M = Mn, **2**; Co, **3**), were also synthesized for comparison. TTF is a well-known conjugated sulfur-rich organic molecule. Pristine TTF-based MOFs have been employed as electrode materials in lithium-ion batteries (LIBs) and HLICs, demonstrating satisfactory electrochemical performance[1,2]. In this work, the TTF-based bimetallic MOF **1** was directly utilized as the electrode material for LIBs. It exhibits enhanced electrochemical performance compared to its isomorphic monometallic electrodes. Comprehensive characterizations reveal that the Mn(II) in MOF **1** is beneficial for the cycling stability and the Co(II) contributes to the high specific capacity. The **1**||NMC 622 full cell delivered a capacity of 154.9 mA h g^{-1} at 100 mA g^{-1} after 200 cycles. The **1**||AC HLIC displays a high specific energy of 141.4 Wh kg^{-1} at a specific power of 0.25 kW kg^{-1}, along with stable long-term cycling performance. The outstanding performance, long-term cycling stability, and low self-discharge rate of the device surpass those of most reported HLICs.



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A REDOX-ACTIVE 2D TTF-Cu MOF WITH PROMOTED PERFORMANCES FOR SUPERCAPATTERY

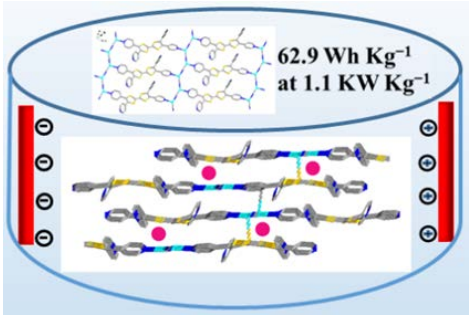
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Keywords: *MOF, two-dimension, redox-active, supercapattery*

Metal−organic frameworks (MOFs) are a unique kind of porous solid material that provides a high degree of chemical and structural tunability by judicious selection of inorganic nodes and organic linkers. MOFs have exhibited great potential applications in electroactive electrodes and supercapatteries [1]. Due to their unique dimension-dependent characteristics, such as short ion transport distances, abundant accessible active sites, and high aspect ratios, two-dimensional (2D) conductive MOFs (c-MOFs) have recently attracted increasing attention as an emerging class of electrode materials. However, since good electrical conductivity is one of the requisites for rapid charge storage, the poor electrical conductivity of most pristine MOFs severely hinders the application of MOF-based electrodes in energy storage. MOFs with redox-active ligands could represent an attractive type of electrode material. Tetrathiafulvalene (TTF) is well-known for its two-step reversible redox process to form stable $TTF^{\bullet+}$ radical cation and TTF^{2+} dication. The electrochemical performances of TTF-based MOFs were preliminarily explored by our group using a three-electrode configuration [2, 3]. Considering that the electrical conductivity of TTF derivatives can be improved by oxidizing TTF to $TTF^{\bullet+}$ radical cation, here, a TTF derivative, tetra(4-pyridyl)-TTF (TTF-$(py)_4$) was selected to construct a new 2D TTF-based complex $[(CuCN)_2(TTF(py)_4)]$ (**1**). The 2D TTF-MOF is assembled by in situ generation of coordinated CN^- from a nontoxic source. Single-crystal X-ray diffraction analysis reveals that compound **1** possesses a two-dimensional layered planar structure, which is further stacked in parallel to form a three-dimensional supramolecular framework. The planar coordination environment of **1** is the first example of a TTF-based MOF. Owing to the unique structure and redox TTF ligand, the electrical conductivity of **1** is significantly increased by five orders of magnitude upon iodine treatment. The iodine-treated **1** (**1**-ox) electrode displays typical battery-type behavior through electrochemical characterizations. The supercapattery based on the **1**-ox positrode and AC negatrode presents a high specific capacity of 266.5 C g^{-1} at a specific current of 1 A g^{-1} with a remarkable specific energy of 62.9 Wh kg^{-1} at a specific power of 1.1 kW kg^{-1}. The excellent electrochemical performance of **1**-ox is one of the best among those reported supercapatteries, demonstrating a new strategy for developing MOF-based electrode materials.



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ZIF-7/POLYETHERIMIDE MIXED MATRIX MEMBRANES (MMMS) FOR HYDROGEN PURIFICATION

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Keywords: *mixed matrix, membrane, hydrogen purification, permeability, selectivity*

Hydrogen is one of the fuels of the future due to its high gravimetric energy density and no greenhouse gas emissions during combustion. Membrane-based separation technologies are sustainable processes due to a 50% operational cost reduction.[1] This presentation will discuss the feasibility of using ZIF-7 and a polyetherimide (PEI) polymer matrix to form MMMs for hydrogen purification. The porosity of the MMM can be altered by thermal treatment after membrane casting. Moreover, the phase change of ZIF-7 from Phase I to Phase III was shown during microwave-assisted synthesis, which reduced the synthesis time from 48 h to 15 min. Lastly, the preparation of ZIF-7/PEI MMMs with ZIF-7 loading 50% (wt.) is discussed for the first time. The hydrogen purification performance of the prepared membranes are evaluated by single-gas permeabilities and selectivities of hydrogen compared to methane and carbon dioxide. The success of this project will open the possibility of using cost-efficient hydrogen purification membranes in future gas networks.

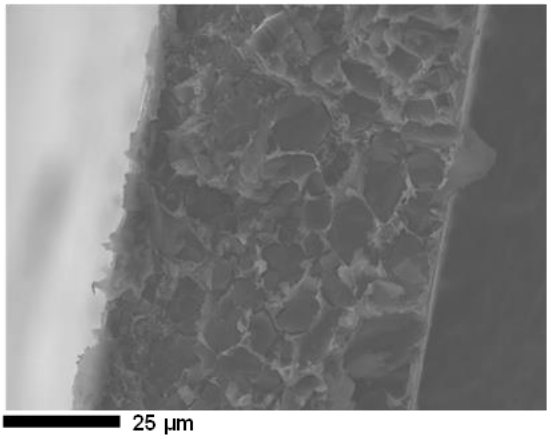


Figure 1 SEM of 50 wt% ZIF-7/PEI MMM

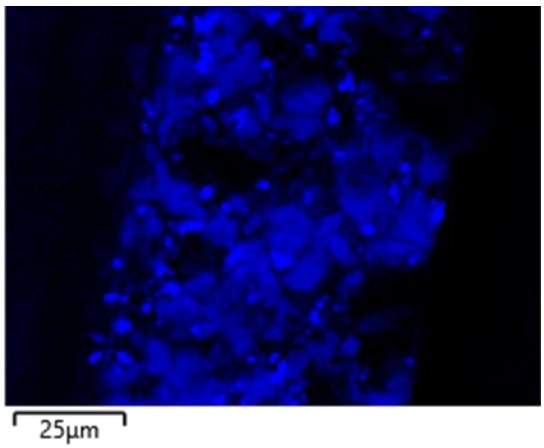


Figure 2 EDX of 50 wt% ZIF-7/PEI MMM. Blue colour highlights presence of Zn from ZIF-7

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NOVEL FLOW REACTOR SYNTHESIS OF HKUST-1 WITH PRECISELY CONTROLLED PHYSICAL PROPERTIES

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Keywords: continuous-*flow synthesis, pilot-scale, green, ambient, HKUST-1*

MOFs perform exceptionally through a range of applications, and their scope for industrial-scale use is wide. In the current market, a large portion of the commercial interest is derived from adsorption-related applications, such as gas separation, CO_2 capture and gas storage.

While the number of commercially available MOFs has increased over time, commercial interest for HKUST-1 has remained despite increasing competition. HKUST-1 exhibits high adsorption capacities toward many gaseous molecules, which is a key property in applications such as gas separation and storage[1]. These promising performance metrics and versatility, coupled with relatively inexpensive precursors make HKUST-1 a great candidate for large scale applications.

For any MOF to be utilised on an industrial-scale, the manufacturing route needs to be scalable and cost-viable. Most commonly, MOF syntheses are reported in batch, which can involve difficulties in reproducibility, scalability and cost-effectiveness. Our approach to MOF synthesis, from laboratory scale upwards, aims to develop and use manufacturing processes that can be scaled to yield large volumes of high quality, cost-effective material. Utilising continuous-flow production to achieve high space-time yields facilitates these goals.

We present our work on the development of an ambient and aqueous-based synthetic process for high quality HKUST-1, using a proprietary, purpose-built continuous-flow reactor system. Using this novel reactor, we can control reagent mixing , stoichiometry dosing and residence time to tune the physical properties of HKUST-1. Such control allows material to be synthesised with a uniform particle size distribution (*Figure 1*), and fast settling into a dense solid layer, which creates faster, lower cost post-synthetic washing. This synthetic route produces the desired product within minutes, and has currently been upscaled to produce tens of kilograms of HKUST-1 per hour, with further upscaling planned.

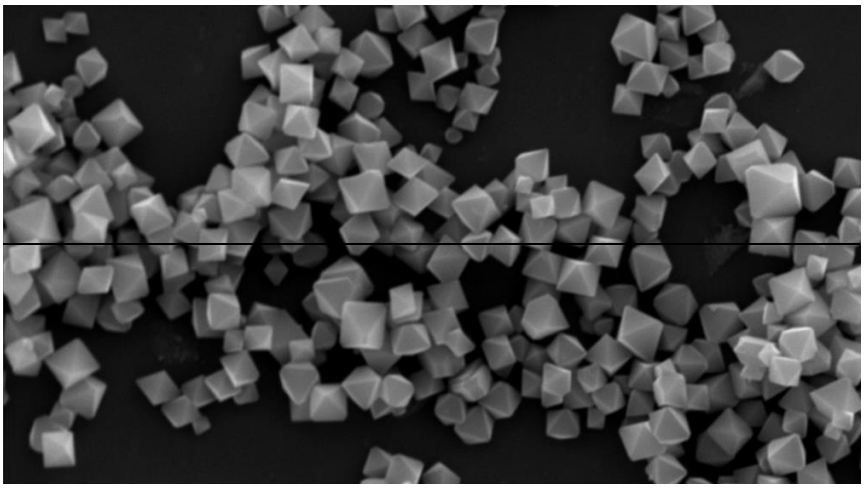


Figure 1. SEM image of HKUST-1 synthesised using the swirl reactor, showing uniform particle size distribution.

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WET GRANULATION OF MOFS: PROCESS DEVELOPMENT AND EVALUATION OF SHAPED SORBENTS

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Keywords: *Wet Granulation Techniques, Mechanical Strength, Adsorption behavior, Pilot-Scale Process*

Porous materials have found broad industrial applications in drying, separation, sensing, gas storage/release, and environmental purification. Among them, Metal-Organic Frameworks (MOFs) represent a distinctive class of sorbents with highly tailorable architectures and tunable chemical functionalities. At ITRI, a pilot-scale MOF production process has been successfully established, incorporating a 3 kL hydrothermal reactor along with integrated purification and drying units. Through systematic process optimization, high-yield MOF synthesis (197 kg per batch) with consistent adsorption performance, comparable to lab-scale results, was achieved.

Despite their superior sorption characteristics, the powdery nature of MOFs poses practical challenges for industrial deployment, including dust generation, handling inefficiencies, and increased pressure drops in packed-bed systems. To address these limitations and enable effective integration into packed-bed systems, this study developed wet granulation techniques, specifically high-shear granulation and extrusion granulation, to transform MOFs into mechanically robust spherical granules. The resulting granules were evaluated in terms of mechanical strength, attrition rate, and water vapor adsorption performance.

Experimental results demonstrated that MOF granules produced via high-shear and extrusion granulation exhibited mechanical strengths of 40 N and 60 N, respectively, with low attrition rates (1.4% and 0.8%). The average particle sizes were 3.6 mm and 2.9 mm, meeting the requirements for packed-bed applications. Through binder selection and process optimization, both types of granules achieved equilibrium water uptakes of ~50% and sorption rates of ~$6.5*10^{-3}$ $g_{H_2O}\cdot min^{-1}\cdot g_{MOF}^{-1}$ surpassing the performance of the original MOF powder (47% uptake) and conventional alumina-based desiccants ($2.37*10^{-3}$ $g_{H_2O}\cdot min^{-1}\cdot g_{MOF}^{-1}$). This enhancement may result from improved binder–MOF interfacial compatibility, which facilitates water transport while preventing pore blockage. The superior mechanical performance of the extrusion granules is possibly due to the uniform stress distribution and directional alignment of binder-MOF domains induced by the extrusion flow field. The developed MOF granules satisfy the structural and functional criteria for industrial use and have been successfully integrated into an adsorption-based compressed air drying system, marking a significant advancement toward real-world deployment of MOF-based sorbents.

Acknowledgments

The authors express their most sincere gratitude to the Energy Administration, Ministry of Economic Affairs, R.O.C., for financially supporting this investigation.

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INTRODUCING MOFGRAPHY: DEVELOPING ADVANCED SEPARATION MATERIALS FOR CHEMICAL PURIFICATION APPLICATIONS

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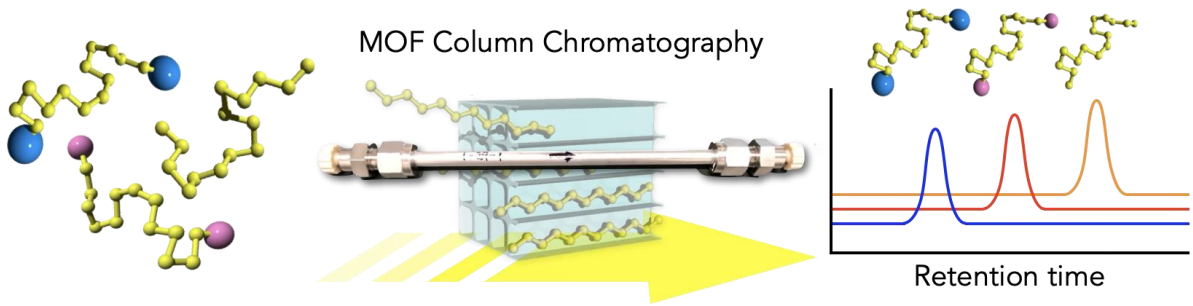
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Keywords: *Industrial applications, chemical purification, chromatography, MOF synthesis*

The industrial implementation of advanced separation processes hinges on the development of new materials platforms that enable high selectivity, low energy and regeneration requirements, as well as robust material lifetimes. In this context, the tunability of metal-organic frameworks (MOFs) provides a powerful platform for addressing conventional separation challenges and enabling new modes of purification—particularly for complex molecular mixtures. For example, in the area of chromatographic (solution-based) macromolecular separations, the matching of the pore size, pore shape, and surface chemistry of the MOF with the target molecule can provide materials that can be used to separate polymers according to their molecular weight, tacticity, or terminal functionality, as well as selective removal of proteins from structurally similar analogs.[1-6]

MOFgraphy Inc. is a newly established start-up based in Tokyo, Japan, focused on supporting the industrial adoption of next-generation separation technologies developed at the University of Tokyo. MOFgraphy offers B2B consulting, technoeconomic assessments of MOF-enabled processes, and end-to-end support for material discovery and optimization, including synthesis and characterization tailored to the needs of client companies. Through its extended network, the company is also positioned to assist with MOF scale-up and integration into functional devices for rapid commercial deployment.

This presentation will introduce the chemistry that underpins the technical solutions offered by MOFgraphy, and outline the types of collaborative opportunities available to potential partners. Key application areas and workflow models will be discussed. The presenter welcomes discussions with both academic and industrial participants throughout the EuroMOF conference, and is particularly interested in exploring the separation challenges faced by industrial companies, with a view toward the co-development of innovative solutions.



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DIRECT MIXING VS. IN-SITU GROWTH OF MOF-74 AND UIO-66 PROMOTED BY GRAPHENE OXIDE FOR CCUS TECHNOLOGIES AND FRUCTOSE DEHYDRATION

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Keywords: *MOFs, shaping, beads, biopolymer, graphene oxide, CO_2 capture*

Despite their widespread recognition as highly porous and crystalline materials, MOFs still face several limitations for real-world applications due to shaping difficulties and low chemical stability [1]. To address these issues, integrating MOFs into moldable biopolymers such chitosan (CS), and alginate (Alg) is considered one of the most recommended strategies by many researchers for developing shaped MOF-based systems without damaging their initial properties [2].

In our recent studies, we employed an *in-situ* growth strategy to synthesize HKUST-1-based binary and ternary composites within chitosan beads containing graphene oxide (GO), achieving high specific surface areas (up to 923 $m^2.g^{-1}$) and improved hydrolytic stability at room temperature [3]. Next, this *in-situ* growth strategy was applied to develop, for the first time, MOF-74-based composites, resulting in robust CS@MOF-74 and CS-GO@MOF-74 (Co) beads with high crystallinity and specific surface areas exceeding 500 $m^2.g^{-1}$. The prepared CS@MOF-74 (Co) composite spheres (Fig. 1a) were used for CO_2 adsorption, demonstrating promising performances of 3.16 $mmol.g^{-1}$ at 298 K and 1 bar, with a high recyclability for multiple cycles [4] ((Fig. 1d).

On the other hand, we explored shaping UiO-66 through an *ex-situ* (direct mixing) growth strategy within alginate matrix to prepare Alg@UiO-66 crystalline composites in the form of beads (Fig. 1b and c) and monoliths with open microporosity (up to 700 $m^2.g^{-1}$). We then applied the same strategy for growing UiO-66-SO_3H with enhanced Brønsted acidity for fructose hydration applications, currently in progress.

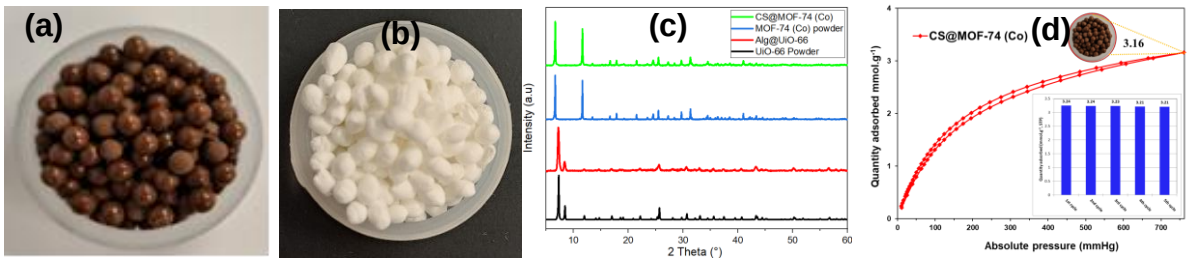


Fig. 1. The as-prepared CS@MOF-74 (Co) (a), Alg@UiO-66 (b), their corresponding PXRD patterns (c), and CO2 adsorption plot of CS@MOF-74 (Co) at 298 K (d).

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METAL-ORGANIC FRAMEWORK BASED FUNCTIONAL GLASSES AND POROUS LIQUIDS

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Keywords: *Porous Liquid, MOF Glass, CO2 to value added products*

Metal-organic frameworks (MOFs) are porous materials well-known for designability, highly ordered crystalline structure and host-guest chemistry.[1,2] The purposeful and controlled introduction of defects and disorders in MOFs at smaller scales is widely used to impart and modulate their structures, properties and functionalities. While crystallinity is not a prerequisite, studies on crystalline MOFs dominate the literature. Glasses are amorphous solids with a high degree of defect and disorder and are both fundamentally intriguing and important functional materials.[3] MOF glasses are a fundamentally new category of glass-forming system where in a designer framework chemistry of crystalline MOFs can be transferred to glassy states otherwise distant in typical glass formers.[4,5] However, limited information is available on the design guidelines to realize melting and glass-forming MOF systems and their structure-property correlation. Alternately, porous liquids (PLs) have gained much interest as they combine the permanent porosity of solids and flow properties of liquids which endow them with novel functionalities that are inaccessible to pure solids and liquids.[6] The high and selective gas uptake aided by efficient mass transport renders them suitable for materials for chemistries involving gaseous reactants.[7] Both the MOG glasses and Porous Liquid chemistry are in their infancy with a huge scope for scientific investigations. In my talk, I will present some of our recent works on the chemical modulation routes to tune T_m, T_g and T_d in MOF glasses and their structure-property correlation. This will be followed by our work on bio-compatible MOF-based porous liquids for one pot direct air CO_2 capture and conversion for CCUS application.

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HYBRID INORGANIC-ORGANIC MULTIFUNCTIONAL MATERIAL UNAM-3: STRUCTURAL FLEXIBILITY, SOLVENT EXCHANGE, AND ELECTRICAL CONDUCTIVITY

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Keywords: *Hybrid materials, polyoxometalates, flexible structures, self-assembly, supramolecular frameworks, semiconductors.*

The design and synthesis of new materials have acquired significant interest for tailored applications in numerous fields and have paved the way for the creation of new multifunctional materials improving stability, applicability, and costs.[1–3] Among these, materials combining electrical conductivity and porosity have only recently emerged, with metal-organic frameworks (MOFs) leading the field despite their inherent insulating nature.[4,5] Hybrid materials that integrate inorganic and organic blocks and assemble via weak interactions, offer a promising alternative, enabling flexible structures, sufficient stability, and the combination or potentiation of electron-driven properties from each block.[6,7] This work presents UNAM-3 (Scheme 1), a novel porous inorganic-organic hybrid material based on the stable and reversible redox-active Keggin polyoxometalate $[SiW_{12}O_{40}]^{-4}$ and the dimeric radical cation of N,N,N'N'-tetraethylbenzidine ($[TEB^{\bullet+}]_2$). These charged molecules assemble via non-classical hydrogen bond interactions between the aromatic rings and terminal oxygen atoms of the polyoxometalate, forming 1D channels capable of reversible solvent exchange by dynamically modulating the framework's volume and symmetry as a function of the solvent's size. As expected, the redox-active components granted electrical conductivity with a value of 4.24 x 10^{-7} S cm^{-1}. To further elucidate the role of each building block, we synthesized two additional hybrid materials: (1) a precursor of UNAM-3 comprising the protonated organic block ($TEBH_2^{2+}$) and the Keggin anion, and (2) $[TEB^{\bullet+}]_2[I_3^-]_2$, a non-porous hybrid material with a conductivity of 1.38 x 10^{-8} S cm^{-1}. The latter comparison underscores the polyoxometalate's dual role in enabling porosity and enhancing conductivity.

Scheme 1. Formation and structure of UNAM-3 with calculated 1D channel voids (Blue).

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ZIF-8 THIN FILMS WITH EMBEDDED IONIC LIQUIDS FOR ULTRA-SENSITIVE CAPACITIVE GAS SENSORS

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Keywords: *chemical sensors, composites, capacitors, volatile organic compounds*

Monitoring volatile organic compounds (VOCs) at trace levels is essential in several applications, including breath disease diagnostics, indoor air quality control and agricultural process optimization. These settings often demand detection of VOCs in part-per-billion (ppb) range. Capacitive MOF sensors with optimized electrode configuration allow detection of low levels of VOCs, with the limit of detection in part-per-million range (ppm) for small polar compounds using laboratory capacitance meters.[1] Therefore, further improvements to sensor sensitivity are necessary for reliable detection of sub-ppm concentrations in real-world applications.

We explore the sensitivity enhancement by embedding ionic liquids (ILs) into the MOF pore network. Although incorporation of IL reduces the overall adsorption capacity, it can enhance VOC uptake at low concentrations when the interaction is favourable. We show that capacitive sensors with embedded 1-butyl-3-methylimidazolium bromide in ZIF-8 host exhibit about 100-fold increase in sensitivity toward methanol (Figure 1). Similar enhancement is observed for other alcohols, but the intensity decreases with increasing chain length. No enhancement is observed for non-polar hexane. To elucidate the mechanisms responsible for sensitivity enhancement, we employed a combination of atmosphere-controlled spectroscopic ellipsometry and broadband dielectric spectroscopy. Ellipsometry revealed increased uptake affinity of IL-embedded MOF toward polar VOCs at low concentrations (about 6-times for methanol), while the recorded dielectric spectra imply the emergence of new polarization contribution at low measurement frequencies. These results reveal synergistic effects in IL-MOF composites that enable ultra-sensitive detection of VOCs using capacitive sensors.

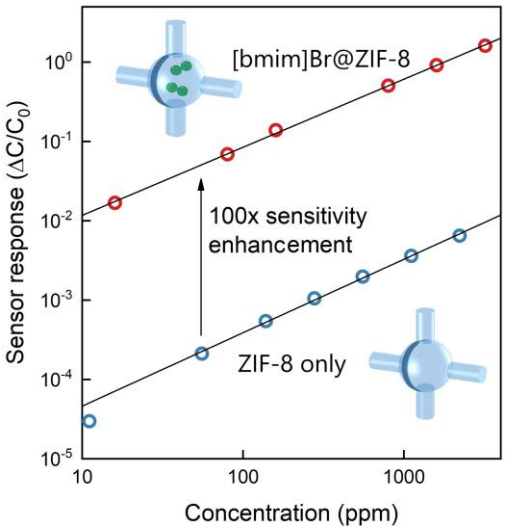


Figure 1: Response of ZIF-8 and IL@ZIF-8 capacitive sensors to low levels of methanol vapour, revealing significant enhancement of sensitivity by ionic liquid incorporation.

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HIERARCHICAL STRUCTURING OF POROUS MOF ADSORBENTS FOR GAS ADSORPTION APPLICATIONS

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Keywords: *microspheres, droplet coagulation, shaping, adsorbents, gas adsorption, MOFs*

The chemical industry is facing major challenges in their transition towards more sustainable processes and dealing with climate change, decarbonization and resource scarcity. Since more than 90% of all chemical processes require catalysts and sorbents, development of advanced materials with specific characteristics tailored to the application is key to improve the overall performance, efficiency and sustainability of the industry. Most developed materials are synthesized in the form of powder, making the shaping process highly important for their use in industrial applications. Moreover, the specific shape highly influences some key characteristics including pressure drop, geometric surface area, packed bed density, mechanical stability and overall catalyst or adsorption performance.

Typical architectures for solid porous materials in packed bed configurations include pellets or microspheres, granules and extrudates. Although pellets, extrudates and granulates are widely commercially applied due to the simplicity and speed of manufacturing, a packed bed of these structures might cause a large pressure drop and mass-transfer limitations which lead to inefficient use of the catalyst or sorbent material. Alternative structures including monoliths are also highly investigated, which offer a reduced pressure drop and mass-diffusion limitation due to the ordered packing and the open channels of the structure. Despite the successful manufacturing methods of coating inert supports or extrusion-based systems, also these methods are showing several drawbacks such as limited catalyst or sorbent loading, while extrusion-based processes are not able to produce complex geometries and are limited by the need of extrusion molds for each geometry. Over the last years, additive manufacturing or 3D-printing has become an emerging technology and has proven its potential in several publications and reviews due to its high geometric flexibility and compatibility with a wide range of possible materials, but might come with high costs and decreased productivity in comparison with alternative shaping technologies. Therefore, it is important to evaluate the different shaping technologies and balance the ad- and disadvantages for each specific application case.

A specific study will be discussed, which involves MOFs and more specifically UiO-66 that are shaped into microspheres using (vibrational) droplet coagulation. A flow of a MOF-containing suspension is solidified upon contact with a coagulation bath. Two different binder routes including phase inversion and alginate-based binders have been explored and evaluated in terms of retainment of the specific surface area, overall porosity and mechanical strength. This work was performed in the framework of the HySTram project (Grant Agreement N° 101058643).

GAS EXCLUSION ZONES IN TYPE-II POROUS LIQUIDS

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Keywords: *Porous Liquids, Gas Separations, Molecular Dynamics*

Porous liquids combine permanent porosity with fluidity and may ultimately find uses which are not possible for conventional liquids or porous solids.[1,2] An important general characteristic of porous liquids is that they exhibit very high gas solubilities. Here, a Type II porous liquid (T2PL) of Noria$_{OEt}$ dissolved in 15-Crown-5 (15C5) is presented which demonstrates a characteristic enhanced CH_4 uptake in comparison to neat 15C5.[3] However, very surprisingly it actually exhibits lower CO_2 solubility than 15C5 at pressures above 1 bar. To our knowledge, this is the first time that a T2PL has been reported with a reduced gas uptake in comparison to the neat solvent on which it's based.

Molecular dynamics modelling reveals that although the pore space does provide a good binding site for gas molecules, there is an 'exclusion zone' around the pore space within which binding of CO_2 molecules is disfavoured compared to binding within the bulk solvent. The unfavourable binding may arise from a number of effects, including i. steric exclusion by the covalent framework of the NoriaOEt host, and ii. higher density of the solvation shell around the Noria$_{OEt}$ host compared to the bulk solvent. Overall, this work provides a more sophisticated understanding of gas solubility in Type II PLs.

It also suggests some additional design considerations for achieving high solubility for a given gas. This is implemented in the design in of a porous liquid based using a cryptophane host dissolved in Cyrene, a biorenewable solvent. Due to the reduced surface steric bulk of the cryptophane in comparison to Noria$_{OEt,}$ and the smaller size of Cyrene in comparison to 15C5, this porous liquid is predicted to have a smaller gas exclusion zone than the Noria$_{OEt}$ in 15C5 porous liquid. Indeed, this porous liquid demonstrates an enhanced CO_2 uptake in comparison to its base-solvent, which illustrates how minimisation of the gas exclusion zones leads to formation of improved T2PLs.

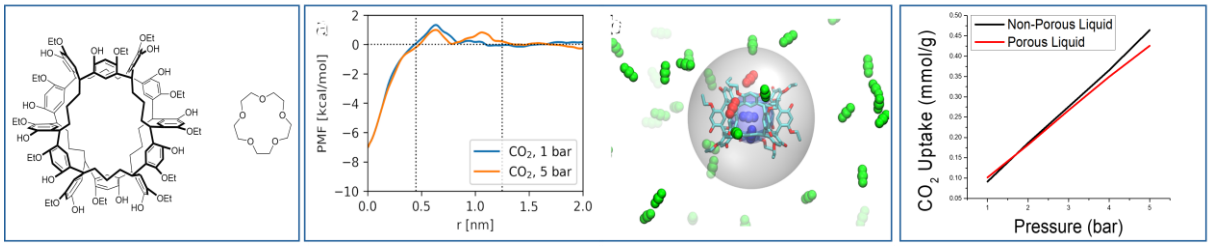


Figure 1 (left) Structures of Noria$_{OEt}$ and 15C5 which are used to form a T2PL. (centre) Graphical summary of MD simulations used to support the formation of a gas exclusion zone in the T2PL. (right) CO_2 uptake measurements of 15C5 and the T2PL showing the effect of the gas exclusion zone on the gas uptake properties of the T2PL.

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FAST SYNTHESIS OF VINYLENE-LINKED COVALENT ORGANIC FRAMEWORKS VIA FAVORABLE INTERMOLECULAR INTERACTIONS

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Keywords: *covalent organic frameworks, vinylene linkage, rapid synthesis, catalysis*

Covalent organic frameworks (COFs) are porous and crystalline materials built from the periodic self-assembly of covalently bonded organic monomers in 2D layers that extend to 3D frameworks. Vinylene-linked COFs are particularly interesting for several applications, including energy storage, electrocatalysis, and metal-free photocatalysis owing to their efficient π-electron delocalization over the C=C bonds, high chemical stability and unique optoelectronic properties, like narrow bandgap and rapid charge carrier mobility.[1] However, most reported syntheses of these COFs typically involve solvothermal methods with controlled atmosphere and pressure, which can be time-consuming and hinder their scalable production and applicability. Recently, solid-state synthesis using benzoic anhydride as catalyst has gathered attention for being an efficient and more viable approach for vinylene-linked COFs. However, this approach still suffers from long reaction times of 3 to 5 days.[2]
Herein, we present our recent results on rapid synthesis of 2D vinylene-linked COFs based on 3,8-dimethyl-4,7-phenanthroline (Phen) via the Knoevenagel reaction.[3] Our studies of COF formation, using 1,3,5-triformylbenzene (TFB) as a counterpart, revealed that the material forms rapidly, with a crystalline framework observed already within 30 min. Nuclear magnetic resonance (NMR) experiments, the synthesis of control COFs, and structure simulations attributed this phenomenon to favorable intermolecular interactions driven by dipole moment of Phen monomer. All Phen-COFs showed suitable optical band gaps for visible light harvesting applications and exhibited photocatalytic activity in dye degradation. Building on this study, we will also present results on extending this approach to other types of vinylene-linked COFs.

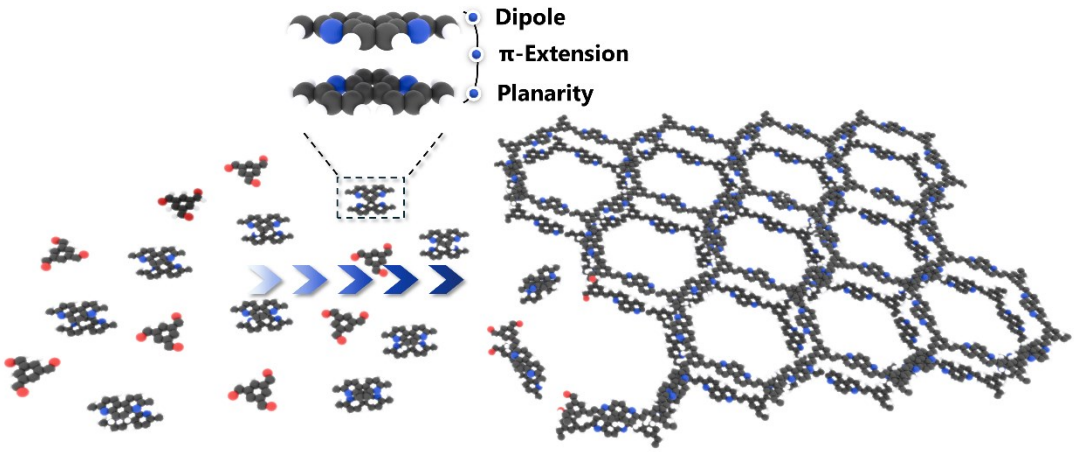


Figure 1: Schematic illustration of the pre-organization of Phen monomers.

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UP-DOWN APPROACH FOR EXPANDING THE CHEMICAL SPACE OF 3D COVALENT ORGANIC FRAMEWORKS

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Keywords: *Covalent Organic Frameworks, Up-down Approach, Reticular Chemistry, Materials Discovery*

Covalent Organic Frameworks (COFs) are a rapidly advancing class of crystalline porous materials composed of organic building units connected through robust covalent bonds. Three-dimensional (3D) COFs, in particular, offer enhanced structural complexity and functional diversity compared to their two-dimensional counterparts. However, the set of reported 3D COF topologies remains disproportionately narrow, despite the vast variety of available organic linkers. To overcome this limitation, we introduce the Up-Down Approach (UDA)—a design strategy originally developed for Zr_6-based metal-organic frameworks [1]—to systematically explore the underutilized chemical space of 3D COFs. Unlike traditional bottom-up synthesis, UDA begins with the identification of feasible topologies and subsequently maps them to synthetically accessible building blocks. Using this algorithmic framework, we discover and validate over 100 novel 3D COF structures that are both chemically diverse and experimentally attainable. This work not only broadens the known landscape of COF topologies but also establishes a new paradigm for rational, high-throughput framework discovery [2]. Up-down approach highlights the untapped potential of modularity and topology in reticular design and opens new avenues for data-driven exploration of porous materials.

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SUPERPROTONIC CONDUCTIVITY IN ZR-BASED METAL-ORGANIC POLYHEDRA

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Keywords: *Metal-Organic Polyhedra, Superprotonic Conductivity, Counterion Impregnation*

Proton conductive materials are crucial components in clean energy technologies, particularly in proton-exchange membrane fuel cells (PEMFCs), which are vital for achieving carbon neutrality. Although Nafion is the most widely used proton-conducting membrane, its limitations—including high cost, temperature sensitivity, and humidity dependence—have driven the search for alternative materials. Recently, porous crystalline solids, such as metal-organic frameworks (MOFs), covalent organic frameworks (COFs), hydrogen-bonded organic frameworks (HOFs), and metal-organic polyhedra (MOPs), have emerged as favorable candidates, due to their high porosity, structural designability, and ordered structures.[1]

Among them, MOPs, consisting of cage-based compounds with weak interaction, have gained attention as a promising class of porous solids.[2] In particular, Zr-based MOPs feature neutrally charged structures, formed by cationic cage molecules charge-balanced by chloride ions. In our previous works, we extended the scope of reticular chemistry to Zr-based MOPs, based on directional packing interactions.[3] Despite their potential, the study of proton conduction in Zr-based MOPs is still in infancy.

Herein, we present UMOP-1 and UMOP-11, as effective Zr-based MOPs platforms for proton conductors *via* modulation of residual cationic species. The lithium-exchanged UMOPs, Li@UMOP-1 and Li@UMOP-11, exhibited superprotonic conductivities of 2.43×10^{-2} and 4.19×10^{-2} S cm^{-1}, respectively, at 363 K and 95% relative humidity (RH)—among the highest values reported for cage-based materials. Compared to conventional Zr-based MOFs, UiO-66 and MOF-808, the UMOP series exhibited enhanced performance, attributed to its ionic framework architecture. Overall, we offer valuable insights into the rational design of next-generation proton conductors.

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DEFECTIVE CE-DOPED MIXED LIGAND-UiO-66 MOFS WITH CONTROLLED FLUORINATION FOR CO_2 CONVERSION: SYNTHESIS AND THOROUGH CHARACTERIZATION

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Keywords: *UiO-66, bimetallic systems, mixed ligands, fluorination, gas adsorption, CO_2 conversion*

UiO-66 is one of the most robust and versatile MOFs, widely employed in gas adsorption, catalysis, and separation. Recently, defect engineering on this material has gained attention: missing linker and cluster defects can be selectively introduced to create exposed metal sites capable of interacting with guest molecules. Additionally, substituting Zr Lewis acid sites with Ce ions (below 17 mol% to avoid pure Ce clusters[1]) can enhance reactivity, particularly for the direct conversion of CO_2 and methanol into dimethyl carbonate (DMC)[2]. This reaction is important for CO_2 fixation, as DMC is a greener alternative to phosgene and dimethyl sulphate, used in polycarbonate synthesis, carbonylations, methylations, and fuel additives.

Studies on Zr and Ce-based MOF-derived oxides have shown that water produced during the reaction deactivates Ce sites, lowering catalytic activity[3]. Using UiO-66 to maintain an even distribution of active sites, could slow water diffusion to Lewis acid centres and improving activity. Moreover, trifluoroacetic acid-modulated UiO-66 catalysts have demonstrated improved performance in DMC synthesis[4], highlighting the role of hydrophobicity in water expulsion.

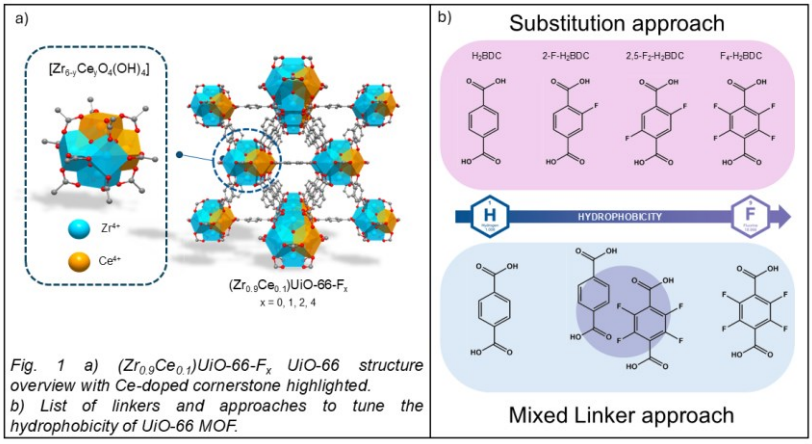


Fig. 1 a) $(Zr_{0.9}Ce_{0.1})UiO\text{-}66\text{-}F_x$ UiO-66 structure overview with Ce-doped cornerstone highlighted. b) List of linkers and approaches to tune the hydrophobicity of UiO-66 MOF.

With this in mind, we succeeded in the synthesis of a series of potential $Zr_{0.9}Ce_{0.1}$-UiO-66 catalytic systems by changing the ligand with fluorine-containing ones and applying a mixed linkers approach by introducing mixtures of fluorinated and non-fluorinated ligands at different ratios (see Fig. 1).

These materials are subject of a deep characterization, involving PXRD, porosimetry, TGA, SEM/EDS, ICP-OES and NMR analysis as well as synchrotron radiation techniques, in particular HR-PXRD and in operando AP-XAS.

Preliminary results have shown that the metals ratio in the final materials follows the stoichiometric amount introduced. Moreover, by increasing the fluorine content, decomposition temperature, BET surface area, N_2 and CO_2 uptake decrease, suggesting reduced stability due to probable electronic and steric effects provided by fluorine groups, responsible also of blocking pores accessibility for guest molecules. In operando AP-XAS studies have also confirmed the reduction of Ce^{4+} centres to Ce^{3+} due to a thermal-induced decoordination of a labile ligand and partial re-oxidation upon O_2 gas exposure, as previously suggested in literature[5].

Further studies on metals distribution, dependence of BET surface area on fluorine content, as well as catalitic activity tests will be conducted to evaluate DMC production and fully understand the structure-to-function relationship in these materials.

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BOTTOM-UP COMPUTATIONAL DESIGN OF SHAPE-SELECTIVE ORGANIC MACROCYCLES FOR HUMID CO_2 CAPTURE

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Keywords: *Carbon capture, Humid flue gas , High-throughput screening, Macrocycles*

Carbon capture and storage is of paramount importance in global endeavors toward ensuring a sustainable energy future. Capturing CO_2 from the realistic flue gas remains changeling due to the low concentration of CO_2 diluted in mostly N_2 along with water. In addition, due to the smaller kinetic diameters and larger molecular dipole of water, the competition of H_2O with CO_2 in the same adsorption sites results in the remarkably decrease of CO_2 working capacity. Here, we introduced a high-throughput computational screening workflow to calculate the binding energy of over 25,000 molecular fragments with both CO_2 and water. The screening results revealed that specific aromatic "clip" and prism-shaped macrocycles exhibited optimal CO_2/H_2O selectivity. Following these findings, two water stable molecular macrocycles with either triangular or square geometries were synthesized, namely (+)-NDI-△ and P4. Dynamic column breakthrough experiments confirmed that these structures maintained their CO_2 capacity even in highly humid conditions, outperforming commercial benchmark materials. This bottom-up design strategy could be applied to other porous materials based on molecular organic building blocks.

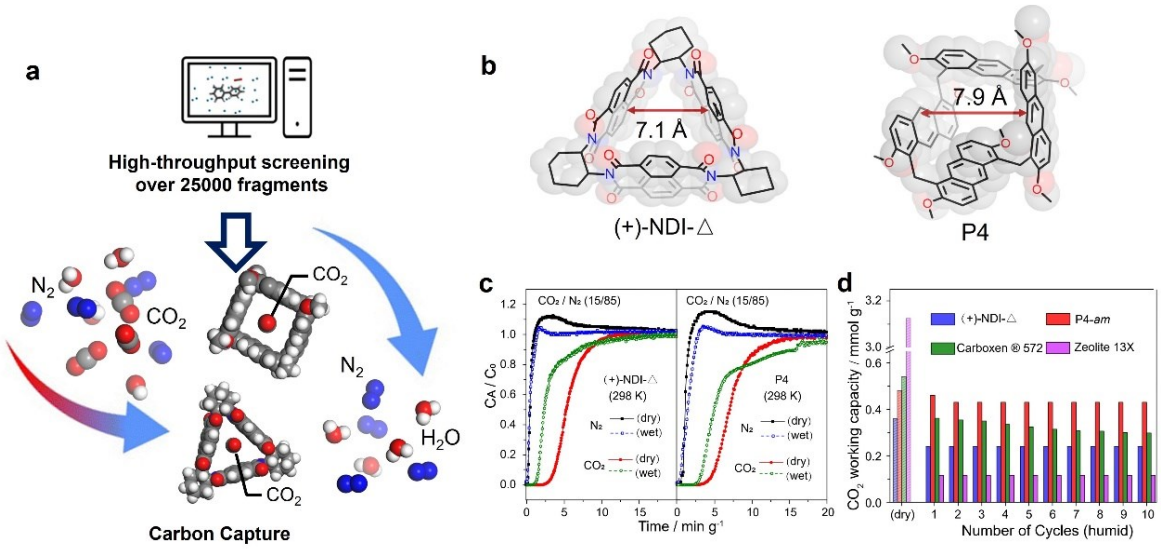


Figure 1. High-throughput screening of molecular fragments (a) used in the rational design of triangular and square organic macrocycles (b) for efficient carbon capture under humid conditions (c and d).

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SURFACE-CONFINED NANOPOROUS SUPRAMOLECULAR NETWORKS STABILIZED BY DIPOLE-DIPOLE INTERACTIONS

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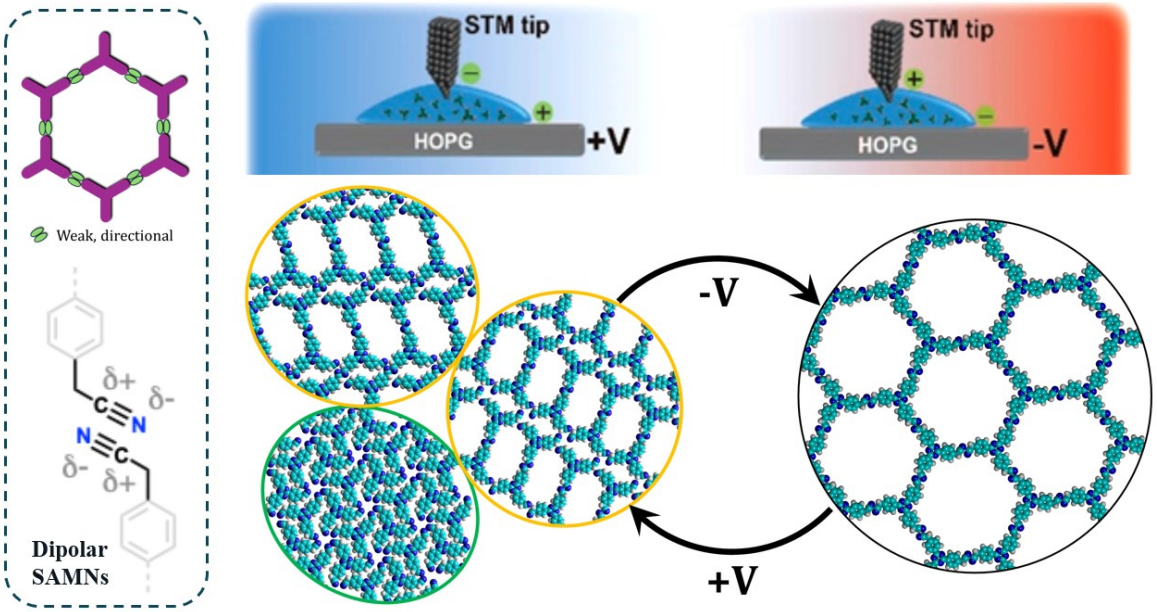
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Keywords: *self-assembled molecular networks (SAMNs), dipole-dipole interactions, porous materials.*

Porous materials have evolved from rigid, strongly bonded inorganic materials such as zeolites to modular and adaptable metal-organic and covalent organic frameworks (MOFs and COFs) based on reversible intermolecular interactions. The trend towards weak and/or reversible interactions continues, where recent research has explored porous materials based on even weaker interactions, such as hydrogen bonding and electrostatic forces.
Building on this trend, here we demonstrate the formation of honeycomb porous supramolecular networks driven by weak, yet directional dipole-dipole interactions formed at the solution-solid interface. High-resolution scanning tunneling microscopy (STM) and molecular modeling reveal how these interactions guide self-assembly and structural stability. We further report on electric field-mediated switching behavior within these SAMNs and their ability to host guest molecular species. In this work, the growing significance of weak intermolecular forces in the design of porous materials has been emphasized, opening new possibilities for dynamic and reconfigurable architectures.



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ENGINEERING POROSITY MODULATION, MULTI-STIMULI RESPONSIVITY AND ORTHOGONAL ISOMERIZATION IN POROUS SWITCHABLE FRAMEWORKS

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Keywords: *Porous Aromatic Frameworks, Molecular switches, Stimuli-responsive materials*

Porous aromatic frameworks (PAFs) possess a low-density, yet robust scaffold with a well-defined topology, which facilitates the organization of dynamic building blocks such as molecular switches and motors in the solid state. Highly porous and stable architectures, denominated Porous Switchable Frameworks (PSFs), were engineered to support the effective isomerization of molecular switches. Light-responsive PSFs based on a bistable chiroptical overcrowded alkene, endowed with an exceptional surface area up to 3950 m^2 g^{-1}, exhibited quantitative bulk photoisomerization in the solid state. Remarkably, the porosity of the framework and the consequent gas sorption capabilities can be reversibly modulated in response to light and heat.[1] An improved hexadentate switching monomer yielded swellable, hierarchical micro/mesoporous architectures with densely integrated photoswitches.[2] The interplay between hierarchical porosity, a flexible backbone, and the reversible photoisomerization between the two isomers resulted in three unique and distinct porosity states that can be accessed in sequence upon application of external stimuli, creating a sponge-like behavior (Figure 1A). Multi-stimuli responsive, yet structurally robust, spiropyran-based materials were prepared using an innovative *in-situ* solid-state grafting approach, preserving their high porosity.[3] This effective strategy produced dynamic materials that undergo reversible transformation of spiropyran to zwitterionic merocyanine by chemical and physical stimulation, showing potential for pH-active control, modulated gas uptake and release, ion capture and immobilization, and water harvesting (Figure 1B). Furthermore, orthogonal photoswitching PSFs were generated by integrating distinct classes of molecular switches, e.g. o-fluoroazobenzene and nitro-spiropyran, into porous architectures.[4] Different wavelengths of light generate four distinct states that can be selectively populated. The juxtaposition of two or more dynamic elements in flexible frameworks points to the development of complex machinery endowed with collective and emergent properties.

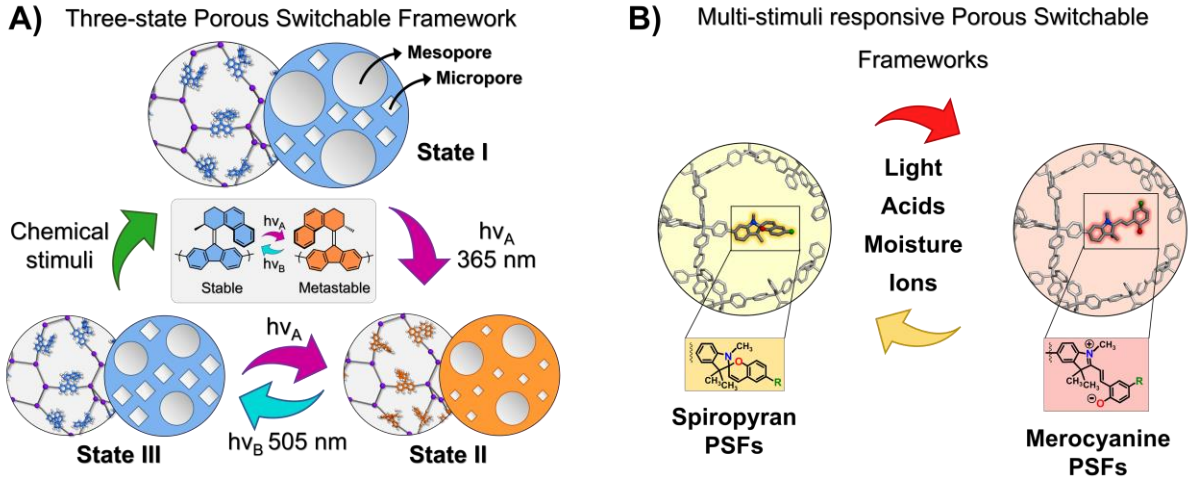


Figure 1

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UNDERSTANDING ION EXCHANGE KINETICS IN A FAMILY OF ORGANIC MOLECULAR CAGES

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Keywords: *Organic Molecular Cages, Ion-exchange, kinetics, ^{79}Br NMR*

Supramolecular chemistry has been a powerful tool in many areas of research, and its most significant application is probably molecular encapsulation. In 1967, Pedersen and coworkers reported the use of macrocyclic compounds, known as crown ethers, for the encapsulation of cations.[1] Currently, a new class of materials has been developed, known as supramolecular cages, which can be classified into two main groups: purely organic and metal-organic hybrids. In this context, purely organic cages are classified as neutral and ionic cages.[2] The latter have a positive charge (usually ammonium salts) that causes the presence of a counterion (anionic species). While the ionic nature of these cationic cages is characterized by low solubility in water and they are only soluble in organic solvents, their use in biological applications is limited.[3] To overcome these limitations, the inclusion of long alkyl chains is used; however, organic chains can modify the nature of the molecular cages.[3] A recent alternative to modify the character of organic and hybrid charged materials is to exchange their counterions.[4]

We have studied the effect of ion exchange on a robust family of cationic organic molecular cages. The objective is to understand the behavior and effect of different nontoxic anions (acetate, carbonate, sulfate, and oxalate). To determine the evolution of ion exchange, we used SEM-EDS, ^{79}Br NMR, and FT-IR. The results indicate that ion exchange is affected by variables such as the molecular cage composition and the anion's pKa. Furthermore, computational simulation shows that the size of these anions modifies their solubility.

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NOVEL TOPOLOGIES OF ZINC IMIDAZOLATE $(ZnIm)_2$ WITH ENCAPSULATED FULERENES

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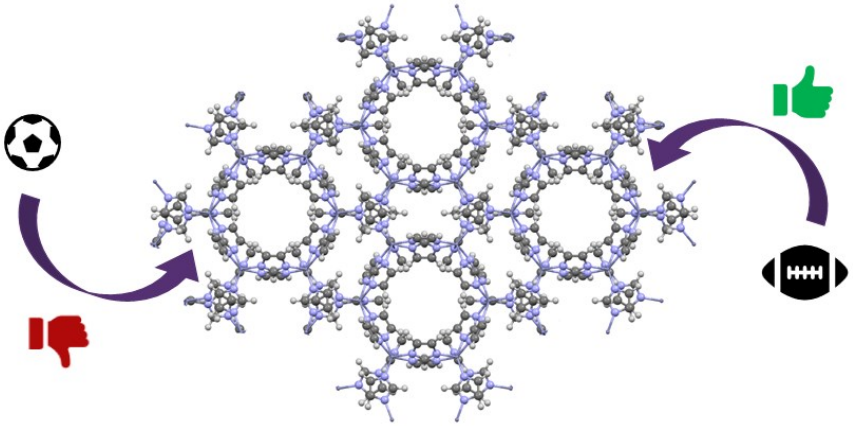
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Keywords: *ZIF, fullerene, topology*

Significance of the simplest member of the zeolitic imidazolate framework (ZIF) materials family, zinc imidazolate ($ZnIm_2$), lies in its remarkable topological diversity where at least 18 distinct topologies have been reported so far.[1] The solvothermal methods predominantly used for preparation of its different topologies are not ideal from a green chemistry standpoint, but also frequently result in (pseudo)polymorphic mixtures. On the other hand, mechanochemical methods have emerged as a promising sustainable alternative for targeted preparation of desired polymorphs using structure-directing effects of different liquids and salts.[2] Furthermore, in materials science studies fullerenes have drawn substantial attention due to their interesting physicochemical properties. ZIF-s have proven to be valuable matrices for encapsulating fullerenes, enabling the formation of novel composite materials with intriguing properties.[3]

In this study, we introduce new solid forms of $ZnIm_2$, synthesized *via* the use of fullerenes as templates and pore-filling agents. We manage to stabilize intrinsically thermodynamically unstable $ZnIm_2$ polymorphic forms through encapsulation of fullerenes, while also introducing supplementary functionalities. Mechanochemical synthesis, used for preparation of new forms, enables the formation of ZIF around the solid template in an exceptionally efficient and stoichiometrically controlled milling process.[4] Comprehensive experimental characterization—including PXRD, IR, SEM, and EPR—alongside rigorous computational exploration utilizing molecular dynamics (MD) and dispersion-corrected periodic density functional theory (DFT) calculations, substantiates our findings.



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DOUBLING DOWN ON BISPIDINES: NOVEL TETRATOPIC LIGANDS FOR COORDINATE POLYMERIZATION

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Keywords: *VOCs, 1D coordination polymers, adsorbents, bispidines*

Refineries, as well as the chemical, pharmaceutical, and automobile industries, along with various human activities, release significant amounts of volatile organic compounds (VOCs) such as halogenated hydrocarbons, aldehydes, and aromatic compounds, which pose environmental and human health risks[1]. With VOC emissions projected to reach 60 teragrams of carbon per year by 2030, effective sequestration strategies are urgently needed. Coordination polymers (CPs) represent a class of hybrid metal–organic materials self-assembled from two components: metal ions and organic ligands[2]. While three-dimensional coordination polymers 3D CPs, particularly metal-organic frameworks (MOFs) have long held a prominent role in VOC adsorption applications, recent efforts have shed light on CPs that lack inherent porosity or possess small, tunable pores and cavities with size and shape complementarity to specific guest molecules. Moreover, although MOFs have traditionally been constructed using simple ligands, the incorporation of structurally complex compounds has emerged as a promising strategy to broaden the scope of accessible materials. Among these, bispidine-based ligands, derivatives of 3,7-diazabicyclo[3.3.1]nonane, have been employed in the synthesis of one-dimensional CPs that exhibit effective and selective VOC adsorption under ambient conditions[3].The rigid yet versatile bispidine scaffold, capable of supporting significant structural modifications, represents a highly attractive platform for the design and development of novel coordination polymers[4].

In this work, we have designed and synthesized tetratopic bispidine ligands which have been then used to obtain novel CPs (Figure 1). They have been synthesized, characterized by SC- and P-XRD and tested for VOCs adsorption applications.

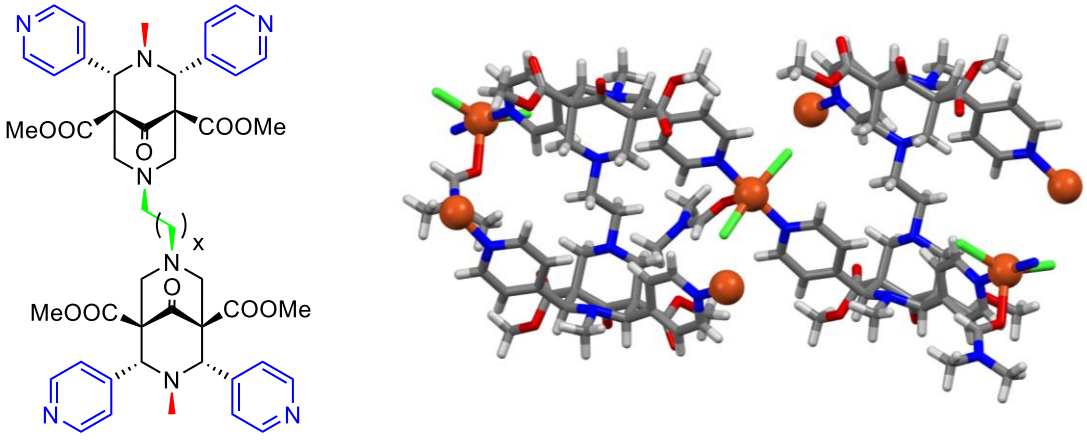


Figure 1: a) Tetratopic bispidine ligands (x = 1-4) and b) Representative 1D coordination polymer obtained with Cu(II) and L1 (x =1).

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STRUCTURAL ANISOTROPY IN COORDINATION POLYMER GLASS INDUCED BY MACROSCOPIC ELONGATION

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Keywords: *Melting, Glass, Anisotropy*

Glassy materials, represented by silica glass, generally feature isotropic properties based on structural isotropy. Formation of anisotropy in glassy structures allows the material to show unique properties including birefringence and uniaxial elasticity.[1] Macroscopic anisotropy is induced by the orientation of the components by processes such as elongation as investigated in glassy organic polymers. Coordination polymer (CP) / MOF glasses have emerged as novel functional glasses, and the control of the properties was demonstrated by the external stimulus-induced structural modulation in the molecular scale.[2][3] However, the macroscopically anisotropic structures and properties are still to be explored.

We studied the anisotropy of a glassy structure of Li(TFSI)(bpp) (**1**, Li(TFSI) = Lithium bis(trifluoromethanesulfonyl)imide, bpp = 1,3-Bis(4-pyridyl)propane). Single-crystal X-ray diffraction analysis revealed that **1** has a one-dimensional chain structure in the crystalline state (Fig. a, b). **1** melted at 139 °C and formed a glassy state below 11 °C. **1** exhibited stringiness and the Weissenberg effect, a well-known phenomenon in organic polymers, in the supercooled liquid state (Fig. c, d).[4] The Weissenberg effect originates from the chain structures of the polymer. This suggests a network containing one-dimensional chains in both the supercooled liquid and glassy states of **1**. Microscopic and macroscopic structural changes induced by external stimuli were elucidated using spectroscopic techniques such as infrared and solid-state nuclear magnetic resonance.

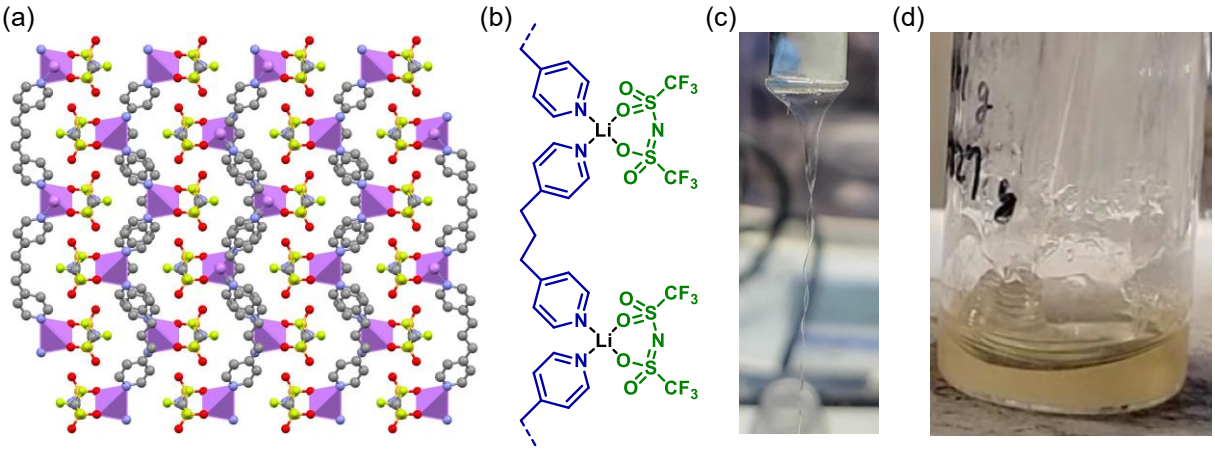


Fig. (a, b) Crystal structure of **1**. (c) Elongated supercooled liquid of **1**.
(d) Weissenberg effect in the supercooled liquid state of **1**.

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Development of cyclodextrin MOFs for food packaging and study of its absorption and release kinetics

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Keywords: *Cyclodextrin, Metal Organic Frameworks, Food Packaging, Kinetics*

The application of volatile compounds like essential oils in fields such as pharmaceuticals and packaging is frequently limited due to their low stability under environmental conditions. To enhance their functionality, Metal–Organic Frameworks (MOFs) offer a promising approach for encapsulation and controlled delivery. However, conventional MOFs can pose toxicity concerns due to the presence of certain metals and organic ligands. In this study, we developed biocompatible MOFs using β-cyclodextrin (β-CD), a compound recognized as GRAS (Generally Recognized as Safe) by the FDA.
The MOFs were prepared through vapor diffusion technique and eugenol was incorporate inside the cavities. Various characterizations were performed to analyze the structure of MOFs.The XRPD peaks at 4.5°, 6.3°, 10.4°, 12.4°, and 19.1° [1, 2]correspond to the crystal planes of (110), (200), (222), (330), and (630), the crystallinity of the MOFs were around 76%. SEM images indicated that the MOFs possessed cuboidal shape with channels of cavities. TGA results showed as slight increase in the degradation temperature from 326.5°C (for β-CD) to 329°C (for β-CD MOFs). FT-IR results confirmed that Eugenol was successfully incorporated inside the MOF cavities and was not present on the surface. Antibacterial testing using S. aureus and E. coli was performed through Kirby Bauer Method. The results showed that MOFs containing eugenol showed antibacterial activities against both the bacterial strains. The loading efficiency of MOFs were around 18±0.5% irrespective of amount of MOFs, The absorbance of eugenol inside the MOFs was monitored over time and pseudo second order model was found to be best fit with R^2 = 0.96492 as compared to that of R^2 = 0.93716 in pseudo first order and R^2 = 0.91244 in Weber-Morris Model. The release kinetics was most suitable for a zero order fit with a R^2 = 0.96345, other models like Korsmeyer–Peppas (R^2=0.8258), Higuchi (R^2=0.7809) and First order (R^2= 0.7548) seemed to be non-suitable. The transition from pseudo-second-order adsorption to zero-order release suggests that the system is effective to first retain the active compound through strong interactions, and then release it in a controlled, steady manner highlighting the potential of β-CD MOFs as a promising platform for sustained delivery applications.

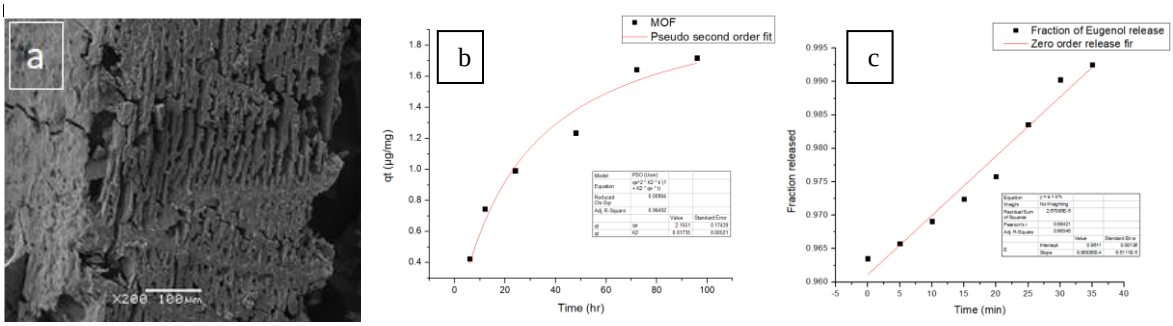


Figure 1: a) SEM images showing MOF cavities, b) Absorption Kinetics following PSO model and c) Release kinetics following Zero-order model

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METAL-ORGANIC FRAMEWORKS IN MATRIX SOLID-PHASE DISPERSION FOR THE EXTRACTION OF PHYTOCHEMICALS FROM *CANNABIS SATIVA* L. AERIAL PARTS

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Keywords: *Cannabis sativa* L., *matrix solid-phase dispersion, metal-organic frameworks*

Cannabis sativa L. is a dioecious herbaceous annual plant, native of Central Asia but easily adaptable to different geographical conditions. This specie could be classified in different chemotypes based on the content of tetrahydrocannabinol (THC), which is the main psychoactive compound in the plant. A distinction is usually made between drug (cannabis) and fiber (hemp) types, based on the higher content of tetrahydrocannabidiol (THC) and cannabidiol (CBD), respectively[1].

The phytochemical composition of *Cannabis sativa* L. is highly diverse, incorporating a wide range of bioactive compounds such as cannabinoids (like the THC aforementioned), and flavonoids as cannflavins and apigenin. All these compounds have important medical, industrial, and recreational interest and, for that reason, the monitoring of these compounds in the plant is of interest. The common approach for the extraction and further determination of cannabinoids is a solid–liquid extraction method using medium to low polarity organic solvents, such as ethanol, methanol and hexane, followed by chromatographic analysis. This methodology implies a high consumption of organic solvents, materials, and energy, and thus it can be considered as a non-sustainable method.

To overcome these limitations in terms of sustainability, matrix solid-phase dispersion (MSPD) have gained attention. This technique involves the direct mechanical blending of the sample (usually a solid) with a solid sorbent, allowing to clean-up and homogenize the matrix while further facilitating the partitioning of the compounds of interest to a compatible extraction solvent. As solid sorbents, metal-organic frameworks (MOFs) are interesting materials due to their exceptionally high surface area, tunable pore structure, and selective adsorption properties[2].

This study focusses on the novel application of the CIM-80(*Al*) MOF in MSPD for the selective extraction of a group of flavonoids and cannabinoids from *Cannabis sativa* L in combination with high-performance liquid chromatography and diode array detection (HPLC-DAD), thus proving the ability of these crystalline materials to succeed with complex plant samples.

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Acknowledgments

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SELF-ASSEMBLY OF UNCHARTED POLYHEDRA PREDICTED BY GRAPH CONVERSION

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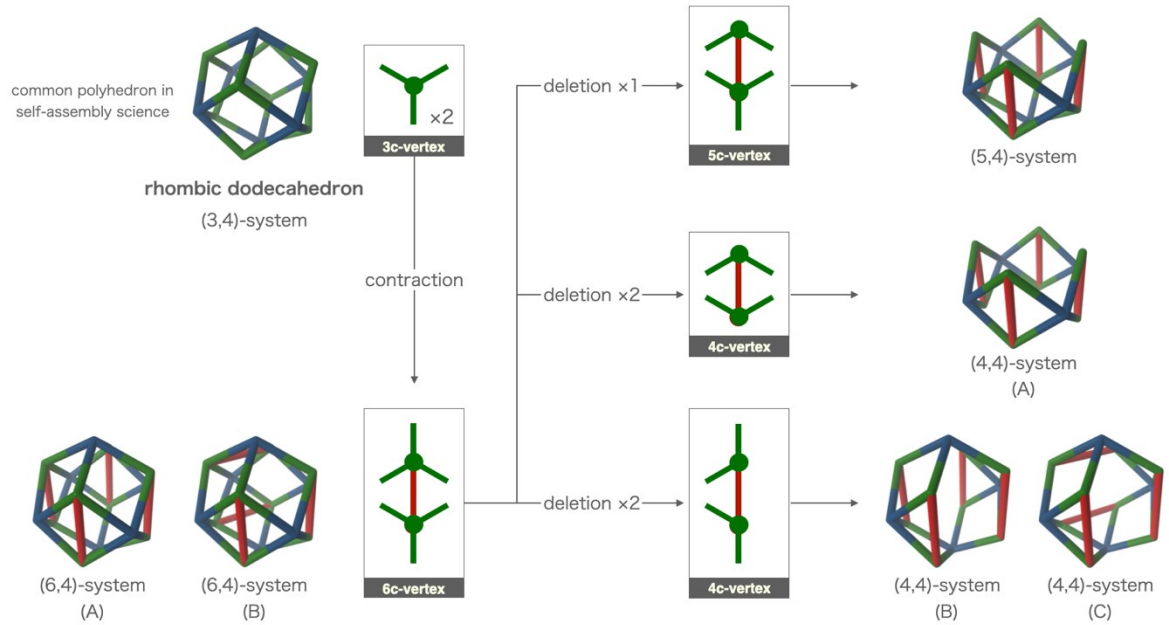
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Keywords: *metal-organic polyhedra, ligand design, graph topology*

The topology variation of polyhedral molecules that can be synthesized through self-assembly is strongly limited. According to reviews on polyhedral metal complexes, there are only about 20 polyhedral topologies that are well reproducible in synthetic chemistry.[1] Therefore, the development of methods to propose new topologies could advance the chemistry of discrete self-assembly system. In this context, we have been working on exploring novel polyhedral topologies by using graph theory, aiming to build theoretical frameworks and validate them through synthetic chemistry.

A graph in discrete mathematics is a structure made up of “vertices” and “edges”. Self-assembled structures like polyhedral molecules are well-suited for graph theory. For example, the structural principles of icosahedral virus capsids can be mathematically described as a part of the trivalent Goldberg polyhedral group. As an extension of this, the tetravalent Goldberg polyhedral group has also been realized as a form of polyhedral metal complexes.[2] However, this principle assumes that “self-assembly spontaneously selects highly symmetrical structures”. This means that it is not applicable for assembling structures with low symmetry.

To address uncharted low symmetry topologies, we applied graph structure conversion to rhombic dodecahedron and found that there exist several low symmetric derivative polyhedra (Figure). Most of them are successfully synthesized as a form of MOPs and their structures are unambiguously determined by single-crystal X-ray diffraction analysis. As far as we know, each topologies realized here are novel ones. In this presentation, we disclose the essence of graph structure conversion, how to design organic ligands, and crystal structures of symmetry-lowered MOPs.



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DEVELOPMENT OF 2.5-DIMENTIONAL COVALENT ORGANIC FRAMEWORKS WITH HIGH CO2 CAPTURE AND SEPARATION PERFORMANCE

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Keywords: *Porous materials, Covalent organic frameworks, Single crystals, CO_2 capture*

Covalent organic frameworks (COFs) are crystalline porous materials formed by the covalent bonds of building blocks, and various applications have been proposed due to their high design flexibility.[1] Their development has primarily followed two structural dimensions: 2D-COFs offer planar morphologies for membranes but are limited by their crystallinity and domain size. 3D-COFs have superior crystallinity but are less suitable for certain device applications.[2,3] This trade-off between morphology (2D) and crystallinity (3D) is a key challenge.

To address this problem, we have developed a novel class of COFs, **TK-COF-4**/**-5**, synthesized by sub-stoichiometric condensation of tetrahedral amines (**TAM**) and triangular aldehydes (**TFPT**/**TFPB**).[3] The novel COFs present an unprecedented 2.5-dimensional (2.5D) structure, constructed with 3-dimensional covalent bonds yet exhibiting a 2-dimensional layered structure on a macroscopic scale (Fig. 1a). Significantly, this 2.5D structure enables the growth of exceptionally large single crystals (> 0.1 mm, Fig. 1b), overcoming the size limitations of 2D-COFs.[2] Furthermore, the key consequence of the 2.5D-COFs is the formation of ultrahigh-density primary amine groups regularly positioned and oriented perpendicular to the covalent planes.

The unique 2.5D structure, particularly the densely packed and accessible amine functionalities, provides exceptional performance for CO_2 capture applications. **TK-COF-4**/**-5** exhibits a highly desirable combination of high CO_2/N_2 selectivity (IAST selectivity > 100 for a 15:85 CO_2/N_2 mixture gas, Fig. 1c) coupled with remarkably low isosteric heat of adsorption ($Q_{st} \approx 25$ kJ mol^{-1}, Fig. 1c). This simultaneous achievement of high selectivity and low Q_{st} is a significant breakthrough, overcoming the common trade-off observed in many porous materials[3] and offering substantial advantages for energy-efficient CO_2 separation processes by minimizing regeneration energy costs. Our findings indicate that 2.5D-COFs are highly potential candidates for advanced carbon capture applications.

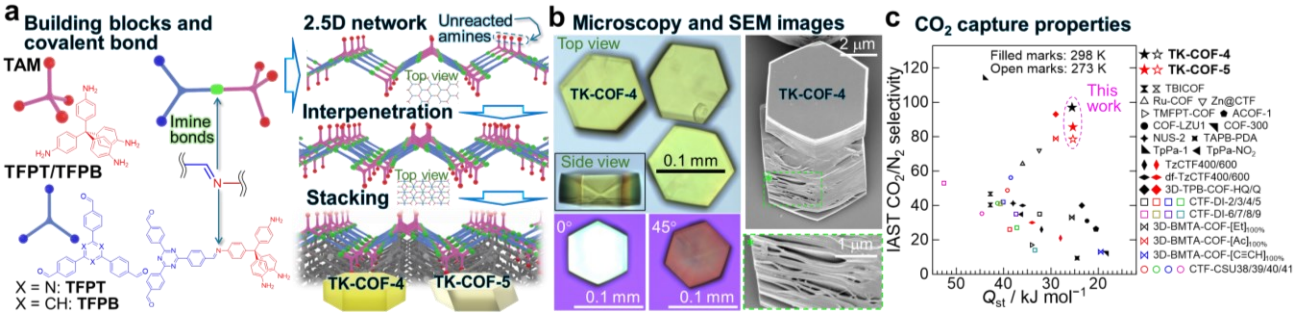


Figure 1 (a) Schematic depiction of 2.5D-COFs formation. (b) Optical micrographs and SEM images of **TK-COF-4**. (c) Comparison of IAST CO_2/N_2 selectivity and Q_{st} with previously reported COFs.

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A MULTIVARIATE LIGAND STRATEGY TO IMPROVE BIOFUNCTIONALITY AND STABILITY IN ENZYME@MAF BIOCOMPOSITES

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Keywords: *Metal-Azolate Frameworks (MAFs), Multivariate ligands (MTV), Biocatalysis*

Enzymes are biological catalysts that are used for a range of biotechnological processes. Despite their wide range of applications, their practical implementation is often limited by their instability in harsh non-native conditions, such as exposure to organic solvents, extreme pH, or proteolytic agents, which can lead to denaturation and significant loss of activity.[1,2] Encapsulation within metal–organic frameworks (MOFs),[2] and in particular within Metal-Azolate Frameworks (MAFs)[2,3], has emerged as a robust strategy to overcome these limitations, offering structural protection and enhance enzymatic activity and performance for a broad range of applications, including sensing and catalysis.[1,2,4]

In the field of MOF chemistry, a multivariate (MTV) synthesis enables the incorporation of diverse functional groups into the framework building blocks, forming isoreticular MOF structures. The MTV-approach preserves the material's intrinsic properties[5,6] while optimizing the pore environment and tailoring specific characteristics, such as hydrophobicity.[7,8,] This strategy can be effectively applied to metal-azolate frameworks (MTV-MAFs) by adjusting the ratio of distinct azolate ligands, thereby fine-tuning the hydrophilic–hydrophobic properties of the framework.[7] This tunability is particularly advantageous for the fabrication of enzyme@MAF biocomposites: controlling the incorporation of different ligands, it is possible to create a favorable microenvironment for the immobilized enzyme.[7,8]

We synthesized a series of enzyme@MTV-MAF biocomposites with sodalite (**sod**) topology, and we screened a large set of synthetic parameters (e.g., ligand ratios) and systematically investigated the physical, chemical and functional properties (e.g., crystallinity, enzymatic activity, encapsulation efficiency) of the biocomposites. We demonstrated that, by controlling the ratio of different azolates in the MTV-MAF, the enzyme@MTV-MAF exhibited an increase of up to 41% in the enzymatic activity, compared to the free enzyme in solution, and a high specific activity of the biocomposites (i.e., up to 6800 U/g). Furthermore, enzyme@MTV-MAF showed that, compared to the free enzyme, the operable pH range for enzymatic activity was extended, allowing for a potential broader range of working environments and applications. In conclusion, enzyme@MTV-MAF composites exhibit enhanced enzymatic activity and stability, establishing MTV-MAF as promising platforms for advanced biosensing and biocatalytic applications. This spontaneous, facile and additive-free preparation of highly active enzyme@MTV-MAF crystalline biocomposites will facilitate the implementation of green chemistry in catalysis and sensing applications.

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ORIGAMIC METAL-ORGANIC FRAMEWORKS AS PROGRAMMABLE MECHANICAL METAMATERIALS

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Keywords: *Origami, Mechanical Metamaterials, Materials Discovery*

The intersection of reticular chemistry and mechanical metamaterials offers exciting avenues for programmable structure and function. Here, we present metal–organic frameworks (MOFs) engineered with origami-inspired motifs to access tunable mechanical properties, including negative Poisson's ratio, foldable architectures, and mechanical anisotropy. Our design principles exploit the modularity of MOF nodes and linkers to guide lattice deformations and shape reconfigurability. We further explore hybrid frameworks integrating photoactive or conductive subcomponents to couple mechanical response with functional output. These architected MOFs exhibit emergent metamaterial behavior with potential applications in molecular robotics, soft matter design, and adaptive porous systems. This work establishes a new design paradigm for synthetic metamaterials grounded in precision chemical synthesis and crystal engineering.

The convergence of reticular chemistry and mechanical metamaterials is opening up novel directions for the design of materials with programmable structure and function. In this work, we present a new class of metal–organic frameworks (MOFs) that incorporate origami-inspired design principles to achieve mechanically tunable and reconfigurable architectures.

By strategically engineering the MOF lattices, we realize frameworks that exhibit unusual mechanical behaviors such as negative Poisson's ratio (auxeticity), directional foldability, and pronounced mechanical anisotropy. These properties emerge not from the chemistry of the building blocks alone, but from the precise spatial arrangement of nodes and linkers—a hallmark of reticular chemistry. Our approach takes full advantage of the modularity and predictability of MOF construction to direct and control lattice deformation pathways.

The resulting materials have potential applications in molecular robotics, soft actuators, adaptive porous systems, and other areas where dynamic, responsive behavior at the molecular scale is desired. This work establishes a new paradigm for synthetic metamaterials, grounded in precision crystal engineering, and highlights the untapped potential of MOFs as platforms for integrating mechanical, structural, and functional design.

QUASIPERIODICITY IN MOIRÉ METAL–ORGANIC FRAMEWORKS

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Keywords: *Quasiperiodicity, Moiré pattern, Metal–Organic Frameworks*

The emergence of quasiperiodicity—non-repeating yet ordered structures with forbidden rotational symmetries—has challenged conventional definitions of crystallinity and opened new avenues in materials design. However, achieving precise control over quasiperiodic length scales remains difficult, as such patterns are typically sensitive to chemical composition and atomic interactions.

In this work, we demonstrate that metal–organic frameworks (MOFs) can serve as a highly tunable platform for realizing dodecagonal quasiperiodic patterns through moiré engineering. By twisting bilayer MOFs composed of triangular lattices, we generate interference patterns that exhibit quasiperiodic order, as confirmed by high-resolution transmission electron microscopy and mathematical analysis. These patterns originate not from intrinsic quasiperiodicity but from the controlled superposition of periodic layers.

Crucially, we achieve angstrom-level modulation of quasiperiodic length scales by tuning geometric parameters within an isoreticular design framework. This approach enables systematic access to quasiperiodicity without requiring building units that directly encode forbidden symmetries.

Our results bridge the conceptual gap between MOFs and quasiperiodicity, highlighting the potential of layered reticular materials for exploring aperiodic order and emergent symmetry. This work opens new directions in the design of structurally programmable porous materials and provides a foundation for future exploration of topological and functional phenomena in quasiperiodic MOF systems.

SPATIALLY ORDERED DEFECTS IN METAL-ORGANIC FRAMEWORKS: TOWARDS PRECISE CONTROL AND PROPERTY OPTIMIZATION

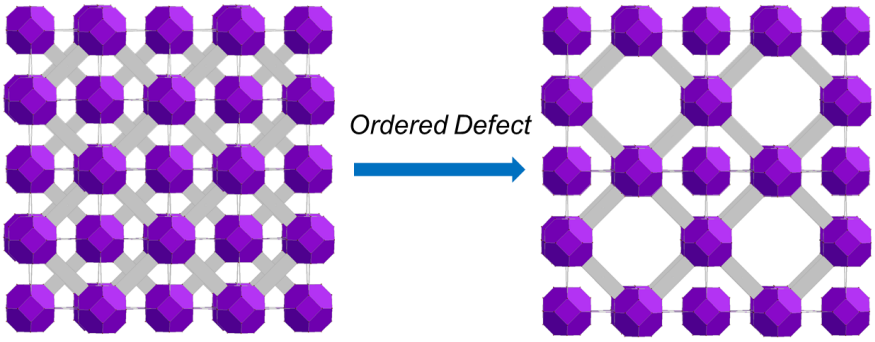
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Keywords: *MOFs, Defect, Controlled synthesis, Structure-property relationship …*

Ideal periodic solids do not exist in nature, as defects are inherently present and critically influence solid-state properties. Metal-Organic Frameworks (MOFs) are no exception, with their performance strongly governed by defect structures. Understanding the defect-property relationship and achieving controlled defect synthesis remain central challenges in MOF research.[1-2] Building on previous efforts to maximize defect density and isolate specific defect types,[3-4] we now focus on controlling the spatial distribution of defects within MOFs. By employing kinetic nucleation-controlled synthesis and thermodynamically guided ligand design, we achieve spatially ordered defect distributions, restoring structural order while strategically enhancing material properties. This ordered defect arrangement significantly improves catalytic activity and separation performance by optimizing active site accessibility and diffusion pathways. Our findings underscore the pivotal role of defect spatial distribution in MOF functionality, providing new insights into defect engineering strategies. This study advances the precise design of MOFs with tailored defect architectures, paving the way for next-generation materials with superior catalytic and separation efficiencies.



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POST-SYNTHETIC MODIFICATION OF LAYERED MOFS CONSTRUCTED FROM TETRAZINE LIGANDS

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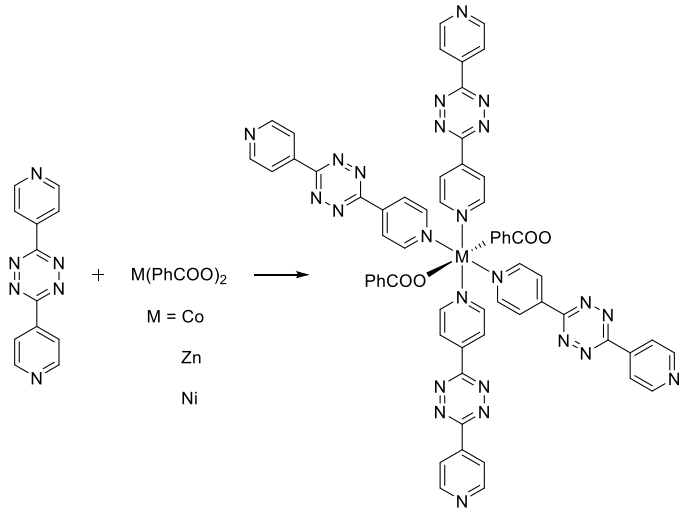
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Keywords: *Tetrazine, Diels-Alder reaction, 2D MOF*

Abstract

Two-dimensional (2D) metal-organic frameworks (MOFs) have attracted significant interest due to their excellent performance, ultrathin structures, and large specific surface areas [1]. Post-synthetic modification (PSM) of frameworks is one of the most widely used tools in the field of MOF-related research. Among various functional groups, 1,2,4,5-tetrazine (s-tetrazine) has attracted considerable attention in coordination chemistry due to its unique electron-deficient nature and the potential for post-synthetic modification via the well-established inverse electron-demand Diels–Alder (D-A) cycloaddition reaction [2]. In this study, a strategy based on the D-A reaction of tetrazine was employed to PSM a layered MOF. The approach involved incorporating tetrazine functional groups into the layered MOF, followed by a D-A reaction to weaken the van der Waals interactions between the layers, thereby facilitating exfoliation into 2D sheets. The feasibility and effectiveness of this method were evaluated by examining various tetrazine-based ligands and their interactions with different alkenyl reagents. This innovative strategy demonstrates a promising route for synthesizing 2D MOFs with enhanced structural and functional tunability.



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HIGH-THROUGHPUT DISCOVERY OF POLYMORPHIC POROUS STRUCTURES IN METHYL-SUBSTITUTED AMMONIUM CHLORIDE SALTS

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Keywords: *Porous organic salts, high-throughput crystallization*

Porous organic salts, constructed through ionic interactions and hydrogen bonding, feature charge-separated, highly polar nanoconfined channels that endow them with unique properties such as adsorption[1], I_2 capture[2], and proton conductivity[3]. Due to the lack of strong directional bonds guiding crystal growth, molecular crystals are often sensitive to crystallization conditions, which can readily lead to the formation of various polymorphic structures. Different packing typically results in significant variations in porosity and channels, thereby offering potential applications across diverse fields.

Herein, we employed high-throughput crystallization on the OT-2 platform to demonstrate the feasibility of forming different porous structures in ammonium chloride salts. By using methyl-substituted triazine amines and systematically adjusting both the acid equivalents and the crystallization solvent, we successfully obtained a series of ammonium chloride salts featuring distinct channel architectures. The presence of sterically hindered substituents adjacent to the amine groups, combined with variation in acid stoichiometry, enabled the formation of structures with different protonation and tautomeric states, which in turn led to diverse packing modes and substantially enriched the structural variety obtained. In one exemplar of the structures with permanent porosity, partially protonated triazine and its tautomeric form can co-assemble into dimers that further organize into porous frameworks.

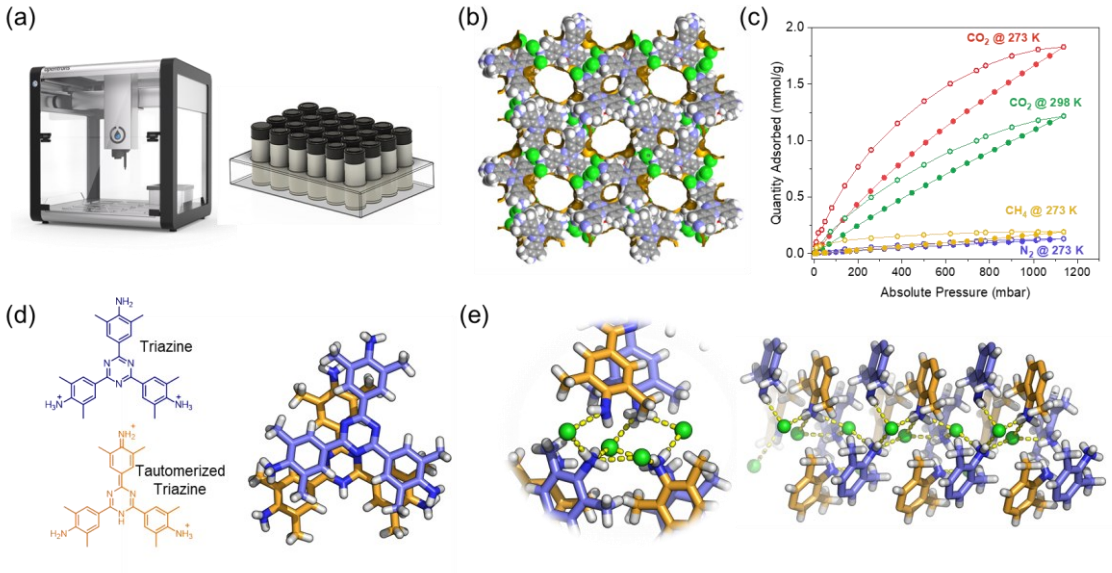


Figure 1. (a) High-throughput crystallization performed using the OT-2 platform and a 24-well rack plate. (b) Obtained porous structure featuring one-dimensional channels. (c) Adsorption isotherm of the porous material. (d) Packing structure of protonated methyl-substituted triazine and its tautomeric form. (e) Detailed ammonium chloride ions interactions.

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SELF-EXPANSION OF METAL–ORGANIC CAGES USING A RING-OPENABLE LIGAND

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Keywords: *Metal–organic cages, Rhodium, Ozonolysis, Ring-opening reaction, Self-expansion*

Metal-organic cages (MOCs) composed of metal ions and organic ligands are highly designable crystalline materials with functional nanopores.[1] To explore the potential functionalities of MOCs, post-synthetic modification is a powerful method for rational alterations of the size and functionality of the nanopores.[2] However, the existing methods based on ligand exchange or defect engineering cannot drastically enlarge their cavity size while preserving the topology of original complex skeletons, often causing structural collapses.

In this study, we have developed a new strategy to expand the MOCs cavities while retaining their topology (Figure 1a).[3] For this purpose, we designed ring-openable ligands with flexible oligomeric chains that tether the two benzene rings of stilbene, whose olefinic bond can be cleaved by ozonolysis.[4] The cavities of the resulting MOCs could be successfully enlarged via the self-expansion method.

Ring-openable ligands **L** were synthesized from hydroxybenzoic acid derivatives in 5 steps (Figure 1a). Rh_6(**L**)$_6$ type MOC **1** was synthesized by mixing an acidic form of the ligand (**L**+2H), Na_2CO_3, and rhodium(II) trifluoroacetate in *N,N*-dimethylacetamide at 100 °C for three days. The formation of MOC **1** as [Rh_6(**L**)$_6$] was confirmed by single crystal X-ray diffraction analysis (SCXRD).

Self-expansion of **1** was carried out by bubbling ozone through the solution of **1** to cleave the C=C bond in the stilbene moiety, followed by treatment with dimethyl sulfide (Figure 2a). Transformation into the expanded MOC structure (**1′**) was evidenced by MALDI-TOF-MS, ^{1}H NMR, UV-vis. The direct synthesis of **1′** or similar MOCs using long flexible linkers was not achievable due to an entropic disadvantage. Thus, highly flexible, expanded MOCs are only accessible via this self-expansion approach using designed linkers.

Owing to its expanded backbone, the expanded MOC **1′** can encapsulate a guest molecule (2,4,6-tri(4-pyridyl)-1,3,5-triazine; **tpt**) whose size is larger than the inner cavity of the original MOC **1**, which was revealed by SCXRD analysis (Figure 1b). Remarkably, the expanded host adaptively captured the guest molecule in an induced-fit manner with the aid of its highly flexible chain.

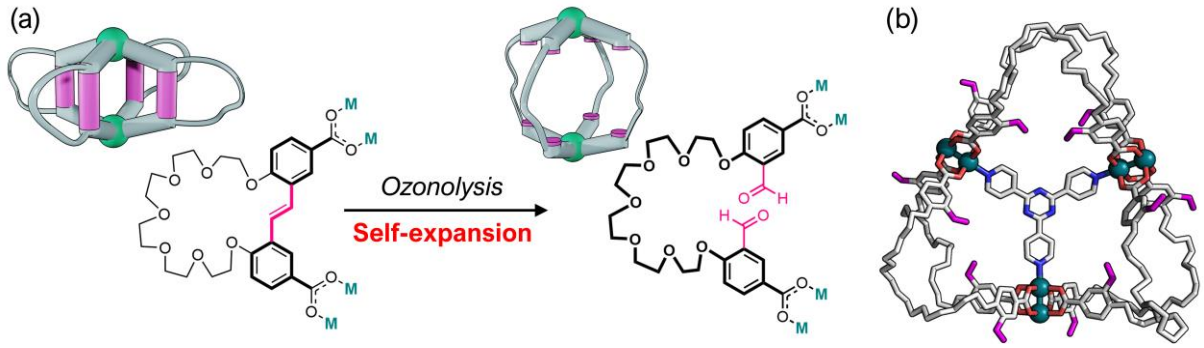


Figure 1. (a) Scheme of the self-expansion of a MOC and the structural transformation of **L**. (b) Single crystal X-ray structure of the expanded MOC **1′** encapsulating **tpt**. Rh ions, N atoms, and O atoms coordinating to Rh ions are shown in green, blue, and red respectively. Aldehyde groups are shown in magenta.

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ELECTRIC FIELD-TRIGGERED DYNAMICS OF 2D COVALENT ORGANIC FRAMEWORK BY *IN SITU* SPECTROELECTROCHEMISTRY

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Keywords: electromagnetic field*, 2D, Covalent organic framework ,Mn, in-situ operando*

Surface-Enhanced Infrared Absorption (SEIRA) enables ultrasensitive detection of vibrational signatures by exploiting intense local electromagnetic fields near nanophotonic structures. When coupled with complementary spectroelectrochemistry (SEC) techniques, such as EPR-SEC, SEIRA-SEC, ATR-IR-SEC, and UV-Vis-SEC, it allows for the identification of reaction intermediates under varying electrochemical potentials. In this work, we demonstrate that the enhanced electric field at the COF–electrode interface induces dynamic structural reorganization of the 2D covalent organic framework (COF) through expansion and translocation mechanisms. These structural changes lead to the formation of distinct intermediate species. We investigate the correlation between intermediate formation and catalyst (COF_{bpyMn})[1] framework dynamics under applied potentials. Our findings highlight the structural complexity and responsiveness of reticular materials, offering valuable insights into their behavior under external stimuli and guiding future studies on dynamic processes in functional organic frameworks.

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ENHANCED ENERGY STORAGE OF A POROUS COORDINATION POLYMER BY INTRODUCING ADDITIONAL TRANSITION METAL

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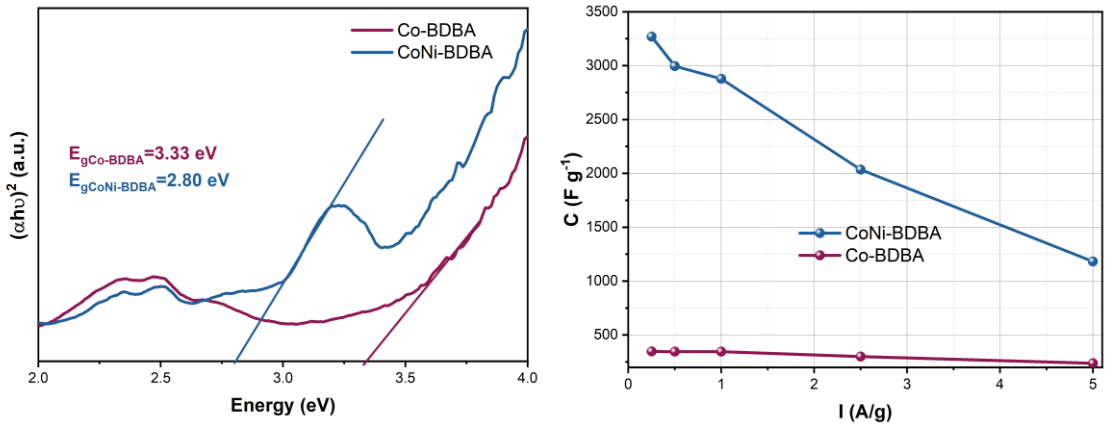
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Keywords: *Energy Storage, Porous Coordination Polymer, Benzene-1,4-diboronic acid, Cobalt, Nickel*

Due to the necessity of reducing climate change rate, moving from carbon-based fuels towards sustainable and renewable energy sources (e.g., solar, wind) is a paramount goal for humankind. However, since renewable energy sources produce energy intermittently, energy storage systems are mandatory.

Recently, it has been previously reported the use of benzene-1,4-diboronic acid (BDBA) as ligand in the construction of a cobalt-based coordination polymer (CPs)[1], which showed outstanding results as electrode for Li-ion batteries. In this work, we synthesized a novel material entitled CoNi-BDBA built up from BDBA, as ligand, Co(II), and Ni(II) as coordination centers in order to use it as electrode in supercapacitor devices. Based on powder X-ray diffraction and XPS analysis, we believe that Ni(II) atoms occupy the same crystallographic sites that Co(II), where Ni(II) substituted some Co(II) randomly in the SBU. The addition of Ni(II) results in enhanced electronic properties of the material, compared to the monometallic material (Co-BDBA). Cyclic voltammetry results indicate that the material has a pseudocapacitor behavior. Furthermore, galvanostatic charge-discharge profiles of CoNi-BDBA present high symmetry. Finally, CoNi-BDBA has a specific capacitance value of 2876 F g^{-1} at 1 A g^{-1} (8 times greater than that of Co-BDBA), value even higher than other CPs[2]. These improved properties can be attributed to the formation of new energetic levels created at introducing Ni(II) atoms[3].



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A PHOTOTAUTOMERIC 3D COVALENT ORGANIC FRAMEWORK FOR RATIOMETRIC FLUORESCENCE HUMIDITY SENSING

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Photo-induced proton transfer is an essential process for designing photocatalysts, bio-imaging, and fluorescence sensing materials. However, deliberate control of the excited/ground states and meticulous manipulation of the excited state intramolecular proton transfer (ESIPT) pathway in the solid materials constitute a significant challenge. Here, we present the integration of a fluorophore into a crystalline, porous, phototautomeric dynamic 3D covalent organic framework (COF) to show guest-induced fluorescence turn-on, emission redshift enhancement, and shortened lifetimes. Theoretical and spectroscopic studies provide mechanistic insights into the Phototautomerism, conformational dynamics, charge transfer coupled with local excitation, and ground-state uphill regulation. We illustrate the sensitive, rapid, steady, and self-calibrated ratiometric fluorescence sensing for a wide range of humidity benefiting from the architectural and chemical robustness and crystallinity of such a 3D COF. These findings provide molecular insights into the design of functional porous materials that integrate host-guest mutual recognition for multiplex molecular sensing for environmental monitoring and biomedical diagnostics applications for the future.

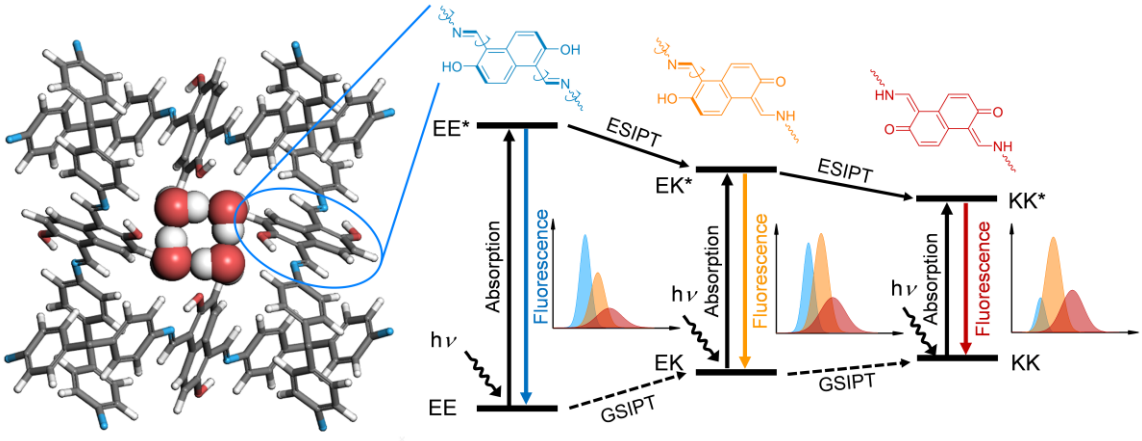


Fig.1 Energy levels for the phototautomerization process of COF-310 with adsorbed water molecules

Keywords: *covalent organic frameworks, proton transfer, ratiometric fluorescence*

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BENCHMARKING SELECTED DENSITY FUNCTIONALS AND DISPERSION CORRECTIONS FOR MOF-5 AND ITS DERIVATIVES

Joshua Edzards,[a,b] Julia Santana Andreo,[a,b] Holger-Dietrich Saßnick,[a] and Caterina Cocchi[a,b]

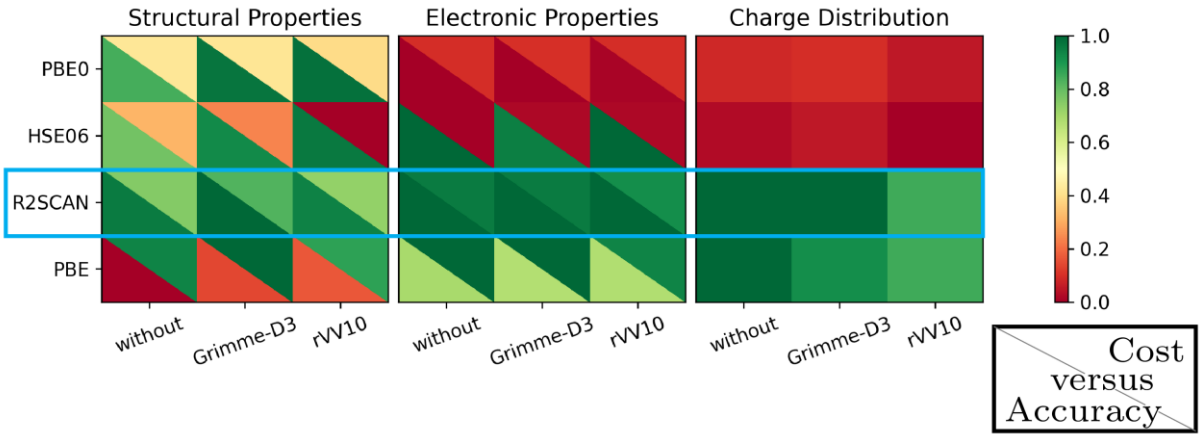
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Keywords: *DFT, Benchmark, Functional, Dispersion Correction, MOF-5*

The rational design of metal-organic frameworks (MOFs) with tailored properties heavily relies on accurate and computationally efficient theoretical methods. In view of high-throughput screening based on ab initio methods like density functional theory (DFT), the selection of appropriate settings and approximations is crucial to obtain reliable results. Here, we benchmark semi-local, meta-GGA, and hybrid DFT functionals in conjunction with van der Waals correction schemes on MOF-5. Building upon a previous high-throughput screening study on its stable derivatives[1], we assess the performance of the functionals in the calculation of structural, and electronic properties, considering different metal nodes and functional groups. Our results show that the meta-GGA functional R2SCAN strikes the best balance between accuracy and computational efficiency. It provides structural parameters that align well with experimental findings and charge distributions comparable to hybrid functionals. Explicit treatment of van der Waals interactions is crucial for accurately describing the structural properties. Our conclusion is that R2SCAN in combination with the Grimme-D3 scheme represents the most favourable approach for high-throughput screening studies on MOFs, offering a reliable approach for predicting their electronic, and structural characteristics[2].



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DYNAMIC STABILITY OF MOF-5 AND ITS DERIVATIVES

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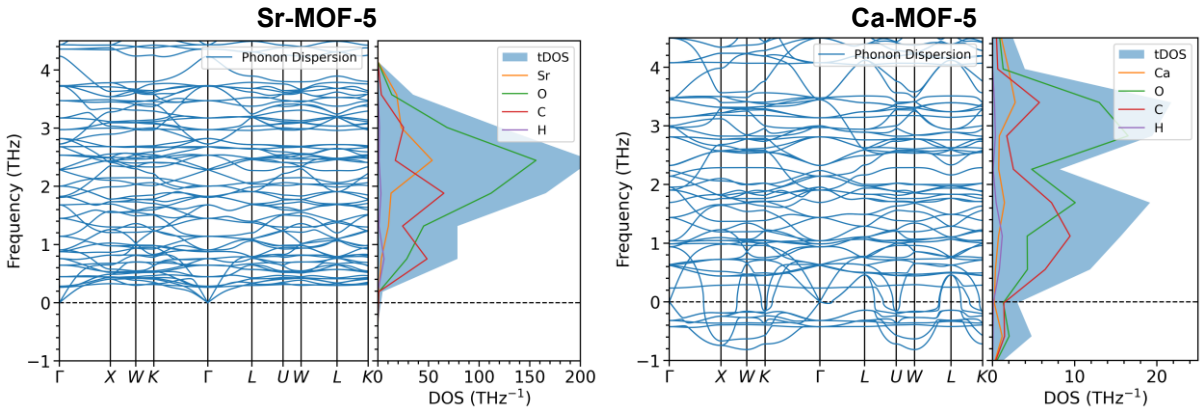
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Keywords: *DFT, Phonons, Stability, Functionals, MOF-5*

Assessing the dynamical stability of computationally predicted structures is crucial in the vast landscape of MOFs to confirm their feasibility for synthesis. Using density functional theory (DFT), we investigate the vibrational properties of MOF-5 in its pristine form or with metal-node substitution and/or organic linker functionalization [1]. Our results reveal that MOF-5 derivatives incorporating Sr and Mg are dynamically stable, evidenced by the absence of imaginary frequencies. In contrast, Ca substitution induces significant instabilities, particularly in the low-frequency regime. Leveraging our earlier benchmark study of exchange-correlation functionals for MOF-5 [2], we exclude the possibility that these effects are artifacts of the adopted approximations. Conversely, we demonstrate that these low-frequency imaginary modes are related to phonon anharmonicities and negative thermal expansion, providing valuable insights for high-throughput screening studies of MOFs.



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FUNCTIONALIZATION OF MONOLITHIC MOF THIN FILMS WITH HYDROCARBON CHAINS TO ACHIEVE SUPERHYDROPHOBIC SURFACES WITH TUNABLE WATER ADHESION STRENGTH

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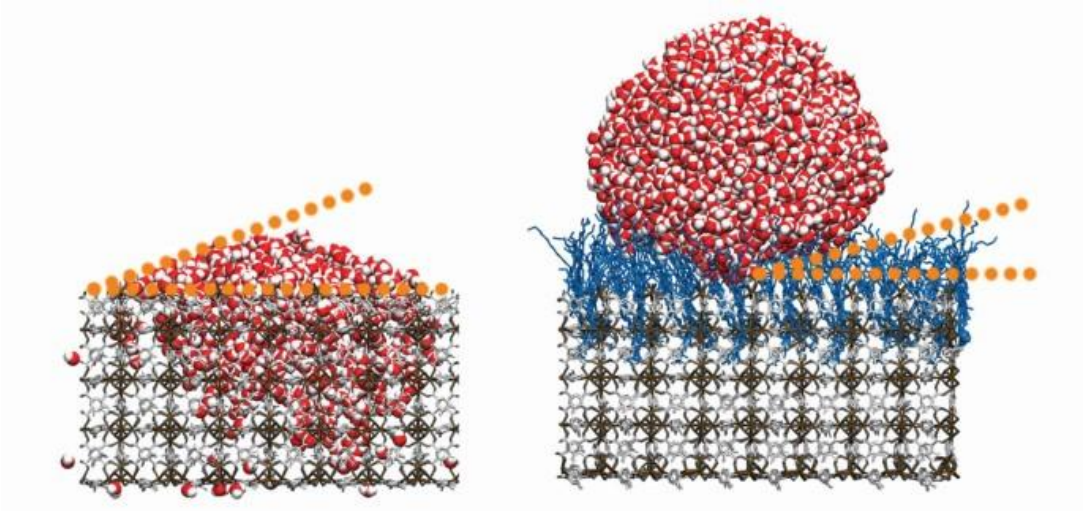
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Keywords: *surface-coordinated metal-organic frameworks, wetting, superhydrophobicity*

Despite the accessible pores render an enormous variety of functionalities for the bulk material in metal–organic frameworks (MOFs), the MOFs' exposed outer surfaces is less investigated while the interface also offer unique characteristics not available when using conventional substrates. By grafting hydrocarbon chains to well-defined surface-coordinated MOFs (SURMOFs) prepared using the layer-by-layer technique, we were able to fabricate superhydrophobic substrates with static water contact angles over 160°. A detailed theoretical modelling of the hydrocarbon chains grafted on the outer SURMOF surface with well-defined spacing between anchoring points reveals that the grafted hydrocarbon chains behave similarly to polymer brushes during wetting, where conformational entropy is traded with mixing entropy. In dry conditions, the chains are coiled and can access many different conformations, as evidenced directly by infrared spectroscopy. During wetting, the entropic contributions from the coiled state lead to a pronounced reduction of the surface free energy, rendering superhydrophobic properties to the functionalized SURMOFs. Additionally, the water adhesion strength could be decreased by increasing the surface roughness on the nanometer scale.



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LEVERAGING MOFS FOR EFFECTIVE ICE RECRYSTALLIZATION INHIBITION

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Keywords: *Ice recrystallisation Inhibition, Metal Organic Framework, MOFs for biological systems, Machine Learning, MOF-design, MD simulations, Cryopreservation.*

Cryopreservation preserves biological materials using methods like slow freezing and vitrification, though thawing often causes damaging ice formation. Vitrification employs cryoprotectants (CPAs), such as ice-binding proteins (IBPs) like antifreeze glycoproteins (AFGPs), which inhibit ice recrystallization via an adsorption-inhibition mechanism. However, due to immunogenicity, high cost, and scalability issues, biomolecules are unsuitable for large-scale use. To overcome this, various organic molecules have been studied for ice recrystallization inhibition (IRI) using experiments and MD simulations. Effective IRI agents typically feature exposed hydroxyl groups for strong ice binding, lattice matching to enhance interaction, and high surface area—all contributing to ice suppression via the Gibbs–Thomson effect [1–3].

A recent study[4,5] experimentally evaluated the IRI activity of a class of MOFs, specifically UiO-66 variants, and found that UiO-66$(OH)_2$ exhibited superior ice growth inhibition compared to other MOFs in the same family. This finding sparked increased interest in the potential of MOFs as effective IRI agents. MOFs consist of metal nodes coordinated with organic linkers, and the vast diversity in metal centers, linker chemistries, and framework topologies provide a high degree of tunability for specific applications. This structural and chemical versatility makes MOFs particularly attractive for tailoring properties critical to IRI performance. Leveraging these advantages, we conducted a comprehensive screening + design of MOFs designed to incorporate key features associated with high IRI activity.

We began by screening for the most effective organic linkers that could mimic the properties of antifreeze glycoproteins (AFGPs). This was done by training a neural network (NN) model to predict mean grain size (MGS), based on data reported by Warren, M. T. et al[6]. The model was then used to predict MGS values for a set of organic linkers, which had been descriptorized using RDKit in a manner like AFGPs. Linkers predicted to result in lower MGS were selected for further ice-binding simulations under varying degrees of supercooling and concentrations, aiming to validate and understand their ice recrystallization inhibition (IRI) activity.

Ice binding MD simulations showed that increasing linker concentration raises hydrogen bonding and reduces ice growth by saturating the surface. Linkers bind to ice crystals through hydrogen-bonding functional groups, creating surface curvature that suppresses growth via the Gibbs–Thomson effect. This mechanism, supported by previous studies [7,8], makes organic linkers effective in controlling ice formation, further supporting MOFs to be used as effective IRI agents. MD simulations were performed on MOFs with the tested organic linkers, as both nanoparticle and surface of varying sizes. Results revealed that the exposed organic linkers bind with ice inducing the Gibbs Thomson effect, which prevents ice growth. They were further tested for different concentrations and degree of supercooling.

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TOWARDS A FUNDAMENTAL UNDERSTANDING OF FORCED LIQUID INTRUSION FOR SHOCK ABSORPTION APPLICATIONS USING MACHINE LEARNING POTENTIALS

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Keywords: *forced liquid intrusion, zeolitic imidazolate frameworks, shock absorbers, machine learning potentials, kinetic Monte Carlo, solid-state modelling, functional materials*

Zeolitic imidazolate frameworks (ZIFs) are a class of nanoporous materials characterised by highly tuneable and interconnected cages. Their peculiar structure opens up a wide variety of exciting applications, including the absorption of mechanical shocks in hydrophobic ZIFs (Fig. 1).[1] In this process, water is forced through the hydrophobic apertures separating the ZIF nanocages, which partially absorbs the energy present in a mechanical shock. Recent studies have shown that the energy absorbed during a single intrusion-extrusion cycle of liquid water in ZIF-8 is strain rate-dependent, with faster shocks resulting in greater energy dissipation and improved shock absorption performance.[1] This behavior can be fine-tuned by adjusting the ZIF material (and consequently, the size, shape, and connectivity of the nanocages), crystallite size, and liquid compositions. Yet, it remains unclear how to design the best ZIF shock absorber that has both a high absorption capacity and remains reusable.

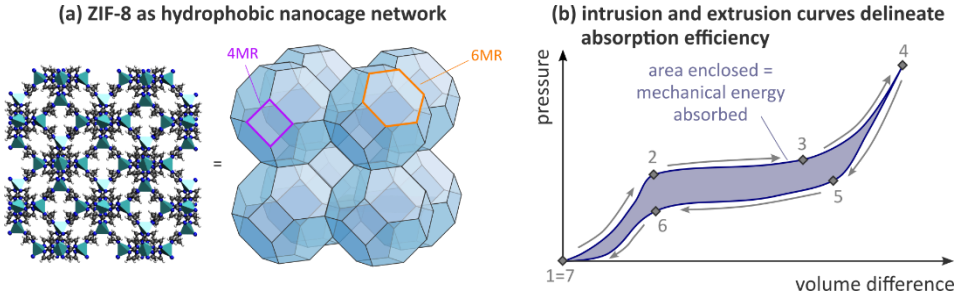


Fig. 1: *(a) ZIF-8 structure of Zn^{2+} nodes and methylimidazolate linkers; (b) Forced liquid intrusion/extrusion cycle and associated energy dissipation. Intrusion occurs between points 2&3 and extrusion between points 5&6.*[1]

Deriving these highly sought-after design rules requires fundamental insight into the interactions between the ZIF and the intruded liquid on the atomic scale, as well as a systematic way to model how these nanoscale interactions affect the macroscopic liquid intrusion that occurs in ZIF crystals of up to several tens of micrometers. Since *ab initio* molecular dynamics methods are computationally too expensive for these length scales, we herein train a machine learning potential (MLP) to capture these interactions with near-quantum accuracy.[2] As the description of hydrogen bonds is of the utmost importance, we will outline the key challenges involved and present our proposed solutions to overcome them. Secondly, new simulation tools that span long time and length scales are necessary to predict macroscopic intrusion properties. Intrusion is inherently a multiscale problem, and deriving macroscopic properties requires realistic crystallite sizes. To address the limitations of current state-of-the-art methods, we develop here a macroscopic kinetic Monte Carlo model (kMC) that is parametrised based on our atomistic MLP simulations. Our multiscale kMC model describes intrusion as a series of hopping events between neighboring nanocages, which reduces the complexity while maintaining a high accuracy due to the MLP-derived parameters. This kMC model builds on three fundamental parameters, all of which can be extracted from our MLP simulations, as outlined in this contribution. With our model, we can already qualitatively predict the experimentally measured intrusion and extrusion pressures as well as intrusion timescales. We will specifically focus on the results for the prototypical ZIF-8 system.

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MACHINE LEARNING-ACCELERATED DEVELOPMENT OF METAL-ORGANIC FRAMEWORKS FOR ENHANCED METHANE CAPTURE

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Keywords: *Machine Learning, Methane Capture, visualization tools*

Methane significantly contributes to global warming, yet effective processes for capturing methane from emission sources are limited.[1] Metal–Organic Frameworks (MOFs) exhibit remarkable tunability in pore environment and geometry, making them highly promising candidates for gas adsorption and separation.[2] Most studies to date have primarily focused on high-pressure methane storage systems for automobiles, while research into low-pressure methane capture remains limited. In this work, we apply a machine learning (ML)-driven screening approach to a large hypothetical MOF database to identify promising materials with high methane capture capacity under ambient conditions. Furthermore, we present the rational design of a novel MOF with three open metal sites, VUF-2 (Victoria University Framework 2), constructed from hexakis(isophthalic acid)benzene and copper clusters. We aim to systematically investigate the effects of open metal site configurations on methane adsorption thermodynamics, supported by experimental validation through controlled synthesis and gas adsorption measurements. Additionally, we have improved the algorithm used for gas adsorption visualization to enhance computational efficiency while maintaining high spatial resolution, enabling molecular-level visualization of adsorption site dynamics. This work establishes a closed-loop methodology that integrates predictive modelling, targeted MOF design, experimental characterization, and adsorption profile visualization, thereby elucidating structure–property relationships at atomic resolution and accelerating the discovery of next-generation methane storage materials.

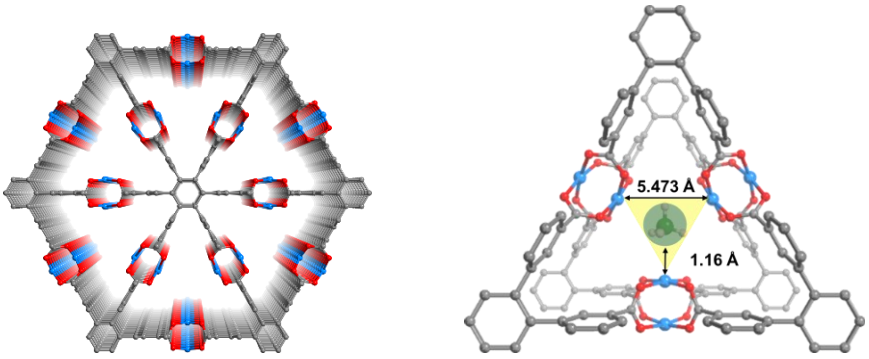


Fig 1. (a) Modelling of VUF-2 (b) Triangular cavity of VUF-2, the methane molecular is treated as modeled as a van der Waals sphere (radius: 2.0 Å)

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FUNCTIONALIZING SURFACE-MOUNTED METAL-ORGANIC FRAMEWORK (SURMOF) FILMS VIA POLYMER CHAIN INSERTION INTO PORE CHANNELS

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Keywords: *SURMOF, wettability, functionalization*

Crystalline pillared-layer $Cu_2(bdc)_2dabco$ surface-mounted metal-organic frameworks (SURMOFs) were synthesized via a layer-by-layer (LbL) deposition method.[1] We achieved functionalization of these SURMOF films through the preferential incorporation of various linear polymer chains—specifically alkanes ($C_{20}H_{42}$/C20), $C_{40}H_{82}$/C40) and polyethylene glycol (PEG)—along the (001) crystallographic direction.[2] Structural characterization using X-ray diffraction (XRD) and infrared reflection-absorption spectroscopy (IRRAS) verified the inclusion of polymeric guests within the nanochannels of the framework, as evidenced by shifts in the form factor and characteristic vibrational modes, indicative of uniform polymer distribution at the molecular level. This polymer infusion approach offers a facile strategy for modifying surface-wetting properties, in contrast to traditional covalent functionalization methods that rely on reactive ligand side groups and are limited to selected MOFs.[3] Notably, the inherently hydrophilic $Cu_2(bdc)_2dabco$ SURMOF exhibited a significant change in wettability: becoming hydrophobic after C20 (~84.7°) and C40 (~113.2°) infusion, and superhydrophilic with PEG (~ 3.9°). The C40-infused SURMOF surface also displayed remarkable slippery property, enabling beaded water droplets to slide off easily when the surface was tilted.

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ATOMICALLY PRECISE ENGINEERING OF SYNERGISTIC ADSORPTION SITES IN A ZIRCONIUM MOF FOR THE HIGHLY EFFICIENT ADSORPTION OF PERFLUOROOCTANOIC ACID

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Keywords: *metal-organic framework, water decontamination, perfluoroalkyl substances, synchrotron characterization, theoretical calculations*

The rising environmental challenges have signaled a global shift to more sustainable practices, with access to clean water being a priority of these efforts. However, the increase in industrial activities over the past decades has brought additional water pollution from man-made substances. Perfluorooctanoic acid (PFOA) is a prominent member of these contaminants.[1] Its extreme persistence against conventional treatments has led to high prevalence in water, widespread bioaccumulation and worldwide health concerns. [1,2] Therefore, more effective strategies are urgently required to fully remediate aqueous sources from PFOA.

In this work[3], we have rationally engineered the zirconium-based metal-organic framework MOF-808 by inserting bimetallic species of a secondary transition element within its cluster nodes (Figure 1A-B). Taking into account the chemical nature of PFOA, this structural modification provides access to several binding sites that enable synergistic interactions with the pollutant. These include coordination bonding, hydrophobic and electrostatic forces, making this material ideal for PFOA capture at environmentally relevant concentrations. The framework achieves complete PFOA removal (Figure 1C) within minutes and maintains performance over multiple regeneration cycles. It also shows exceptional maximum adsorption capacity (3120 $mg_{PFOA}\ g^{-1}$) which surpasses previously reported porous materials. Moreover, ex/in situ synchrotron techniques and theoretical calculations provided unique insights on the structural identity of the framework and the synergistic adsorption mechanism. The results offer a clear design strategy towards high-capacity MOF materials with optimal performance for water remediation from persistent perfluoroalkyl substances.

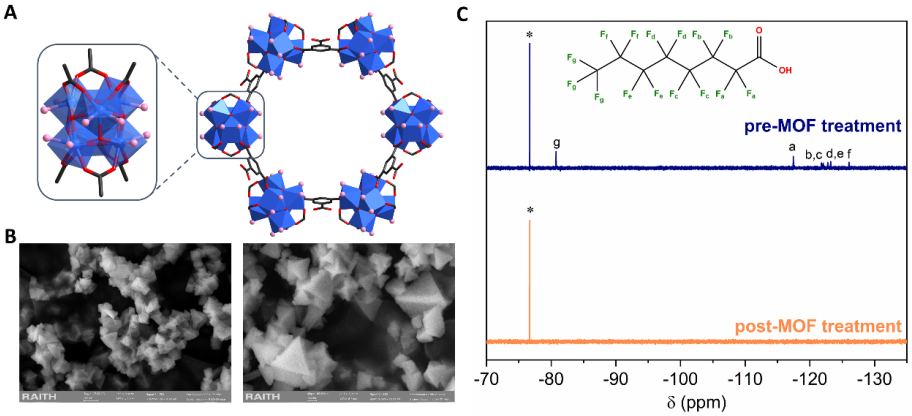


Figure 1. (A) The unsaturated cluster node and resulting hexagonal pores in MOF-808. (Zr: light blue, positions for potential metal insertion: pink). (B) SEM images of MOF-808 before (left) and after metalation (right). ^{19}F-NMR spectra of an aqueous PFOA solution (C_0 = 100 ppm) before and after treatment with the modified MOF, revealing complete pollutant removal.

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ACCESSING CHARGE IN A SERIES OF REDOX-ACTIVE COVALENT ORGANIC FRAMEWORKS (COFS): HARNESSING STRUCTURE-PROPERTY CORRELATION TO PSEUDOBATTERY APPLICATION

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Keywords: *redox-active COFs, electropolymerization, structure-property correlation, charge-storage,* pseudobattery

Abstract: Two-dimensional covalent organic frameworks (2D COFs) constructed from redox-active monomers, so called redox-active COFs (RACOFs)[1], have attracted attention for their utility in charge-storage devices. However, for many of these materials, post-synthetic composite formation is key for their successful use in applications. Furthermore, questions regarding how advantageous RACOFs are in comparison to their amorphous porous polymer (aPOP) analogues still remain. Herein, we mechanochemically synthesized a series of redox-active COFs (TpOMe-DAQ[**x***cis*:**y***trans*]) from 2,4,6-trimethoxy-benzene-1,3,5-tricarbaldehyde (TpOMe) with different ratios of 2,7-diamino-9,10-anthraquinone (DAQ*cis*) and 2,6-diamino-9,10-anthraquinone (DAQ*trans*). Characterization of this polymer series suggested that by increasing the amount of DAQ(*cis*), the materials transitioned from crystalline (COFs) to amorphous (aPOPs). A method for post-synthetic composite formation using the electropolymerization of 3,4-ethylendioxythiophene (EDOT) was developed and optimized which enabled producing ready-to-use electrodes on affordable graphite foil current collectors. This method was applied to the TpOMe-DAQ[**x***cis*:**y***trans*] series as a screening tool to evaluate each material's redox-site accessibility (RSA) in an attempt to probe for any possible structure-property correlations. Ready-to-use electrodes made from the best-performing TpOMe-DAQ polymer via the EDOT-electropolymerization strategy were electrochemically characterized and compared to electrodes prepared by chemical polymerization of EDOT in the same material. The charge-storage potential of ready-to-use electrodes, prepared by EDOT-electropolymerization, was demonstrated by using them as anodes in a beaker-cell-based energy-storage device. This pseudobattery (an intended battery with a significant non-faradaic charge contribution), which used the MnO_2/Mn^{2+} stripping-deposition reaction as the cathode, could operate at 1.1 V and was stable over 1000 cycles at 3C (86% capacity retention). When using the device's full voltage window (1.55 V to 0.45 V), the capacity of the active materials on the graphite foil (excluding the binder) was 73 mAh/g at 3C.

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MOLECULAR RECOGNITION IN $M_{12}L_8$ INTERLOCKED METAL-ORGANIC CAGES

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Keywords: *Metal-Organic Cages, Self-assembly, Dynamic behaviour, Molecular recognition*

Metal-Organic Cages (MOC) represent a great deal for a wide range of potential applications due to their role as porous materials as continuously demonstrated by cutting-edge studies. Connecting MOCs via mechanical bonds is a known approach in which new materials, referred to as polycatenanes made of MOCs (hereafter PC-MOCs), combine the properties of polymers and MOCs.[1] Mechanical bond is the type of bond that allows the mechanically interlocking of two supramolecular groups and the cleavage of a chemical bond is required to separate them.[2]

In this work we explored the topological features and dynamic behaviour of PC of icosahedral $M_{12}L_8$ MOCs (**1**) self-assembled from tris-pyridyl benzene (TPB; denoted L) and a zinc halide (ZnX_2, X = Cl, Br, I; denoted M). The geometry of the cages allows the formation of mechanical bonds to create 1D chains of interlocked nanocages. Solid-state synthesis leads to an amorphous phase (**a1**) representative of the chains collapsed on each other. Inclusion studies of guest molecules like aromatic compounds (e.g. dichlorobenzenes, xylenes, paracetamol…) or small molecules (e.g. methanol, chloroform, carbon dioxide…) were performed using NMR, DFT and X-Ray diffraction techniques. The guests are trapped in the cages in specific binding sites and, thanks to host-guest interactions and a synergic motion of the host structure, allow an amorphous to crystalline transformation where the 1D chains are stacked.[3] A key feature of the crystalline phase of this material (**1**) is the lack of channels between cages, that makes guest exchange seem impossible, which has instead been demonstrated by single crystal to single crystal X-Ray diffraction experiments.[4] We propose a model for the host-guest structure where the pyridines of the ligand act as nanorotors, rotating on themselves to help the inclusion of guest molecules.

Various potential areas of application of **1**, and isostructural compounds, have been carried out. Starting from the capture of Volatile Organic Compounds, guests like xylenes, dichlorobenzenes, nitrobenzene were absorbed by the polycatenanes, allowing studies of preferential capture between them.[4] Preliminary studies were conducted to include an API like paracetamol, elucidating the structure and studying the release in water.[5] Carbon capture technologies were approached studying the effect of the exposure of the material to CO_2 molecules and quantification of such trapping. This supramolecular dynamic system clearly shows the potentialities and opportunities of PC-MOCs.

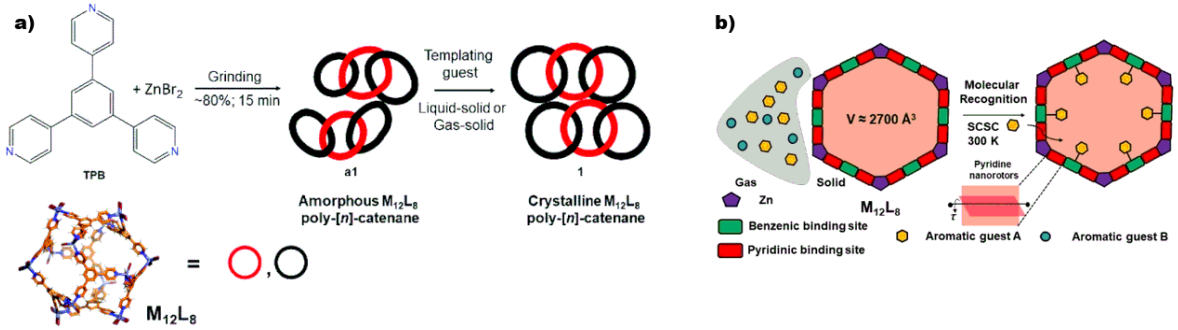


Figure 1: a) Synthesis and amorphous-to-crystalline transformation of $M_{12}L_8$ PC-MOC; b) Molecular recognition in **1** in a gas-solid reaction by means of a SC-SC process.

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LUMINESCENT METAL-ORGANIC FRAMEWORKS AS AN EFFECTIVE ALTERNATIVE FOR HEAVY METAL DETECTION IN AQUEOUS ENVIRONMENT

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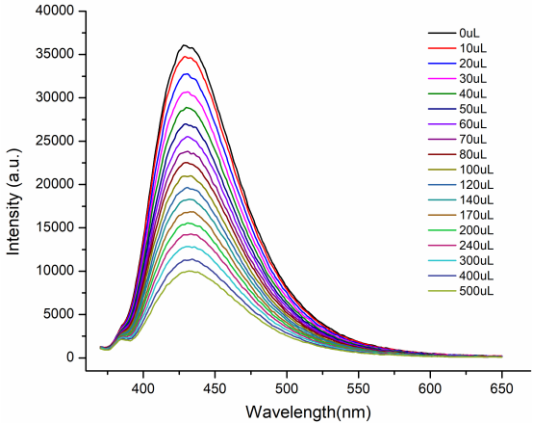
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Keywords: *fluorescent MOF, heavy metal ions, detection, wastewater treatment*

The utilization of metal–organic frameworks in environmental remediation, particularly for the removal of pollutants through adsorption in wastewater, is widespread because of their ease of synthesis, increased adsorption and regeneration ability, and due to the enhancement of their adsorptive properties through ligand functionalization.[1,2] In this contribution we present the synthesis and characterization of two fluorescent MOF materials, bearing the same bridging ligand, aiming to examine the effect of different metal nodes, along with the materials' different structure, on their efficiency in detecting and/or removing heavy metal ions from wastewater. The crystallinity and phase purity of the materials was determined through PXRD measurements, which revealed the structural resemblance to UiO-66 and MIL-53 respectively. The presented MOFs also exhibit stability in aqueous media. Fluorescent titration experiments in water samples with increasing concentrations Cu^{2+} ions and in samples with potentially competitive metal ions show strong evidence of detection, with LOD and LOQ values being several orders of magnitude below the proposed limits of the World Health Organization. In summary, the results reveal a correlation between the metal-ligand combination and the detection capabilities of the resulting material.



Scheme 1. Fluorescence titration of an aqueous suspension of Zr-MOF (0.1 mg mL^{-1}) upon gradual addition of a 10^{-4} M aqueous solution of $CuCl_2$ (λ_{exc} = 340 nm).

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BOOSTING ONE-STEP PROPYLENE PURIFICATION VIA HYDROGEN BONDED FRAMEWORKS WITH OPEN PYRENE SITE

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Keywords: *Hydrogen Bonded Framework, Propane/Propylene Separation*

Olefins are crucial raw materials of the petrochemical industry while propylene (C_3H_6) and ethylene (C_2H_4) are the most important olefins for manufacturing polyethylene and polypropylene[1]. Huge demand of C_3H_6 resulting in the production exceeding 100 million metric tonnes per year in 2020, and the figure is expected to exceed 150 Mt per year in 2050[2]. Notably, the purity of C_3H_6 used for producing polypropylene is needed to be up to 99.5% which is consider as polymer-grade since the excessive impurity may induce an explode during the process of polymerization. The purification of C_3H_6 is highly involved in the separation of C_3H_6 and C_3H_8 while the separation is energy consuming due the low temperature (243 K) and high pressure (0.3 MPa) are engaged during the cryogenic distillation process which is used in current chemical industry[3]. Such high energy consumption not only increases the cost of downstream chemical products of C_3H_6 but also poses great pressure on the environment due to excessive carbon emissions. Therefore, an energy-saving method for separating C_3H_6 from C_3H_8/C_3H_6 mixture is urgently needed. Recently, porous material such as zeolite, metal-organic frameworks (MOFs) and hydrogen-bonded organic frameworks (HOFs) have been demonstrated for being used as adsorbents targeting to purification of C_3H_6. Given that the purification using adsorbents for separating C_3H_6 and C_3H_8 does not involve phase change during the process, such non-thermal process is believed as an ideal alternative to the cryogenic distillation for the energy-saving and environment-friendly perspective.

In our work, we utilize the exposed pyrene sites within the hydrogen-bonded organic framework, whose conjugated π-plane enables the selective capture of C_3H_8 from a C_3H_8/C_3H_6 gas mixture to achieve one-step C_3H_6 purification.

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STABLE TRIPTYCENE HALIDE SALTS WITH HIGH POROSITY

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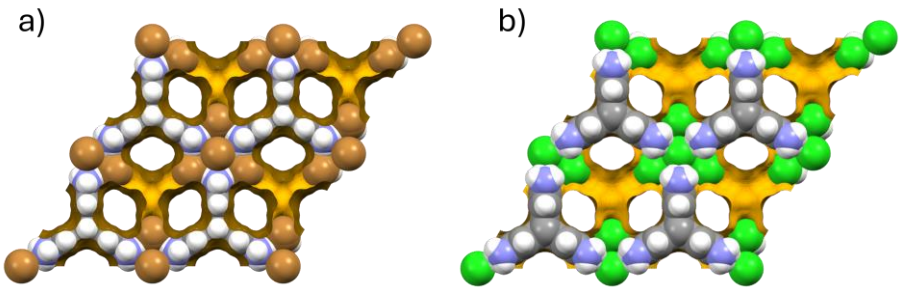
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Keywords: *Porous molecular crystals, porous salts, adsorption*

A subset of porous materials are those characterized by weaker non-covalent interactions, referred to as porous molecular crystals. This leads to distinct properties for porous molecular crystals: for example, it is often quite easy to grow high-quality single crystals, particularly when the intermolecular bonding is weak, and these materials can also be solution processable. However, the more labile intermolecular interactions in porous molecular crystals can have disadvantages. Specifically, it can lead to poor stability and, often, loss of porosity upon activation (that is, removal of solvent from the pores.[1] For materials that use salt interactions, this can be exacerbated by the strong interactions between coordinating solvents and these salts.[2]

To address this challenge, we used high-throughput crystallisations to isolate single crystals of a porous salt, CPOS-7.[3] More recently, we used crystal structure prediction to predict N-MOFs where the global thermodynamic minimum crystal packing was porous, and these materials were stable both to activation and to multiple iodine adsorption/desorption experiments.[4] Nevertheless, it is still the case that most porous salt materials show rather limited porosity, and this porosity is often lost upon activation.

Here, we report two new porous halide salts of triptycene that are stable to activation, exhibiting a type 1 isotherm in the dry state. They also show hydrogen uptakes (5.4 mmol g^{-1}, for T.Br-α and 7.2 mmol/g, for T.Cl-α 1 bar, 77 K) that are competitive amongst all porous materials, and a CO_2 uptake (4.0 mmol g^{-1} for T.Br-α and 4.5 mmol/g for T.Cl-α 1 bar, 273 K) that is the highest reported so far for a porous salt material.



Scheme 1. Space filling structure with voids for a) T.Br-α and b) T.Cl-α.

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ENHANCING PHOTOCATALYTIC HYDROGEN PEROXIDE GENERATION BY TUNING HYDRAZONE LINKAGE DENSITY IN COVALENT ORGANIC FRAMEWORKS

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Keywords: *COFs, Hydrazone linkage, Photocatalysis, Hydrogen Peroxide, Natural sunlight.*

The conversion of solar energy into chemical energy or high-value chemicals has attracted considerable research interest in the context of the global energy crisis. Hydrogen peroxide (H_2O_2) is a versatile and powerful oxidizing agent widely used in chemical synthesis and medical disinfection.H_2O_2 also serves as a clean energy source in fuel cells, generating electricity with zero-carbon emissions.[1] Recently, the sustainable production of H_2O_2 from water and oxygen using covalent organic frameworks (COFs)as photocatalysts has attracted considerable attention; however, systematic studies highlighting the role of linkages in determining photocatalytic performance are scarce.[2] Under these circumstances, herein, we demonstrate that varying the imine and hydrazone linkages within the framework significantly influences photocatalytic H_2O_2 production. COFs with high-density hydrazone linkages, providing optimal docking sites for water and oxygen, enhance H_2O_2 generation activity (1588 μmol g^{-1} h^{-1} from pure water in the air), leading to highly efficient solar-to chemical energy conversion.[3]

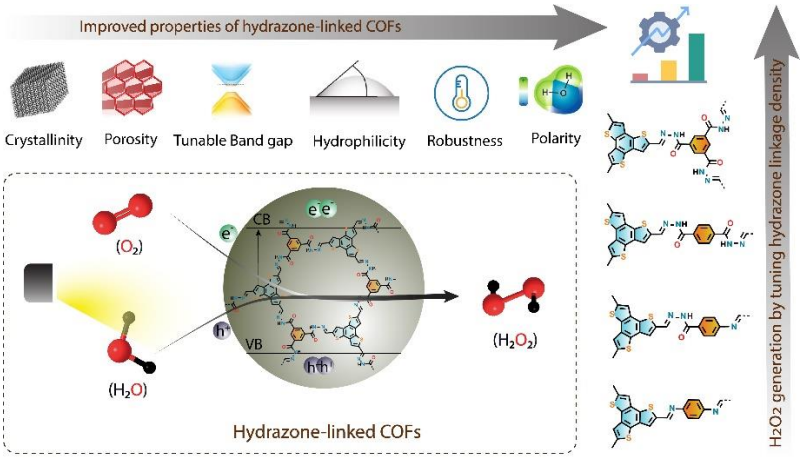


Figure: Application of hydrazone-based covalent organic frameworks for photocatalytic H_2O_2 generation.

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METAL-ORGANIC FRAMEWORK-BASED GREEN POROUS LIQUID FOR ATMOSPHERIC CO_2 CAPTURE & CONVERSION

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Keywords: *Porous Liquids, Catalysis, CO_2 Capture & Conversion, MOF*

Porous Liquids (PLs) have emerged as an exciting new class of materials that combine the intrinsic permanent porosity of solids with the fluidity of liquids. This unique combination imparts novel functionalities that are typically inaccessible to conventional solid or liquid materials. While still in their early stages of development, most research in this area has focused on engineering PLs with high porosity and enhanced selectivity for gas separation, particularly for challenging separations such as CO_2/N_2, CO_2/CH_4, and C_2H_4/C_2H_6.[1,2] Despite their promising capabilities in CO_2 capture and separation, concerns remain regarding the long-term sustainability and practical impact of such approaches. As a result, there is a growing interest in developing PLs capable of permanently fixing CO_2, thereby offering a more sustainable solution to mitigate greenhouse gas emissions and combat climate change.[3–5] In this poster, I will describe my recent advances in the design and synthesis of defect-engineered Metal–Organic Framework (MOF)-based porous liquids that not only exhibit high CO_2 selectivity and uptake but also enable one-step conversion of captured CO_2 into industrially valuable chemicals (Figure 1). This functionality mimics the catalytic behavior of the Carbonic Anhydrase (CA) enzyme, yet the PLs surpass the enzyme in performance due to their enhanced thermal stability and reusability. Compared to neat ionic liquids and conventional MOF systems, these PLs demonstrate superior conversion efficiency under mild conditions. Notably, they also enable Direct Air Capture (DAC) and conversion of atmospheric CO_2 at concentrations as low as ~400 ppm, offering a potentially transformative pathway for climate-positive chemical processes.

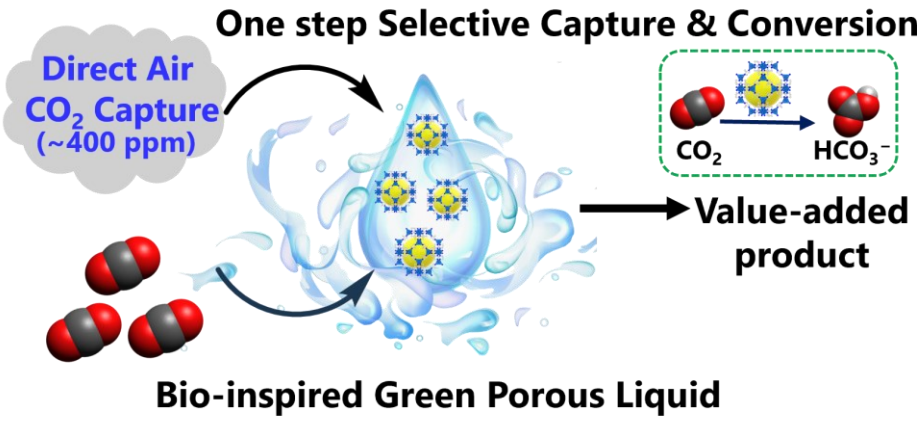


Figure 1. Schematic representation of the design of Porous Liquid for one-pot CO_2 capture and conversion.

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NANO-SPRINGE ENRICHED HIERARCHICAL POROUS MOP/COF HYBRID AEROGEL: EFFICIENT RECOVERY OF GOLD FROM ELECTRONIC WASTE

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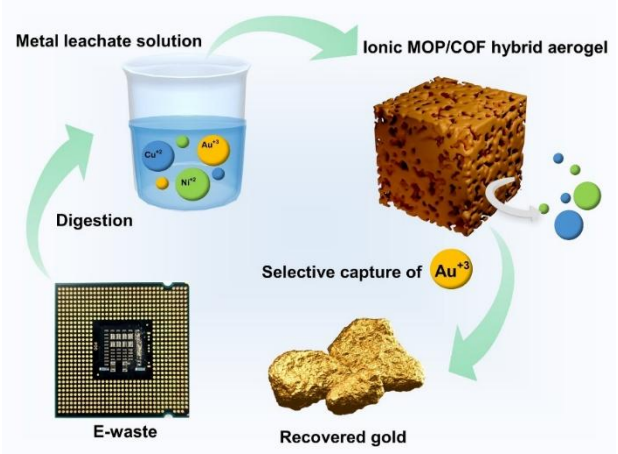
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Keywords: *E-waste, Gold, MOP, Aerogel, COF*

Extraction of gold from secondary resources such as electronic waste (e-waste) has become crucial in recent times to compensate for the gradual scarcity of the noble metal in natural mines. However, designing and synthesizing a suitable material for highly efficient gold recovery is still a great challenge. Herein, we have strategically designed rapid fabrication of an ionic crystalline hybrid aerogel by covalent threading of an amino-functionalized metal-organic polyhedra with an imine-linked chemically stable covalent organic framework at ambient condition. The hierarchically porous ultra-light aerogel featuring imine-rich backbone, high surface area, and cationic sites have shown fast removal, high uptake capacity (2349 mg/g), and excellent selectivity towards gold sequestration. Besides, the aerogel can extract ultra-trace gold-ions from different terrestrial water bodies, aiming towards safe drinking water. This study demonstrates the great potential of the composite materials based on a novel approach to designing a hybrid porous material for efficient gold recovery from complex water matrices.[1]



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COVALENT ORGANIC FRAMEWORKS MEMBRANES FOR PHARMACEUTICALS' EXTRACTION FROM WATERS

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Keywords: *COFs, electrospinning, sulfamethoxazole, fiber, adsorption*

Pharmaceutical compounds, resulting from human activity are increasingly found in water sources, with sulfonamides such as sulfamethoxazole emerging as particularly concerning due to their potential role in antimicrobial resistance, persistence and inefficient removal by conventional wastewater treatments. Therefore, there is an urgent need for selective and efficient methods to monitor their presence in waters at trace levels. .[1] [2] In this work, we develop supported Covalent organic frameworks (COFs) for the efficient extraction and preconcentration of pharmaceutical contaminants from water to enable their identification and quantification in water.
COFs are a class of purely organic and highly crystalline nanoporous structures formed by stacked layers of planar sheets linked through reversible covalent bonds.[3] Their high crystallinity, structural diversity, low density, and permanently uniform pore shape and size render them materials of high interest for adsorption applications, and therefore, COFs are increasingly explored efficient adsorbent materials for water pollutant capture.[4][5] However, their direct usage into practical applications is hindered by its typical powder form which leads to high backpressure and low material retention when packed. Herein, to address this shortcoming and enhance reusability, we propose their immobilization thought electrospinning of COF membranes.

In this work, the potential of the imine-linked COF TpBD-Me_2 to be processed into membranes was investigated. Bulk TpBD-Me_2 had already demonstrated excellent adsorption capacity for various toxins and pharmaceuticals, including sulfamethoxazole. The membranes were prepared by electrospinning a mixture of one of the COF's building blocks with PAN, a non-toxic synthetic polymer, followed by in situ COF growth under optimized conditions. The resulting materials clearly outperformed the bulk COF in the adsorption of sulfamethoxazole (c = 15 mg/L), reaching efficiencies above 95% after 4 hours of incubation, compared to around 78% for the bulk. Currently the membranes are being tested in passive adsorption and are planned to be integrated into filtration systems.

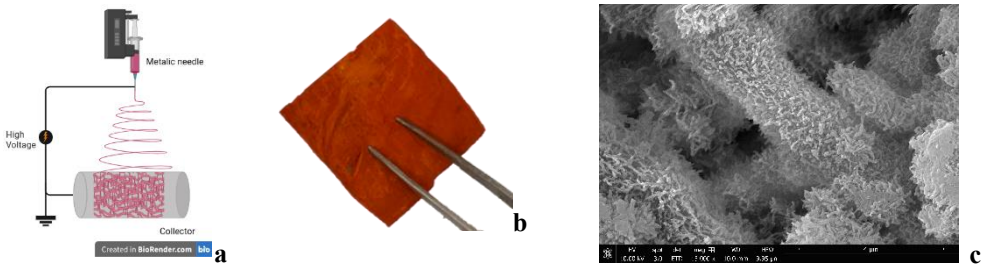


Figure 1 - Illustration of a) the electrospinning process; b) the produced membrane; c) the fiber morphology through SEM

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OVERCOMING DIFFUSION AND STABILITY LIMITATIONS IN METAL-ORGANIC FRAMEWORKS FOR WATER PURIFICATION

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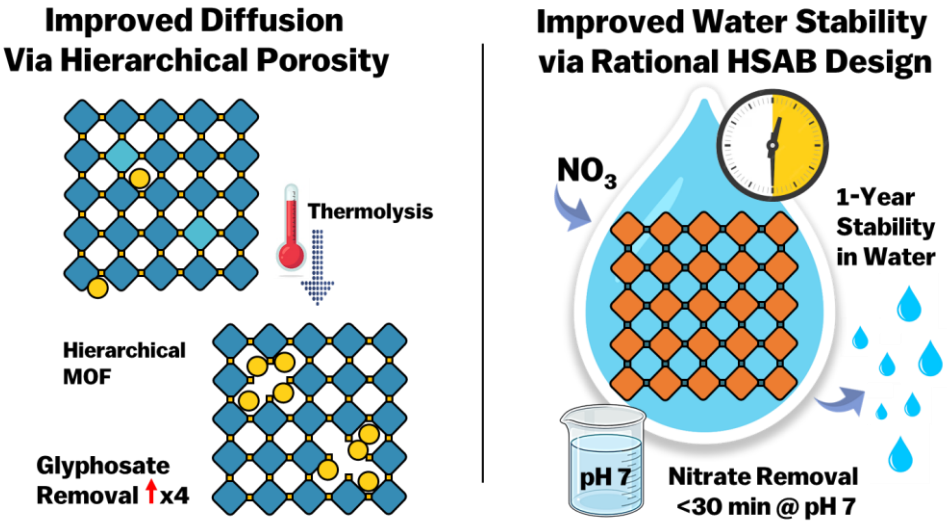
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Keywords: *metal-organic frameworks, water purification, adsorption, water stability*

Metal–organic frameworks (MOFs) hold great promise for water purification, but their application is hindered by limited diffusion and poor long-term water stability. We present a dual design strategy to overcome both challenges without compromising MOF performance.

To address diffusion limitations, we engineered hierarchical pore architectures through selective ligand removal via controlled thermolysis. Applied to mixed-ligand systems (i.e., MIL-125-Ti), this approach introduced mesoporosity while preserving crystallinity and structural integrity [1]. The resulting hierarchical frameworks exhibited significantly enhanced mass transport and adsorption kinetics, particularly for larger organic pollutants (e.g., Glyphosate), with removal rates up to four times higher than the unmodified MOF [2].

In parallel, we synthesized two novel Cu-based MOFs, TUW-1 and TUW-2 [3], specifically designed for aqueous durability. These frameworks demonstrated exceptional water stability, retaining structural integrity after one year of immersion. Rapid nitrate removal under neutral pH (equilibrium in <30 min) highlights their practical relevance. Detailed structural insights were gained through SCXRD and XFEL analyses, revealing key stability factors [4].



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DISORDER DRIVEN TRIPHENYLAMINE BASED MONOLITHIC COVALENT ORGANIC FRAMEWORK FOR THE EFFICIENT REMOVAL OF TOXIC OXO-ANIONS FROM WATER

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Keywords: *Monolithic, Covalent Organic Frameworks, Disordered induced Foam, Hierarchical porosity, Oxoanion removal.*

Covalent Organic Frameworks (COFs) have garnered significant attention for environmental remediation due to their ordered porosity, high surface area and exceptional contaminant removal properties. However, the synthesis of pure-phase monolithic COFs and their application in water remediation is still in the infancy stage. Herein, we developed an industrial-friendly and eco-friendly ball-mill-assisted in-situ gas forming approach for the synthesis of pure phase monolithic COF, named BPTP Foam that efficiently removes the toxic oxoanions from water. This approach induces a hierarchical porous structure, providing high adsorption capacities of 961.54 mg/g for MnO_4^- and 448.09 mg/g for CrO_4^{2-}, with rapid removal times of 1 and 3 min, respectively. Notably, the adsorption capacity for MnO_4^- is the highest among all porous materials reported to date. Density Functional Theory (DFT) and adsorption studies reveal that strong non-covalent interactions between the peripheral oxygen atoms of metal anions and the triphenylamine moieties within the framework contribute to enhanced removal kinetics. The simplicity and scalability of the synthesis method, combined with the high performance of BPTP Foam, make it a promising candidate for large-scale environmental remediation applications.

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OPTIMIZING THE PIEZOCATALYTIC HYDROGEN PRODUCTION ACTIVITY OF METAL-ORGANIC FRAMEWORKS THROUGH PRECISE DEFECT ENGINEERING

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Keywords: *UiO-66, defective engineering, piezocatalytic*

The catalytic efficiency of metal-organic frameworks (MOFs) in piezocatalysis currently is greatly constrained by their low degrees of piezoresponse. Herein, as shown in figure 1a, by using UiO-66 as an experimental platform, we show the feasibity of defect engineering in improving the piezoelectric performance of MOFs, leading to the further improvement of the piezocatalytic hydrogen production activity. Through piezoresponse force microscopy measurements on a series of UiO-66 crystals with precisely controlled defect concentrations, we find that the piezoelectric coefficient of a specifically designed defective UiO-66 can be maximally improved by 5 times as compared to that of its pristine counterpart, as shown in figure 1b. Our molecular dynamics simulations reveal that the enhancement in piezoelectricity of defective UiO-66 is attributed to the additional polarization generated by the flexoelectric effect significant around defects. Piezocatalytic hydrogen evolution tests together with electrochemical analyses and density functional theory calculations further demonstrate that the synergy among the piezoelectric field-accelerated charge separation, defect-mediated carrier transport and lowered energy barrier for surface hydrogen adsorption in defective UiO-66 can significantly enhance catalytic activity, as depicted in figure 1c. The piezocatalytic hydrogen production rate can be almost doubled for a defective UiO-66 with an optimal defect concentration, compared to that of its pristine counterpart at the same reaction condition. This study demonstrates a feasible strategy to enhance the piezocatalytic activity of MOFs through defect engineering, while also providing mechanistic insights into how defect-induced polarization contributes to improved performance. This approach may be extended to other framework materials for future catalytic applications.

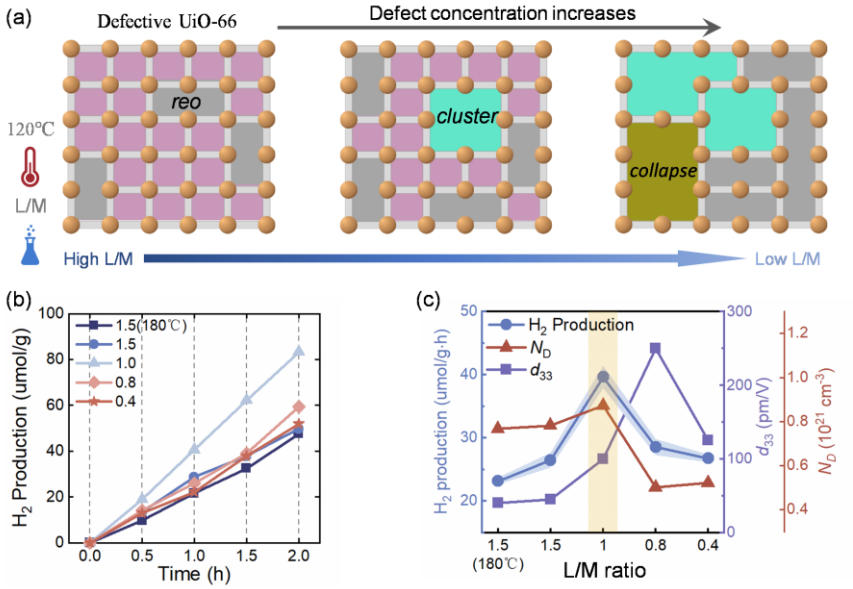


Figure 1. (a) he synthesis principle of defective UiO-66. (b) Results of piezoelectric catalytic hydrogen production comparison of hydrogen evolution under non-ultrasonic conditions. (c) carrier concentration, piezoelectric amplitude measured by PFM, and hydrogen evolution excess of UiO-66-1.5 (180°C), UiO-66-1.5, 1.0, 0.8 and 0.4.

References

PHOTOCATALYTIC ACTIVITY OF COF-BASED MATERIALS MODIFIED WITH CuS QUANTUM DOTS: INFLUENCE OF MONOMER TYPE AND MODIFIER CONTENT

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Keywords: *COF, photocatalysis*

In the face of escalating environmental problems, such as air pollution, water contamination and greenhouse gas emissions, environmental-friendly technologies are receiving increasing attention. One of the processes finding application in such technologies is photocatalysis. Many types of photocatalysts in the form of metal oxides, metal nanoparticles, quantum dots or metal organic frameworks (MOFs) are currently in use. One relatively new group of materials used in photocatalysis is covalent organic frameworks (COFs). Covalent organic frameworks represent novel, rapidly expanding class of highly porous crystalline materials. Their distinctive regular structure is based on organic linkers connected by strong covalent bonds, which translates into high physical and chemical stability of these materials[1]. The polymeric nature of COFs makes their structure extremely amenable to modification, both through the selection and functionalization of individual linkers. The main advantages of COFs include their ease of design, high degree of porosity (and thus high specific surface area), as well as the ability to tailor their properties to specific applications. The presence of donor-acceptor groups in the structure of these materials allows efficient separation of photogenerated electron-hole pairs, which is crucial in photocatalytic reactions[2].

Two series of COF-type materials were developed, differing in the monomer used: TTB-TAPT and TTB-TAPB. The structures were modified with copper(II) sulfide (CuS) quantum dots, and their photocatalytic activity was evaluated in the hydrogen photogeneration reaction and photodegradation of phenol in the liquid phase. The effects of the type of monomer used and the amount of modifier introduced on the properties of the materials obtained were analyzed.

Acknowledgements
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THE FIRST POST-SYNTHETIC MODIFICATION STRATEGY OF VINYLENE-LINKED COVALENT ORGANIC FRAMEWORK FOR BOOSTING PHOTOCATALYTIC PERFORMANCE

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Keywords: *Covalent organic framework (COF), Post-synthetic modification (PSM), Reactive oxygen species (ROS), Photocatalyst*

Dimerization of enamines is an important chemical reaction for synthesizing valuable pharmaceutical compounds. Reactive oxygen species (ROS) are typical catalysts for enamine dimerization, so enhancing ROS generation is an important strategy for improving the reaction.

Covalent organic frameworks (COFs) are emerging porous materials used in various research fields. Among them, vinylene-linked COFs (also known as olefin-linked COFs) have gained attention as photocatalysts due to their extended π-conjugation and robustness arising from the C=C double covalent bond. However, enhancing their photocatalytic performance remains challenging, as methods for controlling their chemical environment have not been reported.

For this reason, we applied the well-known alkene arylation strategy[1] to the olefin-linked COF for the first time to modulate its electronic structure. Consequently, the method successfully enhances ROS generation and boosts the photocatalytic performance of the COF. The detailed synthetic procedures and analytical data will be provided in the poster.

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CLUSTER METALATION AND POST-SYNTHETIC PORE MODIFICATION OF MOF-808 TOWARDS PHOTOCATALYTIC CO_2 REDUCTION TO ETHANOL

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Keywords: *cluster metalation, post-synthetic pore modification, photocatalytic CO_2 reduction, ethanol formation.*

Solar light-driven CO_2 reduction to multi-carbon products (C_{2+}) is a fascinating and challenging endeavour, owing to the complexities of C–C bond formation and the involvement of intricate proton-coupled electron transfer processes. Metal-organic frameworks (MOFs) have enabled the rational design of catalytic centers through pre- or post-synthetic modifications. Herein, we introduce a non-trivial pre-synthetic secondary building unit (SBU) modification strategy for the precise incorporation of heterometal sites into Zr-based MOF-808.[1] Specifically, we design the bimetallic Zr_Fe-MOF nanoparticles through a one-pot synthesis, in which one Zr^{IV} ion in the Zr_6-oxo cluster was substituted with a Fe^{III} ion, yielding a Zr_5Fe-oxo cluster. Furthermore, $[Ru(bpy)_2]^{2+}$ moiety is covalently grafted to the confined space of post-modified Zr_Fe-MBA-MOF, culminating in an integrated catalytic system Zr_Fe-MBA-Ru-MOF (Figure 1).[24] The closer proximity of the highly effective redox couple Fe^{III} center and photosensitizer within the MOF nanospace significantly enhances the photoinduced electron transfer process. Additionally, the cooperative interaction between Zr and Fe centers facilitates the C–C coupling by stabilizing key intermediates during photocatalysis. The Zr_Fe-MBA-Ru-MOF produces 1208 μmol g^{-1} of ethanol with 95.2% selectivity by suppressing other gaseous products in an aqueous medium. The mechanistic insights are unveiled through *in situ* diffuse reflectance FT-IR spectra and DFT calculations. This approach highlights bimetallic Zr_Fe-MOFs design, via SBU engineered within Zr_6-oxo clusters, as efficient catalysts for enhancing CO_2 reduction performance and selectivity.

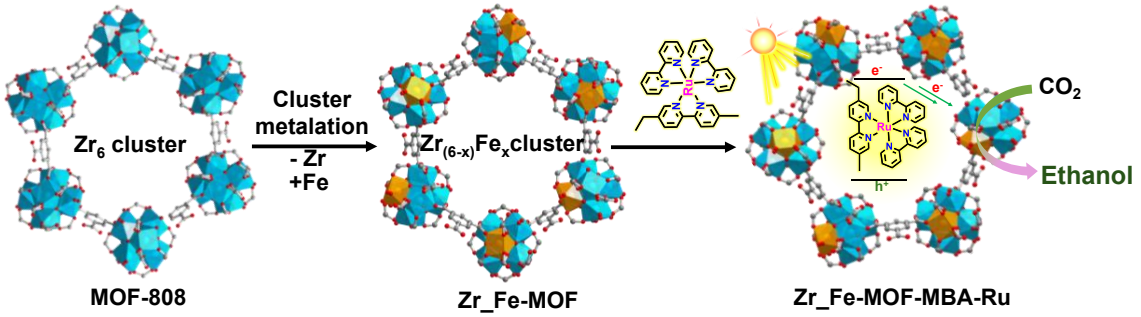


Figure 1: Schematic for the visible light-driven photocatalytic CO_2 reduction by Zr_Fe-MBA-Ru-MOF in pure water.

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TUNING CORE FLEXIBILITY AND CURVATURE IN AZINE-LINKED COVALENT ORGANIC FRAMEWORKS FOR ULTRASENSITIVE IMPEDITIVE SENSING OF GLUCOSE

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Keywords: *covalent organic frameworks, core flexibility, electrochemical sensing, electrochemical impedance spectroscopy, glucose sensing.*

Glucose serves as a key biomarker of metabolic health, requiring continuous and reliable monitoring.[1] While enzymatic glucose sensors dominate current clinical practice, they suffer from susceptibility to biofouling, instability, and costly fabrication processes.[2] Non-enzymatic electrochemical impedimetric sensors present a promising alternative, however, their sensitivity is limited by weak molecular recognition and inefficient charge transport at the sensing interface.[3–5] In this study, we have tuned the core flexibility, curvature, and electronic structure of azine-linked covalent organic frameworks (COFs) through the substitution of the central triazine ring in the C3 symmetric building unit for nitrogen. This modification maximized glucose–framework interactions, thereby enhancing signal transduction and detection sensitivity. The results confirmed the sensitivity and selectivity of the COFs toward glucose, with a linear response over a wide concentration range [1 aM – 5 mM], surpassing previously reported glucose sensors. The sensors exhibited outstanding stability and reproducibility compared to traditional enzymatic sensors, offering a simpler and more practical alternative for integration into wearable and implantable devices. Experimental findings are supported by molecular simulations, which revealed superior sensitivity and specificity toward glucose recognition. This work establishes a versatile design strategy for next-generation COF-based sensors, opening new pathways for ultrasensitive, scalable, and selective molecular detection.

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COMPUTATIONAL INSIGHTS INTO ADVANCED DESIGN OF MIXED MATRIX MEMBRANES FOR GAS SEPARATION

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Keywords: *Gas Separation, Porous Material Geometries, Mixed-Matrix Membranes, Membrane Simulations*

Recently, there has been growing interest in the use of mixed matrix membranes (MMMs) for gas separation processes. The incorporation of structurally diverse porous fillers into a polymeric matrix significantly enhances the influence of filler morphology on membrane performance [1]. Most existing macroscopic predictive models for MMMs are based on analogies between fluid permeability in heterogeneous membranes and thermal or electrical conductivity in composite media. However, these models are generally limited to simplified scenarios involving spherical filler particles and single-gas transport [2]. To overcome these limitations, particularly the challenge of capturing the complex morphologies of porous materials when predicting the effective transport properties of MMMs, we employed a three-dimensional, voxel-based finite element method to model binary gas transport and evaluate both permeability and selectivity. Using this computational framework, we systematically investigated the influence of Platonic-shaped porous fillers, presented here as a case study, on key design criteria for high-performance permselective membranes [3]. Furthermore, we addressed an important unresolved issue in the synthesis and characterization of MMMs, namely the lack of a predictive description of how interfacial defects impact membrane performance. Through our computational platform, we explored the intricate interplay between the geometrical features of interfacial defects, the spatial arrangement of filler particles, and the resulting transport pathways (Figure 1) [4].

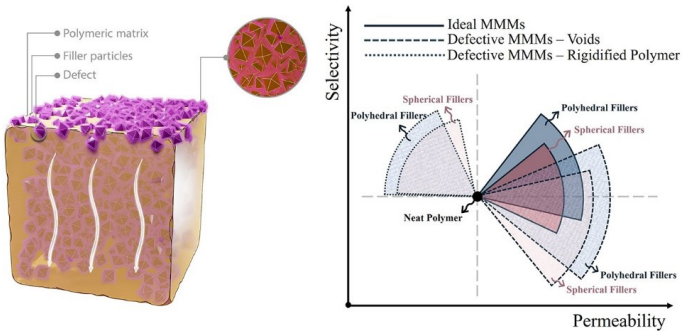


Figure 1. (a) Illustration of MMMs showing particles distributed on the membrane with overlapping defect regions. (b) Impact of variations in filler particle geometry and defect interphase on perm-selectivity [4].

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MULTISCALE COMPUTATIONAL INSIGHTS INTO THE PFOA ADSORPTION BY CHEMICALLY ENGINEERED MOF-808

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Keywords: *Adsorption Mechanisms, Multiscale Simulations, Environmental Remediation*

Metal–Organic Frameworks (MOFs) are crystalline porous materials with tunable chemistry, making them attractive for applications in gas storage, separation, and environmental remediation [1]. This study applies a multiscale computational strategy to examine the adsorption behavior of perfluorooctanoic acid (PFOA) on both unmodified MOF-808 and its iron-functionalized counterpart (Fe-MOF-808). Structural analysis will identify preferred binding sites, while atomistic simulations— including Density Functional Theory (DFT) and Molecular Dynamics (MD)—will elucidate PFOA–MOF interactions. Grand Canonical Monte Carlo (GCMC) simulations will be employed to compute key thermodynamic parameters such as adsorption enthalpies and equilibrium constants. The influence of Fe functionalization on adsorption performance and interaction mechanisms will be critically assessed to determine its role in enhancing pollutant affinity. This comparative analysis aims to inform the rational design of MOFs for environmental applications, offering insights into their efficiency and selectivity for pollutant capture.

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TOPOLOGICAL AND STRUCTURAL DIVERSITY OF ZEOLITIC IMIDAZOLATE FRAMEWORKS EXPLORED THROUGH CRYSTAL STRUCTURE PREDICTION

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Keywords: *crystal structure prediction, zeolitic imidazolate frameworks, polymorphism, machine-learnt potentials*

Zeolitic imidazolate frameworks (ZIFs) are a class of MOFs renowned for their structural and topological diversity, which in turn leads to a wide variety of functional applications from gas storage and separation to catalysis. The principal strategies for targeting new topologies in ZIF design has been metal replacement and introduction of peripheral substituents into imidazolate linkers.[1] However, the most polymorphic ZIF system to date is the unsubstituted zinc imidazolate, Zn(**Im**)$_2$, for which at least 18 different topologies have been isolated.[2] So what is the reason for such topological and structural abundance of Zn(**Im**)$_2$ polymorphs, and can we expect further new structures to be discovered in the future?

This presentation will demonstrate how crystal structure prediction of MOFs, based on the *ab initio* random structure search (AIRSS)[3] and Wyckoff Alignment of Molecules (WAM)[4] algorithms, can be used to uncover the entire structural landscape of Zn(**Im**)$_2$ system. Thanks to the use of machine-learnt potentials (MLPs)[5] for rapid energy ranking of the predicted structures, our structure search has become orders of magnitude faster than what has been possible with periodic density-functional theory (DFT) calculations. This enabled sampling of structures of highest complexity, containing up to 16 formula units of Zn(**Im**)$_2$ per primitive crystallographic unit cell, allowing us to locate multiple experimentally-reported polymorphs on the crystal energy landscape.

The full energy landscape will be examined during the presentation, highlighting the positions of previously reported polymorphs, and exploring the topological diversity of other, so far hypothetical, structures found in the landscape. It will be shown how accelerated high-throughput CSP calculations can facilitate the discovery of promising candidate MOF structures for targeted synthetic screening.

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Gas ADSORPTION MEETS DEEP LEARNING

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Keywords: artificial intelligence, *machine learning, deep learning, neural networks, gas adsorption*

Metal-organic frameworks (MOFs) are promising materials for gas adsorption due to their ultra high porosity and surface area. However, their vast combinatorial space makes traditional material discovery methods inefficient. Recently, machine learning (ML) approaches have been proposed for large-scale screening of MOF databases but their efficacy rely heavily on hand-crafted features. We propose a deep learning (DL) framework[1] for predicting gas adsorption properties of materials, using as one and only descriptor the potential energy surface (PES). The latter uniquely combines the structural properties and the electronic structure of a material in real space, rendering the proposed scheme applicable in any host-guest system for predicting any adsorption property of interest. Furthermore, we have developed a generalized deep learning framework[2] that predicts gas adsorption properties from raw structural information using a point cloud representation of the material. Combining this simplified yet complete representation with DL, introduces a versatile paradigm for data-driven material science, bypassing the obstacles of manually crafted descriptors. Our algorithms were tested for CO_2 adsorption in MOFs, outperforming the conventional ML models in the literature, which rely on geometric descriptors. The proposed methodologies were further validated across different host-guest systems, demonstrating broad applicability in diverse materials and properties.

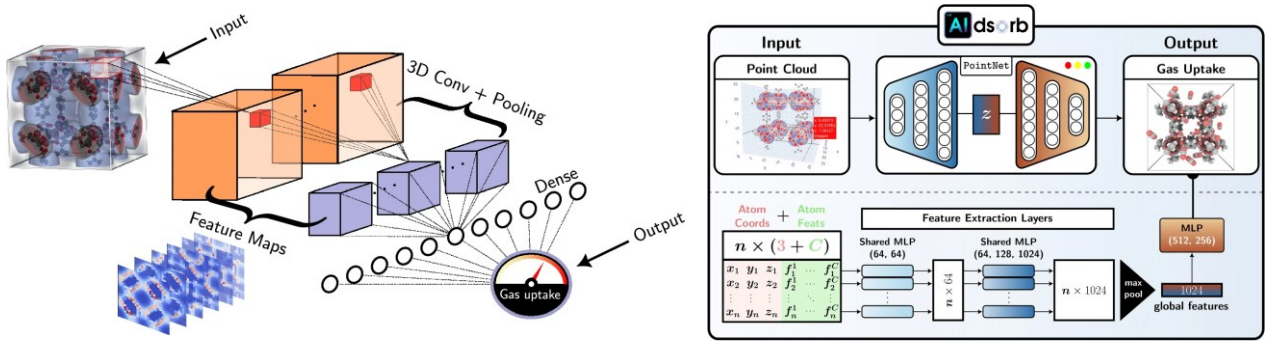


Figure 1: *Deep learning frameworks to predict gas adsorption properties of MOFs using voxelized PES (left) and point clouds (right).*

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MACHINE LEARNING POTENTIALS FOR CRYSTAL STRUCTURE PREDICTION OF MAGNETIC METAL-ORGANIC FRAMEWORKS

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Keywords: *metal-organic frameworks, magnetic materials, crystal structure prediction, machine learning*

Magnetic materials are essential in today's technology, from electric motors to data storage, but inorganic magnets, especially those with rare-earth metals, often lack tunability in their magnetic properties[1]. Metal-organic frameworks (MOFs), consisting of transition metal ions and organic linkers, show promise in enhancing magnetic materials by offering tunability through the arrangement of magnetic ions. These structures allow the metal ions to provide magnetic moments while the organic linkers control the spacing and alignment of the magnetic centers. However, finding the optimal combinations of metals and linkers for desired magnetic properties is complex and time-consuming due to the vast range of possible configurations.

Our method for investigating magnetic MOFs theoretically involves crystal structure prediction (CSP) using ab initio random structure searching (AIRSS)[2], combined with Wyckoff Alignment of Molecules (WAM)[3]. AIRSS generates crystal structures by placing metal nodes and organic linkers into trial unit cells, while WAM analyzes the point group symmetry and identifies compatible crystallographic space groups for each MOF component. This approach enhances efficiency by considering both molecular and crystallographic symmetry. A key step in assessing the feasibility of the generated structures is energy ranking, typically done using periodic density functional theory (DFT). However, since MOFs are large and computationally demanding, we address this challenge by using the machine-learnt potential (MLP). For this MLP approach, we utilize MACE, a machine learning software that combines equivariant message passing with efficient many-body interactions to predict atomic interactions and generate force fields[4].

We evaluated the performance of the MACE foundation models[5] by comparing its predicted energies with those calculated via density functional theory (DFT). The results demonstrate strong agreement, with a low root mean square error (RMSE) of 0.032 eV/atom and a mean absolute error (MAE) of 0.0251 eV/atom. Furthermore, the coefficient of determination (R^2) value of 0.91 indicates a good fit between the MACE-predicted and DFT-calculated energies. These findings suggest that the MACE potential is a promising alternative to DFT for energy ranking in crystal structure prediction (CSP). Based on the energy rankings obtained from MACE, we will select several low-energy candidate structures for further geometry optimization using density-functional theory (DFT) and subsequent structural and magnetic property analysis. With the aid of MLP approach, we aim to predict both the structures and properties of magnetic MOFs before experimental synthesis.

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HOW DOES INTERLAYER SPACING INFLUENCE COVALENT ORGANIC FRAMEWORK BAND GAPS?

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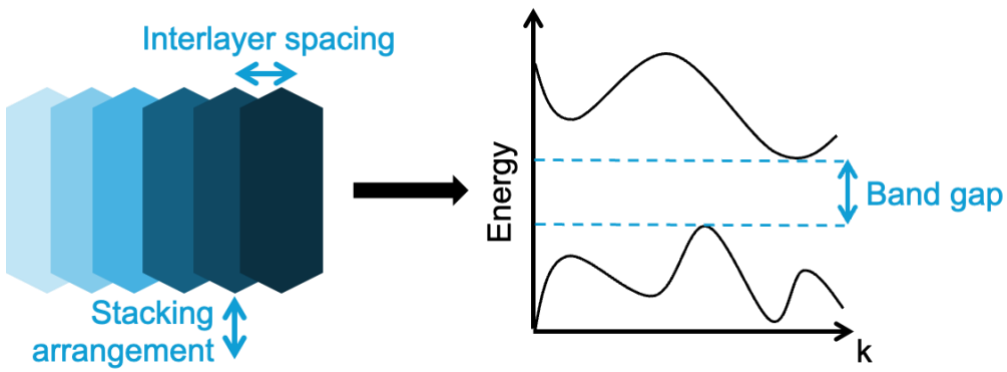
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Keywords: *COFs, electronic structure, interlayer spacing, density functional theory*

Two-dimensional (2D) covalent organic frameworks (COFs) are microporous, layered reticular frameworks with multiple applications.[1] The electronic structure of these semiconducting materials is crucial to their many practical applications and is defined not only by their composition, but also the interlayer stacking mode, which imparts framework stability through non-covalent intermolecular interactions. These interlayer interactions introduce indirect band gaps and band dispersion into the material *via* the intermolecular proximity effect.[2] However, there are limitations to the insight into COF stacking that can be gained experimentally, and in some cases the guidance given by experiment can be misleading.[3] Along with being poorly defined experimentally, to the extent that for some COFs the 001 powder x-ray diffraction (PXRD) peak corresponding to the interlayer spacing can be hidden in the noise of the powder pattern or contribute to a broad peak,[4] COF interlayer spacings are often treated ambiguously using theoretical models,[1,3] and limited research has explored their influence on the COF structure. Therefore, it is prudent to understand in detail how the interlayer spacing and stacking arrangement affect the properties of 2D COF materials.

In this presentation, we use periodic and molecular density functional theory (DFT) models of a subset of 2D COFs of various functionalities and topologies to answer three questions: 1) why do different 2D COFs exhibit different band gaps?, 2) for an individual COF, how do the interlayer spacing and stacking arrangement affect the band gap? and 3) can the trend in electronic properties as a function of interlayer stacking mode calculated using periodic DFT models be reproduced using molecular DFT models? We anticipate that understanding the trends in COF functionality and electronic properties will lead to the design of new COF materials tailored to desired applications.



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A MOFSynth: A COMPUTATIONAL TOOL TOWARD SYNTHETIC LIKELIHOOD PREDICTIONS OF MOFs

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Keywords: *MOFs, Synthesizability, Computational Chemistry*

Metal-Organic Frameworks (MOFs) are a class of crystalline materials with numerous applications including gas storage, catalysis, and drug delivery. Despite their potential, their experimental synthesis poses significant challenges. This study presents a comprehensive investigation into the synthesizability likelihood of MOFs utilizing a novel computational approach. We propose that disparities in energy and geometry between the linker conformation within the MOF structure and its isolated, free gas state are critical factors influencing MOF synthesis. Our user-friendly tool streamlines synthesizability evaluation, requiring minimal expertise in computational chemistry. By deconstructing over 40,000 MOFs from databases including QMOF[1], CoRE[2], and ToBaCCo[3], we analyze key parameters defining linker strain within the MOF unit cell. Our results indicate that QMOF and CoRE contain promising candidates for synthesis, while ToBaCCo exhibits relatively poor synthesizability likelihood due to unoptimized materials. Through extensive analysis, we identify optimal linker candidates for highly synthesizable MOFs. Consistent trends in energy distribution across databases, that are confirmed by high Pearson and Spearman coefficients, suggest the potential for omitting optimization steps, significantly reducing computational costs. This study enhances the understanding of synthetic accessibility in MOF research, offering valuable insights for future advancements in the field.

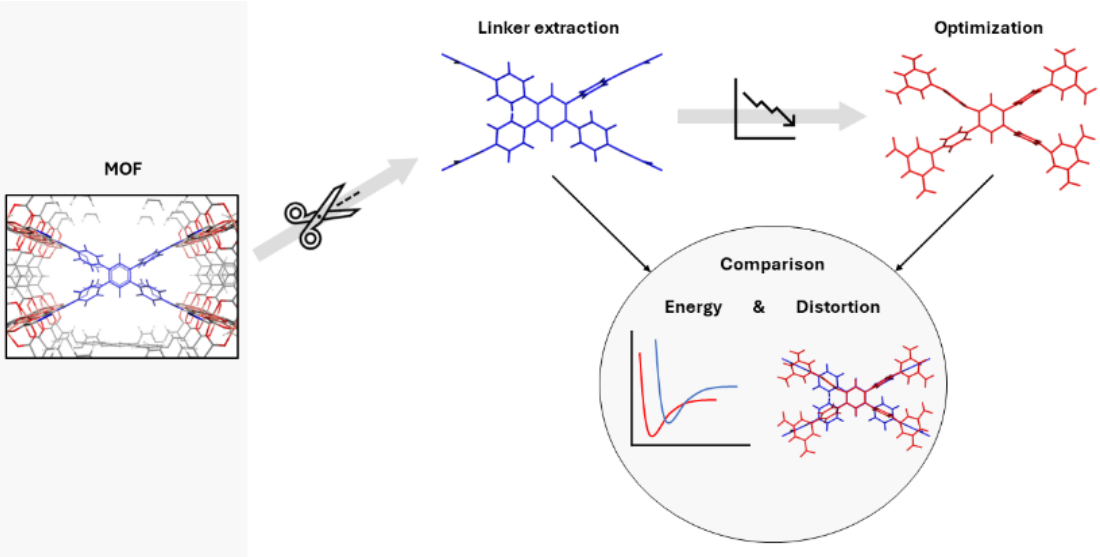


Figure 1: Workflow of synthesizability likelihood evaluation

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DYNAMIC SYNERGY: PROBING MULTI-ELEMENT MOTION IN FLEXIBLE MOFS WITH COMPUTATIONAL MODELING AND SOLID-STATE NMR

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Keywords: *Guest-modulated dynamics, ss-NMR, Rotor energy landscape, Computational modelling*

Understanding dynamic behaviour in metal–organic frameworks (MOFs) through computational methods is essential for capturing local energy landscapes and predicting motion beyond experimental resolution. [1,2] We investigate guest-responsive dynamics in the flexible pillared MOF, featuring bicyclopentane and azopyridine (azpy) rotors that showed ultra-fast dynamics in the 10^7 Hz regime even down to 44 K. In order to elucidate the dynamical mechanism DFT and MM molecular model were employed. Using a "*sum of the parts*" approach, we computed all the unique rotor-rotor, rotor-ligand, and rotor-guest potential energy scans pair-wise by DFT using M06-2X/6-311+G(d) level of theory. We can then construct a 2D potential energy landscape for bicyclopentane rotation for a complete model, with and without guests and varying guest arrangements, by summing the appropriate 1D and 2D PES. This approach significantly reduced the overall computational cost. These DFT PES scans revealed that CO_2 raises rotational barriers from ~1.1 to 1.65 kcal/mol, comprising 21 configurations of CO_2 interacting with the rotors. In contrast, iodine inclusion induces a piston-like framework sliding that lowers barriers to ~0.6 kcal/mol, enhancing rotor mobility. These simulations reproduce the guest-specific dynamic heterogeneity observed by solid-state NMR and synchrotron PXRD. This integrated approach highlights how localised modelling can decode rotor–guest interactions and structural flexibility, enabling the rational design of MOFs with programmable dynamics and selective transport properties.[3]

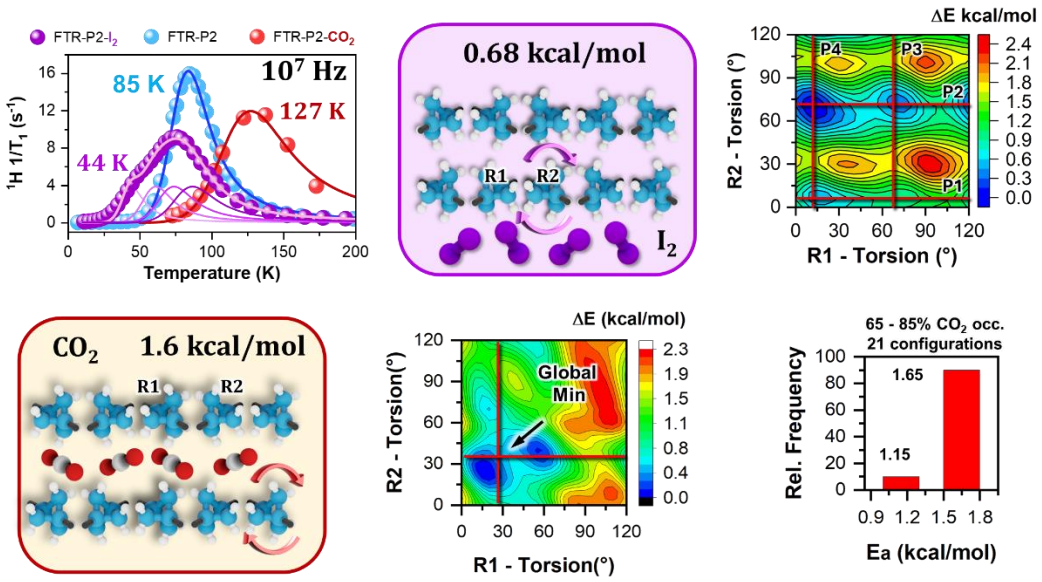


Figure 1. Top-Left - ^1H T_1 relaxation measurements demonstrating the BCP mobility. The models for the Iodine and CO_2 loaded structures, with one of the 2D PES maps for each, to the right.

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TOWARDS GREENER REFRIGERANTS: SIMULATING ADSORPTION REFRIGERATION IN MOFSAND THE ROLE OF CORRELATED DISORDER

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Keywords: *Computational, Simulations, MOFs, Adsorption, Refrigerants, Disorder*

As the effects of climate change become more apparent in the form of rising global temperatures, the necessity for temperature control become more significant.[1] Current refrigerants are low cost and exhibit high performances but these materials possess very high global warming potentials.[2] A greener alternative is a solid-state approach via barocaloric materials which exhibit large adiabatic temperature and isothermal entropy changes upon compression and decompression cycles.[3] In addition, it is estimated that refrigeration technology contributes up to 20 % of the global energy consumption, therefore, any alternative must also match or improve on the efficiencies of current refrigerants (ΔS_{iso} =~520 J kg^{-1} K^{-1} under 15 bar of pressure). [4,5]

Metal-organic frameworks (MOFs) are porous, crystalline materials that are highly modular due to the many metal and linker combinations possible. Notably, certain combinations of metals and linkers have shown to result in a breathing effect wherein the adsorption and desorption of guest molecules are accompanied by a large reversible volume change, entropy change, and by extension, temperature change.[6] Hence, they were recognised as potential barocaloric materials.[5] A crucial flaw with the barocaloric MOFs stems from the volume changes which leads to a reduction in performance as well as mechanical stress that greatly reduce the life-time of these materials.[7]

In this work, we show the outstanding refrigeration potential of a novel, rigid MOF which operates purely from the adsorption of water or carbon dioxide. Using ab initio molecular dynamics (AIMD), we are able to probe the thermal and mechanical stability of the rigid framework, and through grand canonical Monte Carlo (GCMC), the efficiency of the material as a potential adsorption refrigerant. Finally, we utilise umbrella sampling (US) to unveil the potential energy surface related to linker-orientation based disorder in order to further understand the impact of it on the framework properties. Based on their mechanical stability and barocaloric efficiency, we show that rigid MOFs are viable candidates for the next generation of greener refrigerants.

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INSIGHTS INTO THE ELECTROCHEMICAL PROPERTIES OF METAL–ORGANIC FRAMEWORKS FOR APPLICATIONS IN DIVERSE BATTERY CHEMISTRIES

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Keywords: *Metal-Organic Frameworks, Battery, High-throughput, Clustering, Electrodes, Electrolytes*

The growing demand for sustainable energy technologies such as electric vehicles and portable electronics has intensified the need for high-performance efficient energy storage systems. Traditional electrode materials like transition metal oxides and graphite commonly used in conventional batteries are increasingly unreliable and environmentally unfriendly due to the high energy costs associated with their extraction and processing. This has created an urgent need for the discovery of new materials for next-generation battery systems.

Metal-organic frameworks (MOFs) have emerged as promising battery materials due to their tunable porosity, structural diversity, high surface area and crystallinity, which are advantageous for optimizing ion transport, charge storage and chemical stability. However, their practical application is still limited because most studies focus on isolated, highly tailored MOFs that are designed for specific battery chemistries. This fragmented approach hinders the development of a general understanding needed for the systematic integration of MOFs across a broader range of battery technologies.

For this reason, we conducted a comprehensive high-throughput screening of 22,000 curated MOFs with pore-limiting diameters above 2.5 Å by evaluating their interactions with the following guest species Li, Na, K, Ca, Mg, Zn, Al, LiO_2, and LiS. For each MOF, 20–50 host-guest complexes were generated by randomly inserting the guest species into the pores and calculating their interaction energies. We clustered the resulting energy minima to identify distinct interaction energy regimes, selected representative structures (centroids) and computed their band structures, projected density of states and effective masses to assess their charge transport properties. Additionally, we performed nudged elastic band (NEB) calculations to evaluate their ion diffusivity. Finally, we assessed the electrochemical potential of each MOF by determining their maximum guest uptake, open-circuit voltage, theoretical capacity and energy density.

In this talk, I will present the key findings of our study, which include the systematic classification of MOFs as potential anodes, cathodes and solid electrolytes for a wide range of battery chemistry including Li, Na, K, Ca, Mg, Zn, Al, LiO_2, and LiS systems.

FLEXIBLE HOFMANN-TYPE METAL-ORGANIC FRAMEWORKS FOR Xe STORAGE: A MOLECULAR DYNAMICS APPROACH BASED ON MACHINE LEARNING POTENTIAL

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Keywords: *Xe adsorption, Flexible MOF, Machine learning potential*

Flexible metal organic frameworks (MOFs) exhibit various dynamic behaviors including framework expansion/shrinkage and pore opening/closing, offering exceptional potential for gas storage and separation applications. In particular, their characteristic sigmoidal adsorption behavior enables superior storage and separation performance.[1] Here we investigate Xe adsorption behavior in three flexible Hofmann-type MOFs–CoNi-Pipe, NiNi-Pipe, and CoPd-Pipe–by developing machine learning potentials (MLPs) for molecular dynamics (MD) simulations. Our MLPs achieve DFT-level accuracy while enabling large-scale and long-timescale MD simulations with root mean square error (RMSE) values for energy (0.004, 0.001, and 0.009 eV $atom^{-1}$) and force (0.059, 0.018, and 0.056 eV $Å^{-1}$) for Xe-adsorbed CoNi-Pipe, NiNi-Pipe, and CoPd-Pipe, respectively. According to our MLP-based MD simulations, CoNi-Pipe shows the highest Xe mobility, followed by CoPd-Pipe and NiNi-Pipe despite their comparable Xe adsorption energies. Thus, CoNi-Pipe achieves the highest Xe uptake among the three MOFs. We find that framework flexibility plays a key role in Xe diffusion behavior; CoNi-Pipe possesses the most flexible structure, followed by CoPd-Pipe and NiNi-Pipe, a trend that is consistent with the order of the maximum Xe uptake. We further find that for CoPd-Pipe, Xe diffusion is limited at low Xe loadings but significantly improves at higher loadings due to enhanced framework flexibility. This provides a clear explanation for the sigmoidal adsorption behavior observed in CoPd-Pipe. This study highlights a new strategy for understanding the structural dynamics of flexible frameworks during gas adsorption and expands the scope of computational approaches for studying stimuli-responsive materials.

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THEORETICAL INVESTIGATION OF MOF'S LINKER FUNCTIONALIZATION FOR ENHANCING DESALINATION

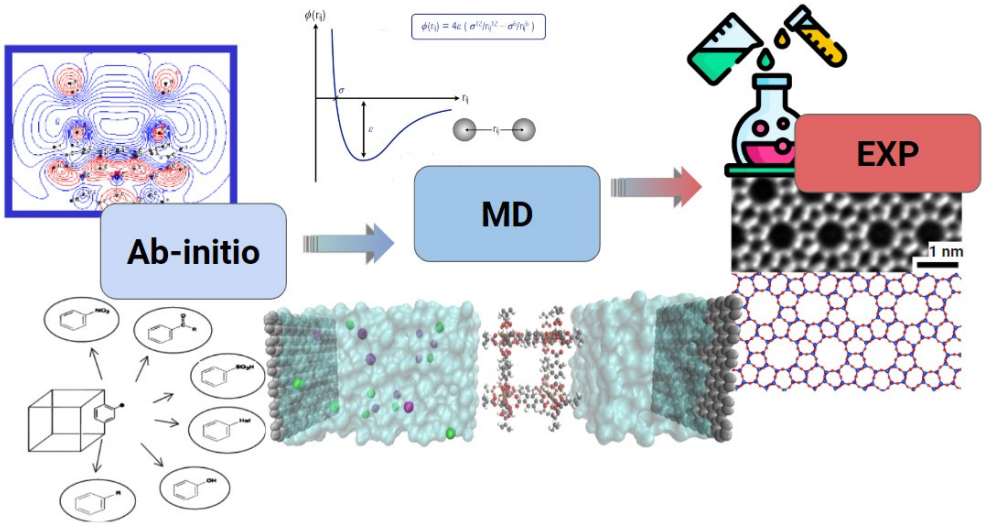
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Keywords: *Metal–Organic Frameworks; Water; Salt; Desalination; Functionalization; Ab initio; Molecular Dynamics*



Water scarcity is a critical issue that affects millions globally. With the increasing population and the escalating impacts of climate change, there is an urgent need for sustainable water treatment solutions. Desalination, plays a pivotal role in addressing this challenge. Our research leverages Metal-Organic Frameworks (MOFs)—highly porous materials composed of metal nodes and organic linkers—to enhance the desalination efficiency. By functionalizing MOF linkers, we improved salt rejection without significantly affecting water permeability, making the desalination process more effective and energy-efficient. We employed a multi-scale computational approach, that can advance the understanding of MOF interactions with water and contaminants, contributing valuable insights to the field of materials science and environmental engineering. Specifically, we conducted extensive ab initio calculations to screen a wide range of functional groups for their binding energy with water and salt ions, using the RI-MP2/def2-TZVPP level of theory [1]. This process led to the creation of a database of substituted benzenes with high salt adsorption potential compared to water. The functional group with optimal selectivity (-PO3H2) was selected for MOF modification and its desalination performance was evaluated through molecular dynamics simulations. It was found that the functionalized MOF reached 100% ion rejection, without significantly affecting water permeability. The results of this research, can guide experimental scientists to design new materials with desired properties and interactions, and facilitate the development of advanced desalination membranes and other water treatment technologies, tailored to specific needs and conditions.

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SIMULATION STUDIES OF VOLATILE ORGANIC COMPOUNDS ADSORPTION AND SEPARATION BY METAL-ORGANIC FRAMEWORK MIL-101(CR)

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Keywords: *MIL-101, volatile organic compounds, molecular simulations, quantum chemical calculations*

Volatile organic compounds (VOCs) are hazardous air pollutants with significant environmental and health impacts [1,2]. Their presence as indoor air pollutants can pose serious risks to both human health and the preservation of cultural heritage artifacts [3,4]. Metal-organic frameworks (MOFs), with their high surface area and tunable pore structures, offer promising solutions for VOC capture and separation. In this work, we combine Grand Canonical Monte Carlo (GCMC) simulations and Density Functional Theory (DFT) calculations to study the adsorption and separation of *n*-butyl acetate and n-dodecane in the metal-organic framework MIL-101(Cr) [5]. The simulations were performed for pure components and binary and ternary mixtures under realistic conditions, including the presence of humid air, to evaluate the competitive adsorption behavior. Particular attention was given to ternary mixtures involving water and the two VOCs to assess separation performance in complex environments. Our results reveal the influence of framework–guest interactions and humidity on adsorption capacity and selectivity, providing valuable insights into the potential of MIL-101(Cr) for VOC capture and separation under practical conditions.

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INTEGRATING MOLECULAR SIMULATIONS AND MACHINE LEARNING TO ASSESS MEMBRANE-BASED CO_2/N_2 and O_2/N_2 SEPARATION PERFORMANCES OF METAL–ORGANIC FRAMEWORKS

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Keywords: *Air separation, MOFs, diffusion, GCMC, molecular dynamics, machine learning*

High-purity oxygen is widely used in various industrial processes, including oxy-fuel combustion and medical applications. The separation of CO_2 from N_2 is vital for post-combustion carbon capture in flue gas treatment, addressing the urgent need to mitigate rising atmospheric CO_2 levels. Metal–organic frameworks (MOFs) offer a promising alternative for air separation thanks to their tunable porosity and high surface area. In this study, we investigated the CO_2/N_2 and O_2/N_2 membrane separation performances of 4009 Computation-Ready, Experimental Metal–Organic Frameworks (CoRE MOFs) through a multiscale approach combining molecular simulations and machine learning. We first performed grand canonical Monte Carlo (GCMC) simulations for CO_2, O_2 and N_2 at 298 K and 1 bar to determine single-component uptakes. These uptakes were then used in equilibrium molecular dynamics (MD) simulations to calculate self-diffusivities under the same conditions. Additionally, MD simulations at infinite dilution were conducted to capture intrinsic diffusion behavior. Using the simulation data, we developed machine learning (ML) models to predict self-diffusivity, incorporating structural features (e.g., PLD, LCD, ASA, porosity, pore volume), energetic descriptors (Q_{st} for CO_2, O_2 and N_2), and uptake values (CO_2, O_2 and N_2 adsorption at 1 bar), as well as log-transformed infinite dilution diffusivity. The most impactful features were found to be diffusivity at infinite dilution, heat of adsorption (Q_{st}), and pore limiting diameter (PLD). To test model generalizability, the trained ML models were evaluated on a distinct set of hypothetical MOFs (hypoMOFs). The predicted and simulated diffusion coefficients (DCs) showed good agreement, with hypoMOFs exhibiting a higher diffusivity range than CoRE MOFs. For CO_2, the diffusion coefficients ranged from 3.6×10^{-8} to 7.8×10^{-4} cm²/s in CoRE MOFs and from 1.5×10^{-4} to 3.4×10^{-3} cm²/s in hypoMOFs. For O_2, the range was 1.76×10^{-6} to 2.42×10^{-3} cm²/s in CoRE MOFs and from 2.33×10^{-5} to 8.16×10^{-3} cm²/s in hypoMOFs. For N_2, the range was 8.52×10^{-7} to 2.71×10^{-3} cm²/s in CoRE MOFs and 1.80×10^{-6} to 1.23×10^{-2} cm²/s in hypoMOFs. Our findings demonstrate the potential of combining high-throughput molecular simulations with interpretable machine learning models to screen MOFs for efficient membrane-based CO_2/N_2 and O_2/N_2 separation, paving the way for the rational design of materials.

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REFINEMENT OF $B_{18}H_{22}$ CLUSTER AND CYCLOHEXANE ARRANGEMENT IN MOF PORES USING HYBRID QM/MM APPROACH

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Keywords: Boron 18, cyclohexane, QM/MM calculation, MOF

Classical molecular dynamic simulations provide valuable information about distribution and arrangement of guest molecules in crystalline materials. When they complement X-ray and electron diffraction, they can significantly facilitate crystal structure solution and give a detail insight into interactions between guest molecules and host metal-organic frameworks (MOFs). However, accuracy of their results strongly depends on used force fields in calculations. Hence, as a step beyond the classical simulations, the hybrid quantum mechanical/molecular mechanical (QM/MM) approach can be utilized to refine the description of interactions between guest molecules and a MOF scaffold.

In this contribution, we focus on arrangement of cyclohexane and $B_{18}H_{22}$ clusters in the well-established prototypical Fujita MOF $[(ZnI_2)_3(tpt)_2]$[1] (tpt = *2,4,6-tris(4-pyridyl)-1,3,5- triazine*). Starting from optimized structures from the quenched molecular dynamics, the adsorbed molecule along with proximal atoms (up to the distance of ca 8 Å) was included into the QM part and the wave function was polarized by atomic charges in the outer region using electronic embedding. Total energies were evaluated within the subtractive scheme utilizing density functional theory (DFT). Optimizing the QM region, refined structures and positions of guest molecules were obtained. Simultaneously, the technique provides access to their electron densities.

Altogether, using this well-described system, the possibility and limitations of combining such an approach with the single crystal X-ray diffraction to enhance the precision of structural determination is investigated.

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APPLYING MACHINE-LEARNING APPROACHES FOR A QUANTITATIVELY RELIABLE DESCRIPTION OF HEAT TRANSPORT IN MOFS

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Keywords: *heat transport, phonons, machine-learned potentials, molecular dynamics, structure-to-property relationships, lattice dynamics*

Heat conduction in MOFs is a crucial requirement for any application in which excess heat needs to be dissipated or supplied (e.g., for gas adsorption/desorption or catalysis). As most MOFs are electrical insulators, they transport heat as lattice vibrations, which can be described either in real space via lattice vibrations or in reciprocal space via phonons. To develop reliable structure-to-property relations for heat transport, an atomistic understanding of the underlying processes is crucial. This can be best achieved via atomistic computer simulations, provided that they are capable of describing the relevant processes accurately.

This raises two fundamental questions: which computational approach should be chosen to describe thermal transport, and how could one reliably describe the involved inter-atomic interactions. For the latter, density functional theory (DFT) would be the natural choice, but DFT is not efficient enough to calculate forces between (tens of) thousands of atoms several million times. At the other end of the computational spectrum would be classical, transferable force fields, but they are way too inaccurate for providing a reliable description of MOF properties. These dilemmas can be resolved by using force fields system-specifically trained against DFT data, where we focus on moment-tensor potentials trained via a specially adapted active learning approach.[1], [2] They yield essentially DFT accuracy at sharply reduced computational costs (with a speedup compared to DFT of approximately 10^{10} estimated for the largest considered systems). This allows a quantitatively reliable description of heat transport processes for MOFs[1] as well as for molecular crystals.[3] Notably, the excellent agreement between experiments (often on single crystals) and simulations is achieved both when extracting thermal conductivities from the particle trajectories of non-equilibrium molecular dynamics simulations[1],[4] as well as when basing the analysis on harmonic and anharmonic phonon properties.[3],[4]

The distinct advantage of considering both approaches is that they provide complementary insight into the physical aspects of heat transport: from an analysis of the real-space effective temperature distribution in MOFs subject to a thermal gradient, one can, for example, identify the connections between linkers and nodes as the bottlenecks to thermal transport in MOF.[4],[5] In contrast, analyzing the phonon dynamics shows that in low thermal-conductivity materials like MOFs or molecular crystals it is not sufficient to describe heat transport merely as a diffusive transport of particle-like phonons. Rather, one also needs to consider coherences contributions arising from phonon tunneling between the lifetime-broadened phonon bands. This has the consequence that not only low-frequency acoustic phonons contribute to heat transport, but that also more complex, higher-lying optical phonons become relevant.

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RELATING PHASE TRANSITIONS OF CONFINED MATERIALS AND TOPOLOGY OF PORE NETWORK

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Keywords: *Phase transitions; Network models; Pore size distribution; Average connectivity; Pore network topology; Statistically-disordered & correlated structures.*

Measuring adsorption/desorption and melting/freezing transitions in porous materials is a common route to obtain information about pore structure. Often it is done by reducing the pore space to a simple collection of individually idealized pores, such as bundles of cylinders with different pore sizes. In this way, the network effects become fully ignored. To describe phase transition behavior in porous solids with complex pore space architectures we exploit statistical network models including cooperative effects emerging due to interpore connectivity.
By considering statistically-disordered random-branching Bethe lattices we show that in addition to more accurate pore size distributions also the average pore connectivity can be assessed. Furthermore, we show that beyond average connectivity, phase transitions are largely insensitive to finer topological details of the pore network.

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EFFECT OF OPEN METAL SITES ON METHANE ADSORPTION IN HKUST-1

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Keywords: *HKUST-1, Methane adsorption, MD simulation, First-principles calculation, Experiment*

Methane is a greenhouse gas with a warming potential 28 times higher than that of carbon dioxide [1], so should be removed to mitigate global warming. However, the removal or decomposition of methane using catalysts is not trivial due to its structure stability. Recently, methane removal by adsorption using metal-organic frameworks (MOFs) has been proposed. MOFs are porous materials composed of metal ions and organic ligands and exhibit high methane adsorption capacity than other materials. Among MOFs, HKUST-1 shows high methane adsorption capacity [2], and the capacity increases after activation. During activation, unsaturated binding sites called open metal sites are created. In the previous studies, the open metal sites in HKUST-1 appear to actively adsorb methane, but the detailed mechanism is unclear. Thus, we investigated the effect of the open metal sites on methane adsorption in HKUST-1 by comparing methane diffusion behaviors of the inactivated and activated structures. Through atomistic simulations and first-principles calculations, we found that the activated structure shows higher methane adsorption capacity and faster methane diffusion coefficient than the inactivated structure. The slow diffusion in the inactivated structure is originated from the stable adsorption sites located in the {100} surface planes, making some of the methane that diffused into the structure come back out. On the other hand, in the activated structure, the open metal sites shift the stable methane adsorption sites toward themselves, which allows methane to continue to diffuse into the structure and increases the methane diffusion coefficient and methane adsorption capacity. This finding would contribute to the increment of methane adsorption in MOFs.

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TOLUENE DETECTION AND CAPTURE USING MOF/POLYMER COMPOSITES

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Keywords: *Metal Organic Frameworks, Adsorption, Toluene sensor*

In the confined and controlled environments of spacecraft habitat, the presence of airborne contaminants poses unique challenges to crew health, equipment longevity and mission success [1]. Among these contaminants, Volatile Organic Compounds (VOCs) such as aromatics (e.g., toluene, siloxanes, and phthalates) are routinely released from payload systems and materials used onboard [2]. Their persistence in enclosed systems with limited ventilation introduces both health and engineering concerns [3]. Toluene, in particular, is a critical target due to its toxicity and prevalence in off-gassing sources.

This work focuses on the detection and capture of toluene using porous Metal-Organic Frameworks (MOFs), specifically DUT-4(Al) and DUT-5(Al), which have demonstrated superior toluene adsorption performance when compared to traditional materials like zeolites and activated carbons [4]. However, these MOFs are too hydrophilic to be applied in space-relevant settings. Our objective is to design MOF-based composites with hydrophobic polymers so as to ensure that these materials can selectively capture contaminants from the space domain in the presence of humidity, conditions encountered during ground and flight tests.

To achieve this overall objective, numerical simulations were first deployed to scan a wide range of hydrophobic polymers to identify the optimal MOF-based composites with the desired toluene selective adsorption in presence of humidity. We employed a computational approach that integrates Density Functional Theory, Grand Canonical Monte Carlo, and Molecular Dynamics simulations which allowed us to construct atomistic models for all MOF-based composites and further explore the structural, energetic, and dynamics features of toluene in the overall composites. We identified the most promising MOFs/hydrophobic polymers composites showing (i) the highest MOF/polymer compatibility, (ii) the best toluene adsorption performance and (iii) the fastest toluene transport. These computational findings guided the fabrication of the corresponding composites and their experimental testing in progress.

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SEMI-REACTIVE FORCE FIELD FOR ZEOLITIC IMIDAZOLATE FRAMEWORKS

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Keywords: Zeolitic Imidazolate Frameworks*, melting, Force Field*

The ability of Zeolitic Imidazolate Frameworks (ZIFs) to undergo amorphisation under physical or chemical stimuli, while largely retaining their defining chemical properties makes them interesting candidates for versatile and easy to process materials. The phase transitions of ZIFs are actively researched, both experimentally as well as computationally. Computational studies can provide atomistic mechanisms of these transitions. While the use of *ab initio* methods is desirable, they can only access small system sizes and time scales, typically picoseconds, which limits their predictive power for these relatively slow transitions. These limitations can be mitigated by using parametrized models, like machine learning potentials or force fields. The former offer close to *ab inito* accuracy, while the latter allow for larger simulations of millions of atoms.

In this work, a semi-reactive derivative of ZIF-FF by Dürholt et al.[1] is presented. This force field describes the nitrogen-zinc interaction via non-bonded potentials. In contrast to previous semi-reactive force fields, the interaction is modelled using higher order potential terms beyond the simple pair potentials like Van-der-Waals and Coulomb interactions. This approach allows the model to adhere more closely to the physical properties of the system. Furthermore, this force field is parametrized using a novel fully-differentiable in-house fitting-engine called JaxFF that is build on the JAX machine learning python library.[2] First tests revealed good agreement between ensemble properties calculated by density functional theory and the semi-reactive ZIF-FF.

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ANALYZING MOLECULE TRANSPORT IN MOF MATERIALS USING KINETIC MONTE CARLO SIMULATION

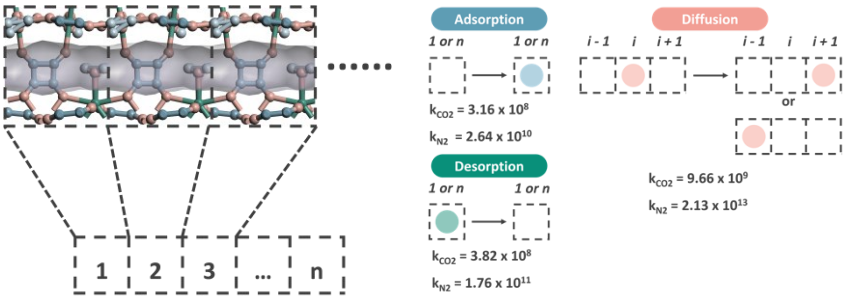
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Keywords: *MOF, Transport Phenomena, Kinetic Monte Carlo, Molecule Dynamic*

As microporous materials continue to have a significant impact in fields such as catalysis, gas adsorption, membrane gas separation, and gas storage, the molecular transport properties within these materials are gaining increasing attention. Metal-organic frameworks (MOFs), a popular class of crystalline microporous materials, have attracted interest for their potential in advancing material design through the study of molecular transport phenomena. Current theoretical models predominantly suggest that gas transport in crystalline microporous materials follows the Solution-Diffusion Model. However, limited discussion exists regarding the relationship between diffusion coefficients and permeability as described by this model, as well as the conditions under which the model is applicable. In this study, we employed density functional theory (DFT) to calculate the rate constants for gas adsorption, desorption and used molecular dynamic (MD) to calculate the rate constants for gas diffusion in MOFs. We further utilized kinetic Monte Carlo (kMC) simulations to replicate gas adsorption and permeation experiments on MOF materials. By comparing the kMC simulation results for two gases with the predictions of the Solution-Diffusion Model, we examined the influence of gas type and crystal size on the model's performance, ultimately defining its applicable scope. Additionally, we proposed a modified model to address scenarios where the Solution-Diffusion Model proves inadequate.



SIMULATING 23NA NMR OF SODIUM-ION-MODIFIED ZIF-62 GLASS

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Keywords: *glasses, NMR, DFT*

ZIF-62 is a mixed-linker metal-organic framework known for its exceptionally high glass-forming ability. Taking inspiration from silicate-based glass techniques, modifying glassy ZIF-62 with Na+ substantially lowers its glass transition temperature, which promises to improve its overall processability[1]. Here, we simulated 23Na NMR via DFT GIPAW on Na-ZIF-62 to determine the mechanisms responsible for its decreased transition temperature. Over 300 Na+ environments were generated and classified according to their match with experimental NMR spectra. We found Na+ substitution in ZIF-62 distorts the framework and reduces connectivity, leading to 4- or 3-coordinated Na+. This contrasts the 6- or 5- coordinated Na+ in Na-modified silicate glasses. The unique structural role of Na+ in Na-modified ZIFs highlights the potential to adapt glass modification principles to MOF-based systems, achieving new structural and functional outcomes.

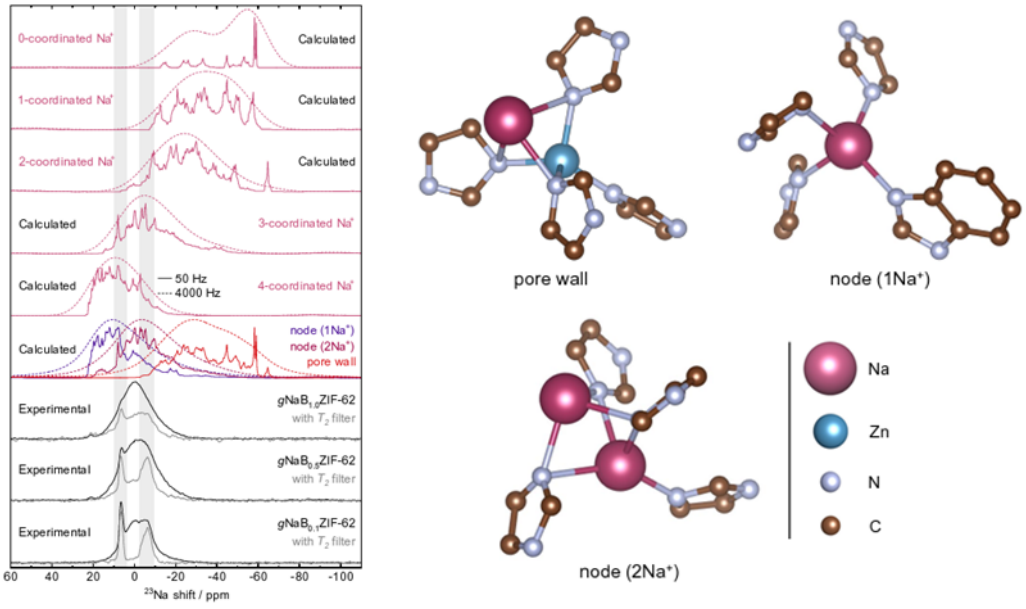


Figure 1 (Adapted from Figure 4 of [1]). NMR and DFT analysis of structural changes during vitrification. Predicted 23Na NMR spectra of Na+ sites in DFT-simulated gNaBxZIF-62 structures, categorised by Na+ occupation in the gNaBxZIF-62 and N–Na+ coordination number. Experimental 23Na NMR (20.0T, 20 kHz MAS) spectra of gNaBxZIF-62 with x = 0.1, 0.5, 1.0. Examples of local structures surrounding Na+ in DFT-simulated gNaBxZIF-62: a MOF pore wall site, a singly occupied node site, and a doubly occupied node site. Gaussian line broadening of 50 Hz (solid) and 4000 Hz (dashed) is applied to calculated spectra to simulate the effect of static disorder.

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FUNCTIONALIZING THE STRUCTURE OF COFS TO ENHANCE THEIR CO_2 UPTAKE CAPABILITY

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Keywords: *COF, CO_2 uptake, DFT, Functionalizing COF*

Global warming is a serious worldwide threat with a significant impact on ecosystems, and CO_2 emission is intimately tied to this threat. The unprecedented challenge to reduce CO_2 emission demands thinking about, focusing on, and designing new materials. Therefore, developing solid-phase adsorbents to efficiently capture CO_2 from the atmosphere plays a critical role [1]. An ideal material to trap CO_2 has a high CO_2 adsorption capacity and a high level of selectivity to enable uptake from the atmosphere as a dilute resource containing different gases. Moreover, it should provide an affordable mechanism to serve economic purposes and remain stable against corrosion for long-term usage. Recently, a promising step forward was established by using covalent organic frameworks (COFs) [2] as porous materials with ordered periodic reticular frameworks and different pore sizes and functional groups. Lyu et al. [3] synthesized COF-609 with a capacity much higher than the first generation of CO_2 capture COFs. Very recently, COF-999 was introduced by Yaghi group [4] which has high capacity for CO_2 uptake from air. COF-999 has cycling stability, low regeneration temperature and facilitates CO_2 uptake in both dry and humid air. The potential capability of COFs to capture CO_2 motivated us to choose them in our research.

In this work, we are modifying the active sites of the COF structure to improve its CO_2 uptake capacity. We carried out electronic structure calculations by density functional theory (DFT). All electronic structure calculations were done with the *Gaussian* 16 program [5]. We used MN15L [6] functional with def2-SVP [7] for carbon and hydrogen atoms while a larger basis set, def2-TZVP [7], was used for the rest of system. To enforce the node geometry of the COF, the carbon coordinates were frozen. CM5 [8] charges are calculated to evaluate the effect of modifications on the interactions with CO_2. As a starting point, we studied COF-999. We manipulated the structure of the chains inside the pore to find how to increase the charge of nitrogen which interacts actively with CO_2. Our results showed that the length of the chains or the presence of more amine groups does not change the CM5 charge of N in the terminal amine groups. While these changes might influence the physisorption of CO_2 due to affecting the available pore space, they do not affect chemisorption. Next, we are functionalizing COF arms by adding metals into their structure. Metal organic frameworks (MOFs) [9] with open metal sites (OMS) have been found to be more active for different catalytic activities. While COFs do not have any metal in the node, our goal is to functionalize them by adding metals not in the node or in the main chain of the linker, but in the side chains of linkers which in principle go into the pore. We use SDD [10] effective core potential for heavy atoms when performing calculations on the metal-functionalized structures. The introduction of OMS influences the charge distribution, enhances the interaction strength with CO_2 and affects the physisorption potential.

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FROM HYBRID DFT FUNCTIONALS TO MACHINE LEARNING INTERATOMIC POTENTIALS FOR MOF

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Keywords: *hybrid functionals, DFT, machine learning, interatomic potentials, f-block elements*

In this work we introduce machine learning interatomic potentials (MLIPs) for the computational design and optimization of metal-organic frameworks (MOFs) by synergizing high-level quantum chemistry and state-of-the-art ML tools.

Moving beyond conventional approaches based on GGA functionals as PBE/plane-wave data, we employ a recently developed cost-effective yet highly accurate method - r^{2}SCAN0pob-3c[1] - that integrates the mGGA functional r^{2}SCAN[2] hybridized with 25% of Hartree-Fock exchange, combined with an all-purpose triple-ζ quality basis set for solids (i.e. POB-TZVP-rev2[3]) and augmented by semiempirical corrections to include dispersion interactions[4] and remove the basis set superposition error (BSSE)[5]. All calculations have been carried out with the CRYSTAL23 code[6].

About four hundred structurally and chemically diverse MOFs, covering a wide range of topologies, metal centers and functional groups, have been carefully selected from the QMOF database[7]. Our dataset includes most of the elements of the periodic table as well as f-block elements - both lanthanides and actinides. The result is a well-curated, ab initio hybrid HF/DFT quality set of data, tailored to capture the nuanced physicochemical behavior across the MOF landscape. Using energy and forces generated through the geometry optimization of 360 MOFs, we collected 16877 configuration data to train a Message Passing Neural Network, as implemented in the MACE code[8], and develop a MLIP that provides a highly accurate prediction of MOF structures, energetics and mechanical responses. To prove it, the MLIP has been rigorously validated against low-temperature (T < 100K) and high-resolution (with R-factors < 5%) experimental structures of MOFs. Results are also compared with MACE foundation models (e.g. MP0 and O-MAT) along with MLIPs derived from the fine-tuning of existing ML models.

Our work not only bridges the gap between DFT-level fidelity of hybrid functionals and molecular-scale efficiency but also takes advantage of the well-tailored small dataset to reduce the computational burden of the ab initio calculations.

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A UNIVERSAL FOUNDATION MODEL FOR TRANSFER LEARNING IN MOLECULAR CRYSTALS

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Keywords: *transfer learning, molecular crystals, transformer model, property prediction.*

The physical and chemical properties of molecular crystals are a combined function of molecular structure and the molecular crystal packing. Tailoring specific packing motifs enables diverse applications—ranging from pharmaceuticals and organic electronics to porous frameworks for gas storage such as hydrogen-bonded organic frameworks (HOFs). However, to design such materials, we need to predict both crystal structure and the resulting physical properties, and this is expensive using traditional computational methods. Machine-learned interatomic potential methods offer major accelerations here, but molecular crystal structure prediction remains challenging due to the weak intermolecular interactions that dictate crystal packing. Moreover, machine-learned interatomic potentials do not accelerate the prediction of all physical properties for molecular crystals. Here we present Molecular Crystal Representation from Transformers (MCRT), a transformer-based model for molecular crystal property prediction that is pre-trained on 706,126 experimental crystal structures extracted from the Cambridge Structural Database (CSD). MCRT employs four different pre-training tasks to extract both local and global representations from the crystals using multi-modal features to encode crystal structure and geometry. MCRT has the potential to serve as a universal foundation model for predicting a range of properties for molecular crystals, achieving state-of-the-art results even when fine-tuned on small-scale datasets. Furthermore, its attention scores offer interpretable insights into the structural factors governing model predictions.

METHANOL-ETHANOL DISCRIMINATION AND SELECTIVE SENSING ENABLED BY MOLECULAR SIEVING IN A CONDUCTIVE MOFS

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Keywords: *conductive metal-organic frameworks, methanol, chemiresistor, density functional theory, molecular dynamics*

Methanol is a hazardous compound due to its high volatility and toxicity, and its resemblance to ethanol increases the risk of accidental ingestion, especially in tainted drinks. Here, we report a selective sensing strategy for methanol based on nanostructured hybrid materials composed of single-walled carbon nanotubes (CNTs) integrated with conductive metal-organic frameworks (cMOFs) made from 2,3,7,8,12,13-hexahydroxytetraazanaphthotetraphene (HHTT) and various metal motifs.[1] Structural motifs within the porous framework play a key role in modulating molecular interactions and transport, enabling enhanced discrimination between methanol and chemically similar compounds, especially ethanol. To understand the origin of this selectivity, we employed density functional theory (DFT) calculations to probe the binding energetics and preferred adsorption sites of methanol and ethanol within the framework. Molecular dynamics (MD) simulations revealed differences in diffusion behavior through the pore environment, particularly highlighting the role of steric hindrance in suppressing ethanol transport. Together, these computational insights elucidate how the material architecture governs gas not only sensitivity but also selectivity and supports the observed sensing behavior. Tests with simulated tainted commercial liquors confirmed the potential utility of the sensor described here in rapid and efficient detection of methanol in counterfeit and tainted popular beverages.

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STUDY OF BORON CLUSTERS AND CYCLOHEXANE MOLECULES ANCHORING IN MOF BY MOLECULAR DYNAMICS

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Keywords: Boron 18, cyclohexane, molecular dynamics, MOF

Crystallographic techniques are powerful tools for determining the structure and spatial arrangement of atoms and molecules in crystalline materials. However, not all molecules are regularly arranged in well-ordered crystals. When high precision methods such as X-ray or electron diffraction are not sufficient in providing detailed structural information, force field based molecular dynamic calculations can offer valuable insights into the position description and behavior of individual molecules within Metal-Organic Frameworks.

Application of molecular dynamics on MOF structures containing boron-18 clusters and cyclohexane molecules can significantly accelerate the process of crystal structure resolution. This approach enables a more detailed description and understanding of anchoring sites and mutual intermolecular interactions within the frameworks.

The first phase of calculations is focused mainly on the preparation of MOFs, their detailed characterization in terms of their crystallinity and number of defects (ligand to metal ratio). Calculations started with the well-established prototypical Fujita MOF [(ZnI2)3(tpt)2],[1] where tpt refers to *2,4,6-tris(4-pyridyl)-1,3,5- triazine*. This MOF will serve as a host structure for the adsorption of non-polar molecules such as cyclohexane's and boron clusters.

Using this well-established system, we will study the possibility and limitations of combining molecular dynamic simulations and single crystal X-ray diffraction to enhance the precision of structural determination.

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Establishing material-transferable design rules for defective metal-organic frameworks and metal halide perovskites through strain engineering

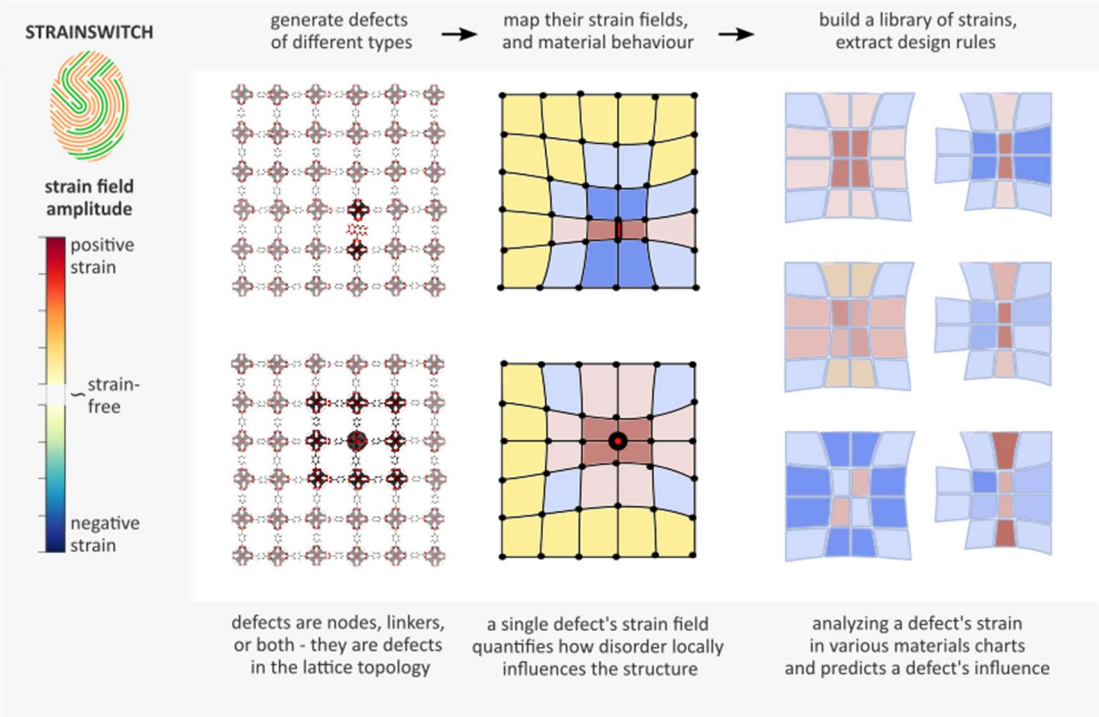
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Keywords: *Strain engineering, disorder, materials chemistry, phase stability, design rules*

When materials such as metal halide perovskites (MHPs) and metal-organic frameworks (MOFs) are subjected to external stimuli (temperature, pressure, gas adsorption), their responses are often accompanied by changes in their overall structure, straining the material *globally*. In contrast, when defects are introduced in these materials, the *local* lattice surrounding the defect adapts, introducing *local* strain. The coupling of these two different strain fields can change the baseline macroscopic response of a material to a given stimulus, *e.g.*, stabilising a phase beyond its stability window in the non-defective variant [1]. This, in turn, can stabilise the opto-electronically active phase in MHPs or tune the porosity-dependent sorption properties of MOFs, among other applications. In this way, strain engineering can endow a material with the desired behaviour by consciously introducing defects.



We herein investigate the properties and dynamics of strain fields in a wide series of defective MOFs and MHPs: the M-IRMOF-L series, in which we introduce disorder in either nodes [M={Zn, Be, Mg, Cd, Ca, Sr, Ba}] or linkers [L={0-8, 10, 12, 14, 16, 18, 20}], and the $CsBX_3$ perovskites, in which we introduce disorder in either the B^{2+} cation [B={Ba, Pb, Ca, Zn}] or the X^- halide anion [X={Cl, Br, I}] [3]. We characterise the dynamic strain fields induced in these disordered materials under temperature and pressure changes using material-transferable machine-learning potentials trained on *ab initio* input [2]. We systematically compare how *different* stimuli in *different* materials with *different* defects lead to *similar* strain fields, as quantified through various analysis techniques [3]. Based on these similarities, we extract material-transferable design rules that are transferable between materials with the same **pcu** topology, paving the way to transfer traditional design rules for MOFs to MHPs and vice versa [3].

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TOWARDS A BENCHMARK FOR MACHINE LEARNING IN MOF SYNTHESIS: INTELLIGENT EXPLORATION OF PARAMETER SPACE

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Keywords: *Machine learning, MOF synthesis, microwave synthesis, parameter space, benchmark dataset, process modelling*

In recent years, machine learning has become increasingly integrated into chemical research, offering powerful tools for predicting structures, reaction pathways, and even guiding synthesis. [1] [2] However, despite its broad applicability, a persistent limitation remains: the lack of comprehensive experimental datasets. In many cases, machine learning models are trained on limited or simulated data, restricting their ability to generalize across systems or to make robust predictions in unexplored regions of the parameter space. Especially in the synthesis of Metal-Organic Frameworks (MOFs), where synthetic outcomes are influenced by a complex interplay of synthesis parameters, this lack of real-world data presents a critical bottleneck.

To address this challenge, we present a large-scale experimental study aimed at generating a benchmark dataset for machine learning in MOF synthesis. Rather than focusing on the optimization of a specific material property, our project targets the systematic exploration of the synthesis parameter space for a selected MOF system. The synthesis conditions are determined iteratively by a machine learning model, which proposes new experimental parameters based on previous outcomes. This enables a data-efficient and intelligent navigation of the parameter space that prioritizes diversity and informativeness over convergence.

A large number of MOF samples are synthesized via a robot-assisted microwave reactor, enabling high-throughput operation. Due to the sequential heating process, individual samples experience varying idle times before and after synthesis, which may introduce minor variability despite efforts to select a system inert at room temperature. Idle times are monitored to account for possible deviations during data interpretation. X-ray diffraction is used to evaluate the resulting material structure, and the collected dataset provides a digital “mirror” of the synthesis space, capturing a wide range of outcomes across varying conditions.

The ultimate goal of this work is to establish a publicly available benchmark that enables the training, testing, and comparison of machine learning models for MOF synthesis. By decoupling model development from real-time experimental validation, this benchmark has the potential to accelerate progress in the data-driven discovery and design of porous materials.

Beyond providing a high-quality dataset for benchmarking, the long-term aim is to facilitate cross-system generalization. Once trained on the generated data, machine learning models may be applied to predict synthesis outcomes for structurally or chemically related MOF systems. This could significantly reduce the experimental effort required when approaching new synthesis targets.

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UNDERSTANDING STRUCTURAL CHARACTERISTICS OF WATER IN CONFINEMENT

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Keywords: Metal-Organic Frameworks, Water Clusters, Hydrogen Bond Networks, Molecular Dynamics

Understanding water behavior under confinement is crucial for optimizing porous materials such as MOFs and COFs for applications in atmospheric water harvesting and treatment.[1] This study systematically compares confined water within MOF-303 against bulk water under identical thermodynamic conditions, varying densities from 0.01-0.6 g/cm^3 using molecular dynamics simulations and graph theory.[2,3] The primary goal is to elucidate how confinement influences structural organization, hydrogen bonding dynamics, and clustering behavior. Our findings reveal significant differences between confined and bulk water, particularly in water clustering dynamics and network connectivity. Confinement notably alters the percolation transition, shifting critical cluster densities compared to bulk water. While bulk water quickly reaches ring formation saturation at relatively low densities, confined water shows delayed ring formation patterns, underscoring unique structural responses to confinement. Network analyses provide detailed atom-level insights into the interactions governing confined water behavior. Confined water networks demonstrate enhanced clustering and distinct topological characteristics compared to bulk water, highlighting the significant impact of specific MOF atomic sites. Certain MOF atoms emerge as critical network hubs, affecting local clustering and influencing the growth or suppression of water clusters. This research advances the fundamental understanding of water behavior under confinement and significantly contributes to the strategic development of MOFs with tailored pore environments optimized for water-related applications.

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CLUSTER-BASED LEARNING TO DESCRIBE DISORDERED METAL-ORGANIC FRAMEWORKS AT THE MESOSCALE

P. Dobbelaere, S. Vandenhaute and V. Van Speybroeck

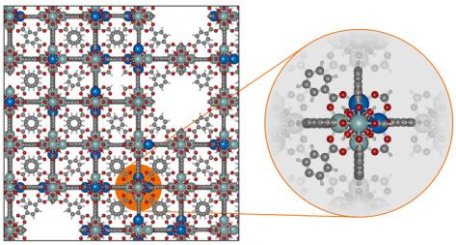
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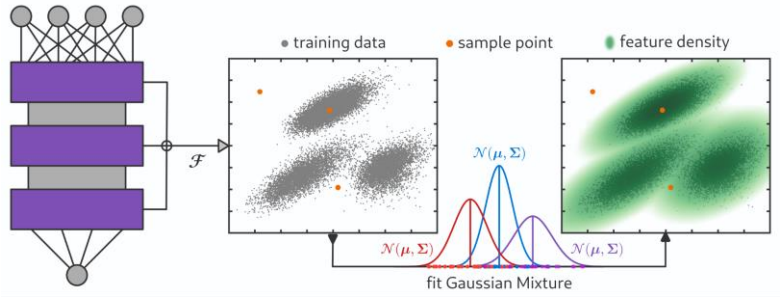
Keywords: *metal-organic frameworks, spatial disorder, machine learning potentials*

Metal-organic frameworks (MOFs) are a spectacularly versatile class of nanoporous materials, with potential applications in (heterogeneous) catalysis, gas sorption, nanosensing and energy storage.[1] By incorporating local spatial defects into their atomic structure, MOFs can be fine-tuned to incorporate desired chemical functionalities. These targeted modifications require a fundamental understanding of the microscopic structure of a material and its macroscopic emergent properties. Successful defect engineering warrants detailed research.

In MOFs, spatial disorder expresses itself across multiple length scales.[2] At the nanoscale, we find point defects such as missing linkers, metal ion substitutions and slightly larger node defects. Zooming out, synthesised crystallites can contain mesopores, regions of phase coexistence and eventually finite crystal boundaries. However, existing computational models often struggle to comprehensively describe disordered phenomena. *Ab initio* methods are restricted by the quantum scaling limit at extended length scales (> 10 nm), and force fields are hampered by a lack of functional flexibility. The recent addition of machine learning potentials (MLPs) to the modelling toolbox promises the combination of high accuracy and efficient evaluation, on the condition that we can collect representative training data. This remains prohibitively expensive, bringing us back to square one.



Here, we introduce a cluster-based learning methodology to develop state-of-the-art MLPs for spatially disordered MOFs. Following a divide-and-conquer approach, we deconstruct large supercells into smaller molecular fragments to circumvent *ab initio* limitations (see figure above). By assembling an appropriate set of finite clusters, it is possible to describe every (local) interaction of the original supercell. Our approach consists of two main components: (i) scan molecular systems and identify out-of-dataset chemical environments using a data-driven uncertainty model exploiting MLP feature space (see figure below), and (ii) encapsulate the corresponding atoms into clusters that replicate the supercell bulk environments. This scheme is embedded into an automated active learning workflow. Our recent preprint shows that cluster-based learning delivers models capable of accurately describing spatial defects in mesoscopic systems with over twenty thousand atoms.[3] Using this methodology, we can simulate (almost) arbitrarily disordered frameworks; a valuable step towards the study of realistic crystallites and an understanding of the role of disorder on MOF behaviour.



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METAL-ORGANIC FRAMEWORKS FOR HYDROGEN/METHANE SEPARATION

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Keywords: *MOF, Adsorption, Separation, Hydrogen, Methane*

Hydrogen is a leading green alternative to fossil fuels for transport and power generation, offering zero greenhouse gas emissions and enabling the transition to carbon neutrality. The European Commission estimates that hydrogen could meet up to 24% of global energy demand by 2050.[1] However, efficient transportation and delivery of hydrogen remains a key challenge. While liquefied hydrogen can be shipped, the high energy cost of liquefaction and long transit times limit its viability for large-scale transport. A promising alternative is blending hydrogen with natural gas in existing pipelines, allowing co-transport with methane and separation near end-use sites.[2] Mixtures containing 10–20% hydrogen by volume can be safely transported without major infrastructure upgrades, providing a cost-effective pathway for widespread adoption of hydrogen energy systems.[3]

Conventional CH_4/H_2 separation methods, such as cryogenic distillation and chemical absorption, are highly energy-intensive. In contrast, pressure swing adsorption (PSA) offers lower energy consumption, high product purity, and operational flexibility. Metal-organic frameworks (MOFs), with their high porosity, large surface area, and tunable chemistry and topology, are promising sorbents for PSA-based CH_4/H_2 separation. However, only a few MOFs have been identified experimentally—often by serendipity—from over 125,000 synthesized structures, while high-throughput computational screenings frequently yield candidates unsuitable for industrial use.[4-6]

In this work, we systematically investigated a series of MOFs that combine ease of synthesis, structural stability, low-cost metal and linker components, and environmental sustainability for thermodynamic CH_4/H_2 separation using detailed atomistic simulations. Grand Canonical Monte Carlo simulations were employed to assess their separation performance and to gain insight into the molecular-level mechanisms governing separation. We identified MOFs exhibiting high selectivity and working capacity, and rationalized their performance in terms of pore size, geometry, and chemical functionality, thereby establishing key structure–property relationships. Guided by these insights, we further explored various tuning strategies—including linker substitution, linker functionalization, and node metal variation—to design novel MOFs with improved separation performance. To complement the thermodynamic analysis, density functional theory calculations were performed to assess framework flexibility and its influence on the separation behaviour, while molecular dynamics simulations were deployed to study the kinetic aspects of separation, ensuring the practical relevance of the materials for PSA processes.

This study provides a comprehensive framework for identifying and optimizing practical MOF candidates for CH_4/H_2 separation, bridging the gap between computational screening and real-world applicability. By integrating thermodynamic, kinetic, and structural analyses, we propose key design principles for next-generation adsorbents tailored for PSA processes. These insights lay the groundwork for experimental efforts and future development of scalable hydrogen purification technologies.

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MACHINE LEARNED POTENTIAL FOR HIGH-THROUGHPUT PHONON CALCULATIONS OF METAL-ORGANIC FRAMEWORKS

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Keywords: *Machine Learning Potentials (MLP), phonons, quasi-harmonic, high-throughput screening*

Metal-organic frameworks (MOFs) have exceptional tunability and porosity, making them ideal candidates for applications in gas storage, catalysis, and sensing. Understanding their lattice dynamics is crucial for analyzing mechanical stability and guest-framework interactions. However, the vast design space of MOFs makes experimental screening impractical, highlighting the urgent need for robust computational models to predict lattice dynamics and guide the discovery of MOFs. Current computational models majorly focus on harmonic phonons, failing to capture important experimentally observed anharmonic effects such as negative thermal expansion in MOFs. To address these challenges, we present the “MACE-MP-MOF0" model specially tailored to produce ab initio quality lattice dynamics which is ready-to-use for a wide chemical space and topologies covering 60% of MOF chemistry. This work proposes an efficient sampling strategy of the MOF phase space to reduce computational costs in DFT dataset generation by a 100 times for fine-tuning MLPs for MOFs. The novelty of this work lies in obtaining accurate phonons and their derived properties like bulk modulus and negative thermal expansion relative to experiments and density functional theory (DFT), as shown in Figure 1 and Table 1, in a high-throughput way which would otherwise be computationally infeasible for MOFs. The systematic benchmarking performed against different levels of theory, from tight-binding DFT to other state-of-the art MLPs, shows that MACE-MP-MOF0 achieves a 50-90% improvement in computational speed and 80% lower mean absolute errors in energies. Benchmarking also reveals that the MACE-MP-MOF0 model is 10 to 100 times more accurate in capturing capturing the covalent interactions in MOFs. Therefore, this model offers a plethora of opportunities to investigate other systems beyond MOFs, such as Covalent Organic Frameworks, where such interactions dominate. The agreement with experiments and DFT highlights MACE-MP-MOF0 as an excellent platform for the materials science community to expedite MOF discovery and synthesis.

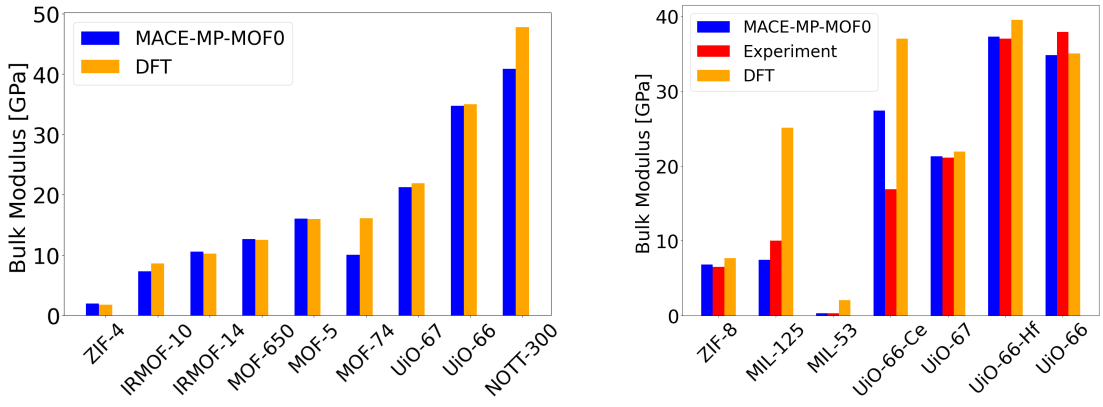


Figure 1. Bulk modulus predictions with MACE-MP-MOF0 for well-known MOFs in literature which are diverse in chemistry and topology, as compared to a) only DFT and b) DFT and Experiments

MOF	MACE-MP-MOF0 [$10^{-6}K^{-1}$]	DFT [$10^{-6}K^{-1}$]
MOF-5 (300 K)	-6.65	−3.5
UiO-66 (350 K)	-9.35	-4

Table 1: Comparison of coefficient of thermal expansion predictions by MACE-MP-MOF0 and DFT at different specified temperatures

MODELLING ELUSIVE ORDER–DISORDER PHASE TRANSITIONS IN METAL–ORGANIC FRAMEWORKS

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Metal–organic frameworks (MOFs) demonstrate complex behaviours in response to thermodynamic stimuli such as changes in temperature, mechanical stress, or guest adsorption. These triggers can induce transitions to disordered states that lack long-range translational order (Fig. 1a).[1–3] Such disordered states are of growing interest for functional applications, owing to their structural adaptability—for example, their ability to dissipate strain without significant material degradation.[1,4] However, experimental and computational challenges in resolving these disordered atomic structures continue to hinder the prediction and rational design of disordered MOFs.

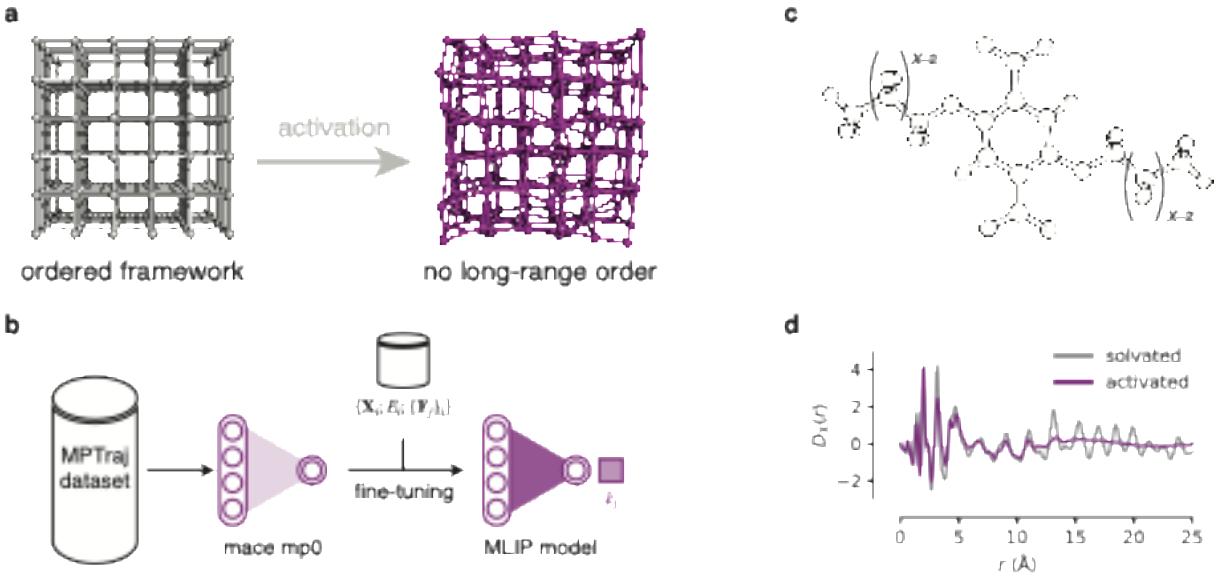


Figure 1. **Overview of this study. a**, Schematic illustration of an order–disorder transition in a MOF. **b**, MOF-5 derivatives investigated in this work with varying alkyl chain lengths on the BDC linker. **c**, Workflow illustrating the use of foundational MLIP models[5] to efficiently train accurate, system-specific potentials. **d**, Trained MLIP models enable direct comparison with experimental total scattering data.[6]

In this work, we address these challenges through an *in silico* approach using machine-learned interatomic potential (MLIP) models (Fig. 1b).[5] We focus on the *efficient* training of models capable of accurately describing, at the level of density functional theory, the transition behaviour of an isoreticular series of MOF-5 derivatives, wherein the benzenedicarboxylate (BDC) ligands are functionalised with alkyl chains of varying lengths (Fig. 1c).[6] We demonstrate that these models achieve an effective balance between accuracy and computational efficiency, enabling us to explore structural transitions in a manner that supports meaningful comparison with experimental total scattering data (Fig. 1d).[6] In doing so, we shed light on the role of linker functionality in modulating the transition behaviour of MOFs.

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PROBING THE ROLES OF SOLVENTS INSIDE METAL-ORGANIC FRAMEWORKS VIA MOLECULAR DYNAMICS SIMULATIONS

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Keywords: *metal-organic frameworks, molecular dynamics, zeolitic imidazolate frameworks*

Metal-organic frameworks (MOFs) are a class of highly versatile materials with a broad range of applications, such as gas storage and separation, water harvesting, platforms for drug deliveries and many more.[1] A major challenge in designing MOFs with precise functional properties is controlling polymorphism, as different polymorphic forms can exhibit entirely distinct structures and behaviours. Zeolitic imidazolate frameworks (ZIFs) based on unsubstituted imidazole are chosen here as an illustrative example, given that more than 18[2] various topologies of Zn**Im**$_2$ have been reported experimentally. Recently,[3] we have shown a systematic approach to employ mechanochemical synthesis coupled with varying structure directing liquid additives (LAs) to obtain 12 unique solid forms of Zn**Im**$_2$. We demonstrated the potential predictive power of periodic density functional theory (DFT) calculations to aid additive screenings and conserve experimental resources, but the dynamic effects of LAs still need to be addressed computationally. Herein, we present the use of molecular dynamics (MD) simulations to explain the formation of specific ZIF polymorphs, by quantifying the energetic effects of incorporation of different guest molecules inside the ZIF pores and using these calculations to rationalize the experimental outcomes of the corresponding mechanochemical reactions.

We here establish an MD simulation methodology[4,5] wherein the zinc-based ZIF structures were constructed first, followed by individual LA molecules being inserted into the pores of each ZIF supercell, until the voids are fully occupied. MD simulations were performed across all LAs used in the experimental synthesis into each ZIF supercell to encounter the energetic variations. We compare the results of MD simulations and mechanochemical synthesis, adding further insight on how specific liquid additives influence the formation of distinct ZIF structures. Overall, this computationally guided approach can further enhance the precision and predictability of mechanochemical MOF synthesis under conditions tailored to yield desired MOF properties.

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SOLVENT-RESPONSIVE PYRAZOLATE PEPTIDE FRAMEWORKS: NAVIGATING THEIR THERMODYNAMIC LANDSCAPE

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Keywords: *flexibility, metal-organic frameworks, computational chemistry*

Peptide-based bispyrazolate frameworks are a promising new class of chemically robust porous materials with adaptive structural responses. Among the experimental structures obtained, the solvent-specific phase transformations observed by the framework with alanine (Zn(Pz-A-Pz), MUV-A)[1] were studied computationally, and the osmotic landscapes[2,3] were constructed (**Fig. 1**). The simulations reproduce the closed-to-open phase transitions in MUV-A and elucidate the thermodynamic and molecular origins of the distinct guest-induced flexibility observed with MeOH and DMF. At low pressures, the closed phase is favored for both solvents, while increasing pressure lowers the energy barrier between states, allowing coexistence and ultimately favoring the open structure (**Fig. 1b,e**). For DMF, simulations predict a 38.6–41.7% unit cell expansion due to solvent intrusion (state B, **Fig. 1c**), in excellent agreement with the experimentally observed 41%. In contrast, the experimental data for MeOH–MUV-A indicate a symmetry change in the open phase, though the extent of expansion could not be directly quantified. Simulations suggest that this corresponds to a smaller expansion (32.3–34.4%), driven by extensive hydrogen bonding and optimal packing of the guest (state D, **Fig. 1c**). These findings confirm a multi-state flexibility modulated by solvent nature and pressure and is consistent with solvent-induced structural changes observed experimentally.

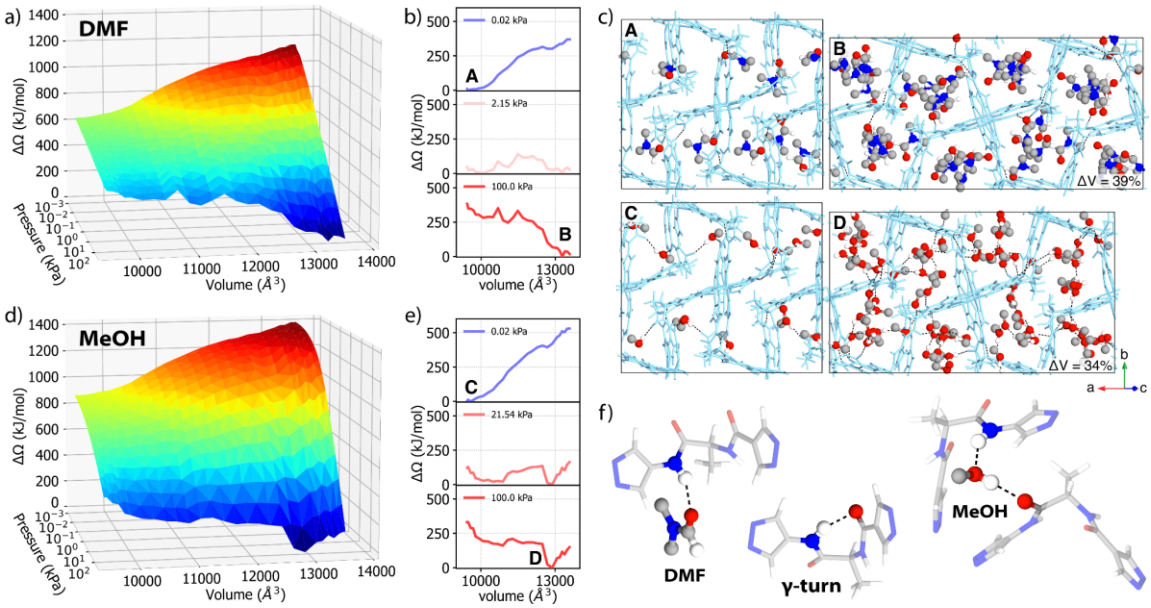


Figure 1. Osmotic surfaces for DMF **(a)** and MeOH **(d)** adsorption/intrusion at 300 K. Osmotic profiles for DMF **(b)** and MeOH **(e)** at selected pressures. **(c)** Representative configurations of the minimum structures indicated in the osmotic profiles, illustrating the closed and open phases of MUV-A (in cyan) with DMF and MeOH (top and bottom rows). **(f)** Solvent–MUV-A hydrogen bonds and intramolecular interactions in the MOF linker (ɣ-turn).

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FIRST-PRINCIPLES MODELING AND ESR IDENTIFICATION OF A NATIVE LINKER-BASED RADICAL IN UIO-66-NH_2 MOF WITH QUANTUM SENSING FUNCTIONALITY

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Keywords: spin center, DFT, ESR, radical, UiO-66

Intrinsic defects profoundly influence MOF properties, yet organic radicals on linkers remain largely overlooked. Here, we identify and structurally assign a native NH• radical residing on the aminoterephthalate linker of UiO-66-NH_2 – a commonly observed but previously uncharacterized ESR-active defect. Using a combination of density functional theory (DFT) and multi-frequency electron spin resonance (ESR), we show that the calculated spin Hamiltonian parameters – *g*-tensor and hyperfine couplings – closely match experiment, confirming both the identity and localization of the radical.

Beyond structural identification, we propose this spin center as a built-in unit for quantum sensing within the MOF. Recent advances in MOF-based quantum sensing highlight their potential for exceptionally high-sensitivity, spatially resolved detection. In contrast to external radical species commonly introduced as sensing units, the NH• radical forms as an intrinsic part of the framework, preserving the porosity, functionality, and chemical stability of the MOF. Its spin density is spatially confined to a single linker and well-isolated by the surrounding structure, yielding remarkably long spin coherence times. These findings position native linker radicals as a promising and underexplored class of quantum-relevant defects in MOFs.

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NANOCONFINED WATER IN HYBRID ZIF-7-8 MOF: A MOLECULAR-LEVEL PERSPECTIVE

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Keywords: *hybrid MOF, free energy landscape, nano-confined water*

Nanoconfined fluids hold great promise across various fields—such as nanotechnology, purification, nanolubrication, and life sciences—but also pose significant challenges due to their properties often differing markedly from those of the bulk phase.[1–2] For instance, the freezing[3] and critical[4] temperatures of water can be tuned depending on the confinement medium.

In this work, we focus on hybrid zeolitic imidazolate frameworks (ZIFs), such as ZIF-7-8, composed of mixed linkers, methylimidazole (mIm) and benzimidazole (bIm). This hybridization results in a material with enhanced thermal stability and novel mechanical behavior.[5] Notably, ZIF-7-8 behaves as a molecular spring during water intrusion/extrusion cycles—unlike ZIF-8 (shock absorber) and ZIF-7 (bumper). Strikingly, these properties emerge even at low bIm concentrations (~1%). Such strong sensitivity to linker composition requires a theoretical explanation, which will enable to develop design principles for optimizing porous materials for target applications.

To elucidate the molecular mechanisms behind this behavior, molecular dynamics simulations were performed on an ideal ZIF-7-8 sample, where a single bIm linker is embedded in a ZIF-8 slab containing 28 cavities (~0.2%). The intrusion free energy profile of this hybrid material was computed and compared with that of pure ZIF-8.[6] Results show that the presence of the bIm linker significantly alters the energetics of water intrusion—not only in the modified cavity but also in neighboring ones—by increasing the free energy barrier. This higher barrier correlates with higher experimental intrusion pressure, stemming from the disruption of the hydrogen bonding network.

These findings introduce a novel strategy to engineer the thermodynamics of confined water through linker-level tuning in MOFs. This molecular-level control of phase behavior lays the groundwork for next-generation technologies in various field such as energy storage, catalysis, and selective filtration.

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COMPUTATIONAL SCREENING OF ZEOLITIC IMIDAZOLATE FRAMEWORKS (ZIFS) FOR OPTICAL SENSING OF VOCS VIA REFRACTIVE INDEX MODULATION

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Keywords: *VOCs, optical sensing, refractive index, dielectric properties*

Volatile Organic Compounds (VOCs) pose a serious threat to indoor air quality, contributing to both short and long-term health issues. Identifying materials capable of selectively and sensitively detecting VOCs is, therefore, essential. Among various sensing strategies, optical detection based on refractive index (RI) changes has shown great promise for detecting VOCs at low concentrations[1]. However, accurately predicting the dielectric and optical properties of crystalline materials using ab initio methods such as periodic Density Functional Theory (DFT) is computationally intensive. To efficiently identify suitable materials from a broader selection, a computational screening approach that balances accuracy and resource demands is imperative.

In this study, we explore the potential of Zeolitic Imidazolate Frameworks (ZIFs), a subclass of MOFs known for their structural tuneability and chemical diversity for RI-based VOC sensing. We begin with a fragment-based method (FBM) developed by *Treger et al.* [2] that decomposes each ZIF into its inorganic node and organic linker components. Polarizabilities are calculated for each fragment using DFT, and the refractive index is estimated through the Clausius-Mossotti relation[3]. This method allows rapid screening while significantly reducing the computational load compared to full periodic DFT calculations. We apply this approach to ten structurally diverse ZIFs, systematically varying in metal composition, linker chemistry, and topology, and evaluate their RI response to three representative VOCs: acetone, toluene, and methanol. As a next step, we assess the validity of the FBM by performing full periodic DFT calculations on selected systems for benchmarking.

Our findings highlight that ZIFs with smaller unit cell volumes, such as ZIF-7 and ZIF-9, both incorporating benzimidazole linkers, exhibit the most pronounced RI changes upon VOC adsorption, followed by ZIF-1. While unit cell size and linker chemistry contribute to this behaviour, the framework topology also plays a critical role. ZIFs with tightly packed, low-porosity structures tend to show more increased RI shifts. This subtle influence arising from the spatial arrangement of building blocks was particularly well-captured by the fragment-based method (FBM). Moreover, the consistency in the RI change trends between FBM and periodic DFT further validates the reliability of this cost-effective approach. Overall, this workflow offers an effective and scalable strategy for discovering advanced materials for optical sensing, paving the way for next-generation VOC detection technologies.

Acknowledgments: Financial support provided by the University of Ghent is sincerely acknowledged. Financial support by the EU-project SENNET, titled "Porous Networks for Gas Sensing," under the Marie Skłodowska-Curie Actions, under the number 101072845 is acknowledged.

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IMPACT OF ELECTRON-PHONON COUPLING AND EXCITONIC EFFECTS ON A BISMUTH MOF PHOTOCATALYST FROM FIRST PRINCIPLES

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Keywords: *Excitons, Charge transfer, Electron-phonon coupling, Many-body perturbation theory*

By promoting light-driven chemical reactions such as the conversion of water and carbon dioxide into added-value chemicals, photocatalysts hold potential for a more sustainable future. MOF photocatalysts display a unique set of photocatalytic properties that derive from the complex interplay of the optoelectronic properties of their building blocks. Understanding how MOFs respond to light and other external perturbations is crucial to control their photocatalytic properties.

Let's take the concept of charge separation, for example. MOFs can display linker-to-metal or metal-to-linker charge transfer, which enhances charge separation and facilitates the utilization of electron and hole. Understanding from first principles how these phenomena occur is by no means trivial. From one side, standard low-cost ground-state DFT approaches are not suitable to treat excited states, and often time-dependent DFT alternatives struggle in correctly capturing charge-transfer states. [1] On another side, it is common practice to only consider static structural models which might not be representative of the room-temperature properties of MOFs – especially given the soft nature of organic linkers that make room for huge renormalization of optoelectronic properties due to phonons.

In this work, we investigate the role of phonons in the excited-state properties of a Bi-MOF photocatalyst.[2,3] We employ the finite-differences approach and Monte Caro sampling[4-6] alongside first-principles GW/BSE calculations to understand the interplay of electrons, phonons and excitons in this MOF. We show how the coordination environment of the Bi atoms can play an important role, and how phonons can greatly renormalize both ground and excited-state properties of this MOF.

Due to the soft nature of the organic linkers, we expect that phonons can modulate the excited-state properties of many MOFs. This work highlights the importance of going beyond static configurations when investigating the fundamental phenomena that underlie the photocatalytic properties of MOFs.

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HIGH-THROUGHPUT ASSESSMENT OF GAS ADSORPTION IN THE REDD-COFFEE DATABASE USING MONTE CARLO SIMULATIONS AND MACHINE LEARNING

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Keywords: *molecular simulations, machine learning, covalent organic frameworks, adsorption*

Covalent organic frameworks (COFs) are porous, crystalline and tunable materials, offering strong promise for gas adsorption and separation applications. This promise caused a rapid increase in the number of both synthetic or hypothetical COFs (hypoCOFs), comprising hundreds of thousands of different structures whose potential to be unlocked by using only experimental methods is impractical. This study aims to comprehensively analyze one of the largest hypoCOF databases (~270,000 structures) for their gas adsorption properties by combining the power of two computational worlds: molecular simulations and machine learning (ML) algorithms. The adsorption data for five industrially important gases (H_2, N_2, CH_4, O_2, and CO_2) were calculated by using both Grand Canonical Monte Carlo simulations and ML algorithms trained with the simulation data of Computation-Ready and Experimental (CoRE) COF database at 1 bar, 298 K condition. Considering the calculation of structural (pore size, surface area, pore volume, porosity), chemical (elemental compositions), and energetic (Henry's constants and heats of gas adsorption) properties of these structures with the gas adsorption properties calculated by molecular simulations and ML, a large data bank comprising of ~7 million data points is presented, ready-to-be used in accelerating the discovery of novel COF materials for gas adsorption applications. Structure-performance and chemical-performance relationships based on simulation and ML results revealed the optimal features for maximizing the gas adsorption properties for selected applications.

Acknowledgement: This study has received funding by the European Union (ERC, STARLET, 101124002). Views and opinions expressed are, however, those of the authors only and do not necessarily reflect those of the European Union or the European Research Council Executive Agency. Neither the European Union nor the granting authority can be held responsible for them.

MODELLING OF ADSORPTION IN METAL-ORGANIC-FRAMEWORKS USING ATOMISTIC FORCE FIELDS

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Keywords: *adsorption, molecular modelling, atomistic force fields, sensor materials*

High-performance chemical sensors are crucial for various applications, such as the early detection of explosives [1,2]. This research focuses on developing an innovative chemical sensor to detect 2,3-Dimethyl-2,3-dinitrobutane (DMDNB), a taggant for identifying manufactured plastic explosives. Metal-organic frameworks (MOFs) are being explored as sensing material due to their highly tunable properties. The sensor's selectivity is based on DMDNB affinity. Adsorption of DMDNB results in a detectable change in capacity via a highly sensitive split-ring resonator [3].
This study uses atomistic simulations to aid in developing a MOF that selectively detects DMDNB even in the presence of moisture, other atmospheric gases, and related compounds. We present two modeling approaches to enhance gas adsorption selectivity in MOFs. The first approach extends previous single-molecule adsorption models to accommodate multi-molecule adsorption scenarios. A
In addition, we demonstrate that experimental selectivity can be successfully modeled in zinc-based MOFs utilizing a mixed supercell structure. This approach involves combining two 2x2x2 supercells of different zinc-based MOFs (ZIF-8 and ZIF-90), enabling more detailed mobility and selectivity simulations.
The charge calculation scheme employed in these simulations is an enhanced version of the charge equilibration (QEq) method, which outperforms density functional theory-derived charges in atomistic force field simulations. This scheme improves the reproducibility of experimental crystal structures, enhances accuracy, and significantly reduces computational requirements, making it efficient for large-scale simulations.

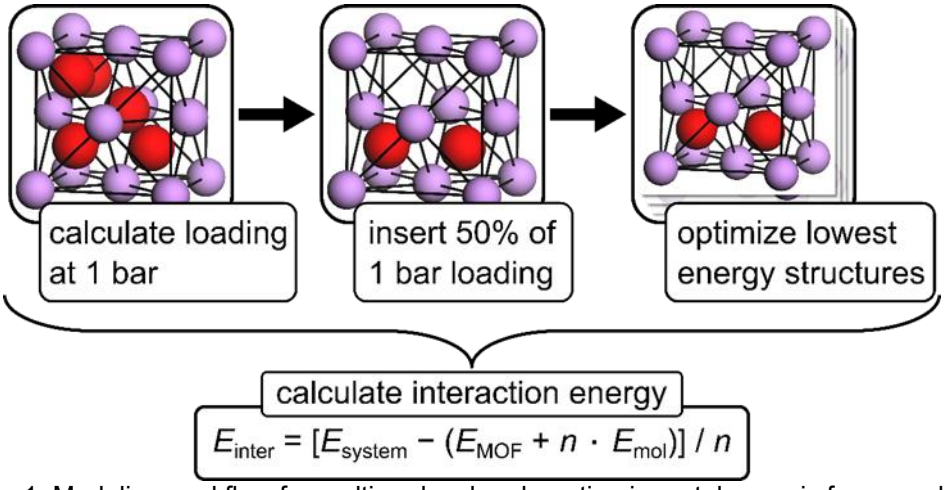


Fig. 1: Modeling workflow for multi-molecule adsorption in metal-organic frameworks.

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DECODING THE SYNERGISTIC ROLES OF AMINES AND PORE CONFINEMENT IN CO_2 CHEMISORPTION BY COFS

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Keywords: *CO_2 capture, chemisorption, amines, confinement, COFs*

The intensification of climate change driven by rising atmospheric CO_2 concentrations has underscored the urgent need for the development of materials capable of efficient CO_2 capture. COFs have emerged as promising candidates, particularly under conditions of moderately high CO_2 concentrations, such as in flue or exhaust gases. However, under low CO_2 partial pressures - such as those encountered in direct air capture - there remains substantial room for the development of high-performance materials.

Aqueous solutions of primary and secondary amines, such as mono-ethanolamine and di-ethanolamine, are currently considered the most cost-effective technology for CO_2 capture under low concentrations. Nonetheless, amine degradation and the high energy demand for regeneration hinder their large-scale application. To reduce these energy requirements, amines and polyamines supported on solid substrates have been proposed as an alternative to aqueous solutions.

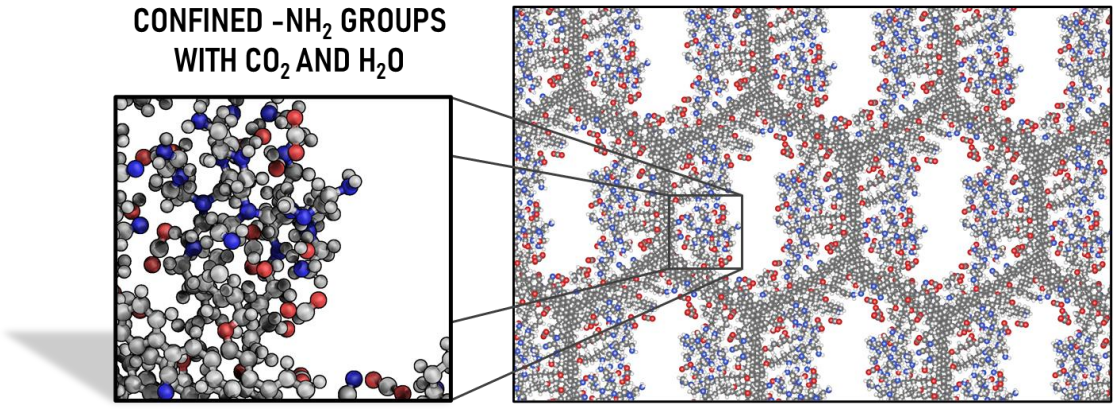


Figure 1. Atomic representation of COF-999 structure with the amine groups interacting with CO_2 and H_2O.

Recently, the incorporation of polyamines into MOFs and COFs, has demonstrated significant potential for the development of materials with high CO_2 affinity from dilute sources, such as ambient air, even under humid conditions.[1,2,3] In contrast to commonly used mesoporous materials, whose larger pore diameters diminish confinement effects, this family of microporous materials can exhibit synergistic interactions between the high affinity of amine groups and the spatial confinement provided by the micropores, increasing both the CO_2 uptake and material stability over multiple adsorption–desorption cycles by several orders of magnitude.

However, the influence of the chemical nature and length of the amine-containing groups incorporated into the MOF/COF pores, as well as the pore size itself, on the CO_2 capture mechanism remains poorly understood. In this work, we employ advanced quantum-calculations simulations to decode how the nature of amine functionalization and its length affect the CO_2 capture mechanism in COFs under both dry and humid conditions, using COF-999 as a prototypical system and exploring a myriad of different amino groups. The insights gained from this study help to establish fundamental structure–property relationships that can inform the rational design of advanced sorbents with improved CO_2 uptake, specially under dilute conditions.

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HIGH-PERFORMANCE HYDROPHOBIC MOFS FOR SELECTIVE ACETONE CAPTURE UNDER HUMID CONDITIONS

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Keywords: *VOCs, acetone, adsorption, capture*

Volatile organic compounds (VOCs) are a class of pollutants that contribute significantly to the deterioration of indoor air quality. Due to their high volatility and toxicity, VOCs pose serious health risks and necessitate effective strategies for their capture. Acetone, a commonly used VOC, is primarily employed as a solvent in products such as paints, coatings, cleaning agents, and personal care products. As a result, indoor activities like home renovations and cleaning with acetone-based products, can lead to its accumulation in enclosed spaces. The primary health effects of acetone inhalation include respiratory tract damage and neurological symptoms, making it crucial to limit its concentration in indoor environments.[1]

In this context, physisorption-based processes utilizing porous materials are particularly compelling for acetone abatement owing to their ease of operation and regeneration. However, capturing this major indoor air pollutant under real-world humid conditions presents a challenge due to the complex task of finding porous adsorbents that combine strong acetone affinity with inherent hydrophobicity. In recent years, metal-organic frameworks (MOFs) have been explored for VOC capture, including acetone.[2] The vast playground of MOFs spanning a wide range of topologies and chemical environments offers a rich platform for designing selective adsorption strategies. Although some MOFs have shown promises for acetone capture, they often fail to selectively adsorb this VOC in the presence of humidity, which is of critical interest in real indoor air conditions.

In this work, we developed a joint computational/experimental approach to identify a MOF capable of selectively capturing acetone over water. Initially, a series of MOFs with varying pore sizes, shapes, and chemical environments was computationally explored using a combination of force field Monte Carlo and Density Functional Theory simulations. This computational screening identified CAU-11(Al) [3] as a top MOF performer, combining high acetone affinity and large acetone uptake at trace concentrations (10 ppm) with remarkable selective adsorption over water. This prediction guided the synthesis of CAU-11(Al) and the exploration of its adsorption performance. Advanced gravimetric measurements confirmed excellent low-pressure acetone uptake, while gas-phase pulse chromatography evidenced high Henry's law constants and adsorption enthalpies in line with the predictions. Beyond confirming the material's outstanding capture performance, the experimental data were further used to refine the force field parameters, enabling a more accurate description of MOF–acetone interactions and a deeper understanding of the adsorption mechanism. Decisively, breakthrough studies on binary acetone/water mixtures further unravelled an excellent potential of this hydrophobic material for selective capture of acetone under humidity, reinforcing its promises for use under real-world acetone capture in humid air environments conditions.

Acknowledgments: This research is funded by 101072845 - SENNET - HORIZON-MSCA-2021-DN-01

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SIMULATING WATER ADSORPTION IN METAL-ORGANIC FRAMEWORKS USING MONTE CARLO AND MACHINE LEARNING INTERATOMIC POTENTIALS

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Keywords: *machine learning, adsorption, Monte Carlo*

Water adsorption in MOFs has been proposed as a mechanism for high-efficiency heating and cooling and for atmospheric water vapor harvesting.[1,2] The tunability of MOFs gives rise to a vast design space of possible materials for such applications that can be difficult to explore through experimentation alone. Computational predictions of relevant thermodynamic properties can be used to accelerate exploration. However, predicting these properties using first-principles simulations is challenging. Density functional theory (DFT) calculations can be prohibitively expensive due to the large unit cell sizes of many MOFs. Classical force fields offer computational efficiency but often cannot accurately describe the energetic interactions between nanoconfined water molecules and MOF atoms without calibration,[3] thus limiting their utility for large-scale screening calculations. We explore an alternate approach based on machine learning potentials, which can achieve DFT-level accuracy at a significantly reduced cost. We train machine learning potentials using DFT calculations and use them to perform Monte Carlo sampling to calculate thermodynamic properties relevant to water adsorption. This poster will illustrate the application of our workflow to the prototypical MOF UiO-66.[4] In particular, I will describe our custom procedure for generating suitable DFT training data and discuss the effects of various hyperparameter choices on the computational cost and accuracy of our machine learning potential. I will discuss the application of advanced Monte Carlo techniques for improving sampling efficiency. Our Monte Carlo methods and machine learning interface are implemented in a custom software package[5] that could be adapted for large-scale screening of other MOFs in future studies.

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BRIDGING GENERIC FORCE FIELDS AND UNIVERSAL MACHINE LEARNING POTENTIALS FOR MOF SCREENING: ETHYLENE CAPTURE IN FOOD APPLICATIONS AS A BENCHMARK

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Keywords: *High-throughput screening, Generic force fields, Universal Machine learning Potentials, MOFs, food applications*

Ethylene, a plant hormone naturally produced by fruits during ripening, accelerates softening and spoilage, leading to premature decay and reduced shelf life in stored produce. This work evaluates the reliability of generic force fields (FF) and universal machine learning potentials (U-MLP) in predicting the selective adsorption of ethylene over water across a diverse MOF library, aiming to address a critical challenge in food storage and packaging.

We employed a multi-database screening approach (see Figure 1), integrating the CSD MOF (2024.3.0), MOSAIC-DB, CoRE-MOF, and QMOF databases alongside advanced structural curation tools (SAMOSA, MOSAIC, CoRE-MOF-tools). Widom's test particle insertion Monte Carlo simulations were applied to sustainable MOFs with pore sizes exceeding the kinetic diameter of ethylene (4.1 Å) to assess their hydrophobicity and ethylene affinity. We identified 118 hydrophobic MOFs combining strong ethylene affinity ($Q_{st,C2H4}$>-25 kJ/mol) with high ethylene over water selectivity ($K_{H,C2H4}/K_{H,H2O}$>1). Further refinement based on linker feasibility yielded 97 experimentally viable MOFs, with six top candidates demonstrating exceptional ethylene uptake at 1 ppm and 10 ppm – critical thresholds for food preservation applications.

To validate FF predictions, we performed state-of-the-art U-MLP-based molecular simulations (using Matlantis' PreFerred Potential [1,2]) and DFT calculations, confirming the overall accuracy and robustness of the FF-based predictions. We further assessed the impact of MOF flexibility and identified specific cases where FF data require cautious interpretation. This work not only identifies high-performance MOFs for ethylene capture in food preservation technologies but also establishes a benchmark computational framework for future MOF design, bridging the gap between high-throughput screening and experimental validation.

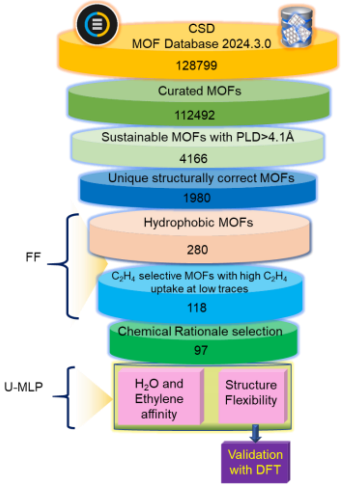


Figure 1: Schematic workflow of an FF/U-MLP/DFT strategy applied to find the most promising MOF candidates for the selective capture of ethylene over water

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THE NEGLECTED ROLE OF THE SURFACE EXPOSURE OF MOFS IN SIMULATING WATER ADSORPTION FOR ATMOSPHERIC WATER HARVESTING

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Keywords: *Metal-Organic Framework, MOF, Atmospheric Water Harvesting, Computational Simulation, Monte Carlo Simulation*

Metal-organic frameworks (MOFs) have emerged as versatile materials with an outstanding potential to enable and enhance atmospheric water harvesting (AWH). MOFs with exceptionally low water condensation pressure, adsorption capacity, recyclability, and resistance to water-induced degradation are great candidates for water harvesting.[1-3]

Understanding the adsorption mechanism is crucial for developing efficient AWH MOFs. Molecular modelling helps us take a deeper look at the adsorption mechanism and identify the parameters that affect the process. This work explores water adsorption in ROS-039, a member of the Regeneration Optimized Sorbents family of MOFs, using Monte Carlo (MC) methods.[3,4]

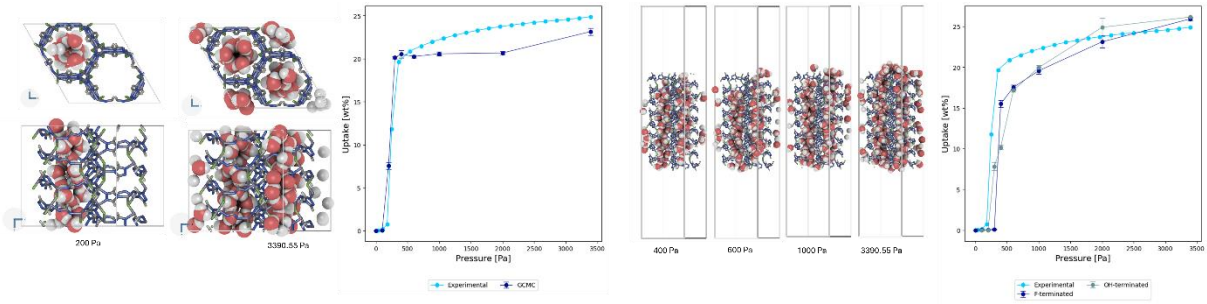


Figure 1- From right to left; snapshots of water adsorbed in ROS-039 bulk model system, the isotherm of water sorption in bulk ROS-039, snapshots of water adsorbed inside and on the surface of the F-terminated 2-D slab model system, adsorption isotherm of water in ROS-039 with exposed surfaces with F or OH termination.

Our grand canonical (GC) and Gibbs ensemble (GE) Monte Carlo simulations revealed that water sorption in ROS-039 is governed by cooperative water sorption, which causes a sharp step in the isotherm. However, the location and steepness of the step in the isotherm is governed by the MOF-water interactions and the MOF topology.

The effect of surface exposure and functionalization was also investigated using 2-D slab models terminated with either F or OH functional groups. The GEMC simulation on these systems showed the effect of surface adsorption in the shape of the adsorption isotherm and the capacity of the MOF as obtained in the adsorption isotherm.

Comparing the bulk and slab models, we can see, while they both show good agreement with the experimental results in terms of the inflection point and the uptake, the slab model helps us understand the adsorption isotherm after the pore filling happens, which is adsorption on the surface of the MOF-crystal.

In summary, this research underscores the importance of the computational approach in understanding water adsorption in MOFs and tailoring them to better perform in desired applications.

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DFT ANALYSIS OF WATER DIFFUSION IN MOF-303

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Keywords: *Density Functional Theory, Transition State Theory, Water Adsorption, Water Diffusion, MOF-303*

Water scarcity is a pressing global challenge, and metal–organic frameworks (MOFs) have emerged as promising materials for atmospheric water harvesting. Among them, MOF-303 ([Al(OH)(PZDC)], where PZDC = 1-H-pyrazole-3,5-dicarboxylate) stands out due to its exceptional water uptake capacity.[1] To advance the design of such materials, it is essential to gain atomistic insight into water adsorption and diffusion mechanisms.

In MOF-303, water molecules can move from cluster to cluster within a pore or from one pore to a neighbored one. We study *intra*-pore and *inter*-pore diffusion at two hydration levels — 3.5 and 8.5 water molecules per asymmetric unit. We use density functional theory (DFT) with the PBE+D3 functional as implemented in VASP. Transition structures are localized using the climbing-image nudged elastic band (CI-NEB) method implemented in MonaLisa[2] and verified by vibrational analysis and intrinsic reaction coordinate (IRC) calculations.

Our results reveal a complex, multi-step diffusion mechanism involving short-lived intermediates. Diffusion barriers show a non-uniform dependence on water loading: at higher loadings, surprisingly, *intra*-pore diffusion becomes hindered due to rigid water clusters at hydrophilic sites, whereas *inter*-pore diffusion is facilitated by MOF distortions that open up diffusion pathways. Figure 1, compares the calculated diffusion barriers for the two water loadings which are governed by the interplay between water–water and water–MOF interactions.

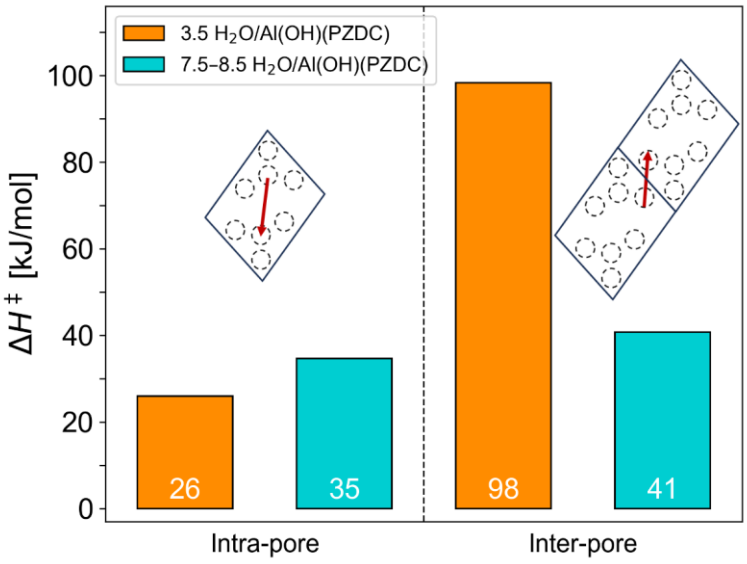


Figure 1. Diffusion barriers, $\Delta H^{\ddagger}$, for *intra*-pore and *inter*-pore water migration in MOF-303 at two water loadings.

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TUNING WATER ADSORPTION PROPERTIES OF MOFS

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Keywords: *water adsorption, heat pump, humidity control*

Thermally driven water-sorption-based technologies offer a sustainable pathway to address rising global energy demands, with applications in dehumidification, water desalination, and heating/cooling systems. The performance of these systems critically depends on the hydrophilicity of adsorbent materials, which must operate within narrow thermodynamic windows. Metal-organic frameworks (MOFs) stand out due to their exceptional tunability in porosity and chemical functionality, achieved through strategic selection of metal nodes and organic linkers. This tunability enables precise control over hydrophilicity by modulating the nature, density, and spatial distribution of hydrophilic sites. MOF/water working pairs have already demonstrated remarkable potential in adsorption-based heat reallocation, atmospheric water harvesting, and moisture regulation.[1-2]

To develop optimal MOF adsorbents, a fundamental understanding of water adsorption mechanisms at the molecular level is essential before scaling to system-level performance. Molecular simulations have emerged as a key tool for predicting adsorption equilibria, elucidating atomistic mechanisms, and guiding experimental efforts. In this work, we present a rational design strategy to fine-tune MOF hydrophilicity, optimizing water adsorption step positions and working capacity for enhanced performance.[3-5] We showcase this approach through case studies leveraging mixed-linker (MTV), polymorphic, and chiral reticular chemistry strategies to engineer hydrolytically stable, high-porosity MOFs. Our findings highlight how microscopic insights can accelerate the discovery of robust adsorbents for next-generation water-sorption technologies.[6-9]

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IMPACT OF PROLINE-FUNCTIONALIZED LINKERS ON DIFFUSION IN UIO-67 FRAMEWORKS – INSIGHTS FROM MOLECULAR DYNAMICS SIMULATIONS

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Keywords: *Metal-organic Framework, Molecular Dynamics, Heterogeneous Catalysis, Diffusion*

Metal-organic frameworks (MOFs) based on the UiO-67 topology offer a tunable platform for designing enzyme-inspired heterogeneous catalysts. In order to shed light on the structural and dynamic reasons for differences of catalytic efficiency of UiO-67 with linkers functionalized by proline (N-acylproline biphenyldicarboxylates) either in meta or ortho position on the organocatalytic aldol reaction of 4-nitrobenzaldehyde with cyclohexanone, we employed here all-atom molecular dynamics (MD) simulations.

First, the spatial arrangement of the catalytic NH groups relative to the Zr groups in the ortho or meta modified UiO-67 revealed configurations suitable for cooperative catalysis.

Furthermore, the functionalized linkers significantly reduce the accessible pore volume – by over 50 % compared to the unmodified UiO-67 – and restrict the diffusion of guest molecules such as solvents and reaction substrates. Diffusitivity analyses revealed a pronounced reduction in guest molecule mobility in both functionalized frameworks, with the meta-substituted variant exhibiting stronger diffusion barriers due to steric blocking of pore windows. Simulations also suggest the product trapping in the pores as a potential rate-limiting factor for the catalytic turn-over.

Our work demonstrates how subtle changes in linker topology and positioning of the organocatalyst can influence the dynamic behavior of catalytic MOFs and highlight the critical role of MD simulations in rational MOF design. Strategies, such as mixed-linker approaches and extended linker frameworks may provide promising pathways to overcome diffusion limitations and optimize catalytic performance.

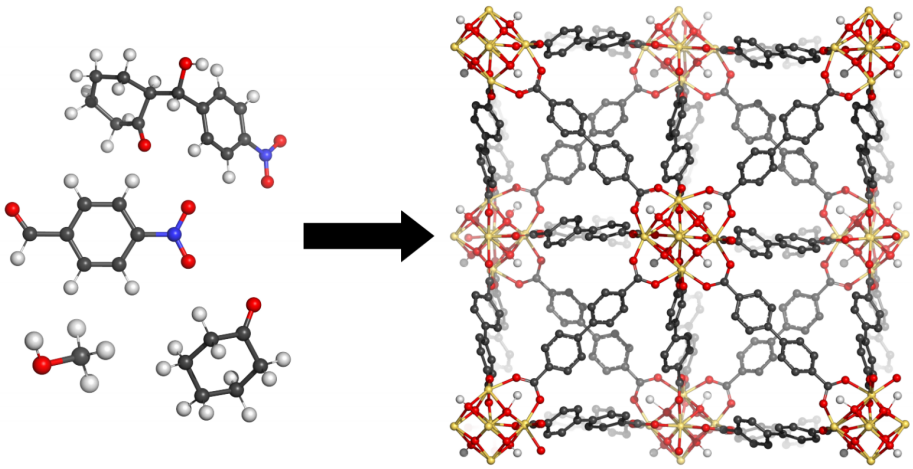


Figure 1: The diffusion of various guest molecules inside UiO-67-based frameworks was investigated using all-atom molecular dynamics simulations.

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NANOSCALE FLEXING MECHANISM OF METAL-ORGANIC FRAMEWORK GA-MIL 53 REVEALED BY IN-SITU ATOMIC FORCE MICROSCOPY

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Keywords: *flexible, MIL-53, atomic force microscopy, phase transitions, breathing*

Flexible metal-organic frameworks (MOFs) display the property of external stimuli induced framework flexibility. MIL-53 MOFs undergo flexing with this behaviour providing potential to enhance functionality in numerous applications.[1] Structural changes during flexing have been determined, but there is a lack of nanoscale information on the pathway by which the actual MOF particles transform. We employ in-situ atomic force microscopy (AFM) to probe the flexing transformations of Ga-MIL-53 [Ga(OH)(1,4-benzenedicarboxylate)] (**1**).

Crystals of **1**·0.75H_2BDC were synthesised and face indexed.[2] **1**·0.75H_2BDC was solvent exchanged with N,N-dimethylformamide (DMF) to form **1**·0.96DMF.[3] Room temperature solvent exchange of DMF in **1**·0.96DMF for ethanol (EtOH) produced **1**·*x*EtOH which could be reversibly solvent exchanged to reform **1**·0.96DMF. The frameworks of **1**·0.96DMF and **1**·*x*EtOH are shown in Figure 1a. **1**·0.96DMF crystals were fixed within an AFM fluid cell and EtOH passed over them to form **1**·*x*EtOH and the reverse process was induced by passing DMF over freshly formed fixed crystals of **1**·*x*EtOH. AFM images were collected from the {011} crystal facets during these transformations using a JPK Ultraspeed II AFM.

The AFM results reveal the pore-expansion transformation of **1**·0.96DMF to **1**·*x*EtOH occurs by wavefronts propagating across {011} facets as shown at an instant in Figure 1b. The wavefronts propagate along <100> directions parallel to the pore direction. The domains behind the wavefronts are regions of newly formed **1**·*x*EtOH. This is schematically represented in Figure 1d. A surface uplift of up to ~7 nm is seen between transformed and untransformed areas without accompanying crack formation. *Ca.* 0.5 nm high ridges running parallel to the <100> directions appear after the passage of the wavefront and may provide a stress relief route for the transformed surface. The pore-contraction transformation from **1**·*x*EtOH to **1**·0.96DMF is observed to occur in a seemingly different manner as depicted in Figure 1c and e. New domains, represented by the brown bands in Figure 1c, are observed to extend along the <100> direction before expanding perpendicular to this direction. These domains are areas of **1**·0.96DMF whose surface is angled at ~161 ° to the surface of **1**·*x*EtOH as shown schematically in Figure 1e. These results are consistent with **1** undergoing a shear mechanism involving layers of unit cells parallel to the (011) and (01$\bar{1}$) planes for the pore expansion and contraction transformations respectively.

In conclusion, these results represent the first nanoscale observations of a MOF during flexing and reveal the layer-by-layer shear mechanism through which flexing occurs. The work also proves the coexistence of different phases within one crystal. The gain in understanding of the processes will aid the design of flexible MOFs and expands the comprehension of flexible phase transformations.

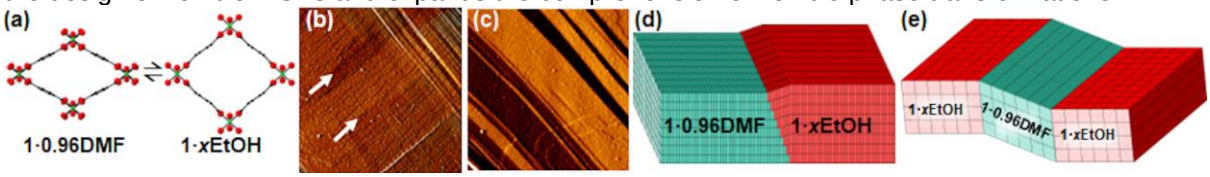


Figure 1. Schematic of the flexing transformation between **1**·0.96DMF and **1**·*x*EtOH (a). AFM images from the transformation of **1**·0.96DMF to **1**·*x*EtOH (b) and **1**·*x*EtOH to **1**·0.96DMF (c). Schematics of the transformation imaged in (b) and (c) shown in (d) and (e) respectively.

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EXPLORING CO_2 CAPTURE DYNAMICS IN CALF-20 MOFS USING POSITRON ANNIHILATION LIFETIME SPECTROSCOPY

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Keywords: *CO_2 adsorption, In situ conditions, CALF-20, Positron annihilation lifetime spectroscopy*

Reducing atmospheric CO_2 levels is crucial to mitigating climate change. This study investigates the effectiveness of the zinc-based metal-organic framework CALF-20 (Zn) for CO_2 capture across varying temperatures. The unique structure of CALF-20 allows it to maintain high CO_2 selectivity and efficiency in a broad range of temperatures.

This study examines CO_2 adsorption mechanism in CALF-20 using in situ positron annihilation lifetime spectroscopy (PALS), in situ powder X-ray diffraction (PXRD), and gas adsorption experiments under varying temperatures (the focus here is on PALS results).Variable-temperature PALS experiments demonstrate that CO_2 molecules are spatially localized within the CALF-20 cages, leaving temperature- and pressure-dependent gaps. Such a dependence is expected based on the changes in positronium lifetimes within the cages (τ_{cage}). The evolution of τ_{cage} with pressure and temperature suggests that CO_2 adsorption begins at cage centers, forming 1D chains, and ultimately adheres to pore walls. Interestingly, positronium intensity in the cages (I_{cage}) correlates with the Langmuir-Freundlich isotherm, reflecting gas uptake behavior. (Fig. 1i, ii).

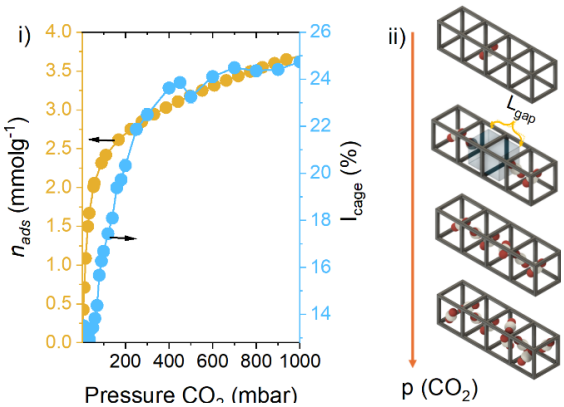


Figure 1. (i) Correlation between o-ps intensity in CALF-20 cages with the amount of adsorbed CO_2 by classical gas adsorption. (ii) arrangement of CO_2 in CALF-20 as a

These findings highlight that PALS plays a critical role in analyzing how gases interact with porous materials. PALS was particularly useful in distinguishing how CO_2 interacts within the material. Additionally, the correlation between I_{cage} and amount of adsorbed gas within the cage reflects an added value of PALS porosimetry as it can be compared to the classical adsorption techniques. For instance, in our published work[1], the fitting of I_{cage} to Sips model hints a presence of heterogeneous adsorption sites on the cage's wall. Yet, it needs further analysis to validate the approach.

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ELECTRIC-FIELD-MEDIATED IN-PLANE HETEROJUNCTION OF 2D COVALENT ORGANIC FRAMEWORKS

Guangyuan Feng[a] and Steven De Feyter[a]

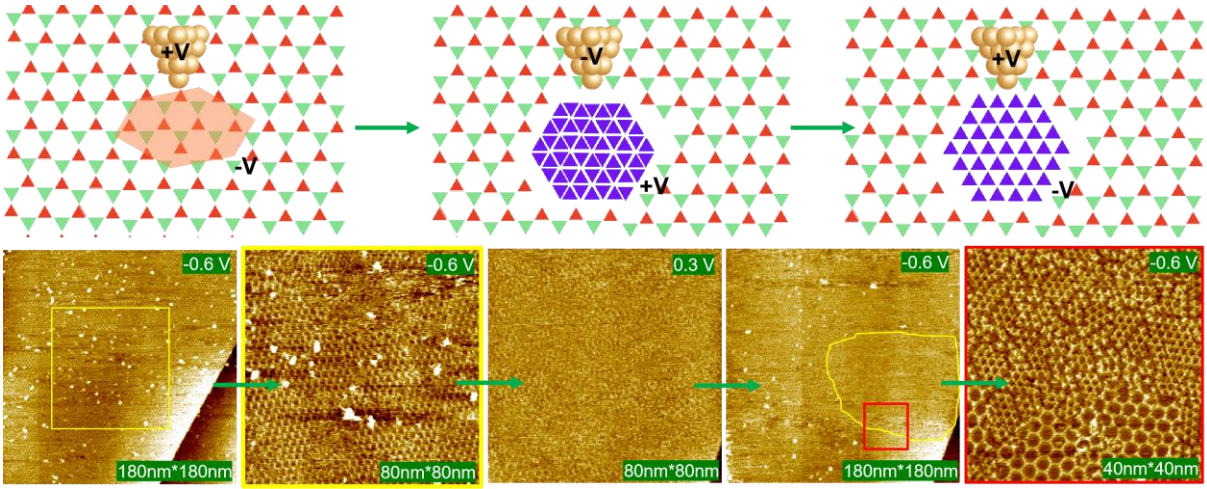
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Keywords: *Electric field-assisted synthesis, In-plane heterojunctions, Monolayer* covalent organic framework

The construction of covalent organic framework (COF) heterojunctions enables the precise integration of COF materials with distinct structures and properties within a single system. This strategy opens new avenues for the rational design of advanced functional materials. In particular, the controlled synthesis of in-plane heterojunctions within two-dimensional COF monolayers, coupled with in situ investigation of their formation mechanisms at the molecular level, is of great significance. Such insights are essential for enhancing material quality and optimizing synthetic methodologies. We recently explored the electric field (EF)-mediated, bias-dependent polymerization and depolymerization processes during boronic acid polymerization using scanning tunneling microscopy (STM).[1] Structural transformations were primarily confined to the scanned region, while the surrounding areas remained unaffected. The observed bond formation and cleavage were attributed to the strong directional electric field established between the STM tip and the substrate. Furthermore, we performed in situ monitoring of the fundamental steps involved in 2D polymerization at the liquid-solid interface—including nucleation, growth, and ripening.[2] These studies underscore the powerful capabilities of STM in unraveling the mechanistic intricacies of 2D polymerization processes.

Building on these insights, we employed boronic acid molecules as "molecular scissors" to achieve localized depolymerization of imine COFs under the influence of an external electric field, followed by bias-induced reformation of boroxine-linked COFs. This enabled structural transformation within the STM-scanned region, leading to the in situ construction of monolayer COF in-plane heterojunctions mediated by an external electric field. By utilizing STM, we directly visualized—at the molecular level—the transformation process, influencing factors, and growth mechanisms of these heterojunctions in real time at the liquid-solid interface. This approach not only deepens our understanding of the dynamic formation of COF heterostructures, but also offers valuable insights for the precise control and tailored design of functional COF-based materials.



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ADVANCED DIFFRACTION TECHNIQUES FOR MOF STRUCTURAL ANALYSIS

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Keywords: *MOF, structure determination, XRPD, electron diffraction*

Metal-organic frameworks (MOFs) are at the forefront of materials science due to their versatile applications in gas storage and separation, drug delivery, imaging, catalysis, and environmental remediation. Precise determination of their crystal structures is essential for optimizing these properties. This work presents an overview of advanced diffraction techniques employed for the structural solution and characterization of MOFs.

We highlight the example of MFU-4-Br, an MFU-4-Type MOF studied for noble gas trapping.[1] Due to the tendency of MOFs to crystallize into very small crystals (<10 µm), and the necessity of such small crystalline sizes for material applications, conventional single-crystal X-ray diffraction methods are often inadequate. Instead, we utilized X-ray powder diffraction (XRPD) and three-dimensional electron diffraction (3DED) to overcome these limitations. Our findings include structural characterizations performed using Rigaku X-ray diffractometers and the Rigaku XtaLAB Synergy-ED electron diffractometer.

We demonstrate the workflow for structural analysis, including indexing, space group determination, crystal model search, and Rietveld refinement. The integration of XRPD and 3DED techniques provides a comprehensive approach to MOF characterization, facilitating the development of novel materials with tailored properties. This presentation aims to showcase the potential of advanced diffraction techniques to enhance the characterization process and overcome traditional limitations.

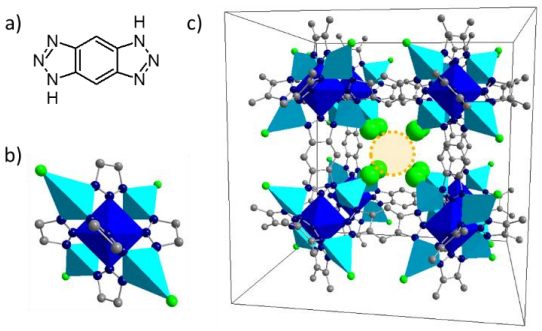


Figure 1. A structure of the (a) benzobistriazole ligand [1H,5H-benzo(1,2-d:4,5-d′)bistriazole], (b) pentanuclear coordination unit featuring the central Zn^{II} ion in an octahedral geometry (dark blue) and four Zn^{II} ions in a tetrahedral coordination environment (turquoise), and (c) unit cell of MFU-4 (CCDC: 723714) with a pore aperture visualized as a yellow circle. Elements: C (grey), H (white), N (blue), Cl (green), Zn^{oct} (dark blue), Zn^{tetr} (turquoise).

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LIQUID-PHASE IN SITU CRYSTALLIZATION AND CHARACTERIZATION USING ELECTRON MICROSCOPY AND DIFFRACTION

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Keywords: *Liquid-phase transmission electron microscopy, 3D electron diffraction*

Liquid-phase electron microscopy (LP-EM) provides a powerful tool for investigating materials in their native liquid environments, offering valuable insights into dynamic processes and structural properties[1]. However, the study of beam-sensitive materials, such as porous Metal-Organic Frameworks (MOFs), is often hindered by challenges like beam-induced damage and radiolysis effects[2]. These challenges can be mitigated through low-dose imaging strategies and the use of advanced nanochannel chips, which allow for precise control of liquid flow and mixing, facilitating high-resolution characterization. To better understand flow behavior in nanochannels, in situ mixing was characterized using an optical microscope equipped with fluorescent filter cubes and a Fluigent microfluidic flow controller. The timescale of diffusive mixing between water and a rhodamine solution was measured, providing critical insights into mixing efficiency and dynamics within the chip.

Additionally, two nanochannel chip designs were employed to support different experimental approaches under liquid-phase conditions. One design enabled in situ mixing and controlled crystallization directly within the nanochannels, allowing real-time observation of crystal growth using transmission electron microscopy (TEM). Another design was optimized to trap pre-formed small crystals, introduced to the chip using the flow system, after external sample preparation. Both chip configurations were explored and compared to evaluate their suitability for studying sensitive materials. For further structural characterization, continuous rotation electron diffraction (cRED) can be used, allowing for accurate and efficient structural analysis with high-completeness 3D data[3].

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DEFECT INDUCED ANISOTROPIC NODE DISTORTION IN AMORPHOUS MOFs: LOW-VALENT ZR SITES AS CATALYTIC HOTSPOTS

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Keywords: *Zr-based MOFs, Cluster Dehydroxylation, Amorphization-Enhanced Catalysis*

Zr-based metal-organic frameworks (MOFs) with well-defined Zr oxo clusters emerged as a promising class of heterogeneous catalysts. Defects on these metal-oxide clusters are central to understanding their reactivity, as they i) replace metal-ligand bonds with more labile terminal groups or ii) lower the valency of the metal sites.[1] Efforts are made to induce missing-linker defects, whereas few studies exist on inducing oxygen vacancies in $Zr_6O_4(OH)_4$ clusters via dehydroxylation, i.e. the removal of μ_3-OH groups from the octahedron faces.[2]

In our work, we used a previously developed thermal treatment method under humid air[3] to induce both missing-linker and Lewis open metal defects through dehydroxylation in DUT-67[4]. We found that the framework undergoes rapid amorphization under the treatment conditions (**Fig. 1a**) and a drastic improved catalytic activity of the amorphous phase in the conversion of glyoxal to glycolic acid (**Fig. 1b**) before it drops again at longer treatment duration. Pair-distribution function analysis reveals that the Zr cluster undergoes an anisotropic distortion visible by a peak splitting of the Zr-Zr distances followed by the formation of bulk zirconia at extended treatment time. These distortions are irreversible and have been previously observed by Chapman *et al.*, who have explained the observed node distortion by a conversion of μ_3-O to μ_2-O groups via molecular simulation (MD)[5] and missing linker defects via density functional theory (DFT) calculations.[6] Complementary to their work, we find that the observed distortions can also be explained by cluster dehydroxylation (Fig. 1a), and the observed distortions are a result of lowering the valency of Zr from 8 to 7, which removes the centro-symmetry of ZrO_8 sites in the pristine clusters. The distortions are irreversible, and the catalyst is stable and cyclable (Fig. 1c). Finally, we propose possible reaction pathways supported by DFT calculations, including the formation of reaction intermediates with low-valent Zr sites and terminal OH groups. The study provides new pathways for engineering defect sites in Zr-based MOFs for catalysis and other applications.

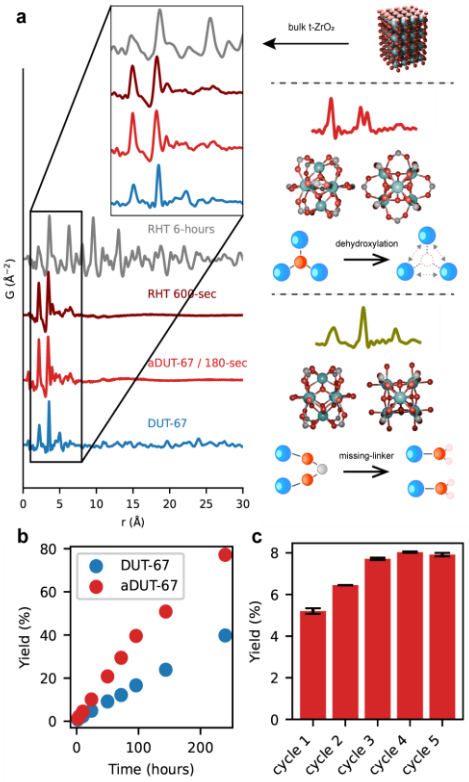


Figure 1 a) Pair distribution functions of pristine MOF and thermally treated samples with exposure times of 180 seconds, 600 seconds, and 6 hours. On the right are structural models with missing linker defects and cluster dehydroxylation together with galculated PDFs. b) shows the yield of glycolic acid as a function of time. c) shows the cyclability of aDUT-67 (180-sec sample).

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REAL-TIME INVESTIGATION OF METAL-ORGANIC-FRAMEWORK SYNTHESIS VIA ULTRASOUND ATTENUATION AND SPECTROSCOPY

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Keywords: *ultrasound, in situ-monitoring, synthesis, spectroscopy, attenuation*

Understanding the complex synthesis of metal-organic frameworks (MOFs) is still a challenge in the field of porous materials. Some models suggest the formation of pre-nucleation building units (PNBUs)[1], whose nature is still widely discussed. For ZIF-8, which is an extensively studied MOF, the formation mechanism is not yet fully understood. While Venna et al. propose a solution- and solid-mediated mechanism[2], Cravillon suggests the involvement of pre-nucleation clusters as well as nanoparticles[3]. In situ methods, such the ultrasound-monitoring (figure 1) allow obtaining additional insights, which are often missed by ex situ characterizations. In addition, ultrasound monitoring is a robust and simple technique, offering a non-destructive analysis with high time resolution[4].

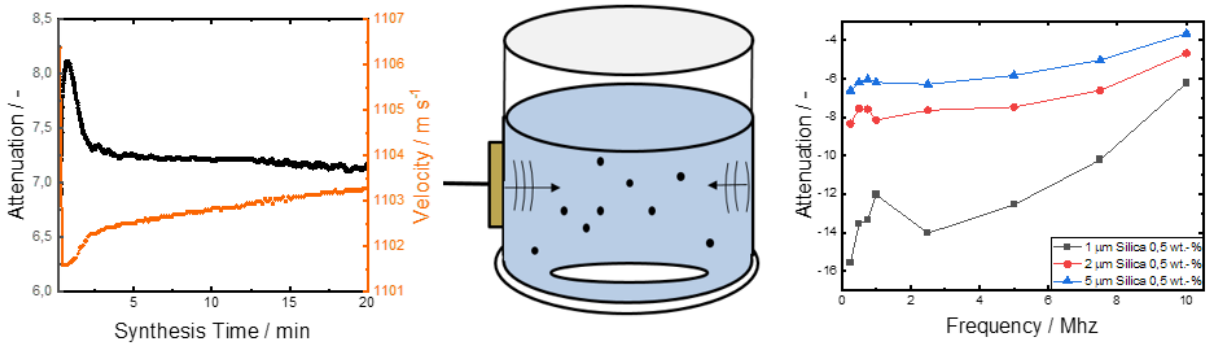


Figure 1: Setup for in situ US-monitoring (center) with exemplary US-signals over time (left) and spectroscopic measurement (right).

Using the pulse echo method, the ultrasound velocity increases continuously from the start of the ZIF-8 synthesis. Since sound propagates faster in solids than in liquids, this increase can be correlated with particle formation. The ultrasound attenuation rises sharply at the beginning of the synthesis, and then gradually decreases until a plateau is reached at the end. Notably, at the attenuation maximum, a change in the velocity trend becomes apparent. Further investigations revealed the formation of an intermediate phase in the early stages of the synthesis, which subsequently transforms into ZIF-8 as the reaction progresses. Ultrasound spectroscopy provides a valuable insight to the particle formation, since the ultrasound attenuation depends both on the particle size within the dispersion as well as on the frequency of the ultrasound wave. Figure 1 shows that attenuation increases as particle size decreases.

This study confirms that ultrasound monitoring is a simple, yet powerful technique for investigating MOF synthesis. This technique can significantly enhance the understanding of synthesis parameters and mechanisms, while also providing real-time insights into the material forming.

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TOWARD A COMPREHENSIVE IN-SITU UNDERSTANDING OF PD/HKUST-1-DERIVED PD/CUO CATALYSTS FOR CO OXIDATION

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Keywords: Metal-organic frameworks, in-situ XPS, in-situ XRD, CO oxidation

Metal-organic frameworks (MOFs) have garnered significant attention as precursors for the fabrication of various nanostructured catalysts due to their high porosity and tunable composition.[1] MOF-derived materials can realize rationally designed structures with uniform dispersion, often inheriting beneficial properties from the parent MOF. To gain crucial insights into this transformation, in-situ X-ray diffraction (XRD) and near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) have proven to be powerful tools for studying the structural evolution of MOFs and their derivatives under operating conditions.

In this study, we utilized a bimetallic MOF, Pd/HKUST-1 (Pd/Cu-BTC),[2] and thermally transformed it into a Pd/CuO composite catalyst, which was then applied for CO oxidation reaction. To unravel the structural dynamics and metal node oxidation state changes during thermal treatment and catalytic operation, in-situ XRD, thermogravimetry–mass spectrometry (TG-MS), and in-situ NAP-XPS were employed. In-situ XRD revealed the progressive collapse of the MOF framework and the temperature-dependent crystallization of CuO and Pd phases under oxidative conditions. TG-MS was used to monitor gas-phase products evolved during the transformation. In parallel, in-situ NAP-XPS provided insights into the redox evolution of Pd and Cu species, indicating dynamic oxidation-reduction behavior crucial for catalytic performance. Notably, the Pd node in the MOF was reduced under thermal treatment conditions, while the Cu node was transformed to CuO.

We further evaluated the catalytic performance of Pd/CuO, Pd, and CuO individually. The MOF-derived Pd/CuO exhibited superior catalytic performance compared to Pd, CuO, and the mixture of Pd and CuO. In-situ XRD and NAP-XPS were used to establish structure–property correlations relevant to CO oxidation, providing insights into real-time structural and electronic changes occurring in both the bulk and surface of the Pd/CuO catalyst (specifically regarding the Cu and Pd species). Additionally, through the use of high-resolution transmission electron microscopy (HRTEM) and density functional theory (DFT) calculations, we discovered that the abundant in-situ generated Pd/CuO interfaces likely play a crucial role in enhancing the catalytic activity of the Pd/CuO composite.

This multi-technique approach offers a thorough explanation of the transformation process from bimetallic MOF precursors to hybrid catalysts. It emphasizes the synergistic roles of Pd and CuO in improving CO oxidation. The study highlights the importance of in-situ characterization for the rational design and optimization of MOF-derived catalytic systems under realistic working conditions.

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USING ELECTRON DIFFRACTION TO UNLOCK THE CRYSTALLINE SPONGE TECHNIQUE

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Keywords: *Electron diffraction, crystalline sponge, MOFs,*

The crystalline sponge technique first developed by Fujta and co-workers is a powerful tool for the elucidation of hard or impossible to crystalize molecules.[1] A single crystal of a porous crystalline material such as $(ZnI_2)_3(tpt)_2$ can be soaked in a solution of the desired analyte which is adsorbed into the porous framework. Single-crystal X-ray diffraction (SCXRD) can then be used to elucidate the structure of the analyte within the crystal's pore environment. This technique is limited, however, by the need for large single crystals that can survive solvent exchange. Electrons interact with matter 10,000 times more strongly than X-rays, breaching the hard lower sample size limit of SCXRD (1 μm): electrons can structurally characterise crystalline particles in the nanometre size regime.[2] This significantly reduces the requirement for the synthesis of large single crystals. Furthermore, smaller crystals are known to be more stable and less susceptible to the loss of crystallinity on solvent exchange and a small particle size will significantly reduce the lengthy soaking times currently required to achieve sufficient analyte loadings for analysis.

As such we are developing a series of MOFs capable of acting as crystalline sponges for use with electron diffraction. This two-pronged approach involves adapting previously known crystalline sponges for electron diffraction as well as creating new systems such as the Cu MOF shown in Figure 1. This system is unsuitable for SCXRD due to its small particle size but with electron diffraction can be used as a carboxylate specific crystalline sponge.

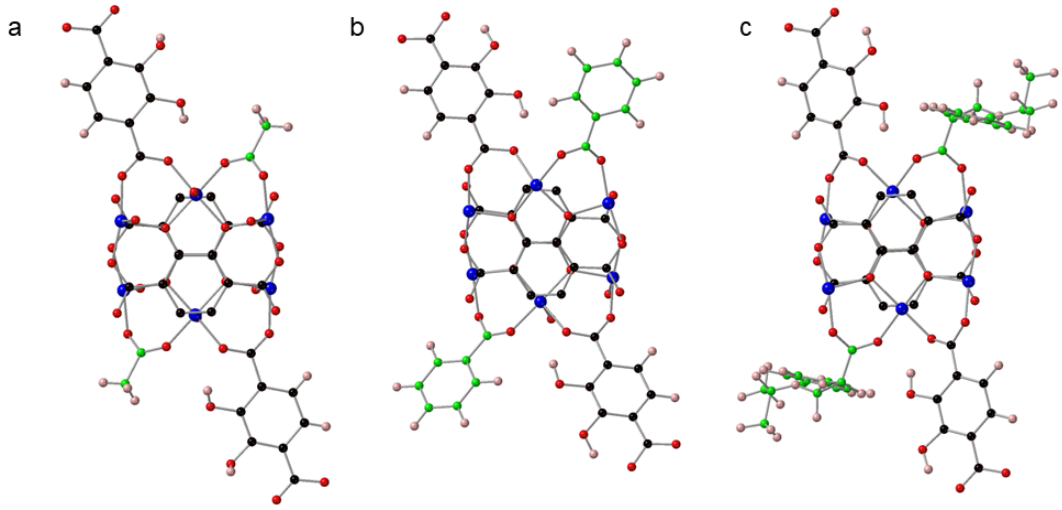


Figure 1: Ball and stick models of a new Cu MOF showing the structure of three different molecules (green): a) acetic acid, b) benzoic acid, c) isobutylphenylpropionic acid.

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PRESSURE-INDUCED STRUCTURAL TRANSITIONS IN ZEOLITIC IMIDAZOLATE FRAMEWORKS

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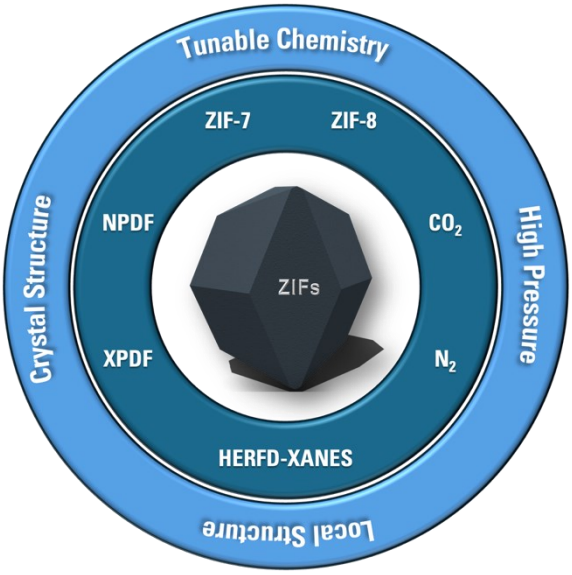
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Keywords: *zeolitic imidazolate frameworks, high pressure, neutron scattering, X-ray scattering, and X-ray spectroscopy*

Zeolitic imidazolate frameworks (ZIFs) are a sub-group of microporous metal organic frameworks (MOFs) with sodalite topologies similar to zeolites, but with more flexibility due to the rotational swinging of the imidazolate-based linkers that bridge metallic nodes.[1] These conformational transitions are commonly referred to as *gate-opening* effects and are reflected by an increase in pore size and gas uptake. The tuneable chemistry coupled with high specific surface areas and good thermal and chemical stabilities, makes ZIFs great candidates for carbon capture, utilisation, and storage (CCUS). Their main application has been the selective adsorption of carbon dioxide (CO_2) from mixtures containing nitrogen (N_2), carbon monoxide (CO), and methane (CH_4).[2] Understanding the performance of these adsorbents in their operating environment is challenging since gas adsorption leads to multiscale structural variations. The holistic elucidation of the adsorption process requires neutron and synchrotron techniques, such as total scattering, which are not hindered by the heterogeneous, multiscale, and multiphase properties of these porous systems.

The structural evolution of ZIFs as a function of CO_2 and N_2 adsorption was investigated using *in situ* neutron pair distribution function (NPDF), X-ray pair distribution function (XPDF), and high-energy resolution fluorescence detection X-ray absorption near-edge structure (HERFD-XANES). ZIFs exhibit conformational and phase transitions that increase the uptake of guest molecules. Phase-to-phase transformations due to pressure and gate-opening (adsorption) and -closing (desorption) have been observed in the short- and long-range structure of zinc methylimidazolate (ZIF-8) and benzimidazolate (ZIF-7) at moderate and high pressures. ZIF-8 is one of the most studied MOFs due to its easy synthesis and good adsorption properties.[3] However, it has a low susceptibility to *gate-opening* effects at industrially relevant temperatures. Improved absorbance has been achieved by varying the organic linker and/or increasing the operating pressure.[4] This study followed the structural transitions of the two ZIFs at different pressures (up to 10 bar) of CO_2, N_2, and an equimolar CO_2/N_2 mixture. By using a combination of neutron and X-ray techniques, we were able to elucidate the interplay between local adsorption phenomena and long- to short-range structure. The mechanistic information obtained from this study will enable the design and development of more effective MOFs for gas adsorption. We anticipate the impact of the novel methodologies used in this study to be far-reaching, creating new science possibilities to the wider materials community.



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INSIDE THE PROCESS OF FORMATION OF ZIF-8@Zn-Al LDH CONVERSION COATINGS ON SURFACE OF AA2024 ALLOY

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Keywords: *ZIF-8; in situ synchrotron, layered double hydroxide (LDH); corrosion protection*

Nowadays, due to severe environmental pollution, serious waste of resources and enormous losses for the world economy, corrosion protection stands out as one of the most important industrial tasks. In this context, metal organic frameworks (MOFs) have recently demonstrated high potential as materials for corrosion protection of various metallic surfaces[1]. This increased interest has been linked to a number of unique properties of MOFs. For example, thanks to their high surface area, and pore volumes, MOFs can be loaded with various inhibiting species, i.e. act as nanocontainers for loading corrosion inhibitors, i.e. nanomaterials capable of controllably storing/releasing functional compounds on demand, e.g. in response to the presence of corrosive agents[2]. In addition, the ligands or metal cations that form MOFs can themselves act as corrosion inhibitors. However, in both cases, MOFs have mainly been used as powder additives to polymer coatings, while the use of MOFs as conversion coatings remains limited due to the challenging process of growing MOFs directly on metallic surfaces. In the current investigation, this obstacle was overcome by surface pre-treatment to promote further MOF formation. Thus, Zn-Al-LDH (layered double hydroxide) firstly grown on the surface of AA2024 aluminium alloy was recrystallised into ZIF-8@Zn-Al-LDH coating. *In situ* synchrotron and *ex situ* XRD analyses showed that recrystallisation of Zn-Al LDH into ZIF-8 was accompanied by intercalation of 2-methylimidazolate into the LDH gallery under the applied treatment conditions (Fig. 1)[3]. Such a complex structure of the coating was beneficial for the corrosion protection of AA2024 alloy as the obtained coating contained an increased amount of 2-methylimidazole inhibitive species. Moreover, it was found that the variation of the treatment condition (95-140 °C, 3-24 h) affected the corrosion protection performance of the ZIF-8@Zn-Al-LDH coatings.

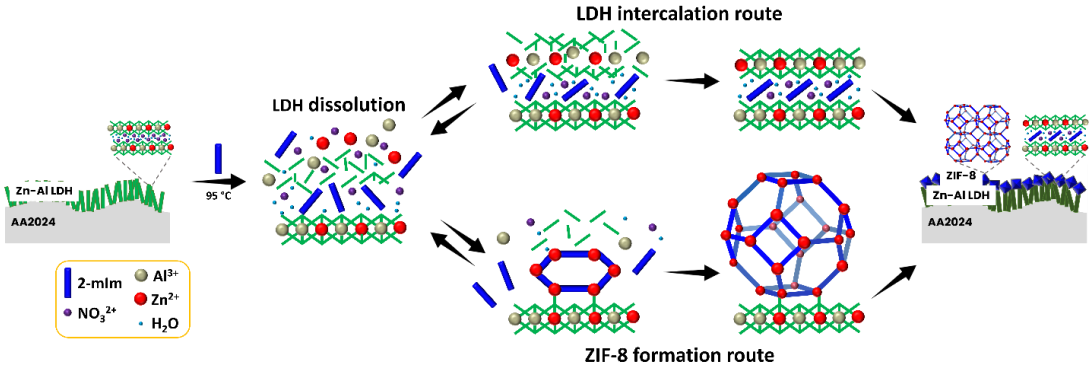


Fig. 1. Processes taking place on the surface of AA2024 alloy covered with Zn-Al LDH after the treatment with methanolic solution of 2-HmIm.

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FTIR STUDY OF SULFATED ZIRCONIA AND UiO-66: COORDINATION MODES AND ACTIVE SITE ACCESSIBILITY

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Keywords: *MOF, functionalization, sulfation, UiO-66-SO_4, ZrO_2-SO_4, carbon monoxide, CD_3CN.*

Functionalizing solids with sulfate groups is a widely used strategy to enhance surface acidity and improve catalytic performance. In this study, we introduced SO_4-groups into the metal-organic framework UiO-66. First, we synthesized a highly defective UiO-66 using benzoic acid as a modulator (sample UiO-66-BA) [1]. Initially, zirconium sites in the defective pores were blocked by benzoate anions. Treatment with hydrochloric acid removed these anions, making the Zr sites accessible (sample UiO-66-FA) [2]. These accessible sites were then functionalized with SO_4-groups (sample UiO-66-SO_4). Sulfate ions can coordinate to Zr centers in monodentate, bidentate, or tridentate modes. To investigate their coordination in UiO-66, we used tetragonal zirconia as a reference system, as its structure mimics the Zr–O clusters in UiO-66 but offers better thermal stability [3]. *In situ* FTIR spectroscopy was used to monitor changes during partial oxygen isotope substitution $^{16}O/^{18}O$ in sulfate groups. The shift of SO_4-related bands without splitting confirmed tridentate coordination on zirconia. Using CO and CD_3CN as probe molecules, we found that hydration changes this to bidentate coordination. Extrapolating these findings to UiO-66, we explored sulfate coordination in the defect pores. Probe molecule studies showed that after sulfation, CO could no longer adsorb on Zr sites, even after activation, suggesting restricted access. In contrast, acetonitrile could still interact with the Zr centers without activation. Combined with the presence of terminal OH groups in the spectra, we concluded that sulfate groups in UiO-66 are coordinated in a bidentate mode, and a tridentate configuration is not achieved, because it requires activation at temperatures exceeding the thermal stability of the MOF.

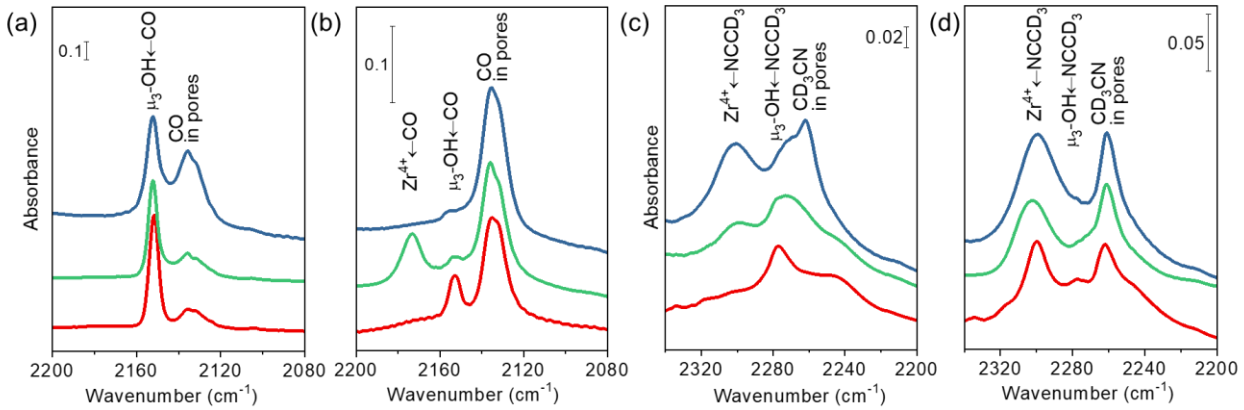


Figure 1. FTIR spectra of the UiO-66 samples: UiO-66-BA (red), UiO-66-FA (green), and UiO-66-SO_4 (blue). Spectra were recorded after exposure to CO (a, b) and CD_3CN (c, d). Panels (a) and (c) show spectra of rehydrated samples, while (b) and (d) correspond to samples dehydrated at 250 °C. Band assignments are indicated in the figure.

Overall, this study highlights how sulfation influences active site accessibility in both zirconia and UiO-66. The presented FTIR-based approach offers a useful protocol for studying the coordination and reactivity of cations in pure and functionalized MOFs.

Research was financially supported by the Bulgarian Science Fund under grant number КП-06-ДВ-1.

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ADSORPTION OF NITROUS OXIDE IN ULTRAMICROPOROUS MAGNESIUM GALLATE

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Keywords: *Nitrous oxide capture, physisorption, in situ synchrotron powder diffraction*

Nitrous oxide (N_2O), a potent greenhouse gas and ozone-depleting substance, yet remains understudied in terms of materials-based capture.[1] Here, we show that magnesium gallate (MgGal), a sustainable ultramicroporous metal-organic framework (MOF), effectively captures N_2O through strong host–guest interactions and a unique phase transition.

Gas sorption isotherms revealed a characteristic inflection point, whose position shifted to lower pressures with increasing temperature, indicating temperature-dependent sorption behavior. A significant uptake was observed well below atmospheric pressure, reaching pore saturation, and the isotherms displayed pronounced hysteresis during desorption, reflecting strong host-guest interactions and indicating potential for gas capture applications.

To uncover the sorption mechanism, we performed in situ synchrotron X-ray powder diffraction under isobaric conditions. These measurements enabled real-time tracking of structural changes in MgGal and identification of the N_2O adsorption sites. Sequential Rietveld refinements during activation revealed a transformation from a dihydrated structure (phase I) to an anhydrous activated form (phase II), accompanied by a symmetry change from the superstructure $P3_1$ to space group $P3_121$, without loss of framework connectivity. This activation process was fully reversible and could be triggered by vacuum treatment. However, when performed in air, phase II was observed but proved to be metastable and gradually decomposed via decarboxylation of the organic linker.[2]

Upon N_2O loading, the activated phase II initially adsorbed a small amount of gas before undergoing a sharp transformation back to the phase I. In this final structure, the N_2O molecules occupy different positions within the pores than in phase II. Volumetric and diffraction-based uptake measurements were in excellent agreement, indicating a total uptake of one N_2O molecule per linker. Sorption isobars extracted by Rietveld refinement further revealed a large adsorption–desorption hysteresis (~37°C), highlighting the kinetic stability of the loaded state. The strong affinity for N_2O was attributed to hydrogen bonding between the gas molecules and hydroxyl groups of the gallate linker, as previously observed for CO_2 by ex situ measurements.[3]

Our results suggest that MOFs with proven CO_2 sorption properties may offer a promising starting point for selective N_2O capture, with implications for environmental remediation and gas separation technologies.

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DEMONSTRATING ZERO SECONDARY EMISSIONS FROM CALF-20 IN SVANTE'S VELOXOTHERM™ CO_2 CAPTURE PROCESS

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Keywords: *Secondary Emission, TCM, PTR-MS, CALF-20, Nitrosamine*

CALF-20, a metal-organic framework (MOF), has demonstrated outstanding performance in CO_2 capture from flue gas streams within the VeloxoTherm™ process, establishing itself as a benchmark sorbent [1]. A key advantage over amine-based liquid and solid sorbent systems is Structured CALF-20's potential for negligible to zero secondary emissions.

This study investigates the formation of potential secondary emission products, including nitrosamines, nitramines, and structured CALF20 degradation byproducts, across gas, liquid (steam condensate), and solid phases while operating Svante filters to capture CO2 from RFCC flue gas TCM. In situ Proton Transfer Reaction-Mass Spectrometry (PTR-MS) was used for the gas analysis. Liquid Chromatography-Mass Spectrometry (LC-MS) was employed in liquid phase analysis; and Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR), among several other methods, was used for the solid phase. We confirm the absence of secondary emission related to nitrosamines, nitramines, or MOF building blocks in the exhaust stream of air at 0.1-ppbV level.

These findings, obtained during an extensive test campaign at the Technology Centre Mongstad (TCM), confirm CALF-20's superior environmental profile and robust operational stability, strengthening its readiness as a leading sorbent technology for large-scale deployment with no measurable secondary emissions under tested conditions.

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A PRACTICAL AND ROBUST APPROACH TO DETERMINING THE EXPERIMENTAL MINIMAL FORMULA OF METAL-ORGANIC FRAMEWORKS

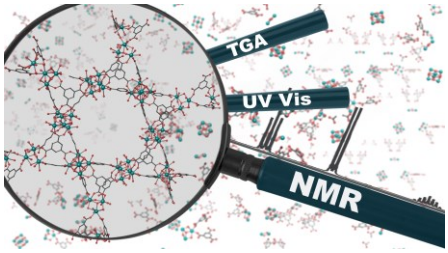
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Keywords: *MOFs, Experimental minimal formulae, qNMR, TGA, UV-Vis spectroscopy*

Metal-organic frameworks (MOFs) have been one of the most advancing classes of materials in the past few years, with immense potential in the fields of catalysis,[1] gas storage,[2] drug delivery,[3] etc. However, the fundamental aspect of determining the precise chemical composition of the synthesised MOFs is lacking sufficient attention, although it is crucial for many advanced applications, such as catalysis.



In this work, we present a simple yet robust methodology to derive the minimal formula of the synthesised MOF material.[4] To achieve this, we combine quantitative Nuclear Magnetic Resonance (qNMR) spectroscopy, Thermogravimetric analysis (TGA), and UV-Vis spectroscopy. We investigated the previously used methodologies that solely rely on TGA and demonstrated why the assumptions that were made in this technique are not justified. We further dive deep into the use of NMR to quantify the different organic molecules present in the framework. We have also shown the crucial influence of digestion methods and relaxation time on the accurate determination of the minimal formula. We also highlight the often-overlooked presence of residual inorganic species, particularly chloride and nitrate ions originating from the precursors such as ZrCl4 or ZrOCl2 (for Zr-based MOFs), or cerium ammonium nitrate (for Ce-based MOFs). These residues can remain embedded within the framework in significant quantities, impacting properties such as catalytic activity and framework stability. Our methodology provides a quantitative means of identifying and accounting for these species.

To align MOF characterisation with practical applications, we introduce the concept of “experimental molar mass” reflecting the true chemical identity of the MOF as synthesised and handled under laboratory conditions. We used our methodology to derive the experimental minimal formula of MOF-808(Zr), UiO-66(Zr), UiO-66(Ce), MOF-5(Zn), MIL-125(Ti), and MIL-100(Fe), to show the generality of our technique. We further extended our work to amorphous coordination networks such as an Al-BDC MOF with no information on its crystal structure. Our work focuses on obtaining a fully charge-balanced and chemically feasible minimal formula. This work thus lays the foundation for a more rigorous, transparent, and application-relevant reporting of MOF compositions and serves as a critical step towards the rational design and development of MOFs in both fundamental research and industrial contexts.

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HIGH CARRIER MOBILITY IN TRIPHENYLENEHEXATHIOL BASED METAL-ORGANIC FRAMEWORKS MEASURED WITH TIME-RESOLVED TERAHERTZ SPECTROSCOPY

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Keywords: *Photoconductive MOF, 2D MOF, THz Spectroscopy, Charge Transport*

Despite some early advances, understanding and controlling the charge transport mechanism within metal-organic frameworks (MOFs) remains a challenging frontier. After some promising results that have been published a few years ago which reported high charge carrier mobility in layered bidimensional MOFs,[1] we recognize the necessity to consolidate and expand those findings. Specifically, in this work we investigate the photoconductivity on a range of π-d conjugated metal triphenylenehexathiol (M-THT) MOFs with several metal nodes, measured in the terahertz (THz) frequency region.

Using a pump-probe scheme (Optical Pump-Terahertz Probe, OPTP), THz spectroscopy can time-resolve the photoconductivity of a system with sub-picosecond resolution. Additionally, while other conventional spectroscopy techniques record the time-integrated intensity of the probe pulse, in THz spectroscopy the time-dependent electric field of the THz pulses is measured, giving access to phase information. This allows characterizing the complex-valued, frequency dependent optical constants of our MOF films in a frequency range that connects the domains of electronics and photonics.

We present substancial reproducibility of the conductivity in a thin film of Fe_2THT_3 MOF. Furthermore, the insights obtained from the experiments on isostructural M-THT seems to indicate that geometry, rather than composition, is the main factor that determines charge transport in this class of materials.

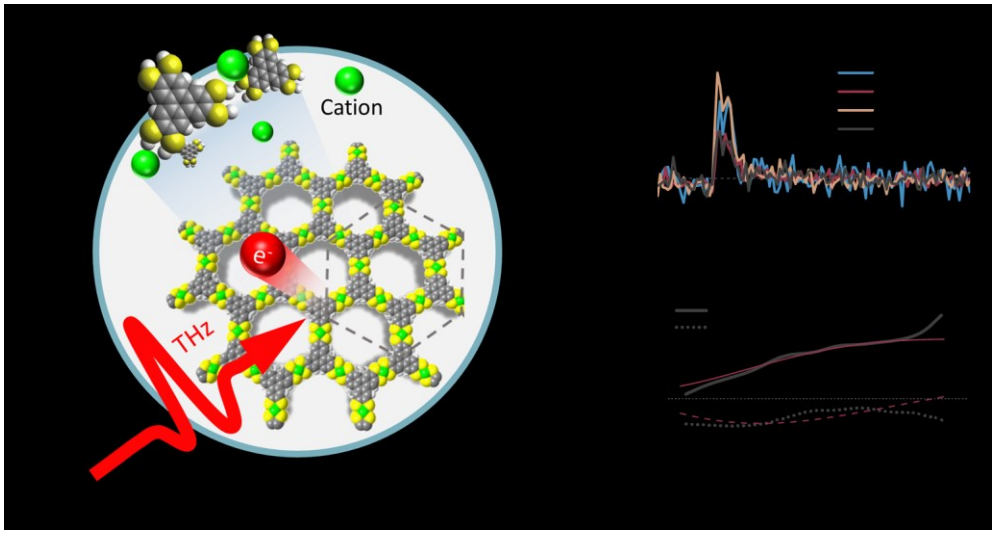


FIGURE 1. a) Graphical representation of metal triphenylenehexathiol (M-THT) MOFs irradiated by THz light. b) Differential transmission in (M-THT) MOFs measured via OPTP. c) Frequency resolved photoconductivity in Fe_2THT_3 MOF (black) and fit according to the Drude-Smith model (burgundy).

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THE ROLE OF CHEMICAL BONDING AND HYDRATION STATE ON THERMAL EXPANSION OF A ZINC-BASED METAL-ORGANIC FRAMEWORK

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Keywords: *Anisotropy, Guest-Responsive Frameworks, PXRD, Single Crystal, Thermal Activation*

Thermal expansion is a fundamental material property that provides direct insights into the bonding forces within a solid. For metal-organic frameworks (MOFs), thermal expansion plays a particularly important role, as their hybrid nature leads to diverse bonding motifs that can result in a highly anisotropic behavior.[1] Thermal expansion is directly linked to the shape of the potential energy wells, hence, to the strength of the underlying chemical bonds. However, to date, no experimental studies have systematically explored, how various types of chemical bonding affect anisotropic thermal expansion. GUT-2, a zinc-based coordination polymer consisting of Zn^{2+} ions and 3-(2-methyl-1H-imidazol-1-yl)propanoate linkers, is shown in Figure 1.[2] Its crystal structure features directional covalent polymer chains, hydrogen bonds and weak van der Waals interactions, making it ideally suited to probe how different bonding types relate to the thermal responsiveness of the framework.

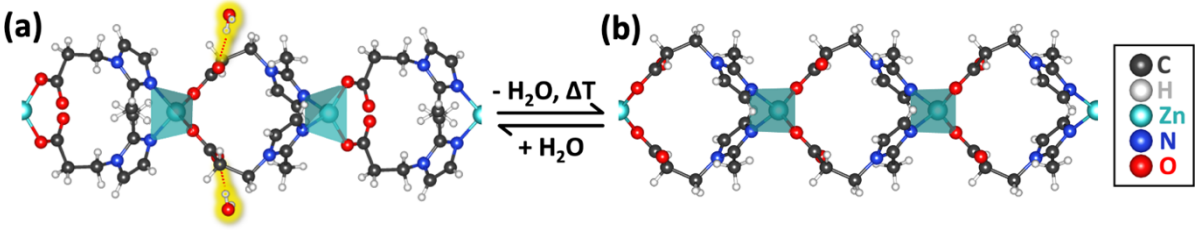


Figure 1. Single polymer strand of (**a**) hydrated GUT-2 where the H_2O molecules (highlighted in yellow) inside the pores can be removed in a reversible reaction by thermal treatment to produce (**b**) its activated form. Exposure to humid air restores the original, hydrated crystal structure.

In the course of my current work[3], we investigated the thermal expansion of GUT-2 by performing temperature-dependent powder X-ray diffraction measurements on activated and hydrated powder samples of GUT-2. Subsequent Rietveld refinements allowed the determination of anisotropic thermal expansion coefficients for both forms. The hydrated structure displays near-zero thermal expansion along the direction of the polymer chains (≈ 2×10^{-6} K^{-1}), reflecting the rigidity imposed by strong covalent bonding. In contrast, moderate expansion (≈ 6×10^{-6} K^{-1}), is observed along the hydrogen-bonded direction, while the highest thermal expansion coefficient (≈ 9×10^{-6} K^{-1}), is found in the van der Waals direction. Dehydration of the MOF removes hydrogen bonds, replacing them with weaker van der Waals interactions causing a doubling of the thermal expansion in the affected direction, highlighting the pivotal role of hydrogen bonding in suppressing structural flexibility.

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ATOMIC-LEVEL INSIGHTS INTO CO_2 ADSORPTION IN A DEFECTIVE AMINO-FUNCTIONALIZED MOF THROUGH *IN SITU* HR-PXRD

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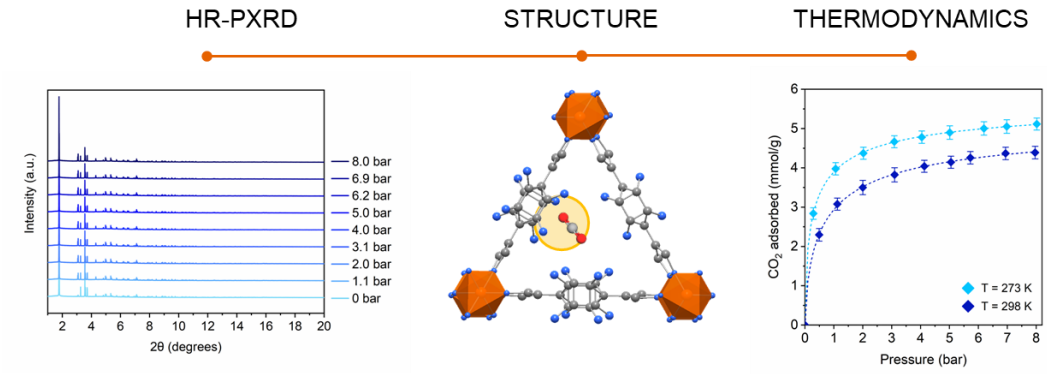
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Keywords: *powder X-ray diffraction, CO_2 adsorption, in situ characterization.*

Rising anthropogenic CO_2 levels necessitate the development of efficient carbon capture and storage (CCS) technologies, with metal-organic frameworks (MOFs) emerging as promising adsorbent platforms. The CO_2 adsorption behavior of these materials is significantly influenced by their tunable microstructural features, including surface area, network topology, and the presence of defective sites[1]. While traditional gas sorption techniques offer valuable macroscopic insights, a comprehensive understanding of the underlying structural and thermodynamic mechanisms is crucial for optimizing adsorbent performance.

Our group recently described the application of a powerful *in situ* high-resolution powder X-ray diffraction (HR-PXRD) protocol[2], performed under controlled CO_2 atmospheres with systematic pressure variations, to directly derive structural adsorption isotherms for the highly stable, pyrazolate-based MOF $Fe_2(BDP)_3$ [H_2BDP = 1,4-bis(1H-pyrazol-4-yl)benzene][3], This approach, coupled with Rietveld refinement and simulated annealing, enabled the precise localization of physisorbed CO_2 molecules and determination of isosteric heats of adsorption, effectively bridging the gap between structural and thermodynamic information[4].

To further validate and expand the scope of this HR-PXRD protocol, the present study focuses on its application to amino-tagged derivatives of $Fe_2(BDP)_3$, namely $Fe_2(BDP)_{3-x}(BDP\text{-}NH_2)_x$ (x = 1.5, 3), explicitly considering the intrinsically defective nature of this family of architectures. By investigating these functionalized materials, we aim to elucidate how the introduction of polar amino groups, known to enhance CO_2 uptake *via* quadrupole interactions, influences the structural and thermodynamic aspects of CO_2 adsorption within the framework, providing an extensive overview of structure-property relationships for advanced CCS applications.



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PERFORMANCE AND NANOCONFINEMENT EFFECTS IN Pd/UiO CATALYSTS FOR THE DIRECT CO_2-TO-METHANOL HYDROGENATION

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Keywords: *post-synthetic functionalisation, heterogeneous catalysis, CO_2 conversion, nanoconfinement, defect effects, operando studies*

Following on our previous research on exploring the behaviour of catalytically active nanoparticles embedded in metal-organic frameworks [1,2], this study interrogates matrix effects Pd nanoparticles supported on a partially functionalised UiO-67(Zr) framework, for the hydrogenation of CO_2 to methanol. In the course of the reaction, although elevated temperatures induced localised distortions in the UiO-67 framework, its overall structural integrity was preserved.

Using a comprehensive suite of characterisation techniques, including *operando* X-ray absorption spectroscopy (XAS) and *operando* X-ray diffraction (XRD), we demonstrate that Pd the particle size and location in relation to the MOF pores has a significant effect on the catalytic performance, particularly on the product selectivity. Further comparison with Pd embedded in the smaller-pore X-UiO-66(Zr), i.e. functionalised, matrix will also be discussed, which reveals a clear nanoconfinement effect and consequent control over the catalytic reaction.

Furthermore, we have recently demonstrated that simple materials processing techniques may lead to improved catalyst performance (**Figure 1**), which is attributed to the role of the UiO MOFs' abundant node chemistry and ability to stabilise defective structures. The proposed MOF contribution to the CO_2 hydrogenation reaction will also be discussed.

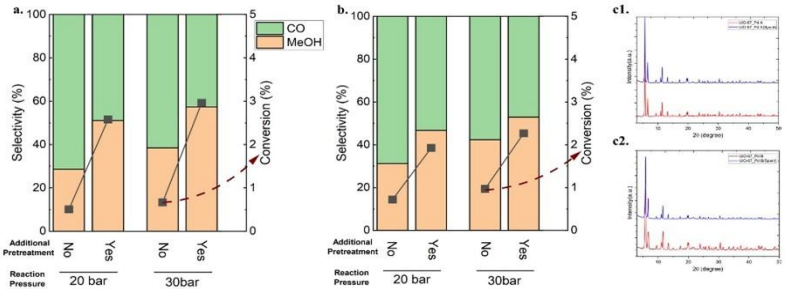


Figure 1. Product selectivity distribution (left axis) and CO_2 conversion (right axis) for catalysts under varying pressure and reaction temperature at 170 °C, with and without additional pretreatment step. The reaction conditions are CO_2/H_2/inert = 1/6/2. Different Pd particle size and locations: a. Pd A and b. Pd B. XRD patterns for pristine and spent samples c1. Pd A and c2. Pd B.

The observed nanoconfinement effect is attributed to their higher surface-to-volume ratio and unique electronic properties, which collectively promote higher catalytic activity and methanol selectivity. In this respect, interactions between the MOF and the guest nanoparticles are primordial [3]. This research provides a deeper understanding of the structure-performance relationships in MOF-supported catalysts and offers valuable insights for optimising MOF-based catalysts and catalytic processes for CO_2 hydrogenation.

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FINE STRUCTURE OF A REDOX ACTIVE METAL-ORGANIC FRAMEWORK UPON 3D ELECTRON DIFFRACTION

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Keywords: *Zeolitic Imidazolate Frameworks, Redox Activity, Electrical Property*

Zeolitic Imidazolate Frameworks (ZIFs) are an important sub-family of Metal-organic Frameworks (MOFs). ZIF-4 is one of the prototypical structures among ZIFs, which possesses the basic components of $M(im)_2$ (M = Co^{2+}/Zn^{2+} and im = imidazolate). Exclusive investigations have been applied on ZIF-4 such as mechanical properties[1] and thermal behaviors[2], however missing of the electrical property has largely limited the catalytic application of this catalogue. Even ZIFs' hierarchical pore structure provide multidimensional paths for charge transfer inside the framework, the big pore size impedes the smooth charge migration. We thus designed two methods to address this problem: the first way is adopting bulky ligands (e.g., functionalizing with phenyl groups) to reduce the pore size and/or then use conductive species to fill up the pore space[3].

The functionalized framework has shown improved ability on Oxygen Evolution Reaction (OER) and Oxygen Reduction Reaction (ORR) comparing to the prototypical framework. However, the real mechanism of this electrochemistry activity still remains unclear despite surface reconstruction has been suggested for similar activity.[4] 3-Dimensional Electron Diffraction (3DED) has to be imported at this point to characterize the structure evolution over the electrochemistry activities.[5] Combining the high-resolution imaging through TEM, the fine structure around the pore area is being revealed. This study paves the way to understand the electrical dynamics in the framed 3D spaces.

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STABILITY AND REDOX BEHAVIOR OF CERIUM-BASED MOFS UNDER NON-THERMAL PLASMA CONDITIONS FOR CO_2 HYDROGENATION

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Keywords: *Cerium Metal-Organic Frameworks, Non-Thermal Plasma, CO_2 hydrogenation, Redox chemistry.*

Metal-Organic Frameworks (MOFs) have been investigated as potential catalysts since their discovery due to their exceptional structural and compositional diversity, tunable porosity and well-defined active sites. However, due to their limited thermal stability, these properties have not been exploited in many thermal catalysis applications, e.g., CO_2 hydrogenation.[1]
A significant decrease of the reaction temperature can be achieved by application of non-thermal plasma (NTP) conditions, opening an attractive field of applications for MOFs. NTP can be tailored to form various highly reactive species (ions, electrons, vibrationally or electronically excited molecules) and opens the way to the electrification of chemical processes.[2] However, there is very little information available on the stability of MOFs under plasma conditions,[3] and no systematic studies have been reported to date.
The stability of the two most widely studied Ce-MOFs (UiO-66 and MIL140) and their analogues in contact with CO_2/H_2 and Ar/H_2 dielectric barrier discharge plasmas has been investigated ex- and in-situ using conventional and synchrotron radiation sources. A custom-made reactor was used to study the redox chemistry of the Ce-MOFs using quasi-simultaneous in situ powder X-ray diffraction and X-ray adsorption spectroscopy. The focus was on investigating the impact of a) the structure and connectivity of the inorganic building unit, b) the composition of the linker molecules and c) the plasma composition and NTP conditions on their stability. As a result, we have identified trends that will help guide the development of MOF / NTP processes and open up new opportunities for future applications.[4]

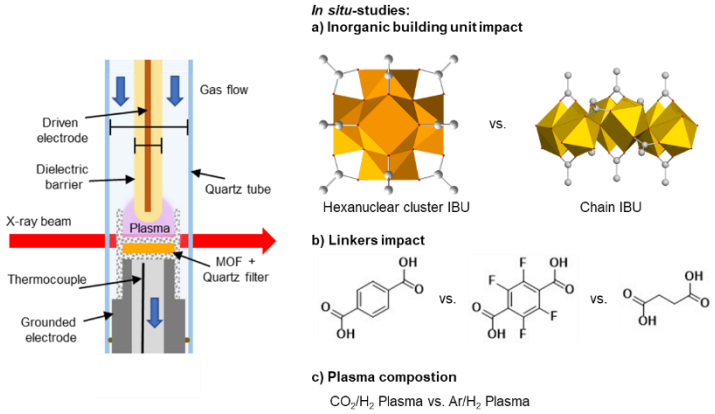


Figure 1 Custom-designed in-situ reactor (left), which was used to study and compare the stability of different seven selected Ce-MOFs, in order to investigate the impact of a) the structure and connectivity of the inorganic building unit, b) the linker molecules (non-fluorinated vs fluorinated linkers and alkyl vs aromatic linkers and c) the plasma compositions and NTP conditions.

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DIAMINE-APPENDED METAL–ORGANIC FRAMEWORKS PROMOTE THE HYDROGENATION OF CO_2 TO METHANOL AT LOW PARTIAL PRESSURES

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Keywords: *metal-organic framework, tandem, catalysis, CO_2 hydrogenation, methanol, Ru-Macho-BH*

Amine-assisted catalytic systems for CO_2 capture and hydrogenation to methanol offer low-temperature alternatives to commercial methods.[1] This study leverages the unique CO_2 adsorption properties of diamine-functionalized metal-organic frameworks (MOFs) to enable tandem CO_2 capture and conversion at low partial pressures. Catalyzed by the Ru-Macho-BH complex, diamine-appended MOFs enhanced methanol yields by up to sixfold at 150 °C and CO_2 pressures as low as 0.5 bar.

Expanded MOF-74-type structures were synthesized by solvothermal methods and functionalized with diamines e2, e2e and ee2 (Fig. 1a).[2] These materials were characterized by powder XRD, SEM, NMR, IR, and gas adsorption measurements. Catalytic tests were performed in batch at 150 °C, with 0.5 – 2 bar CO_2, 50 bar H_2 and Ru-Macho-BH in 1,4-dioxane. Methanol was quantified by GC. Reaction intermediates were analyzed by NMR, and the catalytic species were monitored by Ru K-edge XAS, NMR and IR.

All MOFs exhibited high CO_2 uptake below 150 mbar (Fig. 1a). e2- and e2e-MOFs enhanced methanol production at low CO_2 pressures (Fig. 1b), with activity being influenced by the diamine motif (e2e > e2 > ee2), consistent with the corresponding CO_2 heats of adsorption.[2] Sorption tests in the presence of dioxane showed that under confinement, carbamate concentration at 2.4 bar increased from 0.04 M (homogeneous) to 0.77 M (MOF). Solid-state NMR confirmed carbonylated intermediates stabilized within the pores, while methanol predominantly diffused out. XAS revealed identical catalytic species in both MOF-based and homogeneous systems, indicating a common mechanism (Fig. 1c). ATR-IR demonstrated that the MOF suppressed catalyst coordination to formed CO.

This work highlights the role of diamine-functionalized MOFs in modulating both CO_2 adsorption and the local catalytic environment, leading to enhanced methanol formation under low-pressure conditions. These findings are supported by an extensive spectroscopic study elucidating changes in adsorption behavior and catalyst–substrate interactions.

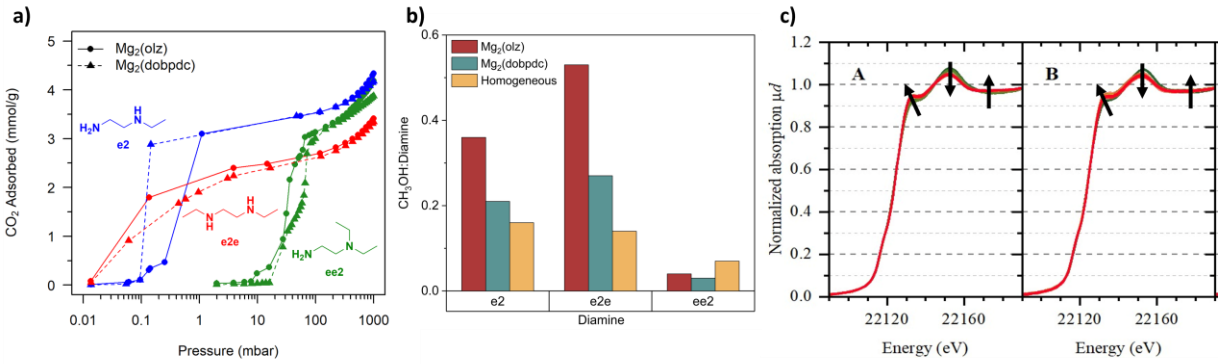


Fig 1. a) CO_2 adsorption isotherms at 25 °C for the diamine-Mg_2(olz) and -Mg_2(dobpdc) b) Batch reaction results for the Ru-catalyzed CO_2 hydrogenation to methanol at 2 bar CO_2, 50 bar H_2, 5 mol% [Ru] in 1,4-dioxane, 150 °C and 22 h. c) *In-situ* Ru K-edge XANES of e2e-Mg_2(olz) (A) and liquid e2e (B) systems at conditions equal to b).

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ILLUMINATING CHARGE TRANSFER MECHANISMS IN PHOTOACTIVE MOFs DURING CO_2 PHOTOREDUCTION

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Keywords: *photoactive MOFs, artificial photosynthesis, porphyrin, charge transfer mechanism, CO_2*

Artificial photosynthesis holds promise for sustainable energy conversion, yet understanding and controlling the underlying photochemical mechanisms remains a major challenge. Metal-organic frameworks (MOFs), especially those incorporating photoactive porphyrin linkers, are attractive platforms due to their tunable structures and high surface areas. In this study, we investigate the mechanism of CO_2 photoreduction in the Zr-based porphyrinic MOF PCN-223 using a multi-spectroscopic approach.

Previous mechanistic models propose electron transfer from the excited porphyrin to the Zr_6-oxo node, enabling CO_2 reduction at the cluster site.[1-3] However, through a combination of X-ray absorption spectroscopy (XAS), electron paramagnetic resonance (EPR), UV-vis, transient absorption, and FTIR spectroscopy, we demonstrate that no Zr^{3+} species form under illumination. Instead, photoexcitation induces the formation of an organic radical within the porphyrin linker network.

Transient absorption and UV-vis data suggest the formation of a symmetry-breaking radical pair on the porphyrin P, ($P^{\bullet+}/P^{\bullet-}$) within the MOF, enabled by strong excitonic coupling and close spatial arrangement of porphyrin units. The sacrificial electron donor triethanolamine (TEOA) selectively quenches the $P^{\bullet+}$ species, allowing the $P^{\bullet-}$ to reduce CO_2 to formate. ATR-FTIR confirms the formation of $HCOO^-$ and the stabilization of the radical under light in the presence of TEOA.

Our findings challenge the prevailing assumption of cluster-centered catalysis and reveal a previously overlooked linker-to-substrate charge transfer mechanism. This work highlights the importance of linker electronic structure, radical stabilization, and spatial preorganization in MOF pores for efficient photocatalysis. The insights gained open new directions for designing MOFs that mimic the photophysical principles of natural photosynthesis through cooperative linker dynamics.

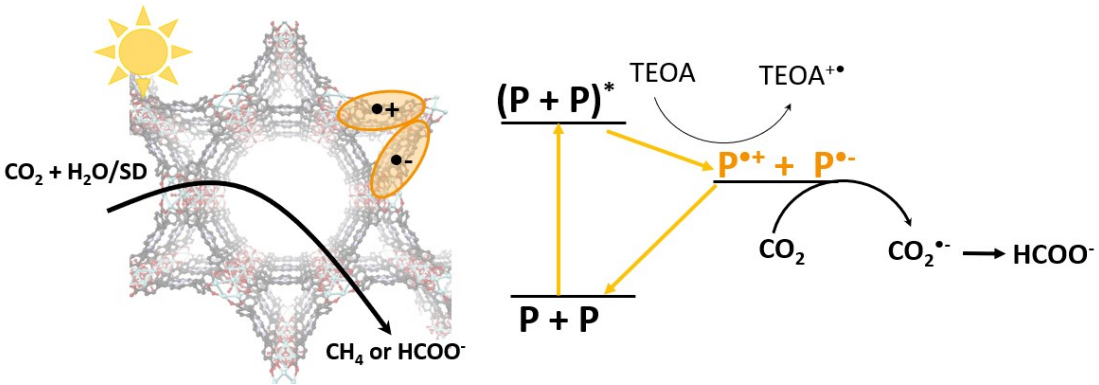


Figure 1: New proposed CO_2 photoreduction mechanism. SD = sacrificial donor, TEOA = Triethanolamine, P = porphyrin.

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CORRELATING THE STRUCTURAL TRANSFORMATION AND ELECTROCATALYTIC PROPERTIES OF ZIF-67 DURING PYROLYSIS

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Keywords: *MOF pyrolysis, in situ X-ray scattering and absorption spectroscopy, electrocatalysis*

Over the past decade metal-organic frameworks (MOFs) have attracted increasing attention as electrocatalysts. Despite the benefits of MOFs of offering high chemical tuneability, large surface areas and a homogeneous distribution of metal atoms, MOFs often restructure or degrade during the catalytic reaction.[1] Pyrolysis, i.e. heating of the pristine MOF under inert conditions, has emerged as a popular strategy to produce chemically stable materials denoted MOF-derived nanomaterials (MDNs). MDNs are typically composed of metal and/or metal oxide nanoparticles in a carbonaceous matrix, but several properties of the parent MOFs, e.g. porosity and morphology, are often preserved during pyrolysis.[2] Furthermore, the graphitic carbon matrix in the MDNs may prevent particle agglomeration and improves the electrical conductivity in comparison with the parent MOF.[3]

Despite of showing good electrocatalytic performance, mechanistic insight into the transition from MOF to MDN is generally poorly understood. Furthermore, the effect of the pyrolysis conditions on the catalytic activity and the structure-activity relationships of the MDNs is generally lacking. However, few recent studies have focused on the transient phase behavior and time/temperature dependence of MOFs during pyrolysis by using X-ray scattering and/or X-ray absorption spectroscopy.[3-5]

In the study,[6] we open up the 'black box' of the pyrolysis process of cobalt-based ZIF-67, by elucidating the thermal decomposition (from room temperature to 550 °C) based on *in situ* X-ray absorption spectroscopy and total scattering followed by pair-distribution function analysis. In order to correlate the structure and electrocatalytic performance towards the oxygen evolution reaction (OER), a series of samples were prepared by low-temperature pyrolysis (*ex situ*) at approx. 550 °C for different durations, i.e. at conditions similar to the *in situ* series. We demonstrate that the phase transition from MOF to MDN can be halted at different stages.

During the pyrolysis process ZIF-67 is firstly transformed from pristine to disordered ZIF-67 followed by a gradual transition from the porous MOF framework into metallic cobalt nanoparticles embedded in a nitrogen-doped carbonaceous matrix. Amongst the best ZIF-67 derived catalysts for OER were materials prepared by pyrolysis at 550 °C for 8 or 12 hours. The cobalt particles in these materials can be described with a bimodal size distribution of 1-2 nm and 7-9 nm, respectively. We propose that the catalytic performance depends on both the size of the nanoparticles, the degree of graphitization of the carbon matrix, and the electrochemical active surface area.[6]

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UiO-66 SUPPORTED COPPER-ZINC CATALYSTS FOR CARBON DIOXIDE-TO-METHANOL CONVERSION: STRUCTURE–ACTIVITY INSIGHTS FROM IN SITU X-RAY STUDIES

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Keywords: UiO-66, carbon dioxide conversion, methanol production, heterogeneous catalysis, in situ characterization.

Background and motivation: Metal-organic frameworks (MOFs) are emerging candidates for carbon dioxide (CO_2)-to-methanol conversion due to their dual role in CO_2 capture and catalytic hydrogenation.[1,2] We focus on zirconium-based UiO-66 MOF functionalized with copper and zinc introduced by wetness impregnation. The catalyst is evaluated for its activity at relatively low temperatures and under low CO_2 partial pressures, relevant for valorizing CO_2 in diluted industrial streams.

Materials and methods: The catalysts were characterized by transmission electron microscopy (TEM) and scanning transmission electron microscopy with energy-dispersive X-ray spectroscopy (STEM-EDX), confirming high metal dispersion (fig. 1a–f). Catalytic tests were performed in a plug-flow reactor equipped with an online gas chromatograph, under CO_2 to H_2 ratios of 1:8, 1:17, and 1:35, at a total pressure of 40 bar. In situ synchrotron X-ray diffraction (SXRD), copper and zinc K-edge X-ray absorption spectroscopy (XAS) measurements were performed at ESRF BM23, simultaneously tracking catalyst structure and metal state under catalysis conditions (fig. 1g–h).

Results and discussion: No methanol production was observed with bare UiO-66, and UiO-66 functionalized with Cu and Zn (1.9 wt.% Cu, 5.5 wt.% Zn) showed increasing methanol productivity and selectivity as the CO_2 concentration decreased from 1:8 to 1:35, (fig. 1i,j). While it was demonstrated that enriched H_2-flows are favorable to methanol production[3], this trend was much less pronounced with a conventional $CuO/ZnO/Al_2O_3$ (CZA) catalyst tested under the same pressures and temperatures, highlighting the role of the MOF in enabling activity at relatively low temperatures. Still, methanol productivity of the MOF-based system remains lower than that of CZA when normalized to metal content. The intrinsic CO_2 adsorption capacity of UiO-66, however, supports its dual function as both adsorbent [4] and catalytic host – particularly under low CO_2 partial pressures. In situ SXRD confirmed the structural stability of the MOF under 10 bar pressures and elevated temperatures. Linear combination fitting of the X-ray absorption near edge structure (XANES) spectra (fig. 1g) and plotted spectra of the extended X-ray absorption fine structure (EXAFS, fig. 1h) both acquired in situ indicated a mixture of metallic Cu, Cu_2O, and possibly Cu–Zn alloy. These findings suggest a dynamic distribution of copper species which can be possibly influenced by hydrogen partial pressure and correlate with changes in the catalytic performance.

Conclusion: This study demonstrates the applicability of Cu-Zn functionalized UiO-66 for methanol synthesis from CO_2. Notable performance under low CO_2 partial pressures and relatively mild temperatures highlights its potential for flue gas valorization. In situ XAS and SXRD confirm the structural stability of the material and provide direct insight into the evolution of Cu and Zn species during reaction. The coexistence of metallic Cu, Cu_2O, and possibly Cu-Zn alloyed forms under operating conditions suggests a dynamic speciation of copper, which may play a role in the observed catalytic behavior.

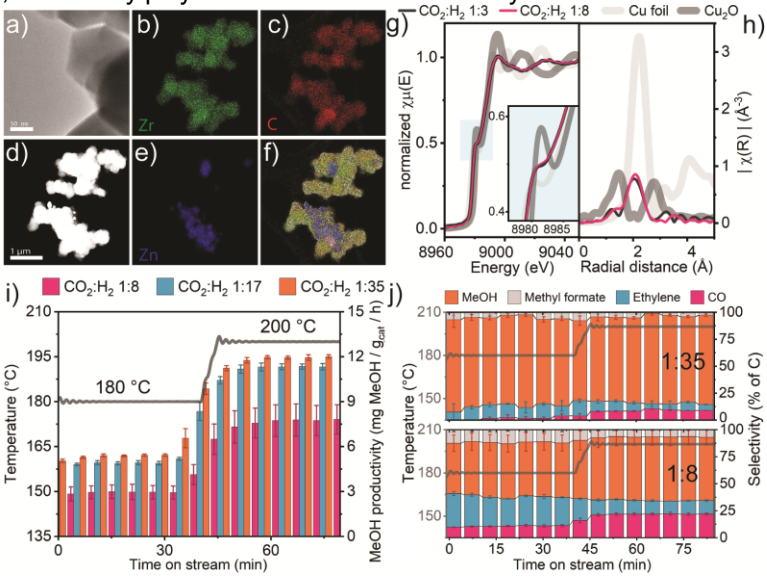


Figure 1. (a–f) TEM and STEM-EDX images: a - pristine UiO-66, d – UiO+Cu-Zn and (b,c,e,f) its element maps: zirconium, carbon, zinc, overlay; copper TEM grid was used; (g–h) in situ copper K-edge XANES and EXAFS during reaction under 1:3 and 1:8 CO_2:H_2, 10 bar, 180 °C, 5 – 15 mg catalyst, 30 mL/min, 2 h on stream; Cu foil and Cu_2O as reference; i) Methanol productivity at different CO_2:H_2 ratios. Conditions: 40 bar; CO_2:H_2 1:8, 1:17, 1:35; 180 and 200 °C, 100 mg catalyst + 100 mg SiC; GHSV 20 700 h^{-1}; (j) Selectivity at 1:35 (top) and 1:8 CO_2:H_2 (bottom) ratios.

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METAL-ORGANIC FRAMEWORKS FOR ENHANCED ANTIBACTERIAL WOUND HEALING

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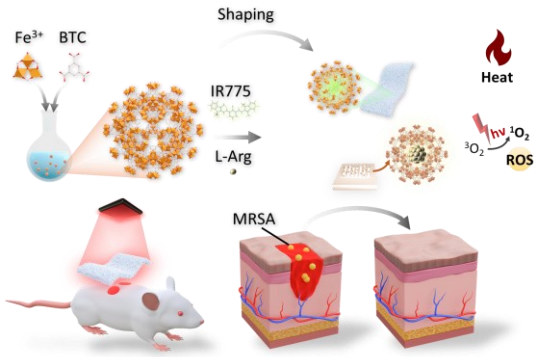
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Keywords: *Metal-Organic Frameworks (MOFs), Phototherapy (PTT/PDT), Nitric Oxide (NO) Release Antibacterial Wound Healing, Methicillin-Resistant Staphylococcus aureus (MRSA)*

The increasing prevalence of antibiotic-resistant bacteria necessitates alternative therapeutic strategies for infection control and wound healing.[1] This study explores the potential of metal-organic frameworks (MOFs)[2] as multifunctional platforms for antibacterial treatment through photothermal/photodynamic therapy (PTT/PDT) [3] and controlled nitric oxide (NO)[4] release.

Here we will first present MIL-100(Fe)@IR775 nanoparticles synthesized via a green method,[5] demonstrating enhanced photostability and strong antibacterial efficacy against methicillin-resistant *Staphylococcus aureus* (MRSA) under LED irradiation.[6] The MOF structure prevents photobleaching and aggregation-caused quenching, allowing for repeated photothermal therapy. In vitro and in vivo studies confirm up to 98.5% bacterial eradication and rapid wound healing. Additionally, MIL-100(Fe)@L-arginine microneedles were developed for controlled NO release. L-arginine, encapsulated within MIL-100(Fe), reacts with hydrogen peroxide generated by lactate oxidase, producing NO and hydroxyl radicals for synergistic antibacterial action. This strategy effectively enhances bacterial clearance and promotes wound repair.



Scheme of the MOF-enhanced dressings for drug-resistant bacteria in wound care

These findings highlight MOF-based platforms as promising alternatives for combating drug-resistant infections and accelerating wound healing. The integration of phototherapy and NO-based treatment provides a versatile and effective approach for advanced wound care applications.

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DECIPHERING INTERFACIAL INTERACTIONS IN A DUAL-FUNCTIONAL MOF@COF COMPOSITE FOR WATER REMEDIATION

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Keywords: *Metal-organic framework, covalent-organic framework, composite, interface, pair distribution function.*

MOF@COF composites have emerged as a promising class of engineered materials, combining the high porosity and tunability of metal-organic frameworks (MOFs) with the chemical and mechanical robustness of covalent-organic frameworks (COFs).[1] Despite their potential, the structural features and the nature of interfacial interactions remain underexplored.[2] In this study, a Fe-MOF@COF composite is presented, exhibiting dual functionality in the efficient adsorption and degradation of organic pollutants from water. The enhanced performance is attributed to the unique properties of the MOF-COF interface, where synergistic interactions between the two materials play a critical role. A detailed structural investigation was conducted using an analysis methodology based on the pair distribution function (PDF) to gain deeper insights into interfacial interactions. The findings were further supported by diffuse reflectance spectroscopy (DRS) and vapor adsorption isotherms, revealing a well-defined porous interface enriched with π-π stacking interactions between the MOF and COF backbones. This interfacial architecture enables simultaneous capture and degradation of bisphenol A (BPA), a common water contaminant, under continuous flow conditions.[3] Overall, this work demonstrates a rational design and characterization strategy for MOF@COF composites targeting multifunctional water treatment applications.

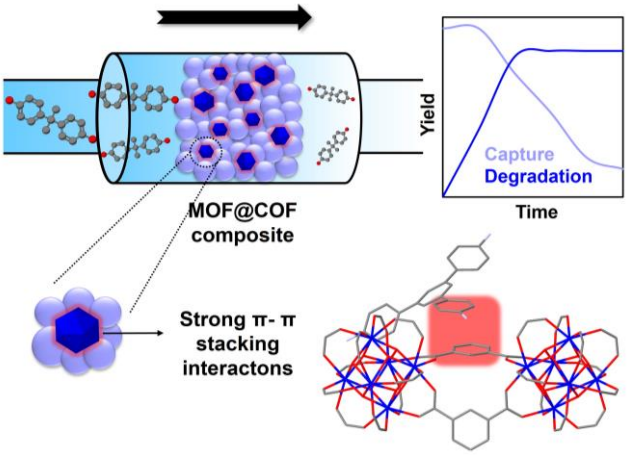


Figure 1. Depiction of the dual role of the FeMOF@COF composite and the nature of its interfacial interactions.

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MOF-ON-MOF HETEROSTRUCTURE THIN FILM: A RATIONAL DESIGN STRATEGY TO INVESTIGATE EMERGENT INTERFACIAL PHENOMENA

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Keywords: *MOF Heterostructure thin film, Interfacial electronic phenomena, Metallic Conduction*

Interfacial phenomena often emerge uniquely when materials are miniaturized into heterostructured thin films. In this study, we report the fabrication of a heterostructured thin film composed of a Mott insulator (Cu-TCNQ) (TCNQ = 7,7,8,8-tetracyanoquinodimethane) and a band insulator (Cu-BPyDC) (BPyDC = 2,2′-bipyridene-4,4′-dicarboxylate) using a layer-by-layer assembly approach. Electrical transport measurements across the heterostructure reveal emergent interfacial metallic conduction at the junction between the Mott and band insulators.[1] First-principles density functional theory (DFT) calculations further substantiate the origin of this metallic behavior, providing insights into the electronic structure at the interface. Beyond this specific system, other heterostructures of metal–organic frameworks (MOFs) have also been explored, each exhibiting unique interfacial phenomena.[2-5] These findings highlight an unexplored frontier in the field of MOFs, where interfacial electronic phenomena have remained largely elusive. This work opens new avenues for investigating and engineering emergent interfacial properties in rationally designed MOF-based heterostructured thin films.

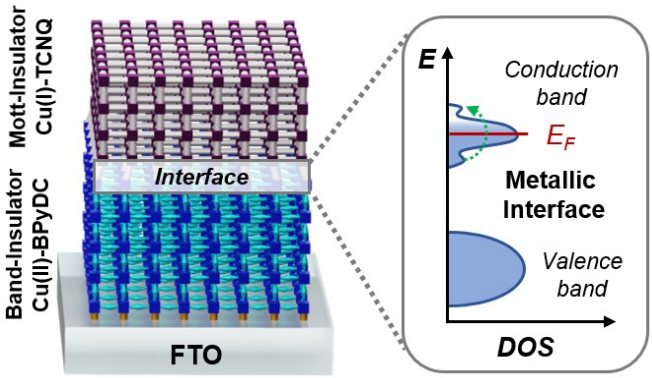


Figure 1: Schematic representation of heterostructure MOF thin film of Band-insulator (Cu(II)-BPyDC) and Mott-insulator (Cu(I)-TCNQ) indicating metallic-interface.

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IN SITU ENTRAPMENT OF MR-TADF EMITTER DIKTA IN METAL-ORGANIC FRAMEWORK MOF-5 AND THEIR PHOTOPHYSICAL PROPERTIES

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Keywords: *MOFs, MR-TADF, Entrapment, Photophysical Properties, Anisotropy*

Here we report the first attempt to synthesize a highly emissive microporous metal-organic framework (MOF) by entrapment of a multi-resonant thermally activated delayed fluorescence emitter called DiKTa (quinolino-[3,2,1-*de*]acridine-5,9-dione). This molecule is known for its narrowband emission, which makes it an interesting candidate for the application in organic light-emitting diodes (OLED's). Due to its suitable pore size, we chose MOF-5 as the MOF, based on the dimensions of DiKTa molecules. The MOF syntheses as well as the entrapment were carried out by a solvothermal in situ synthesis. We focused the synthesis on the production of MOF-5 single crystals. Four DiKTa@MOF-5 composites with different DiKTa loading were successfully synthesized as single crystals. The photophysical and structural properties of these composites were comprehensively analyzed and compared with those of pure DiKTa in both solid-state and solution. The reported DiKTA@MOF-5 composites show good emissions depending on their loading and slightly broader FWHM values compared to DiKTa in solution. Lifetime measurements of the composites yielded results comparable to those observed for DiKTa in solution, with values varying depending on the concentration of DiKTa in the composite. The measured lifetimes included both prompt and delayed components, confirming the concept of a solid solution. Using fluorescence anisotropy measurements, we were able to determine the preferred orientation of individual DiKTa molecules in the MOF matrix. In addition to the decrease in the respective BET surface areas, the powder X-ray diffraction (PXRD) of each composite provided valuable insights into how different DiKTa loadings affected the structural integrity and stability of the MOF-5 matrix. This shows how dye and MOF affect each other.

STRUCTURE-INFORMED MODULATION OF ZEOLITIC IMIDAZOLATE FRAMEWORKS

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Keywords: *Structure-Informed Design, Zeolitic Imidazolate Frameworks, Nanomachines, Pore Structures*

Zeolitic imidazolate frameworks (ZIFs), long appreciated for their structural diversity and chemical stability, present a deceptively familiar landscape. Yet beneath this familiarity lies a hidden layer of geometrical logic that governs their mechanical, thermal, and adsorptive behavior. In this presentation, we explore how subtle modulations in framework geometry—hinge-like coordination motifs,[1] linker functionalities,[2] and high-entropy compositional tuning[3]—can be strategically leveraged to unlock programmable deformations, pore breathing, and stimuli-adaptive responses.

By treating ZIFs not as static architectures but as dynamic, reconfigurable systems, we reveal design rules that couple geometric flexibility with emergent functions such as selective hydrogen isotope separation. These insights, rooted in a structure-informed approach, reframe ZIFs not merely as crystalline solids, but as tunable mechanical platforms—capable of responding, transforming, and performing in ways previously overlooked.

Collectively, these findings establish a foundation for a structure-informed paradigm in ZIF research, wherein geometric principles, compositional complexity, and emerging digital methodologies[4] converge to guide the rational design and accelerated discovery of next-generation adaptive framework materials.

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CONTROLLING THE SELF-ASSEMBLY AND MECHANICAL PROPERTIES OF ISOSTRUCTURAL DISULFIDE-BASED METAL–ORGANIC NANOTUBES

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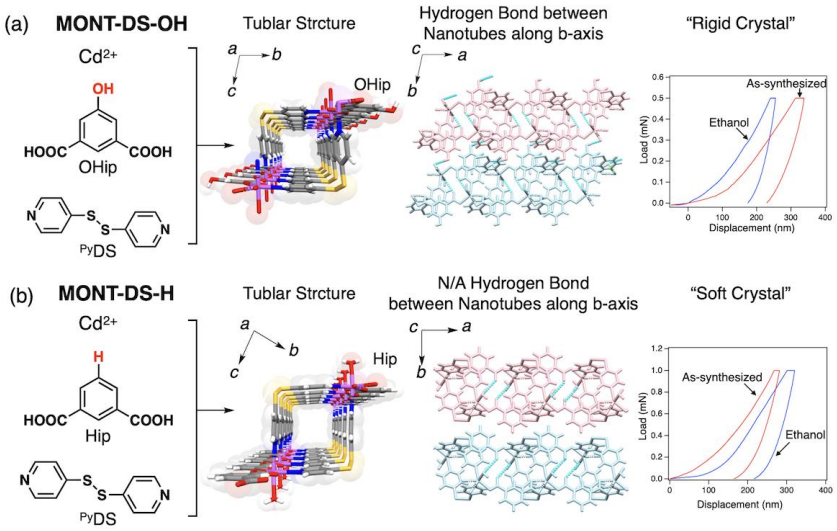
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Keywords: *Mechanical force response, Metal-organic nanotubes, hydrogen Bond*

Metal–organic nanotubes (MONTs), an emerging subclass of metal–organic frameworks (MOFs), combine the unique advantages of one-dimensional tubular architectures with tailorable physicochemical properties.[1] Despite their potential, MONTs remain underexplored compared to their well-established 2D [2] and 3D [3] MOF counterparts, largely due to the synthetic challenge of directing tubular assembly. To date, only a limited number of MONTs have been reported, with most studies focusing primarily on structural characterization. Controlling the elasticity of MONTs by modulating intertubular interactions presents a critical barrier to advancing their functionality, as it demands a fundamental understanding of assembly mechanisms and their direct correlation to mechanical behavior.

In this study, we reported the rational design and synthesis of isostructural MONTs through the self-assembly of cadmium ions (Cd^{2+}), 4,4'-Dipyridyl Disulfide(^{py}DS), and isophthalate derivatives (Hip^{2-} or $OHip^{2-}$). The crystal structures revealed that two Cd^{2+} were connected by two ^{py}DS to form a coordination square $[2Cd^{2+}(^{py}DS)_2]^{4+}$, which one-dimensionally connected with the assistant of isophthalate to form a metal−organic nanotube. Moreover, the substituents at 5 positions of isophthalate pointed out to the adjacent nanotube, offering a powerful strategy for tuning the intertubular interactions. In MONT-DS-OH, robust hydrogen bonding between neighboring nanotubes, with hydroxyl groups as donors, enhanced mechanical properties and minimized solvent effects on elasticity (Fig. 1a). In contrast, MONT-DS-H, lacking this network, displayed solvent-dependent stacking and significant variability in elasticity (Fig. 1b). This approach provides a versatile strategy for designing a series of responsive MONT systems with tunable intertubular interactions.



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MODULATING INTRINSIC CHARGE MOBILITY BY TUNING Π-Π INTERACTION DISTANCES IN THREE ISOSTRUCTURAL POROUS MOLECULAR CONDUCTORS

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Keywords: *metal-organic framework, porous coordination polymer, electrical conductivity, charge mobility, redox activity*

Metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) have recently emerged as a class of electron-conductive porous materials that are promising for practical applications such as the active materials for batteries, supercapacitors and sensors.[1] Several strategies have thus been established to engender conductivity in framework materials in the past two decades. Although numerous endeavors have been made to achieve high conductivity, challenges still remain. For example, despite their very high conductivity, two-dimensional (2D) π-d conjugated MOFs are only very rarely obtained as single crystals suitable for single-crystal X-ray diffraction (SXRD) analysis, and thus their electronic states have not been well studied. In contrast, MOFs constructed based on through-space approach exhibit low conductivity due to an insufficient number of charge carriers. Thus, the exploration of rational design strategies and novel synthetic methods for highly crystalline conducting MOFs is necessary to understand their intricate nature.

We previously proposed the concept of porous molecular conductor (PMC) as the fusion of MOFs and molecular conductors, utilizing the redox-active naphthalenediimide (NDI)-based ligand and synthesized the first PMC (noted as PMC-1).[2] PMC-1 contains $NDI^{\bullet-}$ species and forms one-dimensional (1D) infinite π-stacking columns with uniform distance. However, its semiconducting nature suggests the existence of a charge-ordering state. In this work, we systematically designed and synthesized three isostructural PMCs, noted as **PMC-3-X**, (X = Cl, Br and I). SXRD analysis reveals that each **PMC-3-X** presents two crystallographically independent NDI moieties and thus forms two types of π-stacking distances. Employing numerous characterization techniques, we will demonstrate how the carrier mobility correlates with the π-π interaction distances in the three **PMC-3-X**.

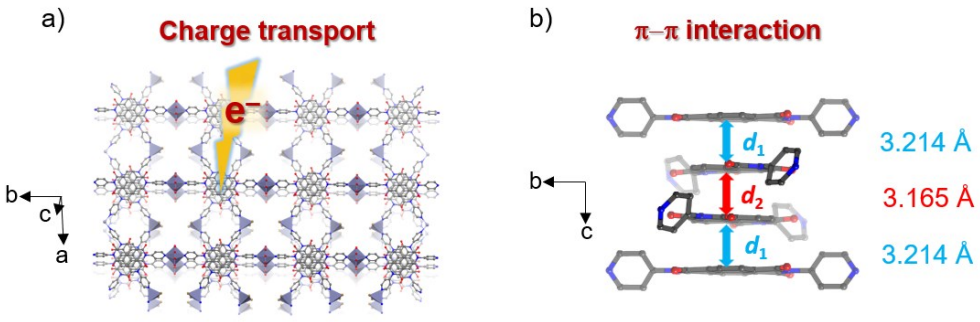


Fig. 1. a) Crystal structure and b) 1D infinite π-stacked column of **PMC-3-Br** .

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COVALENT ORGANIC FRAMEWORK EMBEDDED WITH SINGLE CU-SITES FOR PHOTOCATALYTIC REACTION

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Keywords: *CO_2 photocatalytic reduction, Covalent Organic Frameworks.*

Photocatalytic CO_2 reduction has attracted growing interest, as the direct conversion of CO_2 into value-added chemicals not only mitigates greenhouse gas emissions but also addresses the energy crisis simultaneously. Due to the thermodynamic stability of CO_2 molecules, the reduction reaction is an endothermic process, making it inherently unfavorable. Although numerous inorganic semiconductors have been developed to enhance the activity and selectivity of CO_2 photoreduction, several limitations—such as poor light-harvesting efficiency, inefficient charge separation, and weak CO_2 adsorption—remain critical bottlenecks in this process.[1] One promising strategy to overcome these challenges involves constructing hybrid photocatalytic systems by integrating transition metals into covalent organic frameworks (COFs).

Two-dimensional (2D) covalent organic frameworks (COFs) are considered an ideal platform for immobilizing molecular metal catalysts, including single-atom catalysts. COFs are constructed from rigid organic building blocks linked via strong yet reversible covalent bonds. As a class of crystalline porous polymers, COFs exhibit high crystallinity, porosity, stability, and tunable functional properties.[2] Through atomically precise design of organic units, COFs with optimized structural and optoelectronic characteristics can be synthesized. Their fully π-conjugated structures not only enhance light absorption but also promote charge carrier transport while suppressing the recombination of photogenerated electron-hole pairs. Among the commonly used building blocks, 2,2'-bipyridine and porphyrin are particularly effective for coordinating transition metals within the 1D pore channels of COFs.[3] The incorporation of single metal atoms into COFs facilitates CO_2 adsorption and enables efficient transfer of photogenerated charges from the framework to the active metal sites. Owing to these advantages, COFs have been successfully employed in photocatalytic CO_2 reduction.

In this study, a pyrene-bipyridine COF (Py-BPy COF) functionalized with Cu single-atom sites was investigated for photocatalytic CO_2 reduction. The structure of the Cu-Py-BPy-COF was systematically characterized by varying the Cu loading amount to elucidate the interaction between the COF matrix and metal atoms. Additionally, a solvothermally synthesized Cu-Py-BPy-COF thin film was successfully fabricated. The electrical and optical properties of the material were comprehensively analyzed. This work provides fundamental insights into the COF-Cu interaction and elucidates how the catalytic properties are influenced by incremental Cu loading.

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LUMINESCENT LANTHANIDE-BASED METAL−ORGANIC FRAMEWORKS AS AMBIENT OXYGEN GAS SENSORS WITH RAPID RESPONSE

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Keywords: *O_2 sensor, lanthanide MOF, luminescence, photosensitizer*

It is necessary to meet the growing demands in sensor technology with new material classes for the development of novel stable chemical sensors. Within the realm of gas sensing, researchers have developed both resistive and optical sensors designed for detecting various gases.[1] Regarding optical triplet oxygen sensing, the conventional approach involves incorporation of dyes into oxygen-permeable porous polymers, silica, or zeolites, serving as supporting matrices.[2] Alternatively, modulation of the surface charge distribution of semiconductors may also increase the sensitivity.[3] However, their relatively slow response and recovery as well as their limited selectivity hamper utilization of those sensors in real-life applications.

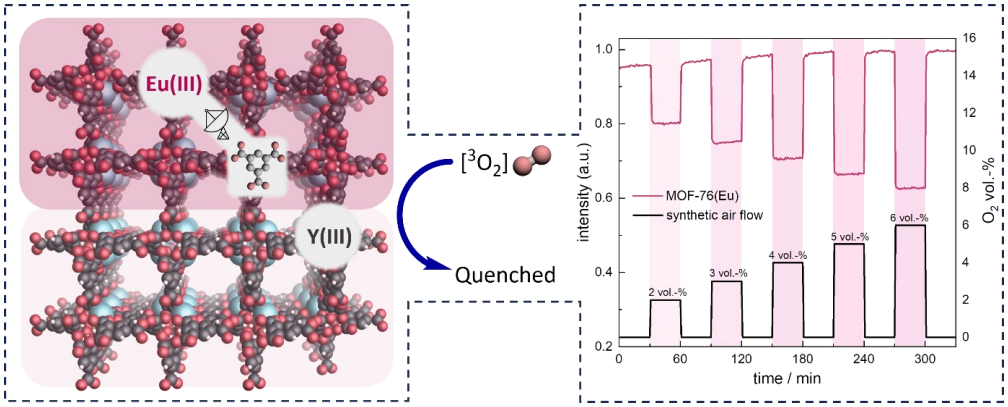


Figure 1. Sensitive and reversible oxygen sensing performance of luminescent MOF-76(Eu) based on suppression of the antenna effect detected by λ_{em} = 616 nm at λ_{ex} = 290 nm under five different oxygen concentration.

We report that the metal-organic framework MOF-76(Eu) and its isostructural frameworks after yttrium incorporation, denoted as MOF-76(Eu/Y), exhibit a remarkably reversible and rapid response and recovery behavior towards varying O_2 concentrations. The underlying principle is based on emission quenching be interaction between triplet O_2 and triplet states in the organic linker molecules in the MOF. To monitor this reversible responsive behavior, we perform time-resolved fluorescence measurements under variable O_2 concentrations by mixing N_2 and synthetic air, within time spans ranging from seconds to hours. Besides, Time-correlated Single Photon Counting (TCSPS) experiments reveal that quenching is mostly static, evidenced by the unaltered lifetime of lanthanide metal centers. Notably, we also found that the incorporation of yttrium accelerates the response to O_2 at room temperature compared to pure Eu-MOF, which may be attributed to a changed distance between luminescent Eu centers.

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DUAL-PSA PROCESS FOR THE SEPARATION OF H_2, CH_4, AND C_2H_6 WITH THE MOF MIL-100(FE)

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Keywords: *H_2/CH_4/C_2H_6 separation, Dual-PSA, Recycle, MIL-100(Fe)*

H_2 has garnered increased attention as a highly efficient and clean energy vector that can be produced via CH_4 decomposition without causing CO_x emissions. To purify H_2 for fuel cell applications (>99.97%) and to generate pure CH_4 (>90%, with trace levels of C_2 hydrocarbons) for natural gas grids, a subsequent separation technology, namely dual-pressure swing adsorption (dual-PSA), is required [1]. Since the 1990s, metal-organic frameworks (MOFs) have been extensively studied for various applications. Notably, the MOF MIL-100(Fe) offers high CH_4 adsorption capacity and stability [2]. This work aims to design a two-stage PSA process, packed with MIL-100(Fe) and featuring a recycling stream, to separate H_2 from CH_4, along with minor C_2H_6 amounts, from the exhaust gas of a typical CH_4 decomposition non-thermal plasma reactor, at 303 K and 1 bar, containing either a low or high H_2 content (*i.e.*, 27.8%/63.4%/8.8% H_2/CH_4/C_2H_6 or 57.1%/31.1%/11.7% H_2/CH_4/C_2H_6).

Single-component adsorption equilibrium isotherms were measured at 303, 313, and 333 K, over a pressure range of 0-5 bar, using a magnetic suspension microbalance. Breakthrough curves were performed at 1 bar and 308 K on a lab-scale fixed-bed unit with a 0.775 m bed length. The Langmuir equation accurately describes pure-component adsorption, and the extended Langmuir equation is used to represent multicomponent adsorption equilibria. A mathematical model was developed to predict the breakthrough curves through the gPROMS ModelBuilder. The experimental breakthrough results were in good agreement with the predictions, validating the model, which was then used to design, simulate, and optimize a dual-PSA system with recycle using a fresh feed with either a low or high H_2 content. A seven-step cycle was considered for each PSA unit for both studied fresh feed compositions. The corresponding cycle extensions for a four-column unit, applied to PSA 1 and PSA 2, for both studied fresh feed compositions, are shown in **Fig. 1**, alongside the ratios between each cycle step time and the feed time. The optimal result obtained for the low H_2 content case was 99.991% H_2 purity, with an 87.2% H_2 recovery rate. In comparison, the optimal result obtained for the high H_2 content case yielded a 99.991% H_2 purity with a 96.8% H_2 recovery and an energy consumption of 46.8 (vs. 105.9) W h mol_{H2}^{-1}.

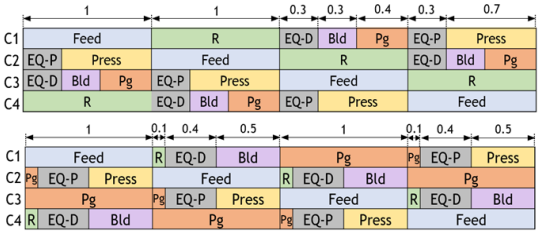


Fig. 1 - Extension of cycle PSA 1 (above) and PSA 2 (below) to a four-column unit.

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DEVELOPMENT OF A NOVEL Mg-FUMARATE-MOF (DUT-153) WITH EXTRAORDINARY TUNABILITY OF ADSORPTION PROPERTIES

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Keywords: *MOF, gas adsorption, gas separation*

Metal–organic frameworks (MOFs) are among the most promising materials for gas adsorption and separation applications. In addition to their exceptionally high and accessible surface areas, MOFs are particularly attractive due to their structural tunability.[1] This unique feature allows for not only adjusting the surface affinity toward specific adsorptives but also tailoring the framework to selectively separate gas molecules based on size.[2]

$[Mg_3(DMF)_2(fum)_3]\cdot(DMF)$ (DUT-153), a novel Mg-fumarate (fum) MOF, demonstrates an interesting ability to adjust its adsorption behavior through the solvent molecules coordinated to the metal centers. As illustrated in Figures 1a and 1b, a key characteristic of this three-dimensional MOF is the presence of DMF molecules, blocking the channel-like pores. In addition to one uncoordinated DMF molecule pro formula unit, two DMF molecules are coordinated to magnesium and protrude into the pores, preventing gas adsorption.

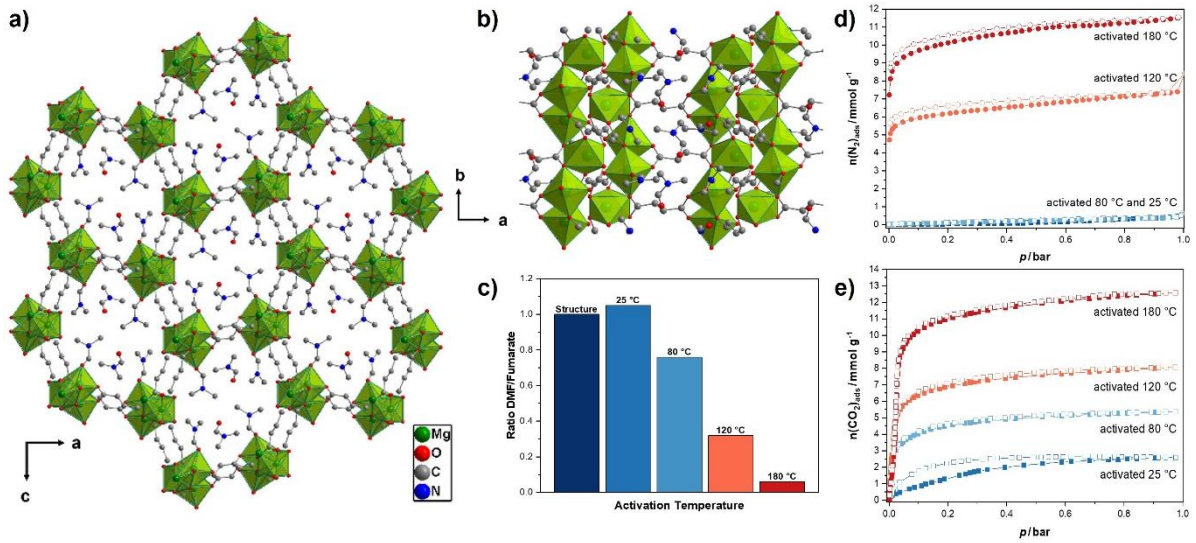


Figure 1: Crystal structure of DUT-153 along the (a) *b*-axis and (b) *c*-axis. (Mg green, O red, N blue, C grey, H omitted). (c) Ratio of DMF to fumarate based on ^{1}H-NMR experiments, (d) N_2-physisorption and (e) CO_2-physisorption on DUT-153 after activation at different temperatures.

Such structure enables controlled tuning of pore accessibility by selective removal of solvent molecules. During the desolvation process, the DMF is removed stepwise, resulting in variable pore diameters. The relationship between solvent content and pore size was explored through theoretical calculations of pore accessibility, which were experimentally validated using ^{1}H-NMR spectroscopy (Figure 1c), as well as nitrogen and carbon dioxide physisorption measurements (Figures 1d and 1e). Physisorption experiments revealed substantial differences in gas uptake, attributed to the varying kinetic diameters of the respective gases, and they are in line with the expectation from the given pore diameters. Thus, by regulating the solvent content in DUT-153, the pore accessibility can be finely tuned. This allows for the optimization of pore size to achieve gas separation through size exclusion, with selectivity that can be dynamically adjusted based on the degree of solvation.

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CRYSTAL ENGINEERING SQUARE-LATTICE COORDINATION NETWORKS FOR ATMOSPHERIC WATER HARVESTING

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Keywords: *Azolate Coordination Networks, Atmospheric Water Harvesting, Crystal Engineering*

As freshwater supplies continue to dwindle, finding sustainable water sources is becoming ever more urgent. Although water covers 70% of the Earth's surface, just 0.4% of freshwater is readily accessible to humans. Traditional water harvesting methods—like rainwater collection, groundwater extraction, and desalination—rely heavily on liquid water availability and are often unfeasible in arid or landlocked regions.[1] Atmospheric water harvesting (AWH) offers a promising alternative, tapping into the atmosphere's vast reservoir of around 15 trillion litres of water vapour. AWH is typically achieved through fog collection, cooling air below its dew point, or sorbent-assisted harvesting.[2] As the first two depend heavily on local climate and geography, our work focuses on the third: sorbent-assisted AWH using azolate-based coordination networks.

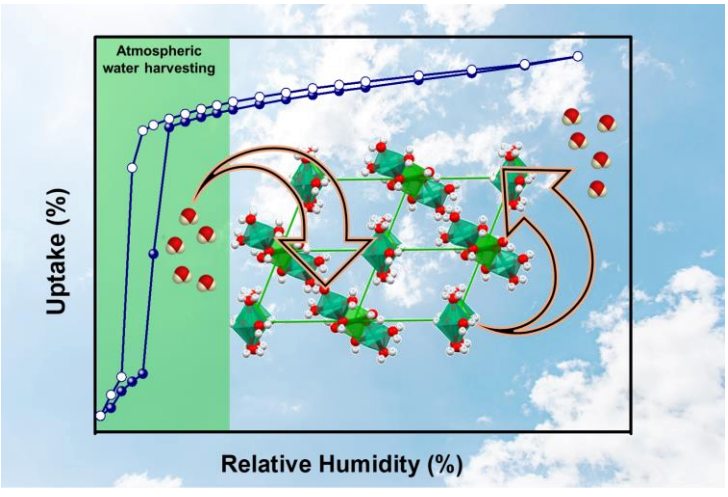
These materials are attractive for moisture capture due to their crystallinity, structural tunability, high surface area, and water stability. Azolate coordination networks (ACNs) are built from metal ions—usually transition metals—and azole linkers, which are five-membered nitrogen-containing aromatic rings. Incorporating a third inorganic linker, such as hexafluorosilicate (SiF_6^{2-}), hexafluorogermanate (GeF_6^{2-}), or hexafluorostannate (SnF_6^{2-}), introduces a further level of tunability.[3] This modularity makes ACNs excellent candidates for crystal engineering aimed at AWH. Ideal sorbents should feature an *S*-shaped isotherm for high working capacity, minimal desorption hysteresis, low regeneration temperatures (<60 °C), fast sorption kinetics, and long-term cycling stability in humid conditions.[4]

Herein, starting from a bifunctional pyridyl-tetrazole linker, our work reports a crystal engineering study of a modular platform of three new Cu(II) coordination networks with square-lattice (**sql**) topology. Upon introducing SiF_6^{2-}, GeF_6^{2-}, and SnF_6^{2-} anions, two distinct types of ACNs were obtained in relation to structures, and sorption properties thereof. The SiF_6^{2-} and GeF_6^{2-} analogues adopt isostructural frameworks within the *Pca2₁* space group and display classic type-I water sorption profiles. Conversely, the SnF_6^{2-} ACN crystallizes in the *P2₁/n* space group and undergoes single-crystal-to-single-crystal (SCSC) transformations upon water uptake. Notably, this phase evolution is accompanied by an *S*-shaped water sorption isotherm with a sharp inflection at ~8% relative humidity (RH), underscoring its potential for AWH. This low RH threshold for water uptake positions the SnF_6^{2-} ACN as a promising candidate for efficient moisture capture in arid environments, particularly below 30% RH. Detailed SCSC and powder X-ray diffraction phase characterizations allowed us to determine the absolute structures of all hydrated, semihydrated, and dehydrated phases within the tripartite phase diagram of SnF_6^{2-}-functionalized ACN — a key step towards guiding the future crystal engineering of AWH-relevant sorbents, *a priori*.

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DEFECT-ENGINEERED HKUST-1 WITH CU(I) SITES FOR ENHANCED HYDROGEN STORAGE

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Keywords: *Metal–organic frameworks, Defect engineering, Fragment linker, Missing linker, Hydrogen storage*

As global efforts to reduce greenhouse gas emissions intensify, hydrogen has emerged as a promising clean energy carrier due to its high energy density and carbon neutrality. Nevertheless, safe and efficient hydrogen storage, particularly under ambient conditions, remains a significant challenge. Metal-organic frameworks (MOFs), such as HKUST-1, have attracted attention for hydrogen storage applications owing to their high surface areas and tunable porosity; however, their performance still falls short of the targets set by the U.S. Department of Energy (DOE). In this study, we propose a defect-engineering strategy to enhance hydrogen storage by introducing unsaturated Cu(I) sites and linker vacancies into the HKUST-1 framework. Among the synthesized materials, DMT-HK-30F exhibited the highest hydrogen uptake, achieving 2.55 wt% at 77 K and 100 kPa, and 0.93 wt% at 298 K and 7 MPa. These values represent significant improvements of 41% and 48%, respectively, compared to pristine HKUST-1. Our findings highlight defect control and Cu(I) site enrichment as effective approaches to enhancing hydrogen storage performance in MOF-based materials[1].

Acknowledgments

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HOW TO ASSESS THE THERMODYNAMIC EQUILIBRIUM OF ADSORPTION FOR IN-VACUUM DECONTAMINATION?

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Keywords: *Polanyi's adsorption potential theory, thermodynamic equilibrium, in-vacuum adsorption.*

Advanced experimental devices are required for space exploration. However, the performance of such space instruments is increasingly sensitive to molecular contamination from outgassing. Volatile molecules emitted from coatings and pumps can deposit on critical surfaces, potentially compromising instrument functionality and mission success even for trace concentrations (a few ppm).[1] The removal of these contaminants using porous adsorbents has emerged as a promising approach. The assessment of the adsorption capacity of porous materials at low contaminant concentrations is crucial. Hence, robust strategies are needed to ensure that thermodynamic equilibrium is achieved, thereby replicating real-world adsorption conditions. In this contribution, static adsorption experiments of several contaminants such as water, siloxanes and *n*-alkanes were performed on Al-fumarate and other porous materials. To rigorously verify thermodynamic equilibrium across all concentration ranges, we applied Polanyi's adsorption potential theory, enabling reliable extrapolation of the real adsorption capacity at low concentrations.

The adsorption of small siloxanes such as hexamethyldisiloxane (L2) and *n*-alkanes exhibits distinct behaviors depending on the nature of the adsorbent: Type I and Type IV adsorption isotherms for the microporous and mesoporous materials, respectively. Microporous materials such as Al-fumarate demonstrate high efficiency for the capture of low-concentration contaminants. Nevertheless, the study of the "low pressure" part of the adsorption isotherms (<10% of saturated pressure) reveals that thermodynamic equilibrium, as assessed by Polanyi's adsorption potential theory, is difficult to achieve even after extended equilibration times (a few hours). Only experiments carried out at elevated temperatures (>40 °C) approach equilibrium. As Polanyi's adsorption potential theory leads to a characteristic temperature-independent curve for an adsorbate-adsorbent system, it is possible to extrapolate equilibrium isotherms for all temperature ranges, a critical requirement for low-concentration adsorption applications. Applying this approach, we demonstrated that for temperatures lower than 40 °C, results from direct experimental measurements of L2 on Al-fumarate highly differ from the real adsorption capacities at equilibrium (Figure 1), and these differences are exacerbated for low concentrations.

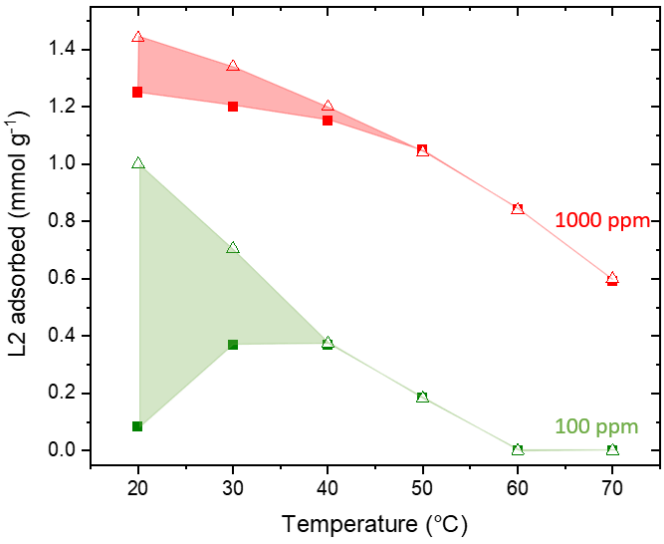


Figure 1: Comparison of adsorbed quantities of L2 on Al-fumarate at 20 °C obtained from direct experimental measurements (full square symbols) and by extrapolation using Polanyi's adsorption potential theory (empty triangle symbols). Colored areas highlight the differences between experimental and real adsorption capacities at equilibrium.

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LUMINESCENT MOF GLASSES VIA LIQUID PHASE MIXING WITH CHELATING ORGANIC LUMINOPHORE COLIGANDS

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Keywords: *metal-organic framework (MOF) glasses, circularly polarized luminescence (CPL), chirality, ZIF-62, BINAP*

In recent years, the search for metal-organic framework (MOF) glasses has emerged as a significant objective in material research because glassy MOFs exhibit outstanding performance in various applications, including mechanics, gas separation and catalysis[1]. However, studies on the optical properties of MOF glasses remain limited[2-4], so systematic investigations in these directions are of high importance for this developing area of materials chemistry. Over the past decade, chiral luminescent materials have received growing attention due to properties such as circularly polarized luminescence (CPL) and chiroptical switching, which are key for the development of emerging technologies in 3D imaging, 3D displays and quantum computing[5]. To date, the formation of MOFs glasses was demonstrated for a few meltable zeolitic imidazolate frameworks (ZIFs), a subfamily of MOFs based on divalent metal ions (i.e. Zn^{2+}, Co^{2+} or Fe^{2+}) and imidazolate-type linkers. Among ZIFs, ZIF-62 (chemical composition $M(im)_{2-x}(bim)_x$; M^{2+} = Zn^{2+} or Co^{2+}, im^- = imidazolate, bim^- = benzimidazolate, $x \leq 0.5$)[6] and its derivatives are of particular relevance due to their relatively low melting point (well below 400 °C for some derivatives), high thermal stability, mouldability of the liquid phase and transparency of the derived glass[7].

This work reports the design, synthesis and characterization of ZIF-62 glasses which are functionalized with chiral organic luminophores: (*R*)- and (*S*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP). We demonstrate how the liquid ZIF-62 can be employed as a matrix for chiral organic luminophores to derive luminescent ZIF composite glasses with interesting optical properties. Variable temperature powder X-ray diffraction, X-ray total scattering with pair distribution function analysis, IR spectroscopy, scanning electron microscopy, solution and solid-state nuclear magnetic resonance, extended X-ray absorption fine structure spectroscopy, thermogravimetric analysis and differential scanning calorimetry provide the first insights into the liquid phase blending the ZIF-62 with chiral organic luminophores, the structure and thermal properties of these new composite glasses. UV-Vis and luminescence spectroscopy reveal optical properties distinct from the pure ZIF glass and the pure organic luminophores, showcasing the utility of these luminescent composite glasses in optics and photonics.

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AN HETEROMETALLIC CU(II)−PD(II) MOF FOR CO_2 CAPTURE AND CH_4 STORAGE

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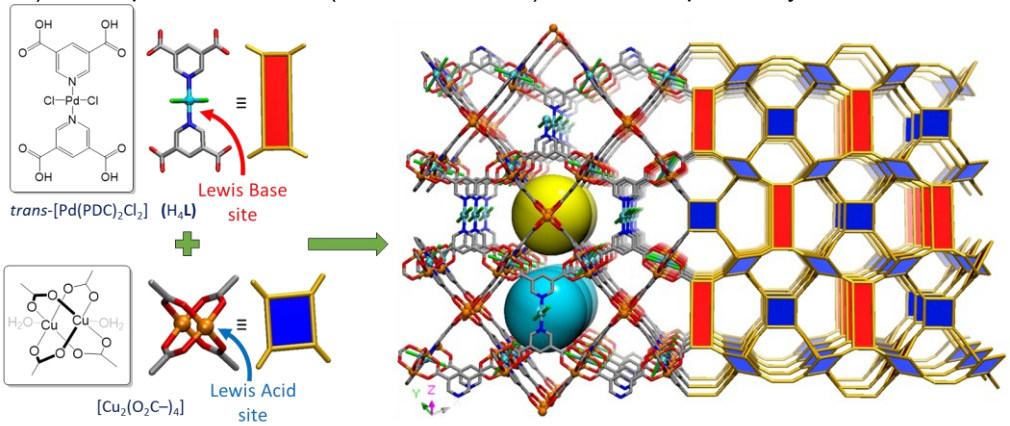
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Keywords: Metal–organic framework, *unsaturated metal sites, dynamic column breakthrough*

The presence of high-density strong binding sites within the porous framework of MOFs has proven to be an excellent approach for achieving enhanced performance in terms of gas uptake and selectivity [1]. Here we report on the thorough characterization and extensive investigation of the gas sorption and separation properties of a bimetallic Cu(II)-Pd(II) MOF with nbo-topology, designated hereafter as NbO-Pd-1´[2]. Its structure features a unique combination of Cu^{2+} open metal sites (Lewis acid sites) and exposed Pd^{2+} ions (Lewis base sites) that act cooperatively to enhance adsorption.



Ar (87 K) and N_2 (77 K) adsorption isotherms revealed reversible type-I adsorption isotherms, a pore size distribution centered at 9.5 Å, BET area of 1400 $m^2\ g^{-1}$ and total pore volume of 0.50 $cm^3\ g^{-1}$. A series of CO_2, CH_4 and N_2 adsorption measurements were performed using both gravimetric and volumetric techniques over a wide range of pressures (0-100 bar) and temperatures (100-300K), that allowed the determination of key thermodynamic and kinetic parameters. Indicatively, CO_2 sorption analysis revealed high gravimetric and exceptional volumetric capacities at 298 K and 19.5 bar, despite the rather modest specific surface area and total pore volume value, positioning NbO-Pd-1´ among the top-performing MOFs for CO_2 capture. The synergistic interaction between the Cu and Pd sites yields one of the highest CO_2 adsorption efficiencies per unit surface area among leading MOFs reported so far, highlighting the critical role of the presence of accessible metal sites in enhancing CO_2 affinity. On the other hand, CH_4 sorption studies demonstrated a high volumetric capacity at 65 bar and 298 K, achieving ~80% of the DOE target at 298 K (i.e. 263 cm^3 (STP) cm^{-3} at 65 bar), with NbO-Pd-1´ ranking among the best MOFs in CH_4 adsorbed phase density and adsorption capacity per unit surface area. Dynamic breakthrough experiments, corroborating theoretical predictions, further confirmed the capability of NbO-Pd-1´ for selective CO_2 adsorption as complete separation was achieved for CO_2/CH_4 and CO_2/N_2 mixtures under application-relevant conditions.Kinetic studies indicated rapid equilibrium for all measured gases, a key feature for achieving high productivity in swing adsorption processes, suggesting that the demonstrated separation behaviour occurs predominantly due to thermodynamic reasons.

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AN HETEROMETALLIC CU(II)−PD(II) MOF FOR CO_2 CAPTURE AND CH_4 STORAGE

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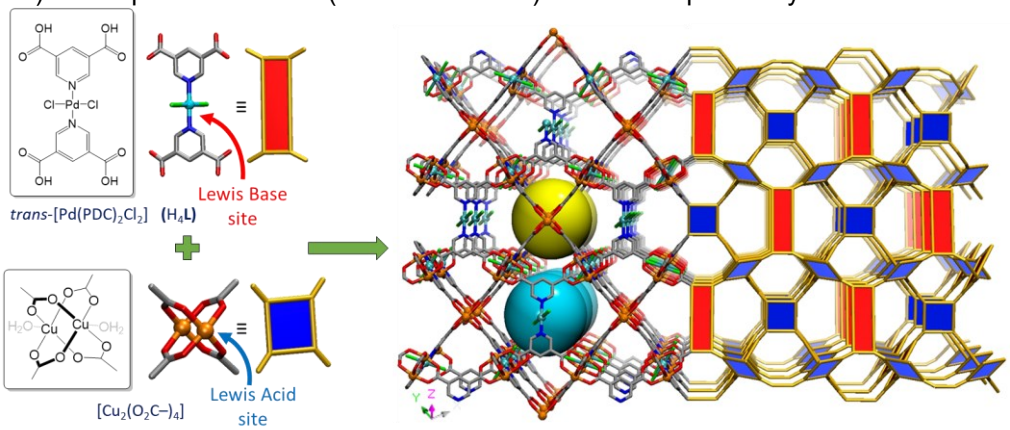
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Keywords: Metal–organic framework, *unsaturated metal sites, dynamic column breakthrough*

The presence of high-density strong binding sites within the porous framework of MOFs has proven to be an excellent approach for achieving enhanced performance in terms of gas uptake and selectivity [1]. Here we report on the thorough characterization and extensive investigation of the gas sorption and separation properties of a bimetallic Cu(II)-Pd(II) MOF with nbo-topology, designated hereafter as NbO-Pd-1´[2]. Its structure features a unique combination of Cu^{2+} open metal sites (Lewis acid sites) and exposed Pd^{2+} ions (Lewis base sites) that act cooperatively to enhance adsorption.



Ar (87 K) and N_2 (77 K) adsorption isotherms revealed reversible type-I adsorption isotherms, a pore size distribution centered at 9.5 Å, BET area of 1400 $m^2\ g^{-1}$ and total pore volume of 0.50 $cm^3\ g^{-1}$. A series of CO_2, CH_4 and N_2 adsorption measurements were performed using both gravimetric and volumetric techniques over a wide range of pressures (0-100 bar) and temperatures (100-300K), that allowed the determination of key thermodynamic and kinetic parameters. Indicatively, CO_2 sorption analysis revealed high gravimetric and exceptional volumetric capacities at 298 K and 19.5 bar, despite the rather modest specific surface area and total pore volume value, positioning NbO-Pd-1´ among the top-performing MOFs for CO_2 capture. The synergistic interaction between the Cu and Pd sites yields one of the highest CO_2 adsorption efficiencies per unit surface area among leading MOFs reported so far, highlighting the critical role of the presence of accessible metal sites in enhancing CO_2 affinity. On the other hand, CH_4 sorption studies demonstrated a high volumetric capacity at 65 bar and 298 K, achieving ~80% of the DOE target at 298 K (i.e. 263 cm^3 (STP) cm^{-3} at 65 bar), with NbO-Pd-1´ ranking among the best MOFs in CH_4 adsorbed phase density and adsorption capacity per unit surface area. Dynamic breakthrough experiments, corroborating theoretical predictions, further confirmed the capability of NbO-Pd-1´ for selective CO_2 adsorption as complete separation was achieved for CO_2/CH_4 and CO_2/N_2 mixtures under application-relevant conditions.Kinetic studies indicated rapid equilibrium for all measured gases, a key feature for achieving high productivity in swing adsorption processes, suggesting that the demonstrated separation behaviour occurs predominantly due to thermodynamic reasons.

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SWITCHABLE COOPERATIVE CO_2 ADSORPTION MECHANISM IN MULTIVARIATE MIL-140A(Ce) MOFs

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Keywords: *multivariate-MOFs, cooperative adsorption, flexibility, fluorination*

The concept of Multivariate MOFs (MTV-MOFs) relies on integrating diverse functionalities by combining multiple linkers, metals, or secondary building units within a single, well-ordered structure. The result is a fine control over tunable chemical environments and multifunctionality in a single material.[1] In this work, we bring the mixed-linker MTV concept to the phase-change F4_MIL-140A(Ce) MOF, proposing a fundamental study aimed at uncovering the structural requirements behind its peculiar CO_2-induced responsive behaviour (Figure 1).

Built from Ce^{IV} and tetrafluorobenzenedicaboxylate linker (F4-BDC), F4_MIL-140A(Ce) exhibits a cooperative CO_2 adsorption mechanism linked to concerted ring rotation, resulting in a non-hysteretic step-shaped adsorption isotherm. Such peculiar phenomenon is absent for gases like N_2, CH_4, and C_2H_2, resulting in high CO_2 selectivities over these gases.[2] Our recent findings reveal that the removal of a single fluorine atom from the MOF ligand suppresses CO_2-induced flexibility, with reduced steric demand from the less fluorinated linkers as the key factor improving accessibility to the Ce^{IV} sites, thereby eliminating the need for cooperative ring rotation to accommodate CO_2 and ultimately leading the partially fluorinated analogues (F*x*_MIL-140A(Ce), *x* = 2, 3) to exhibit classic Langmuir-type I adsorption profiles.[3]

However, it remains an open question whether the CO_2-induced concerted ring rotation depends on a specific fluorination threshold and whether the position of the fluorine atoms on the aromatic ring plays a role. To answer these questions, we developed a series of F4:F*x*_MIL-140A(Ce) architectures by systematically tuning the F4-H_2BDC:F*x*-H_2BDC ratios (*x* = 1, 2, 3), thereby precisely modulating the degree of fluorination at the molecular level. PXRD analysis confirmed the formation of single-crystalline MIL-140A phases across the series, confirming the solid solution nature of these mixed-linker materials. Interestingly, we found that even small amounts of F4-H_2BDC were sufficient to direct the formation of pure MIL-140A phases, enabling access to the MIL-140A phase even for ligands that typically do not yield it under the same synthetic conditions. The CO_2 adsorption isotherms reveal that the cooperative CO_2 adsorption is retained when the average degree of fluorination of the organic linkers exceeds 80%. Notably, regardless of the identity of the linker used alongside F4-H_2BDC, the step in the isotherm consistently occurs at the same pressure.

Altogether, our results reveal that the linker perfluorinated structure is central to triggering the cooperativity in MIL-140A(Ce), and by tuning the fluorination degree, such responsiveness can be selectively activated or suppressed, allowing for a tailored and switchable gas adsorption behaviour.

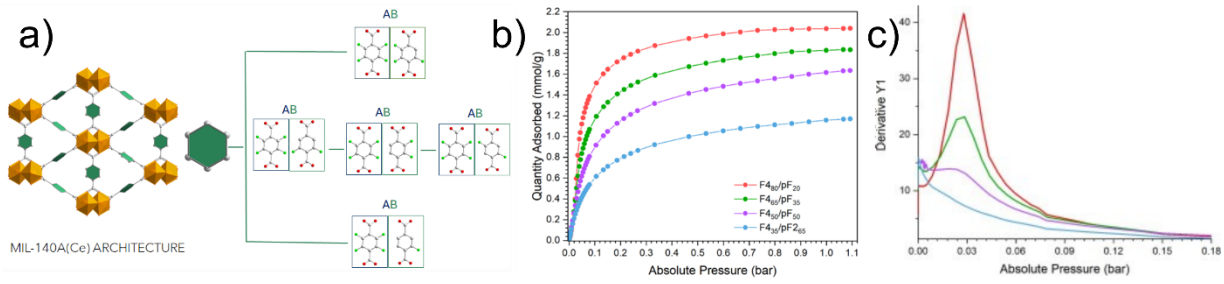


Figure 1. Mixed-linker F4:F*x*_MIL-140A(Ce) a); CO_2 adsorption isotherms of F4:*p*F2_MIL-140A(Ce) at different F4/*p*F2-BDC ratios b); first derivative of CO_2 adsorption isotherms c)

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STRUCTURED MOF-BASED HYBRID ADSORBENTS FOR POST-COMBUSTION CO_2 CAPTURE BY VACUUM/PRESSURE SWING ADSORPTION

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Keywords: *MOF structuring, vacuum/pressure swing adsorption, techno-economic optimization*

MOF-based hybrid adsorbents for carbon capture are gaining increased attention as they can enhance key performance properties and scalability of MOFs [1]. However, their application in large-scale settings under continuous flue gas flow is hindered by processing issues such as dustiness, clustering, and pressure drops in fixed bed columns associated with their micro-crystalline powder nature. Therefore, shaping micron-sized polycrystalline MOF powders into structured forms of millimeter dimensions while preserving porosity and functionality represents an effective yet challenging approach to address these drawbacks [2]. In this work, a water-stable MOF (MIL-101(Cr)) was hybridized with graphene oxide (GO) yielding a hybrid adsorbent with enhanced CO_2 capture performance, and the hybrid was then structured into millimeter-sized hierarchically porous polymer-based beads with ultra-high MOF loading for direct industrial carbon capture applications using a facile and scalable method [2]. The powdered hybrid adsorbent with an optimum GO loading of 6 wt.% exhibited a 55% higher CO_2 adsorption capacity and a 48% higher CO_2/N_2 selectivity than those of the parent MOF at 298 K and 1 bar, while the structured analogue retained the physicochemical characteristics and CO_2 capture performance of the individual MOF crystals. A dynamic simulation of a cyclic Vacuum/Pressure Swing Adsorption (V/PSA) process, targeted at CO_2 capture and compression from the flue gas emitted by a coal-fired power plant, was executed considering the resulting structured adsorbent and compared with other structured MOFs (ZIF-8 and UiO-66) [3,4]. This simulation was grounded in a detailed mathematical model, developed and run within gPROMS software, and its accuracy was validated against experimental data. Parametric sensitivity analyses were performed, and the V/PSA process was optimized to maximize CO_2 purity and recovery while minimizing costs. The resulting structured MOF hybrid adsorbent, cost-optimal operating conditions, module configuration, and train schedule of the V/PSA-based CO_2 capture will be presented and discussed.

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DIRECT GROWTH OF METAL-ORGANIC FRAMEWORKS ON GEOPOLYMERS: A NOVEL APPROACH FOR THE SHAPING OF POROUS MATERIALS

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Keywords: Metal-Organic Frameworks, Direct growth, Geopolymers

Metal-organic frameworks (MOFs) are well known for their high porosity, tunable pore structures or their exceptional gas sorption properties, making them promising candidates for a variety of applications. Nevertheless, their integration into practical applications faces challenges, particularly in terms of immobilization on substrates (shaping).

This study introduces an innovative approach for the direct growth of MOFs on a geopolymer support, a class of amorphous aluminosilicate materials known for their excellent mechanical strength and chemical stability. By taking advantage of the reactive nature of the geopolymer matrix, we achieve MOF nucleation and growth through a simple and scalable synthesis process in one-step.

The direct growth method of the well-known UiO-66, a Zr-based MOF, has been developed and the final material has been evaluated for gas sorption (CO_2 and N_2O) showed in **Figure 1**.

Our results demonstrate the feasibility and versatility of MOF-geopolymer composites, showing the way for the development of advanced adsorbent materials with tailor-made functionalities for a variety of environmental and potentially industrial applications.

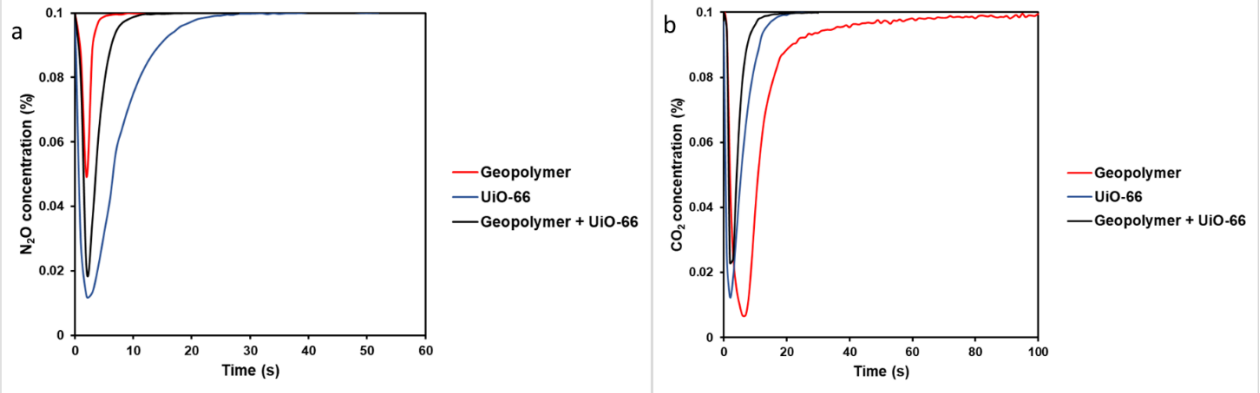


Figure 1 : Breakthrough curve (A) N2O sorption and (B) CO2 sorption.

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AN ADAPTIVE METAL-ORGANIC FRAMEWORK DISCRIMINATES XYLENE ISOMERS BY SHAPE-RESPONSIVE DEFORMATION[1]

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Keywords: *adsorption separation, xylene isomers, MOFs, flexibility, shape-responsive*

The separation of xylene isomers, especially para-xylene, is a crucial but challenging process in the chemical industry due to their similar molecular dimensions. Here, a flexible metal–organic framework, $Ni(ina)_2$, (ina = isonicotinic acid) is employed to effectively discriminate xylene isomers. The adsorbent with adaptive deformation accommodates the shapes of isomer molecules, thereby translating their subtle shape differences into characteristic framework deformation energies. Through a combination of multiple local flexibility behaviors, $Ni(ina)_2$ exhibits guest-specific structural transformations that energetically favor para-xylene over other isomers. Single-crystal X-ray diffraction, in situ powder X-ray diffraction, and theoretical investigations validate this “adaptive fitting” mechanism, where the degree of structural deformation scales with the mismatch between the molecular shape and pore geometry. As a result, $Ni(ina)_2$ achieves exceptional para-xylene selectivity in both liquid and vapor phase separations, maintaining a high para-xylene purity and productivity. This work demonstrates a novel strategy of exploiting framework flexibility to address challenging molecular separations.

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TOPOTACTIC CONVERSION OF TITANIUM-OXO CLUSTERS (TOCS) TO A STABLE TOC-BASED METAL–ORGANIC FRAMEWORK WITH SELECTIVE ADSORPTION OF CATIONIC DYES

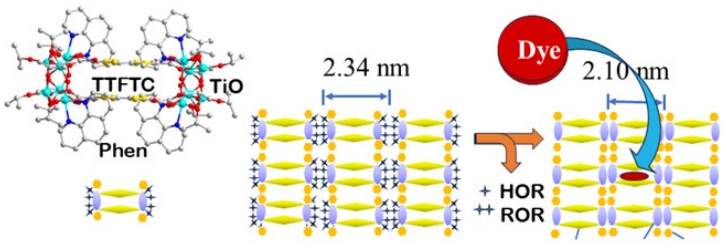
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Keywords: *titanium-oxo-cluster, MOF, adsorption*

Titanium-oxo clusters (TOCs) have attracted considerable attention because they can be used as precursors to prepare titanium-oxo materials for various applications. TOC-based MOFs combine the outstanding features of TOCs with the intrinsic properties of MOFs and extend the application of TOCs to fields that require highly stable and porous frameworks. Generally, the preparation of TOC-MOFs uses separate TOCs to react with the organic linker. However, due to the extreme reactivity of titanium precursors and the ligand coordination space requirement, there have been only a few TOC-MOF examples (in the crystalline state) after more than 10 years of continuous effort. Therefore, the development of different approaches for TOC-MOFs is urgently needed. Very recently, Yaghi et al. prepared a series of TOC-MOF glasses (TOC-MOFs in glass state), groundbreaking the morphology and concept of classic TOC-MOFs[1]. Topotactic conversion has been used to prepare oriented TiO_2 materials using titanate as a presusor[2]. To the best of our knowledge, there have been no reports on the preparation of TOC-MOFs using the topotactic conversion of TOC itself. The key challenge is utilizing functional ligands to regulate the stability and configuration of clusters. In this work, we present a new strategy for the topotactic conversion of ligand-modified TOCs for the preparation of two-dimensional (2D) TOC-MOF. Herein, tetrathiafulvalene-tetracarboxylate (TTFTC) and phenanthroline (phen) were chosen as functional ligands to construct a new TOC. TTFTC was selected because of its ability to serve as a linker for constructing a cyclic structure and because of its key role in adsorption, and the introduction of phen is anticipated to replace some isopropanol groups and to modulate the configuration of TOCs. A rectangular ring TOC, formulated as $[Ti_6O_6(O^iPr)_8(TTFTC)(phen)_2]_2$ •6THF•$2CH_2Cl_2$•$2C_3H_7OH$ (**1**, TTFTC-Ti_{12}, TTFTC = tetrathiafulvalene-tetracarboxylate), was crystallographically characterized. An intracluster ligand-to-ligand (TTF-to-phen) charge transfer was found in **1** for TOCs for the first time. The orientation of phen and the strong chelation of phen and TTFTC with the TiO cluster enable **1** to undergo topotactic conversion through the condensation of isopropanol groups without destroying the ring structure, thus forming a stable TOC-MOF P**1**, as verified by comprehensive characterization. The atomic-level information for P1 was obtained via titanium K-edge extended X-ray absorption fine structure analysis (Ti-EXAFS), which indicate that the TiO structure in P**1** was similar to that in **1** and differs from that in TiO2, suggesting that the TOC core in **1** remained basically in P**1**. P**1** effectively adsorbs cationic dyes, especially crystal violet (CV), with an experimental adsorption capacity (qex) of up to 789.2 mg/g at 298 K. Such a high value has rarely been reported. Moreover, P**1** can rapidly and selectively adsorb CV dye from mixed dyes. The structure–property relationship of the cyclic hosts to guest dyes was discussed based on the crystal structures and the calculated models.



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MICROPOROUS POLYIMIDE AEROGELS: MULTISCALE POROSITY FOR EFFICIENT CO_2 SEPARATION

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Keywords: *Carbon capture, hierarchical structures, porous organic polymer network*

The ongoing issue of climate change is closely correlated with the increase in the atmospheric CO_2 concentration.[1] This underlines the necessity for the development and implementation of carbon capture technologies. A promising approach is the utilization of porous solid adsorbents for carbon capture via physisorption. In this context, microporous organic polyimides (MOPIs) stand out as a group of materials with outstanding potential. Due to their large proportion of ultramicropores, MOPIs exhibit a particularly high affinity towards CO_2, thereby enabling the effective separation of CO_2 from gas mixtures.[2]

One challenge of these materials is the low rate of gas diffusivity within the ultramicropores leading to limited mass transport.[3] A possible solution is the implementation of continuous multiscale porosity to enhance the accessibility of the ultramicropores. Our previous work demonstrated two approaches to create hierarchical structures in MOPIs, one involves a volatile solvent to crate bubbles within the material, the other method utilizes electrospinning to fabricate a nonwoven with multiscale porosity.[4,5] There are many more approaches reported in literature ranging from hard templating to 3D-printing.[6] One promising approach which has not yet been employed for this class of materials is supercritical drying. In this work, we utilized supercritical drying with CO_2 to fabricate an aerogel with multi scale porosity using the literature known MOPI-system MOPI-IV as a model compound.[2]

The preparation of the MOPI-IV aerogel follows a well-established synthesis. The resulting gel was activated by solvent extraction followed by supercritical drying with CO_2 to prevent the collapse of the gel network. The resulting MOPI-aerogel was characterized by XRD, solid-state-NMR, SEM and dynamic and static physisorption experiments, confirming the successful formation of an amorphous, ultramicroporous network. Static physisorption experiments reveal high surface area and good CO_2 capacity and selectivity towards N_2. Dynamic column break through experiments indicate that the multi scale porosity of the MOPI-aerogel has a positive influence in the separation performance of the material. A comparison with an air-dried sample confirms that the supercritical drying process successfully introduced a significant amount of mesopores while simultaneously not affecting the ultramicroporosity. SEM-images reveal the hierarchical structure of the material showing small particles (~50 nm diameter) that are connected with each other to form an open pore network with large windows.

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THERMAL MANAGEMENT IN MOFS THROUGH HIGH-CONDUCTIVITY GRAPHITE INCORPORATION

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Keywords: *Hydrogen adsorption, MOFs, Graphite flakes, thermal conductivity*

Hydrogen is widely recognized as a key energy carrier for the development of sustainable technologies, primarily due to large amount of energy stored in this molecule (in gravimetric basis; 120 kJ/g), and the benefits of the reaction products, i.e. H_2O when used in fuel cells.[1] However, its practical application is severely limited by its low volumetric energy density, even under highly compressed conditions, which poses a significant challenge for its storage. Solid-state storage using porous adsorbents has emerged as a promising strategy to enhance volumetric efficiency under moderate pressure conditions. Among the available materials, metal-organic frameworks (MOFs) stand out due to their exceptionally high surface area, tunable pore structure, and favorable adsorption properties.[2] Despite these advantages, adsorption/desorption processes are accompanied by significant thermal effects, i.e., adsorption is exothermic while desorption is endothermic, resulting in temperature spikes during charging and discharging cycles. Effective heat dissipation is therefore essential to maintain system's efficiency. Unfortunately, many MOFs suffer from inherently low thermal conductivity (below 2 W m−1 K−1),[3] limiting their ability to handle these temperature variations. Moreover, their mechanical and structural stability under compression or shaping is often inadequate for practical use.[4] To address these limitations, the incorporation of thermally conductive additives such as graphite flakes has proven effective in enhancing both thermal management and mechanical robustness.[5] In this work, we aim to develop MOF-based composites with improved thermal conductivity through graphite integration, providing a pathway toward more efficient and resilient hydrogen storage systems.

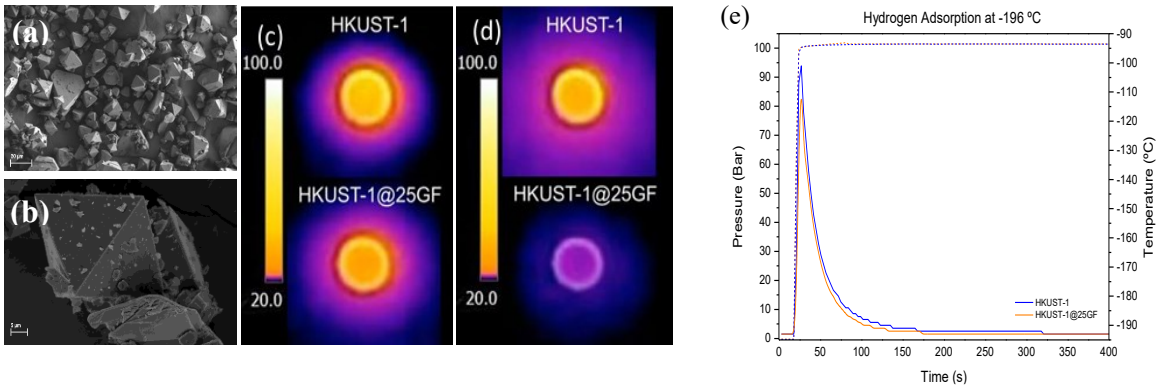


Fig. 1. FESEM images of pure HKUST-1 (a) and its composite (b). Snapshots of the thermogravimetric camera in the cooling process upon thermal heating on a ceramic surface at (c) t = 0s and (d) t = 10s, and (e) comparison of the thermal effects in both materials upon hydrogen adsorption.

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INVERSE GAS CHROMATOGRAPHY STUDY OF N- AND BRANCHED ALKANE ADSORPTION ON CAU-10-CH_3

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Keywords: *adsorption, inverse gas chromatography, Henry constant, shape selectivity*

Rising energy consumption and industrial activities have prioritized air pollution regulation for many countries and organizations. Volatile organic compounds (VOCs), significant air pollutants from industrial processes, household products, and construction materials, pose severe threats due to their toxicity and carcinogenic properties. Adsorption is an efficient method for the removal of such VOCs.

In this work, inverse gas chromatography (IGC) was used to study the adsorption of a range of organic compounds on the MOF CAU-10-CH_3 at very low concentration. IGC is an effective method for characterizing the surface properties of porous solids, requiring minimal sample preparation and offering shorter experimental times compared to other techniques[1].

The Al based MOF CAU-10-CH_3, consists of infinite helical chains of cis-connected, corner-sharing AlO_6 octahedra, which are connected into a 3-D framework by 5-methylisophthalate anions. CAU-10-CH_3 has high thermal stability up to 350°C and a pore size of 5.9 Å [2]. This MOF was synthesised according to the method described by Reinsch et al. [2].

First of all, our findings reveal an unusual nonmonotonic increase of Henry adsorption constants with the carbon number for *n*-alkanes, marked by a local minimum, signifying the presence of a chain coiling effect due to a combination of strong entropic and energetic effects (Figure 1). This effect is a result of the combination of small pores connected by larger cages and was reported before for small pore zeolites such as CHA-type zeolite [3].

Secondly, CAU-10-CH_3 also demonstrates significant selectivity in adsorption of *n*-alkanes and branched alkanes. The size of the pores and the shape of the molecules guide to this shape and size selectivity. In most cases, the less bulky isomers are adsorbed preferentially in terms of adsorption equilibrium and kinetics. This is also the case for isomers of hexane, heptane and octane on CAU-10-CH_3 (Figure 2). But remarkably, CAU-10-CH_3 shows inverse shape selectivity for smaller isomers, e.g. with 2-methylbutane being selectively adsorbed over *n*-pentane [4]. The confined pore space of this methyl-functionalised MOF thus offers interesting perspectives for specific, shape selective molecular separations.

To distinguish shape-selective adsorption from differences in adsorption based on physicochemical parameters, the Henry-adsorption constant is plotted against the boiling point (Figure 3). In nonselective adsorption, a linear trend is expected, with *n*-alkanes, iso-alkanes, and aromatics aligning along a single line [5]. However, as shown in Figure 3, no such correlation is observed, due to the specific pore system of this MOF. In this paper, the observed tendencies will be discussed in terms of molecular and adsorbent properties.

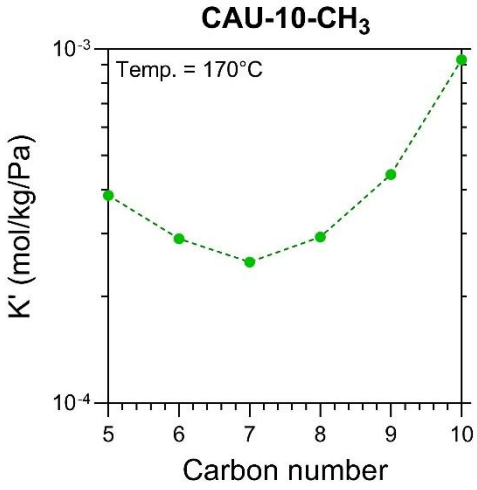


Figure 1. Henry constant as a function of carbon number for CAU-10-CH_3 at 170 ˚C.

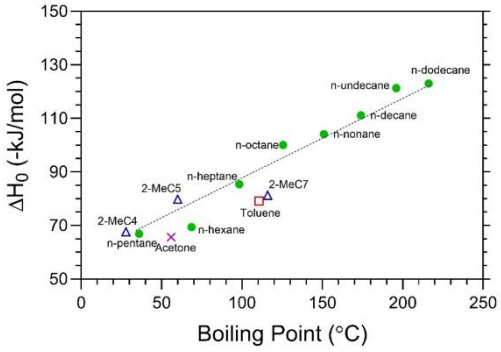


Figure 2. Adsorption enthalpy as a function of boiling point on CAU-10-CH_3.

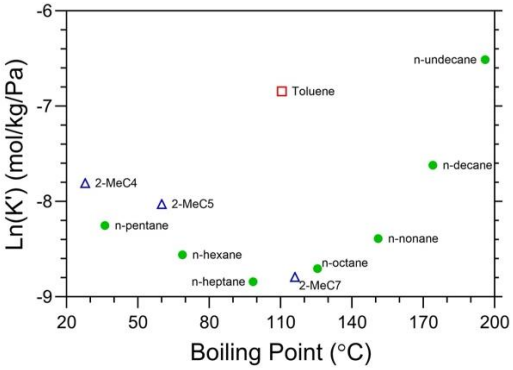


Figure 3. logarithm of Henry adsorption constant (at 180°c) as a function of boiling point on CAU-10-CH_3.

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ADSORPTIVE SEPARATION OF WATER-ALCOHOL MIXTURES USING POROUS COORDINATION POLYMER

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Keywords: *Separations, molecular sieves, dehydration, porous coordination polymers*

Industrial separation processes, such as the purification of chemicals and fuels, often rely on energy-intensive distillation, which accounts for a significant fraction of global energy consumption [1]. Adsorption-based separation techniques offer a promising alternative, potentially reducing energy demands by an order of magnitude [2]. We report a water-born, peptide-based coordination polymer (Figure 1A) that exhibits highly selective water adsorption from aqueous alcohol mixtures (Figure 1B) [3]. This material enables for the first time the efficient separation of water(H_2O)/methanol(MeOH) mixtures and even the challenging water/ethanol azeotrope through a precise molecular sieving mechanism. The performance of the adsorbent is demonstrated through dynamic vapor-phase adsorption measurements, revealing its exceptional selectivity and recyclability (Figures 1C, 1D). Comprehensive structural characterization, coupled with theoretical calculations, elucidates the underlying mechanism of water adsorption, highlighting the role of hydrogen bonding and host-guest interactions in driving this unique selectivity.

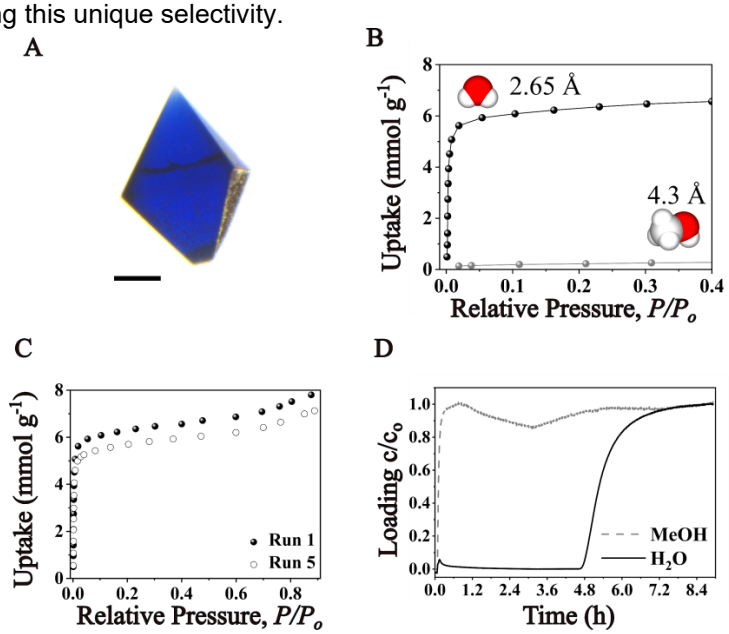


Figure 1 (A) Representative optical microscope image of the single-crystalline peptide-based coordination polymer (scale-bar 20 µm). (B) Single component vapor adsorption isotherms for Water (black) and Methanol (grey) vapors (inset: kinetic diameters for the respective molecules). (C) Water vapor adsorption isotherms before (Run 1) and after (Run 5) multiple sorption cycles of common alcohols. (D) Multi-component dynamic vapor-phase adsorption measurement of a 95.5:4.5 mixture of MeOH:H_2O.

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BOOSTING ETHANE/ETHYLENE SELECTIVITY AND ETHANE UPTAKE THROUGH CF_3-ENGINEERED UIO-66 FRAMEWORKS

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Keywords: *Metal-organic framework (MOF), Fragmented linker, adsorption, ethane, ethylene*

Ethylene (C_2H_4) is one of the most important industrial chemicals, serving as a crucial raw material for plastics and numerous other chemical products. Energy-efficient production of high-purity ethylene involves the adsorptive separation of ethylene from ethane, utilizing ethane-selective adsorbents with high C_2H_6/C_2H_4 selectivity, substantial ethane adsorption capacity, and easy ethane regeneration. In this work, we synthesized a series of novel metal-organic framework (MOF) materials (UiO-66-nCF_3, n = 25, 50, 60, and 75) using CF_3-functionalized fragmented linkers at varying ratios. Among these materials, UiO-66-50CF_3 exhibited outstanding performance, achieving a high C_2H_6/C_2H_4 selectivity (2.04) and an impressive ethane uptake (2.5 mmol/g). Furthermore, UiO-66-50CF_3 demonstrated excellent breakthrough separation performance, maintained good stability, and exhibited strong cyclability over 10 consecutive cycles, highlighting its potential applicability in practical adsorption processes[1].

Acknowledgements

This work was supported by the Korea Environment Industry & Technology Institute (KEITI) through the Center of plasma process for organic material recycling Project, funded by the Korean Ministry of Environment (MOE) (2022003670001). This work was also supported by a grant from the National Research Foundation of Korea (NRF) funded by the Korean government (MSIT) (RS-2023-00302697).

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SELECTION AND CHARACTERIZATION OF SOLID SORBENTS FOR APPLICATION IN POST-COMBUSTION CARBON DIOXIDE CAPTURE

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Keywords: *solid sorbent, post-combustion carbon dioxide capture*

Post-Combustion Carbon Dioxide Capture (PCC) is one of the technologies to capture carbon dioxide (CO_2) from fossil-fuel based power plants. A typical composition of the flue gas is 15 to 16 percent (%) concentration of CO_2 from flue gas, 73 to 77 % nitrogen gas (N_2), 5 to 7 % of water, 3 to 4 % of oxygen gas (O_2), and parts per million (ppm) of toxic gas (CO, NO_x, SO_x) at 40 to 60 ^oC under ambient pressure (1 atm). [1]-[3] The challenges of CO_2 capture by thermal swing adsorption processes lie in the identification of appropriate sorbent materials, possessing high efficiency and high durability under operating conditions. Various parameters need to be considered and investigated, when aiming for a high CO_2 capture performance, namely CO_2 selectivity, working capacity, sorption kinetics, thermal and chemical stability / tolerance to impurities and regeneration of sorbent, cycling performance test. In this work, CO_2 adsorption uptake of different adsorbent materials including ceramic, polymer, and metal organic framework (MOFs) studied by volumetric adsorption (single gas adsorption), gravimetric adsorption (co adsorption of gases) and breakthrough rig**.** Furthermore, the stability of the materials was investigated by thermal gravimetric analysis (TGA), powder x-ray diffraction (PXRD), fourier transform infrared spectroscopy (FTIR) and a scanning transmission electron microscopic (STEM) mode equipped with an energy dispersive X-ray spectroscopy (EDS) considering the conditions for the high temperature regeneration process and for simple stability of the sorbents in steam or water atmosphere.

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TUNING PORE SIZE OF MIL-101 AND ITS INFLUENCE ON WATER ADSORPTION KINETICS

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Keywords: *MIL-101, Water adsorption, Defect, Linker substitution*

Metal-organic frameworks (MOFs) are a group of porous crystalline materials composed of various metal nodes and organic linkers, which realize diverse framework structures and pore network structures. The adsorption properties of MOFs have been extensively studied, and they are expected to be applied in various industrial fields. Countless combinations of metal nodes and organic linkers for MOF synthesis enable us to tune their adsorption properties.

The water adsorption properties of MOFs attracted attention, as some MOFs exhibited higher water uptake or faster water adsorption rate than conventional materials such as silica gel or zeolites, which are currently used in industrial fields for dehumidification. The water adsorption rate is one of the most important factors determining the performance of dehumidification devices. Faster adsorption rate can enhance device processing performance and add value by improving their adaptability to dehumidification for larger air volume. To improve the performance of dehumidification devices, the development of water adsorbents with both high water uptake and fast adsorption rate is required.

MIL-101(Cr) is one of the promising MOFs for dehumidification applications due to its great water uptake and fast adsorption rate[1]. Trivalent chromium ions and terephthalate ligands in MIL-101(Cr) form three different size cages, which are available for water adsorptions in its crystal structure[2][3]. The water adsorption property of MIL-101(Cr) has been tailored by substituting functionalized linkers. The proportion of functionalized linkers to the original terephthalate ligands and their hydrophobicity influenced the maximum uptake of water and adsorption pressure of MIL-101(Cr)[4][5]. These characteristics are substantially beneficial to design adsorbents for high-spec dehumidification devices.

In this study, we explored substituted linkers of MIL-101(Cr) to expand the pore size for faster water diffusion in MIL-101(Cr). We will discuss the relationship between water adsorption rate and tuned pore size distribution of MIL-101(Cr).

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Thorough Characterisation of a Series of Ultra-microporous MOFs FOR HYDROGEN STORAGE AND ISOTOPE SEPARATION

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Keywords: *MOF, hydrogen storage, isotope separation …*

Ultra-microporous Metal Organic Frameworks (pore sizes smaller than 0.7nm) have gained prominence among DAC adsorbents due to their high porosity and reversible CO_2 adsorption at low concentrations [1].

H_2/D_2 isotope separation [2] has generated global interest because of the vast applications of D_2 in the pharmaceutical industry, nuclear energy, and fundamental research. The classical separation technique based on size-based exclusion is ineffective for isotopes given their nearly identical diameter, shape, and chemical properties. Conventional separation approaches (cryogenic distillation, Girdler Sulfide process) are energy and time-consuming with low separation factors. As a promising alternative, kinetic quantum sieving (KQS) based on nanoconfined space was first proposed in 1995 by Beenakker et al [3]. Oh, et al [4] experimentally determined the optimum pore aperture for quantum cryo sieving to be in the range of 0.3nm-0.34nm.

Therefore, to explore the potential for hydrogen storage and isotope separation, we investigated a series of ultramicroporous MOFs. At first, the materials were characterized using Argon isotherm data at 87K to get detailed information about their pore structure and pore size [5]. Then, low-temperature hydrogen and deuterium isotherms have been measured to assess framework flexibility. Alongside, high pressure hydrogen isotherms were recorded to draw a structure-property relationship directly.

Finally, isotope separation performance has been studied using the Thermal Desorption Spectroscopy technique. In this method, a small (typically 3-5 mg) amount of sample is exposed to a gas or isotope mixture at a pressure (Pexp) for a time (texp) at a constant temperature (T_{exp}). Following exposure, the remaining gas molecules are removed by evacuating the sample chamber to achieve high vacuum conditions. Finally, a linear heating ramp (0.1 K/s) is applied to activate desorption, and the desorbing molecules are detected continuously by the quadrupole mass spectrometer [6]. The amount of desorbed gas molecules is proportional to the area under the desorption peak after careful calibration of the instrument with $Pd_{95}Ce_5$ alloy. These findings will be explored further in the poster.

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PORE SIZE ENGINEERING OF NH_2-UIO-66 VIA MODULATING AGENTS: IMPLICATIONS FOR ENHANCED CO_2 ADSORPTION

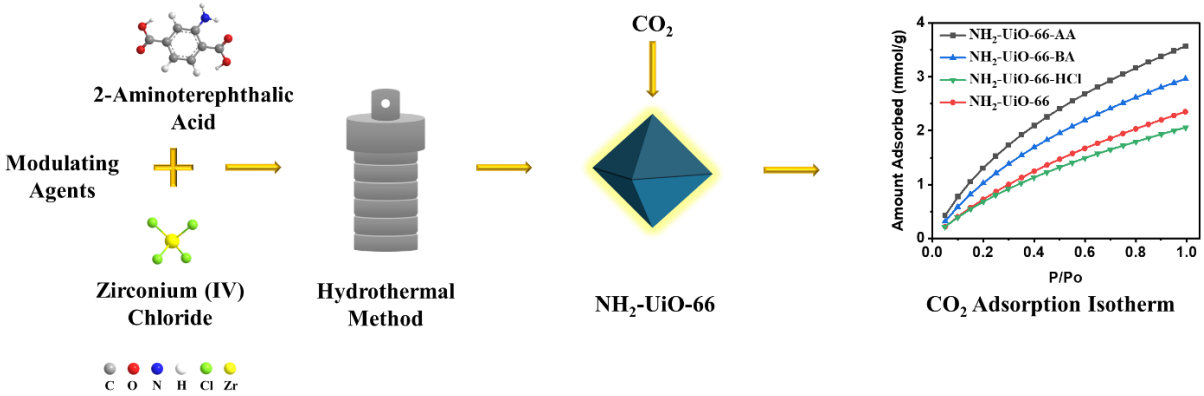
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Keywords: NH_2-UiO-66-X, Metal Organic Frameworks (MOFs), Modulating agents, CO_2 adsorption

The rapid increase in the concentration of atmospheric CO_2 has gained the attention of the scientific community for the development of advanced porous material with efficient CO_2 capture and separation capabilities [1]. Among them, amine functionalized UiO-66, a subclass of Metal Organic Frameworks (MOFs) has emerged as a promising porous material due to its thermal and chemical stability, and its affinity to absorb CO_2 [2-3]. However, the pore size engineering of MOFs remains challenging due to the lack of standard synthesis protocols for precise pore size control. This work explores the role of various organic and inorganic modulating agents in controlling the pore size and structural defects, which impacts the overall CO_2 adsorption behavior. A series of NH_2-UiO-66-X (X represents the various modulating agents) is synthesized via solvothermal method using different modulating agents. The crystal structure and morphology of NH_2-UiO-66-X were analyzed by XRD, FESEM. The functional and textural characteristics were analyzed by FTIR spectroscopy and BET techniques. The CO_2 adsorption capacity was evaluated using a gas sorption analyzer at 298 K across a pressure range between 30 to 760 torr. Additionally, the thermodynamic parameters were estimated by studying the adsorption of CO_2 at different temperatures (25, 40, and 60 °C). Among the various MOFs studied, acetic acid modulated NH_2-UiO-66 exhibits the highest CO_2 adsorption capacity of 3.56 mmol/g at 25 °C and 760 torr pressure. This study offers an inside into a rational design strategy for enhanced CO_2 adsorption capacity, influence of modulating agents, their concentration on crystallinity, porosity, and surface functionality of the MOFs.



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TUNING GATE-OPENING PRESSURE IN FLEXIBLE ZEOLITIC IMIDAZOLATE FRAMEWORKS FOR INVERSE OLEFIN/PARAFFIN SEPARATION

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Keywords: *zeolitic imidazole framework, flexible MOF, gas separation, olefin purification*

The industrial production of polypropylene requires a flow of the starting monomer propylene with a very high purity. To do so, it is separated from its parafin counterpart propane in the very energetic-demanding cryogenic distillation process[1]. The use of efficient sorbents to selectively capture the parafin (propane) from the olefin/paraffin (propylene/propane) mixture is a convenient alternative to distillation, and this can be attained by the use of flexible metal organic frameworks (MOFs).[2] In this work, we explore the ZIF-7 MOF containing Zn^{2+} ions and benzimidazole linkers yielding a sodalite type structure (Fig. 1a). This MOF show gate opening phenomena with increasing gas pressures, which can be leveraged to efficiently separate paraffins in a pressure swing adsorption (PSA) process.[3] We explore isoreticular systems with different metals (*e.g.* ZIF-9, containing Co^{2+}) and with different functionalized ligands post-synthetically introduced (Fig. 1b), in order to change the gate opening pressures and thus optimize olefin/paraffin separation. Some of our results have shown that the use of Co^{2+} as node allows to move the gate opening pressures to higher values, which would reduce the energy input for PSA. Overall we present a very versatile technology to prepare and tune selective sorbents that can efficiently separate gases under the desired conditions.

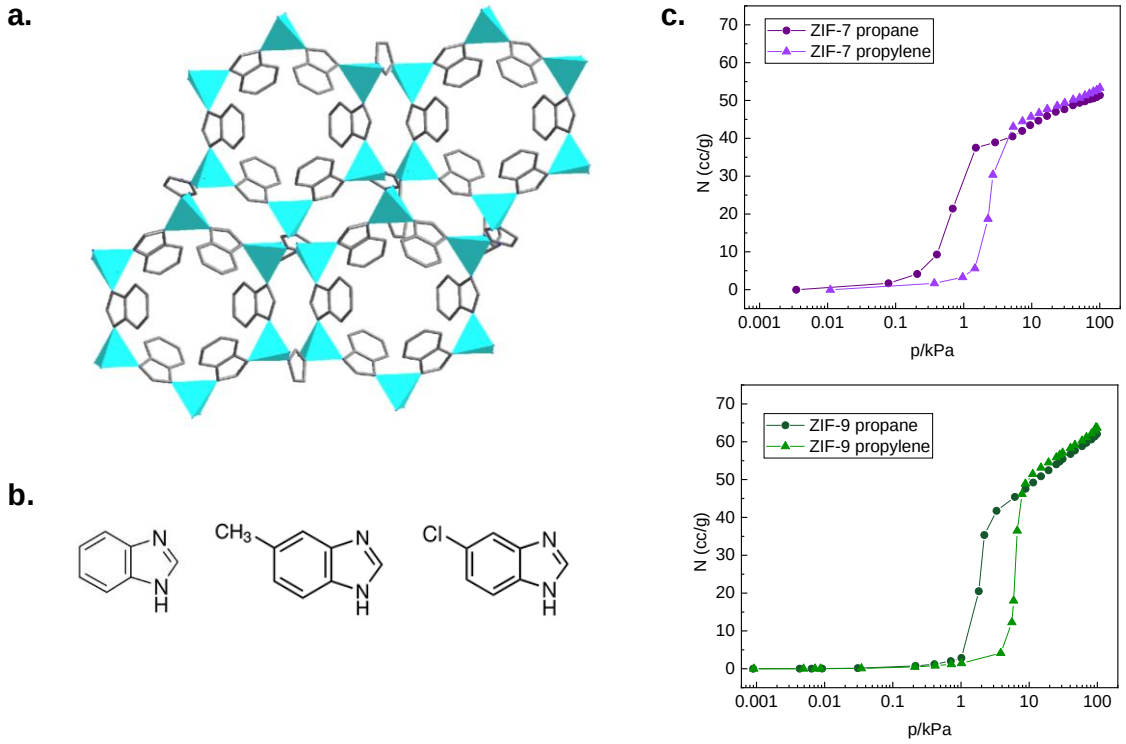


Figure 1. (a) ZIF-7 3D **sod** structure. (b) Benzimidazole linker and functionalized 5-methylbenzimidazole and 5-chlorobenzimidazole. (c) Propane and propylene adsorption isotherms for ZIF-7(Zn) and ZIF-9(Co).

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NANOSTRUCTURED METAL-ORGANIC FRAMEWORK PERCOLATION NETWORKS FOR CHEMIRESISTIVE GAS SENSING VIA POLYSTYRENE NANOPARTICLES

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Keywords: *Nanostructure, percolation networks, metal-organic frameworks, gas sensing*

The practical deployment of conductive metal-organic frameworks (c-MOFs) in chemiresistive gas sensors is often constrained by low sensitivity, particularly when thick films are used. Although c-MOF nano-thin films have been explored to enhance performance,[1] their restricted surface area and inefficient gas diffusion pathways have resulted in only modest improvements.

In chemiresistive gas sensors, percolation theory explains how sensor sensitivity is enhanced by tuning the sensing material to operate near the percolation threshold.[2] Percolation phenomenon refers to the sharp increase in electrical conductance that occurs when the amount of conductive material surpasses a critical concentration during deposition (Figure 1a). By engineering the material to be close to this threshold, even small changes in conductive pathways—such as those induced by gas adsorption—can produce a significant influence on conductivity. This strategy can be achieved by fine-tuning bottom-up deposition parameters to precisely control the formation of percolation network.

In parallel, template-assisted nanostructuring is a common technique for fabricating nanostructured materials with precise control over morphology and internal architecture. By using templates like polystyrene nanospheres, well-defined hollow or porous structures can be formed through material deposition and subsequent template removal. This strategy has been widely applied in creating sensitive sensors from polymers and c-MOFs.[3]

Herein, we developed nanostructured $Cu_3(HHTP)_2$ percolation networks by integrating bottom-up electrochemical deposition with top-down template-assisted nanostructuring techniques. By varying the deposition times, sensors with differing growth stages and electrical conductivities were obtained. Porous and hollow structures were formed by utilizing the polystyrene template. Figure 1b presents an SEM image of the nanostructured $Cu_3(HHTP)_2$ percolation network prepared over 90 seconds on Pt interdigitated electrodes with 5-μm gaps. The response-recovery curve to ammonia ranging from 0.5 to 5 ppm for the optimal sensor is depicted in Figure 1c. As illustrated in Figure 1d, the sensor exhibits a remarkable response of 68.17% ± 4.58% to 5 ppm ammonia, significantly outperforming sensors with conventional percolation networks (17.06% ± 0.45%) or drop-casting thick films (4.73% ± 0.33%).

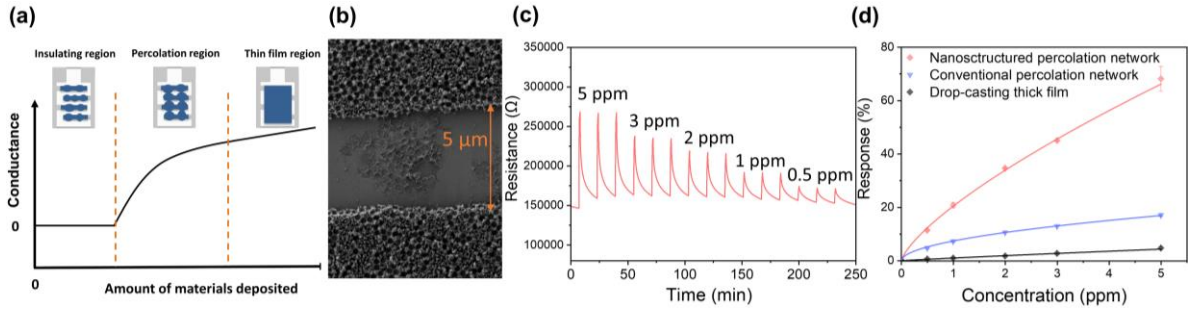


Figure 1 (a) An idealized percolation curve. (b) A SEM image of nanostructured percolation network on interdigitated electrodes (5-μm gap). (c) A typical sensing response-recovery curve of a nanostructured percolation network. (d) Response-concentration curves of sensors with different morphologies.

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BINARY SEPARATION OF CIS AND TRANS-2-BUTENE ON NBOFFIVE-1-NI AND AIFFIVE-1-NI

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Keywords: *Adsorption separation, Cis-/trans-2-butene, Metal-Organic Frameworks (MOFs), NbOFFIVE-1-Ni, AlFFIVE-1-Ni, Gate-opening*

This study investigates the separation of cis-2-butene and trans-2-butene using NbOFFIVE-1-Ni and AlFFIVE-1-Ni materials, derivatives of the fluorinated SIFSIX family of MOFs. Effective separation of these isomers is crucial for the petrochemical industry, with Cis-2-Butene serving as a feedstock for maleic acid, butadiene, and polymers, while Trans-2-Butene is vital for propylene production through ethylene metathesis [1]. Conventional extractive distillation faces challenges due to 2-Butene's high reactivity and copolymerization tendencies at high temperatures, necessitating energy-efficient alternatives aligned with sustainable development goals [2].

Structurally, NbOFFIVE-1-Ni and AlFFIVE-1-Ni consist of M'(II)-pyrazine square-grid layers pillared with $[NbOF5]2-$ or $[AlF5(H2O)]2-$ inorganic building blocks, respectively [3]. These materials exhibit distinct properties with apparent surface areas of 280 m^2/g and 258 m^2/g, and pore volumes of 0.095 cm^3/g and 0.102 cm^3/g, respectively [4]. NbOFFIVE-1-Ni features a pore window size of 3.14 Å and a confined pore space, while AlFFIVE-1-Ni offers a larger pore window of 4.84 Å with potential open metal sites, enhancing its adsorption capacity [5]. Given the kinetic diameters of cis- and trans-2-butene (4.94 Å and 4.31 Å, respectively), both materials are suitable for selective separation [6].

Single-component adsorption isotherms (Fig. 1a) and b)) reveal distinct behaviors: NbOFFIVE-1-Ni exhibits a notable gate-opening effect for trans-2-Butene under specific pressures, significantly enhancing selectivity. In contrast, AlFFIVE-1-Ni shows gradual adsorption through size sieving without gate-opening, yet it demonstrates preferential adsorption of trans-2-Butene over cis-2-Butene. Pure dynamic capacities at 23°C and 1 bar are 0.15 mmol/g (cis) and 1.74 mmol/g (trans) for NbOFFIVE-1-Ni, and higher at 1.59 mmol/g (cis) and 3.13 mmol/g (trans) for AlFFIVE-1-Ni. Binary dynamic breakthrough experiments (Fig. 1c) and d)) confirm these findings across various feed concentrations, temperatures, and flow rates. NbOFFIVE-1-Ni generally demonstrates superior separation performance due to its gate-opening capability, though both materials perform comparably under conditions where gate-opening is absent.

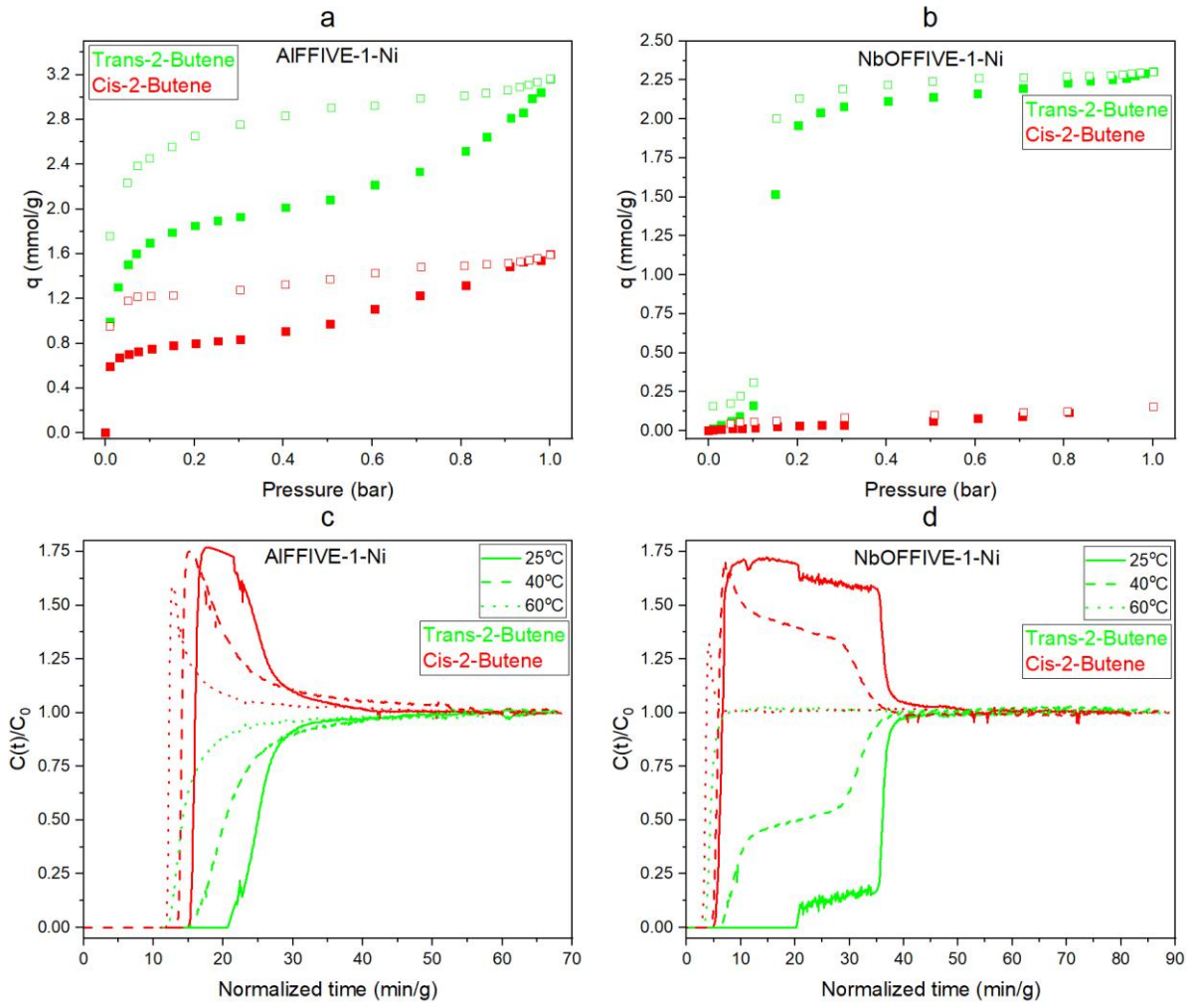


Fig. 1: Single-component gas adsorption isotherm results, trans-2-butene (green) and cis-2-butene (red) adsorption (solid points) and desorption (empty points) isotherms at 25 °C a) AlFFIVE-1-Ni on b) on NbOFFIVE-1-Ni. c) and d) effect of temperature in binary breakthrough curves for trans-2-butene (green line) and cis-2-butene (red line): with total feed flow rate of 2 Nml/min and 50%-50% composition of cis- and trans-2-butene at 1 bar.

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THIAZOLO-THIAZOLATE FLEXMOFS FOR EFFICIENT N-BUTANE STORAGE

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Keywords: *n-butane, gas storage, UAM-1X, in-situ techniques, flexMOF*

In recent years, flexible metal–organic frameworks (MOFs) have attracted significant attention due to their remarkable structural adaptability and high potential for applications in gas storage and separation technologies. Storing gases under high pressure poses several challenges, including the risk of leakage caused by container failure and the requirement for specialized, costly infrastructure. These issues are particularly critical in the case of toxic or flammable gases. Consequently, the development of alternative storage methods such as adsorption-based systems that operate under ambient conditions has become increasingly important.

UAM-1O and UAM-1S are isostructural metal–organic frameworks composed of zinc cations, 2,5-di(pyridine-4-yl)thiazolo[5,4-*d*]thiazole linkers, and dicarboxylate ligands: 4,4'-oxydibenzoate in UAM-1O and 4,4'-thiodibenzoate in UAM-1S. The two frameworks differ by a single atom- oxygen or sulfur within the angular dicarboxylate group. Despite this subtle variation, they exhibit markedly different structural adaptation mechanisms: UAM-1S undergoes a continuous transformation, while UAM-1O responds through a gating structural transition.[2,3]

In our recent studies, we investigated the potential of these materials for n-butane storage. Experimental results revealed that UAM-1O adsorbs up to 80 cm^3/g of n-butane, while UAM-1S adsorbs approximately 65 cm^3/g. Notably, the gas is not completely desorbed, with around 55 cm^3/g retained in the pores of UAM-1O and about 60 cm^3/g in UAM-1S. The adsorption-induced phase transitions were monitored using in situ techniques, including time-resolved powder X-ray diffraction (PXRD), as well as Raman spectroscopy (Figure 1). Remarkably, the presence of n-butane within the pores was still detectable several weeks after the sorption experiments, as confirmed by ex situ IR spectroscopy and PXRD analyses.[4]

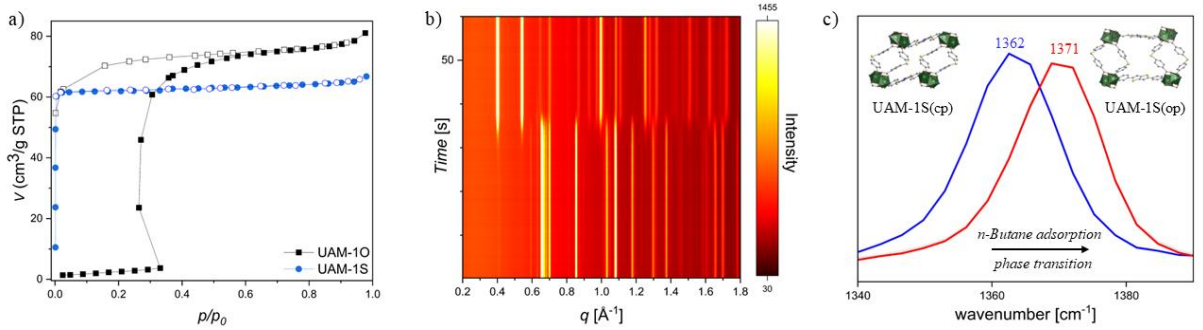


Figure 1 *a) n-Butane adsorption isotherms (closed symbols adsorption; open syblos desorption; 273 K). b) Time-resloevd PXRD during n-butane adsorption and c) corresponding* in situ *Raman spectra during n-butane adsorption.*

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NOVEL *PCL*-UIO-66-UREA MOF FOR THE SELECTIVE ADSORPTION AND DETECTION OF NITRO COMPOUNDS IN SPLIT-RING RESONATOR-BASED SENSORS

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Keywords: *Pore design, pre-crosslinked MOF, room temperature synthesis, vapor sorption, sensor*

Nitro compounds, which are mostly anthropogenic, pose significant threat to human health, whether through their acute toxicity or because of their usage in many explosive compounds. In the latter case, plastic explosives are laced with volatile taggants such as 2,3-dimethyl-2,3-dinitrobutane to make detection easier. Therefore, the detection and adsorption of nitro compounds is of vital importance to societal safety.

Herein, we present a highly porous UiO-66 urea derivative and probe its selectivity towards nitro compounds from the gas phase using vapor sorption methods. UiO-66, the archetypical Zr-MOF, is composed of Zr_6 clusters and terephthalic acid (H_2bdc) linkers and is a suitable platform due to its high stability towards water. Due to the strong interaction with nitro groups through two hydrogen bonds, a urea modification of UiO-66 was pursued. Because a H_2bdc-Urea derivate could not be obtained synthetically, two linker molecules were bridged pre-synthetically through a urea functionality, thus obtaining the *pre-crosslinked* (*pcl*)-H_2bdc-Urea linker. Due to the thermal lability of the linker, a room temperature approach using pre-precipitated Zr_6 clusters was adapted. [1]

The obtained *pcl*-UiO-66-Urea was investigated and compared to other UiO-66 derivatives regarding its selectivity towards nitroethane using static vapor sorption at 298 K.

The *pcl*-UiO-66-Urea MOF is to be incorporated into a split-ring resonator (SRR) sensor. SRRs are a type of LC resonant circuit capable of detecting small changes in the electrical permittivity of the medium within the capacitor gap. [2] Consequently, analyte incorporation within the MOF pore system results in detectable changes in permittivity. Such a sensor could enable a much broader range of analytes and MOFs for gas sensing applications, as no change of physical properties of the MOF are required upon analyte incorporation.

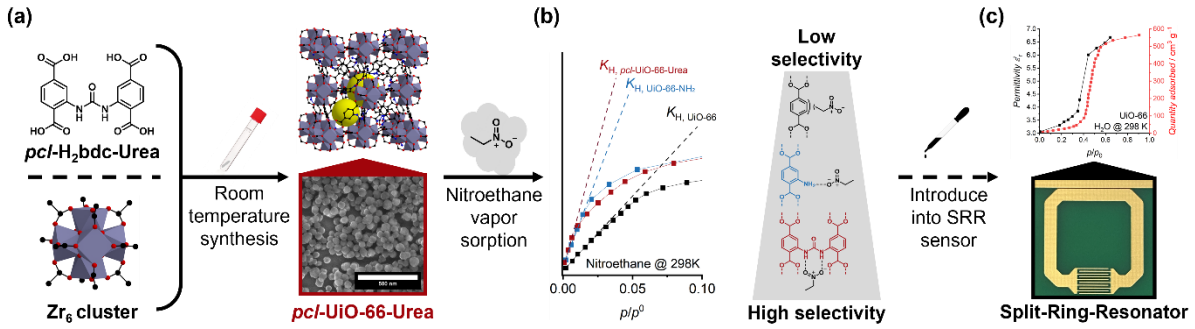


Fig. 1: Synthesis of *pcl*-UiO-66-Urea MOF through a room temperature approach **(a)**, determination of nitro compound selectivity through nitroethane vapor sorption and Henry constant K_H evaluation **(b)** and planned introduction into SRR sensor with exemplary measurement reproducing a water vapor sorption isotherm using UiO-66 **(c)**.

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CO_2 Capture VPSA Pilot Unit using MIL-160(Al) and MIL-120(Al): experimental and simulation study

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Keywords: *CO_2 capture, VPSA, MIL-160(Al), MIL-120(Al)*

Power generation and carbon-intensive industries significantly contribute to CO_2 emissions, making their reduction crucial. Carbon capture technology is essential for achieving net zero emissions by 2050. However, the current amine-based absorption process has limitations such as high energy demands and solvent degradation. CO_2 separation by adsorption is a promising alternative due to potential lower energy consumption and reduced environmental impact. Novel materials like Metal Organic Frameworks (MOFs) have been developed to improve adsorption-based carbon capture, but their performance needs further refinement for large-scale industrial use. In the framework of H2020-MOF4AIR project (https://www.mof4air.eu/) which aims to develop and promote the use of MOFs for CO_2 capture in energy and industrial sectors, several MOFs have been evaluated for use in a Vacuum Pressure Swing Adsorption (VPSA) process. Among these, MIL-160(Al) ($Al(OH)(O_2C–C_4H_2O–CO_2)$) which is an easily scalable 3D Al-based MOF showing pore size between 4 to 6 Å [1][2], and MIL-120(Al) – $Al_4(OH)_8(C_{10}O_8H_2)\ xH_2O$ (x=4.8~5) showing pore size of 4.7 to 5.4 Å [3] were investigated. As represented in Table 1, MIL-120(Al) exhibits higher working capacity, selectivity and bulk density than MIL-160(Al) which could lead to better performance in process for this material. Nevertheless, previous studies have shown that process performance and adsorption metrics are not always clearly related [4][5]. Both MOFs, synthesized at kg-scale and shaped into pellets, were tested on a lab-scale pilot (3 columns of 1.1L) using a 3-bed 6-step cycle (adsorption, heavy reflux, co-current evacuation, counter-current evacuation, light reflux, light product pressurization) with a flue gas composition of 15/85 CO_2/N_2 at 1 Nm^3/h [5]. A design of experiments was employed to investigate five variables: adsorption time (100-400 s), reflux time (40-300 s), co-current evacuation time (20-40 s) and pressure (0.4-0.6 bar), and light reflux flow rate (0.1-0.3 Nm^3/h). Adsorption pressure was maintained at 2 bars, and counter-current evacuation pressure at 0.1 bar for all tests. Under these optimized conditions, MIL-120(Al) and MIL-160(Al) can achieve purity and recovery higher than 90%. Investigation of the performance of these MOFs was completed by simulation of the laboratory scale VPSA pilot using Aspen Adsorption. Kinetic measurements, breakthrough curves and pilot experiments were also used to determine the parameters of a linear driving force model and adjust the heat transfer coefficients [6]. Simulation was used to study the effect of the different parameters studied. Concentration and adsorbed amount inside the column were studied in-depth by simulation to understand the difference between the two materials and the link with other properties such as adsorption isotherms, kinetic, heat of adsorption and bulk density.

Table 1: Adsorption metrics of MIL-160(Al) et MIL-120(Al).

	MIL-160(Al)	MIL-120(Al)
Working capacity (0.15 to 0.015 bar CO_2, 30°C) [mmol/g]	0.91	1.49
CO_2/N_2 IAST selectivity (30°C, 1bar, 15/85 CO_2/N_2) [/]	34	94.7
Heat of adsorption [kJ/mol]	30	36
Bulk density [kg/m^3]	419	684

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ZINC-TRIAZOLATE-CARBOXYLATE METAL ORGANIC FRAMEWORKS FOR CO2 CAPTURE

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Keywords: *Metal Organic Framework, CO2 capture, CALF-20*

CALF-20 (Calgary Framework 20) is an excellent metal-organic framework (MOF) sorbent for point source CO2 capture. In collaboration with BASF, Svante has scaled up and used CALF-20 in our industrial CO2 capture pilot plants. In this work, we are presenting new Svante MOFs (SMOFs) developed by thorough studies on the functionality and pore structures of CALF-20-related zinc-triazolate-carboxylate MOFs.

Two new triazolate carboxylate MOFs (SMOF-537 and SMOF-572) were developed using short carboxylate as pillars and bifunctional triazolates as layers. SMOF-572 showed interesting CO2/water selectivity. The potential of SMOF-572 as CO2 capture sorbent was investigated from both material and process perspectives.

SMOF-46 constructed with Zn, diaminotriazolate and oxalate, has higher CO2 uptake at low CO2 concentration (CO2<10%) compared to CALF20, and excellent CO2 uptake at even lower CO2 region (CO2<4%). SMOF-46 showed great stability under air, moisture, water, and steam.

Green synthesis with water under ambient pressure has been demonstrated, which could facilitate scaling up routes. This study provided great insights into the optimal CO2 and water uptakes of ultramicroporous MOFs for CO2 capture from wet flue gas.

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HARNESSING TI-BASED MOF FOR TARGETED ADSORPTION AND VISIBLE-LIGHT DEGRADATION OF ORGANIC POLLUTANTS

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Keywords: *photocatalysis, COK-47, dye degradation, adsorption*

Access to clean water is a global priority, which is emphasized by the UN's Sustainable Development Goal 6 (SDG6). With synthetic dyes from textile industries contributing significantly to water pollution, developing efficient and sustainable remediation technologies is crucial. Current methods face challenges like slow degradation rates and by-product formation, making photocatalytic advanced oxidation processes (AOPs) a promising alternative. Metal-organic frameworks (MOFs), particularly those with Ti-based secondary-building units (SBUs), offer unique advantages such as high surface areas, tunability, and hydrolytic stability.

In this study [1], we invistigate COK-47, a novel Ti-based MOF featuring 2D SBUs linked by biphenyl dicarboxylic acid ligands [2], synthesized via a microwave-assisted method towards water purification (**Figure 1**). COK-47 exhibits exceptional hydrolytic stability, high adsorption capacity, and superior dye-degradation performance under UV, visible, and solar light, surpassing conventional TiO_2 and MIL-125-Ti photocatalysts. Notably, its unique surface properties enable selective degradation of cationic dyes while resisting anionic pollutants, making it ideal for targeted oxidation reactions. Mechanistic insights reveal the pivotal role of superoxide radicals and highlight the framework's enhanced charge separation and transport capabilities, attributed to its 2D architecture. Additionally, COK-47 demonstrates excellent stability and reusability, positioning it as a versatile photocatalyst for water purification, organic transformations, and water splitting under visible light.

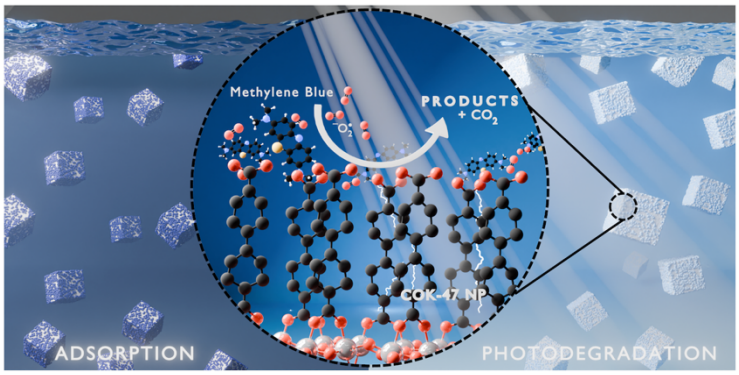


Figure 1. Schematics showing adsorption and photodegradation processes on the COK-47 MOF.

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FLUORENONE-CONTAINING FLEXIBLE ZR-/HF-BASED MOF FOR SELECTIVE KETONE ADSORPTION

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Keywords: *zirconium MOFs*, *VOC adsorption, flexibility, solvatochromism*

Volatile organic compounds (VOCs), particularly ketones, are major air pollutants released by industrial processes that pose serious environmental and health risks due to their toxicity and contribution to poor air quality. [1] Highly selective metal–organic frameworks (MOFs) are promising materials for VOC capture and separation due to their tunable properties – such as large specific surface area, pore size, and adaptable chemical functionalization. [2]

In this work, we present new flexible isomorphous Zr/Hf-based MOFs, containing a fluorenone-bearing linker (DUT–207, DUT = Dresden University of Technology). The use of Zr/Hf nodes ensures high chemical, mechanical and thermal stability, making the framework suitable for demanding separations, whereas the fluorenone moiety is particularly interesting due to its solvatochromic properties in a range of solvents.
According to the single crystal X-ray analysis, the combination of a tetratopic linker and a 10-connected Zr-/Hf-cluster resulted in an unusual MOF topology (Figure 1). [3] The SBUs are connected by six linker molecules, two of which bind to the same cluster through two of their carboxylate groups each, causing the tetratopic linker to act as a tritopic node. Upon partial desolvation of the framework, an unprecedented phase transformation occurs. A second phase transformation is observed upon removal of further solvent molecules. During this process, the 0D SBUs merge into 1D chains, which is accompanied by a significant contraction of the unit cell.

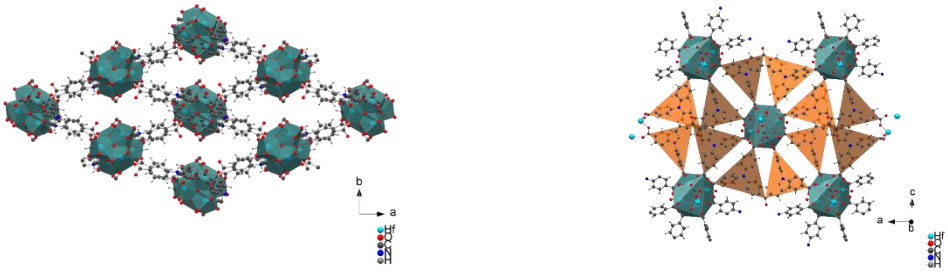


Figure 1. Left: Crystal structure of DUT-207-I (as synthesized), view along c-axis. **Right:** Topological deconstruction of the MOF (3,8-c net, 3,8T220).

Notably, the desolvated DUT-207 phase is nearly inaccessible to N_2 at 77 K and CO_2 at 195 K, but shows exceptional selectivity for ketone adsorption while showing minimal uptake of other VOCs such as diethyl ether or tetrahydrofuran.
DUT-207 exhibits distinct solvatochromic behavior in the presence of ketones, qualifying itself not only as an effective adsorbent but also as a potential chemical sensor. Thus, the dynamic structural flexibility in DUT-207 enables tunable host–guest interactions and enhances selective guest recognition, making it a promising material for advanced VOC separation and sensing applications.

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METAL-ORGANIC FRAMEWORKS FOR DIRECT AIR CAPTURE: BENCHMARKING AGAINST INDUSTRIAL STANDARDS

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Keywords: MOFs, DAC, Lewatit VP OC 1065, Porous Materials

Metal-Organic Frameworks (MOFs) continue to demonstrate immense potential across a variety of applications due to their exceptional structural tunability, high surface areas, and diverse functionalities. As global warming continues to wreak havoc due to the rising number of severe weather events, the need for advanced materials capable of selectively adsorbing carbon dioxide, the primary contributor to global warming, from the atmosphere continues to grow.[1] Over the past 200 years, the concentration of CO2 in the atmosphere has risen by roughly 50%.[2]

MOFs and their exceptional tunability allow for the possibility of capturing carbon dioxide in a wide range of climates around the globe. In this work, a series of MOFs were investigated for direct air capture (DAC) and benchmarked against Lewatit VP OC 1065, a commonly used material for assessing DAC. MOFs offer greater flexibility compared to conventional sorbents, allowing for tunability of carbon capture in varying climates.

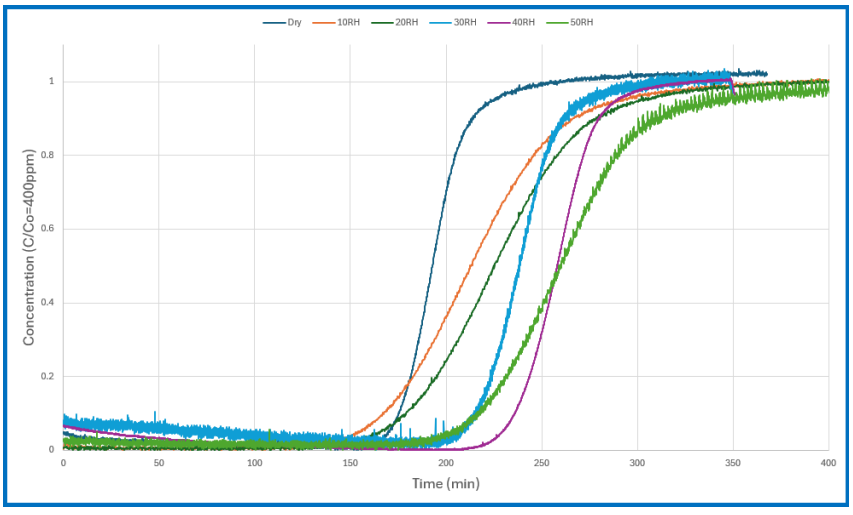


Figure 1. Lewatit VP OC 1065 CO_2 adsorption breakthrough curves collected under DAC conditions (400 ppm CO_2 in N_2) for benchmarking purposes.

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HIGH PERFROMANCE METHANE STORAGE VIA A FLEXIBLE COVALENT-ORGANIC FRAMEWORK WITH MULTI-STEP ISOTHERM

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Keywords: *Covalent Organic Framework, Methane Storage*

Methane is one of the most spotlighted bridgehead-energy source toward carbon-neutral economy. Therefore, carrying and storing methane is a crucial issue. However, current methane storage technology requires exceptional high-pressure such as 250 bar or cryogenic conditions such as -160 ^{o}C, resulting in high cost and safety issue. Therefore, storing methane at milder conditions is a crucial issue. Adsorbed natural gas (ANG) technology using porous materials such as metal-organic framework(MOF), covalent-organic framework(COF), porous organic polymer(POP) has emerged as a promising alternative. ANG technology could provide comparable methane storage under milder conditions (65-100 bar and 273-298 K) offering safety and economic advantages.

We synthesized flexible imine-based COF and evaluated its methane storage performance. The flexible COF showed high adsorption amount at high pressure and low adsorption amount at low pressure leading to higher working capacity. The flexible COF showed enhanced methane storage performance compared with the rigid one, proving its strategy effective. Detailed synthetic scheme and specific properties will be presented in the poster.

LEAD, LOCKED AWAY: POROUS Zr-BASED COORDINATION POLYMER FOR RAPID AND SELECTIVE REMOVAL OF Pb^{2+} FROM WATER

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Keywords: *Porous Coordination Polymer, Water Purification, Selective Lead Adsorption, Porous Materials*

Lead contamination in water represents an urgent global health crisis, impacting both under-developed and industrialized nations. In rapidly industrializing regions, inadequate water treatment and accelerating industrial discharge have created a perfect storm of heavy metal pollution [1,2]. Among various contaminants, Lead (Pb^{2+}) is especially insidious due to its persistence in ecosystems and severe, irreversible health effects [3]. This underscores a sobering truth: lead remains a pervasive threat even in nations with advanced infrastructure, demanding effective remediation strategies.

Among various approaches, adsorption stands out as particularly advantageous due to its cost-effectiveness, operational simplicity, minimal energy requirements, and potential for pollutant recovery rather than mere phase transfer [4]. However, for an adsorbent material to achieve commercial viability and "ideal" status, it must satisfy multiple critical criteria: scalable production processes, economic feasibility, long-term stability, regenerative capacity, and high densities of accessible adsorption sites that facilitate rapid and selective removal of large quantities of targeted contaminants.

To address these demands, we developed a Zr-based coordination polymer (Zr-PCP1), an economical, environmentally friendly material rich in strong binding sites with high selectivity for Pb^{2+}. Zr-PCP1 retains a considerable number of chelating groups, enabling it to readily capture Pb^{2+} ions and exhibit exceptional selectivity, recyclability, and capacity compared to commercial resins (Lewatit TP 207, Lewatit TP 260, Diaion WK100 (Dk-100)) (Figure 1 (a)). Notably, even at low Pb^{2+} concentrations (1 ppm) and in the presence of a high excess of competing ions (1:100), Zr-PCP1 maintained remarkable Pb^{2+} removal efficiency, significantly outperforming all tested commercial resins (Figure 1 (b). Additionally, the adsorbed Pb^{2+} ions could be easily exchanged with protons in acidic solutions (HCl), enabling cost-effective regeneration and reuse of the material.

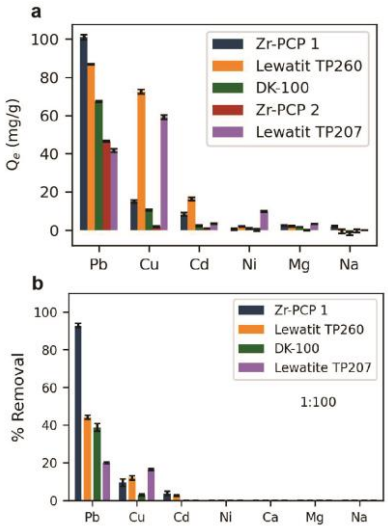


Figure 1 (a) Selectivity experiment with initial metal ion concentration of 100 mg/L (b) Selectivity experiments with the initial Pb^{2+} concentration of 1 mg/L, whereas the concentrations of each interfering ion are 100 mg/L.

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TAILORING ALUMINUM MOFs FOR ENHANCED WATER POLLUTANTS ADSORPTION

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Keywords: *Aluminum-based MOFs, multivariate MOFs, pollutants adsorption.*

The large surface areas of metal-organic frameworks (MOFs) and their easy tuneability and structural diversity have made them attractive candidates for wide range of applications including gas separation, catalysis, drug delivery, and environmental remediation [1]. Among reported MOFs, aluminum-based MOFs are particularly appealing due to their high chemical stability, low toxicity, and sustainability. Recently, incorporating multiple organic linkers within a single MOF structure has been explored as a strategy to fine-tune their physicochemical properties, potentially enhancing their adsorption performance for specific analytes in environmental applications [2].

In this work, a group of aluminum-based MOFs were synthesized following a solvothermal approach, incorporating two different organic linkers to introduce structural and chemical diversity. The resulting materials were characterized using powder X-ray diffraction (PXRD), Fourier-transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), and nitrogen adsorption isotherms to assess their crystallinity, adequate presence of functional groups, proper composition, and porosity. The adsorption capabilities of these MOFs were further evaluated for the removal of a selected group of organic pollutants from water. For that purpose, a UV-DAD detector was employed to monitor the concentration of the contaminants during the adsorption, providing insight into the efficiency and selectivity of the MOFs synthesized, as a function of their structural modification. The experiments were performed to mimic adsorption in real environmental scenarios (multicomponent contaminants in waters).

The results demonstrate that the incorporation of multiple organic linkers in aluminum-based MOFs has been achieved, influencing their physicochemical properties and adsorption capacity. The synthesized materials exhibited promising performance for the adsorption of organic contaminants from water, highlighting their potential as efficient sorbents in analytical monitoring applications. The ability to tailor MOF structures through linker selection offers a valuable approach to optimize their adsorption properties, paving the way for further advancements in sustainable analytical microextraction technologies.

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Acknowledgements

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UNPRECEDENTED SELECTIVITY FOR As^{3+} IN A THIOL-BASED Zr-MOF: THE ROLE OF DEFECTS AND DISORDER

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Keywords: *MOF, disorder, porous adsorbent, arsenic, adsorption, chelation*

While zirconium-metal-organic frameworks (Zr-MOFs) show promise for arsenic remediation, their practical implementation faces critical challenges: poor capture of the neutral arsenite (As^{3+} - H_3AsO_3)[1] and limited selectivity for arsenate (As^{5+} - $HAsO_4^{2-}$) in the presence of certain competing ions.[2,3] To overcome these limitations, this study introduces two structurally distinct Zr-MOFs constructed with a thiol decorated linker. Using pair distribution function analysis (PDF), we observe that the ***bct*** framework exhibits high crystallinity, while the ***fcu*** analogue is highly disordered with only limited long-range order (**Figure 1a**). We find that the ***fcu*** analogue outperforms the ***bct*** analogue in both As^{5+} and As^{3+} adsorption (**Figure 1b**). Compared to the non-thiolated Zr-MOF benchmark - UiO-66 - the thiol-functionalized ***fcu*** framework exhibits superior uptake of both arsenic species, even in the presence of competing phosphates (**Figure 1c**). Through comprehensive structural analysis combining PDF, X-ray absorption spectroscopy (XAS), and solid-state NMR (ssNMR), we uncover the underlying mechanisms driving the superior performance at the molecular level. Comparative studies with analogous thiol-free Zr-MOFs reveal that the thiol groups enable strong covalent sulfur-arsenic interactions. Moreover, DFT calculations and XAS analysis illuminate an unexpected mechanism: framework defects create dangling ligands in the MOF pores that enhance As^{3+} interaction through strategic disorder. This finding challenges the conventional wisdom that high crystallinity is essential for MOF performance in ion capture, suggesting instead that controlled defect engineering can significantly enhance functional properties.

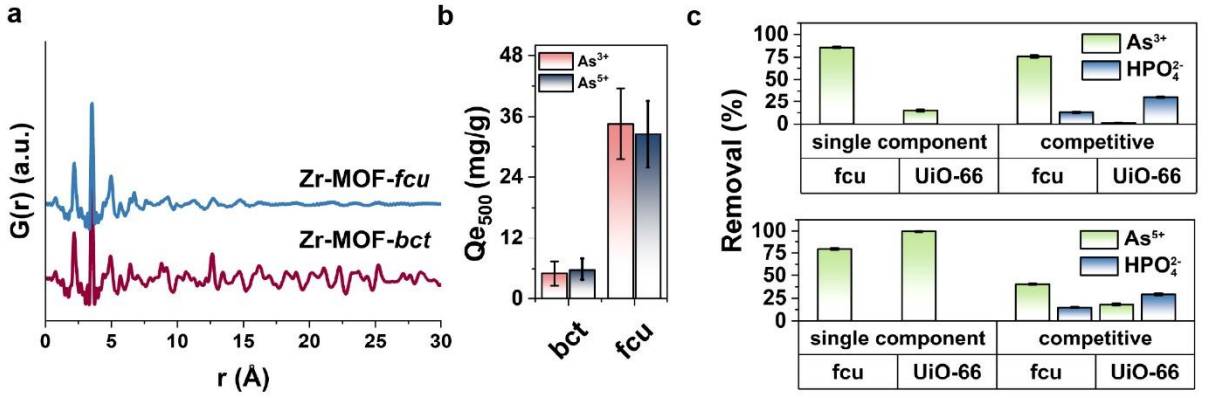


Figure 1. a) PDF of Zr-MOF-*bct* (red) and Zr-MOF-***fcu*** (blue), b) calculated Q_e from Freundlich fit of the adsorption isotherms at equilibrium concentration of 500ppb for As^{3+} and As^{5+}, c) competitive arsenic/phosphate batch adsorption experiments for Zr-MOF-***fcu*** and UiO-66 in aqueous solution containing 1:10 arsenic : phosphate concentration.

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INFLUENCE OF HUMIDITY ON THE SORPTION OF CO_2 IN MOFS: STABILITY AND SELECTIVITY

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Keywords: *CO_2, Carbon Capture, Water, Stability, Selectivity, MOF*

Solid porous sorbents such as zeolites, MOFs, and finely divided metal oxides are some of the most promising candidates for the implementation of carbon capture (CC), both for direct air capture (DAC) solutions and point sources. All of these materials owe their high CO_2 sorption capacity to their high surface areas and pore characteristics. However, each class of material exhibits different selectivity and stability properties. MOFs, in particular, can be tailored to have specific selectivity, while their structure and morphology can be affected if exposed to moisture [1].

Translating promising lab-scale materials to industrial deployment requires realistic screening of their performance in process-relevant conditions. A key challenge is to identify sorbents with sufficient working capacity across the full range of CO_2 concentrations (from 400 ppm to 100%) and to assess whether they retain their affinity for CO_2 in the presence of moisture and over repeated adsorption-desorption cycles[2].

Water molecules compete with CO_2 for sorption sites in many materials (zeolites and most MOFs). In others, the presence of a certain amount of humidity can increase the total amount adsorbed or speed up the sorption kinetics, as in the case of amine-based materials[3] and alkali or alkaline earth metal carbonation processes[4]. For many MOFs, however, moisture can induce framework degradation, reduce pore volume, and significantly lower sorption capacity.

Understanding the impact of humidity on stability, selectivity, and sorption dynamics is critical for evaluating porous materials in CCUS applications. In this study, we present experimental methodologies—including gravimetric analysis and breakthrough experiments—to assess water and CO_2 uptake from multicomponent mixtures. We apply these techniques to both commercial and novel MOFs, providing case studies that highlight their performance under realistic operating conditions.

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EVALUATION OF MOF MATERIALS FOR CO_2-CAPTURE

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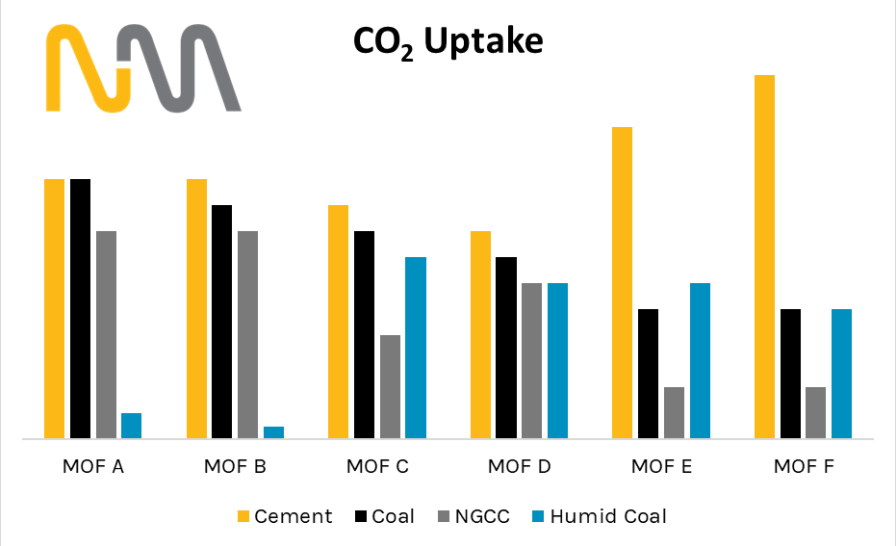
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Keywords: *CO_2-capture, post-combustion, DAC, sorption, DVS, breakthrough analysis, industrialization*

MOF materials are gaining tremendous attention in the field of carbon capture, and various pilot-scale systems are beginning to emerge in industries ranging from cement, steel, coal, biomass, natural gas turbines and even direct-air-capture. However, the unique demands of these different industrial processes means that there is no “one-size-fits-all” MOF material. As such, tailoring MOFs to meet specific operational requirements is a critical step toward their widespread implementation.

In this work, state-of-the-art MOF sorbents are evaluated using advanced techniques across a range of industrially relevant conditions, considering their CO_2 sorption performance under different CO_2 concentrations, temperatures, and humidities. The results reveal insights into how an ideal, application-specific MOF can be selected, and guide the development and optimization of new materials. This comprehensive approach provides a clearer path for transitioning from lab-scale materials to real-world deployment.



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SYNTHESIS AND DESIGN OF ZIRCONIUM METAL ORGANIC FRAMEWORK FOR EFFICIENT PHOTOREDUCTION OF CO_2

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Keywords: *Zr MOF, TNDI, Photocatalysis, CO_2 reduction, Formate, CO*

Reducing CO_2 to useful products such as formate is of immense industrial importance. In the present report, we have studied the CO_2 reduction performance of a Zr MOF and its Titanium-exchanged analogues. A naphthalene diimide tetracarboxylic acid (TNDI) linker-based metal-organic framework with Zirconium metal was synthesized for effective photocatalytic CO_2 reduction in aqueous medium [1,2] This MOF was thoroughly characterized using techniques like PXRD, TGA, N_2 BET, UV-Vis spectroscopy, EPR and SEM. This water-stable MOF was able to achieve formate production at a rate of 38 $\mu molg^{-1}h^{-1}$. Higher production rates and yields were achieved through the post-synthetic metal exchange of Zr with Ti.[3,4] The new mixed metal MOF with 20% and 30% exchange of Zr with Ti metal resulted in the reduction of the band gap of the pristine MOF which led to a higher production rate of 50 $\mu molg^{-1}h^{-1}$ and 71 $\mu molg^{-1}h^{-1}$ of formate, respectively. Inspired by this work, a new analogous Zr MOF with another redox active linker has been synthesized, and characterized, and its photocatalytic activity has been thoroughly checked. The redox active ligand serves as a hotspot for charge transport and helps in the reduction process further. This new framework gave a selective reduction (67%) of CO_2 to CO with a production of 1.22 $mmolg^{-1}$ of the catalyst. Using *in situ* SERS (Surface Enhanced Raman Spectroscopy), the mechanism of photochemical reduction over the MOF catalyst surface is studied in detail. [5,6] The work majorly focuses on the synthesis of novel Zr MOFs with redox active linkers for photocatalytic CO_2 reduction.

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ANTHRACENE-BASED POROUS POLYMERS FOR CHEMICAL SENSING AND PHOTOCATALYTIC GOLD RECOVERY

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Keywords: anthracene porous polymer*, sensing, gold-adsorption, gold-photoreduction*

The increasing release of organic and inorganic pollutants, particularly nitroaromatic compounds and metals, presents a risk to both the environment and human health. That is why sensing methods based on fluorescence quenching offer a simple, sensitive, and cost-effective approach for their detection and removal.[1] Anthracene, an organic molecule formed by the lineal fusion of three benzene rings, is known for its excellent solid-state emission properties. Its ease of functionalization at the 2,6-positions is particularly effective, as it maintains molecular planarity and enhances π-conjugation and charge transport.[2] As a result, in this work we presented the synthesis and characterization of three novel anthracene-based porous polymer and the performance of Pol-A as sensor and its ability to adsorb gold.

A series of anthracene-based polymers were synthesized by Suzuki-Miyaura cross-coupling using anthracene, anthraquinone and 9,10-dihydroanthracene as structural photoactive building units and 1,3,5-triphenylbenzene as comonomer (Figure 1). These new polymers were fully characterized by ^{13}C-NMR in solid state, N_2 adsorption/desorption isotherms, FT-IR spectroscopy, thermogravimetrical analysis, UV-visible spectroscopy and cyclic voltammetry.

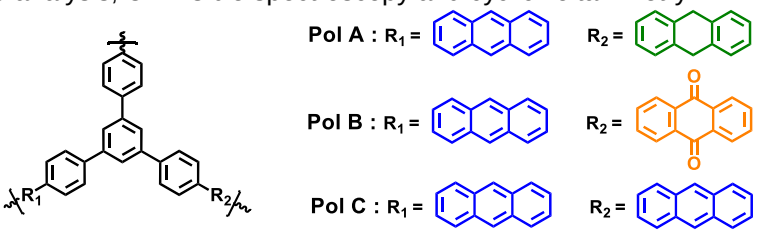


Figure 1. Anthracene-based polymers.

Pol-A was chosen to explore the potential of these materials as sensors and/or photocatalysts. Pol-A was evaluated as sensor to the detect nitroaromatic compounds (NACs) and ions. It is selective for 4-nitrophenol (4-NP) with a K_{sv} value of 2.10x10^4 M^{-1} (Figure 2a) and for Au^{3+} with a K_{sv} value of 1.06x10^4 M^{-1} (Figure 2b) in THF:H_2O (1:1). In view of the high selectivity of Au^{3+}, we studied the adsorption of gold(III) in the polymer and their consecutive photocatalytic reduction to Au(0). We found that Pol-A has high gold adsorption capacity (Figure 2c) and also, after being washed with aqua regia, it can be recycled up to three times without losing capacity. This can be advantageous in the treatment of electronic wastewater.

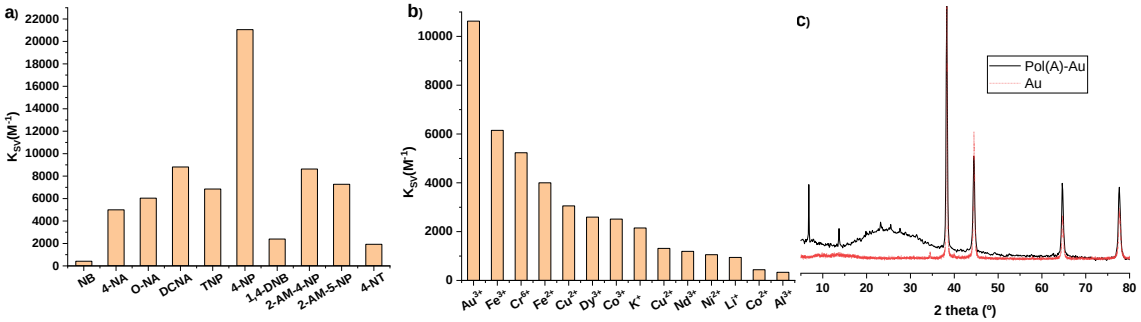


Figure 2. Stern-Volmer constants for a) NACs and b) ions. c) PXRD spectra of Pol-A after gold-adsorption.

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PHOTOINDUCED SPIN CENTERS IN PHOTOCATALYTIC METAL-ORGANIC FRAMEWORK UIO-66

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Keywords: *MOF, photocatalysis, EPR, DFT, trPL*

Metal-organic frameworks (MOFs) are promising candidates for advanced photocatalytically active materials. These porous crystalline compounds possess large active surface areas and structural tunability, making them highly competitive with oxides, the well-established material class for photocatalysis. However, due to their complex organic and coordination chemistry composition, the photophysical mechanisms involved in the photocatalytic processes in MOFs remain poorly understood. In this study, electron paramagnetic resonance (EPR) spectroscopy and time-resolved photoluminescence spectroscopy (trPL) are employed to investigate the fundamental processes of electron and hole generation, along with charge carrier capture events that lead to the formation of various radical species in UiO-66, an archetypical MOF photocatalyst. A variety of photoinduced electron spin centers is detected and subsequently analyzed and identified with the aid of density-functional theory (DFT) calculations. Under UV illumination, the symmetry, g-tensors, and lifetimes of three distinct contributions are revealed: a surface O_2-radical, a light-induced electron-hole pair, and a triplet exciton. Notably, the latter was observed to emit delayed fluorescence. These findings provide new insights into the photoinduced charge transfer processes underlying the photocatalytic activity in UiO-66, paving the way for further investigations of photogenerated spin centers in this and related MOF materials. [1]

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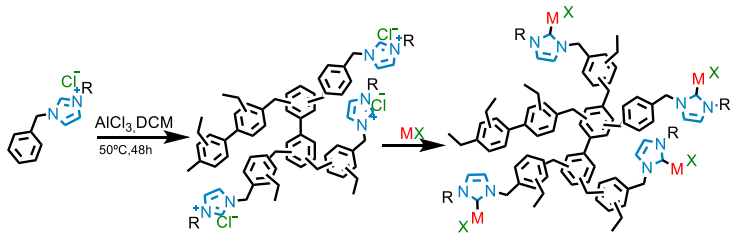
THREE-COMPONENT COUPLING OF CO_2 FOR THE SYNTHESIS OF CARBAMATES AND CARBONATES USING METAL-SUPPORTED HYPERCROSSLINKED N-HETEROCYCLIC CARBENE POLYMER CATALYSTS

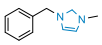
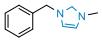
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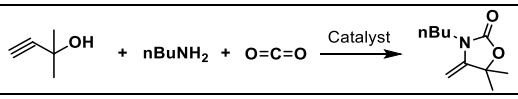
Keywords: N-heterocyclic carbene, CO_2 conversion

A new family of N-heterocyclic carbene-Cu and -Ag complexes has been synthesized from imidazolium chloride-based hypercrosslinked polymers. These complexes enhance CO_2 adsorption capacity and exhibit robustness and insolubility, making them ideal heterogeneous catalysts for CO_2 conversion. They were used in three-component CO_2 coupling reactions, producing cyclic carbamates from propargylic alcohol and primary amines, or asymmetric carbonates using primary alcohols.[1] The synthesis of these materials is performed by Friedel-Crafts reations using a crosslinked agent and $AlCl_3$ as catalyst[2] and a subsequent post-functionalization using Ag_2O and CuI to include the metal in the structure.



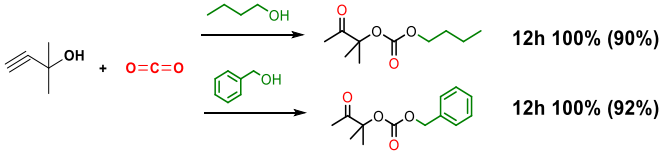
Name	R	M/X
HCP-NHC-Ag	CH_3	Ag/Cl
HCP-NHC-Cu	CH_3	Cu/I
HCP-*Bis*NHC-Ag		Ag/Cl
HCP-*Bis*NHC-Cu		Cu/I

First, a comprehensive study of the synthesis of cyclic carbamate using 2-methylbut-3-yn-2-ol and butylamine as model substrates is carried out using 120°C, 5 bar CO_2 pressure, 5 mol% catalyst and acetonitrile as solvent. The study begins by comparing the four synthesized catalysts, showing the results in the following table.



Entry	Catalyst	t (h)	Conv (%)	Sel. (%)
1	HCP-NHC-Ag	9	85	99
2	HCP-NHC-Cu	5	100	99
3	HCP-*Bis*NHC-Ag	9	100	98
4	**HCP-*Bis*NHC-Cu**	**4**	**100**	**99**

The reaction was also carried out using a bulkiest amine, such as benzylamine, and using the best catalyst of the series (HCP-*Bis*NHC-Cu) achieving 100% conversion and high selectivity (99%). Additionally, to expand the study to other multicomponent reactions with CO_2 and propargylic alcohol, HCP-*Bis*NHC-Cu was used in the synthesis of asymmetric carbonates, employing butyl alcohol and benzyl alcohol as reagents.



Acknowledgment. This work was supported by CATCO2NVERS funded by the European Union´s Horizon 2020 research and innovation program under grant agreement No 101000580 and MICIU/AEI/10.13039/501100011033 FEDER, UE through PID2023-146114NB-C22

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MULTIMETALLIC ZIF-DERIVED HIGH-ENTROPY ALLOY CATALYST FOR *p*-NITROPHENOL HYDROGENATION

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Keywords: *PNP hydrogenation, high-entropy alloy (HEA), multimetallic ZIF, ZIF-derived carbon (ZDC)*

High-entropy alloy (HEA) nanoparticles (NPs) have been proposed to be catalytically active. However, possible particle aggregation and uneven elemental distribution degrade the HEA catalytic ability. It is challenging in HEA NP preparation. Adopting the ligand-mediation method for metal cation separation[1], research on obtaining HEA NPs from multimetallic MOF/ZIF-derived materials is emerging[2]. Nonetheless, discussions on the correlation between MOF/ZIF-derived material properties and catalytic performance are rare.

In this research, we pyrolyzed multimetallic ZIF at various temperatures (500~800°C) for MgCoNiCuZn HEA NPs on ZIF-derived carbon (ZDC) applied to *p*-nitrophenol (PNP) hydrogenation to *p*-aminophenol. It was found that the apparent rate constant and turnover frequency (TOF) increase with pyrolytic temperature. However, ZDC at 500°C showed the highest apparent rate constant and TOF among ZDCs, much faster than conventional transition metals and comparable to noble metals in the literature. It is attributed the smallest HEA NP size and homogeneous elemental distribution in ZDC at 500°C. In addition, the PNP reduction mechanism is prone to be the Eley-Rideal (ER) model in our HEA on ZDC catalyst.

To investigate the catalytic activity in HEA NPs on ZDC, density functional theory (DFT) calculations were employed. With the optimization of HEA configuration, the adsorption energies of the reducing agent (BH_4^-) were evaluated. DFT calculations reveal that compared to Co FCC, HEA shows weaker adsorption strength, resulting in higher activity and faster reaction kinetics. Moreover, the ER mechanism is proven to occur for the HEA instead of the Langmuir–Hinshelwood (LH) model. The report shows that MOF/ZIF pyrolysis is feasible for HEA NP preparation, and the catalytic ability is highly dependent on pyrolytic conditions.

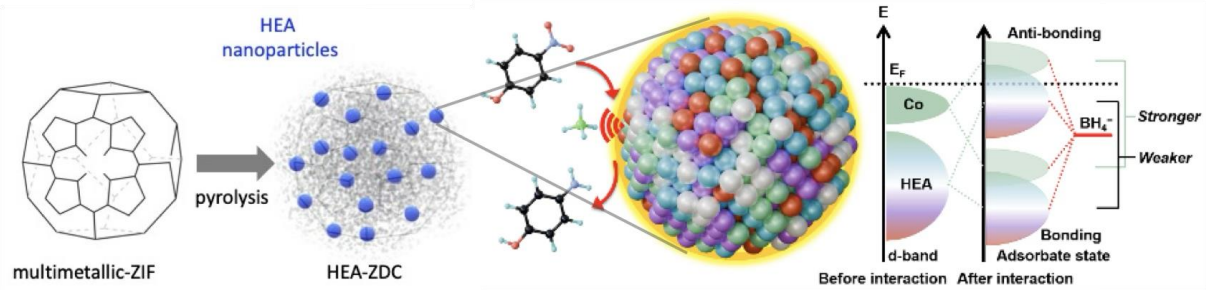


Figure 1. Scheme of MOF pyrolysis and HEA simulation for PNP reduction.

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SULFONATE-FUNCTIONALIZED IONIC METAL–ORGANIC FRAMEWORK FOR MODULATING THE SELECTIVITY OF ELECTROCHEMICAL SENSORS AND ELECTROCATALYTIC AMMONIA PRODUCTION

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Keywords: *Electrocatalysis, Ion-gating membrane, Microenvironment, Porous coating, Zirconium-based MOF*

Metal–organic frameworks (MOFs) with ultrahigh surface areas and interconnected porosity have been considered as attractive materials for electrocatalysis and other electrochemical applications. But the poor stability in water and low electrical conductivity of most MOFs strongly restrict the design and direct use of structurally robust and electrochemically active MOFs. The development of stable group(IV) metal-based MOFs, such as Zr-based MOFs (Zr-MOFs), has allowed the use of MOFs in aqueous media while preserving their structures, but the poorly conducting nature of these MOFs still limits their performances in electrocatalysis [1,2].

Since 2018, our research group has worked on the electrochemistry of chemically stable group(IV) metal-based MOFs in aqueous electrolytes and their use in various electrochemical applications. Rather than serving the MOF as the electrochemically active material, herein, a unique concept of utilizing electrochemically “inactive” and “non-catalytic” MOFs in electrocatalysis is proposed. The porous and stable MOF thin film can modulate the microenvironment near the underlying surface of the electrocatalyst and thus adjust the selectivity of complicated electrochemical reactions. The material design of the underlying electrocatalytic material and the highly porous MOF coating can thus be fully decoupled.

To demonstrate this concept, in this work, a water-stable Zr-MOF, MOF-808, was selected to post-synthetically immobilize the sulfonate-based ligands. By coating a thin film of this “anionic MOF” on the active electrode surface, cationic species can be concentrated near the catalyst surface, which boosts the selectivity toward targeted cationic reactants against undesired anionic reactants during the electrochemical processes. Such ionic Zr-MOF thin films can enhance the selectivity of electrochemical dopamine sensors [3], and can also act as the “proton reservoir” to boost the selectivity of electrocatalytic nitrate reduction to produce ammonia [4]; see Figure 1. In both cases, the Zr-MOF thin film can outperform the conventionally used Nafion thin films with optimized thicknesses. Findings here shed light on the use of such porous and ionic MOFs as advanced alternatives to Nafion for adjusting the selectivity and reactivity of complicated electrocatalytic and sensing systems.

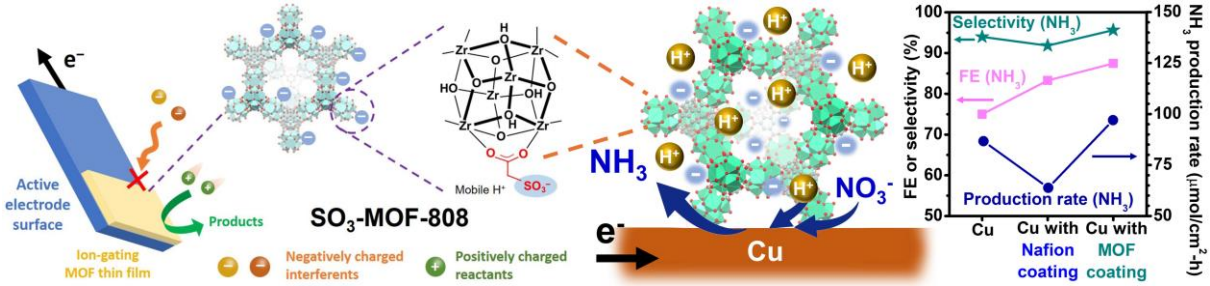


Figure 1. Anionic Zr-MOF coatings to enhance the selectivity of electrocatalysis-based sensors and electrocatalytic ammonia production.

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TUNABLE ISOMETRIC DONOR-ACCEPTOR WURSTER-TYPE COVALENT ORGANIC FRAMEWORK PHOTOCATHODES

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Keywords: *Imine COF synthesis, electron donor-acceptor units, photoelectrochemical water splitting*

Covalent organic frameworks (COFs) provide a unique combination of ordered structures, high porosity, and tailorable functionalities in nanoscale reaction spaces. In this study, we report the synthesis of a series of isostructural, photoactive Wurster-type COFs achieved by manipulating the chemical and electronic nature of the Wurster aromatic amine building blocks (Figure 1). A series of donor-acceptor-donor (D-A-D) Wurster building block molecules was synthesized by incorporating heteroaromatic acceptors with varying strengths between triphenylamine donor groups. These tailored building blocks were integrated into a 2D COF scaffold, resulting in highly crystalline structures and similar morphologies across all COFs (Figure 2). Remarkably, this structural uniformity was also achieved in the synthesis of homogeneous and oriented thin films. Steady-state photoluminescence revealed a tunable red-shift in COF film emission exceeding 100 nm, demonstrating effective manipulation of their optical properties by the predesign of the acceptor unit strength. Furthermore, photoelectrochemical (PEC) water splitting studies exhibited a doubled current density (8.1 µA cm^{-2} at 0.2 V_{RHE}) for the COF with the strongest acceptor unit. These findings highlight the potential of Wurster D-A-D COFs in photoelectrochemical water splitting devices and pave the way for further exploration of chemical functionality-reactivity-property relationships in this promising class of photoactive materials.[1]

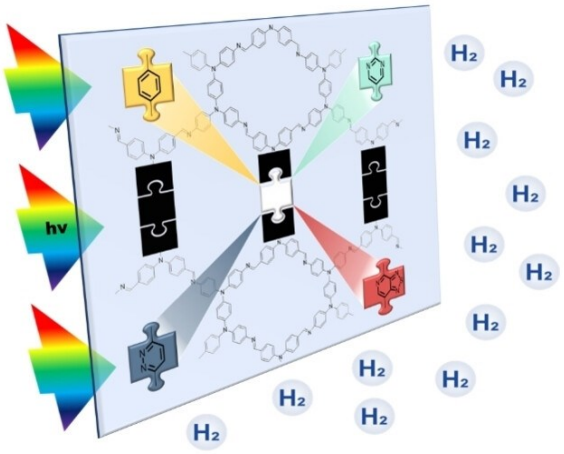


Figure 1: D-A-D COF series for PEC water splitting.[1]

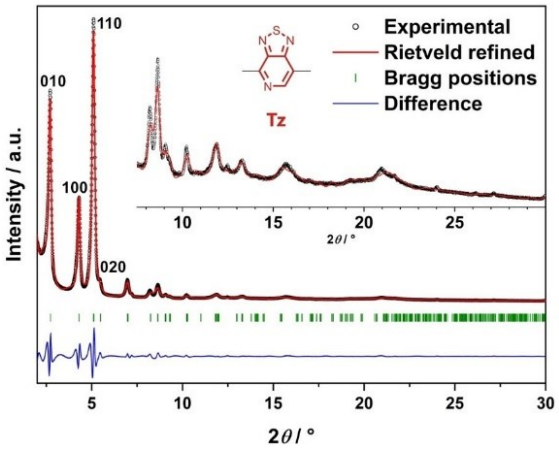


Figure 2: Simulated and experimental PXRD pattern of thiadiazolopyridine containing COF.[1]

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PHOTOTHERMAL EFFECT IN MOF-BASED CATALYSTS TO BOOST CO_2 CONVERSION

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Keywords: *Metal-organic frameworks, solar-driven, CO_2 hydrogenation, photothermal catalysis, bimetallic nanoparticles*

Transforming CO_2 into commercially valuable chemicals, such as methane, formic acid, methanol, and ethanol, offers a promising pathway toward developing a low-carbon chemical industry. CO_2 is a thermodynamically stable and chemically inert molecule, making its activation challenging and requiring an external energy input to drive the reaction. Photothermal catalysis is an emerging field that integrates both photochemical and thermal processes to drive chemical reactions. Unlike traditional photocatalysis, which relies solely on light-induced redox reactions, photothermal catalysis harnesses the heat generated when light, particularly from the visible to infrared (IR) spectrum, irradiates a material. This localized heating effect raises the catalyst's temperature without the need for external heating sources, effectively promoting endothermic reactions.

Metal–organic frameworks (MOFs) are emerging as highly promising platforms for photothermal catalysis. Known for their high porosity, MOFs have long been used as supports or hosts for metal nanoparticles (NPs) across a wide range of catalytic applications, including conventional thermocatalytic CO_2 hydrogenation reactions.[1] However, their potential in photothermal catalytic CO2 conversion remains relatively underexplored, despite growing recognition of their unique advantages in this field. Numerous studies have demonstrated that Zr-based supports exhibit excellent CO_2 adsorption capabilities. Among them, UiO-66 stands out as one of the most widely investigated Zr-based MOFs. Jiang et al. reported Pd_3Cu@UiO-66 composites for CO_2 hydrogenation under photo-thermal conditions.[2] Defect sites on the Zr–oxo cluster can effectively capture and activate CO_2 molecules. Notably, the MOF linker plays a crucial role by harvesting solar energy and generating photo-induced electrons, which are transferred to the Zr–oxo cluster, thereby enhancing the rate of CO_2 activation. This structural modification led to enhanced CO_2 adsorption capacity and significantly improved activity for methanol production. Li et al. reported Cu_6Pd@UiO-66 for CO_2 hydrogenation under photo-thermal conditions.[3] Copper and a small amount of palladium are encapsulated within the UiO-66 cage using a dual-solvent-sonication method, forming ultrafine Cu_2O/Cu–Pd clusters. The Cu–Cu_2O component acts as an electron-rich center to boost CO_2 adsorption and activation, while the presence of Pd facilitates efficient H_2 activation. Owing to the electronegativity difference between Cu and Pd, electrons preferentially transfer from Cu to Pd, creating an asymmetric electron distribution. This electron imbalance facilitates C–C coupling, enhancing the conversion of CO_2 into ethanol. However, the utilisation of solar light is limited because of the poor light absorption of UiO-66.

Recently, our group discovered that Zr–ferrocene (Zr–Fc) MOFs exhibit excellent intrinsic photothermal properties.[4] To further improve solar energy utilization, we developed a novel hybrid solar-driven catalyst by integrating Cu-Pd bimetallic nanoparticles into photothermal Zr–Fc MOF for efficient CO_2 conversion. We believe this foundational work could be extended to a wide range of unexplored Zr-based MOFs, serving as active supports for the development of new, highly efficient photothermal catalysts for CO_2 conversion.

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MODULATOR ENGINEERING TO BIFUNCTIONAL METAL-ORGANIC FRAMEWORK FOR SYNERGISTIC CATALYSIS

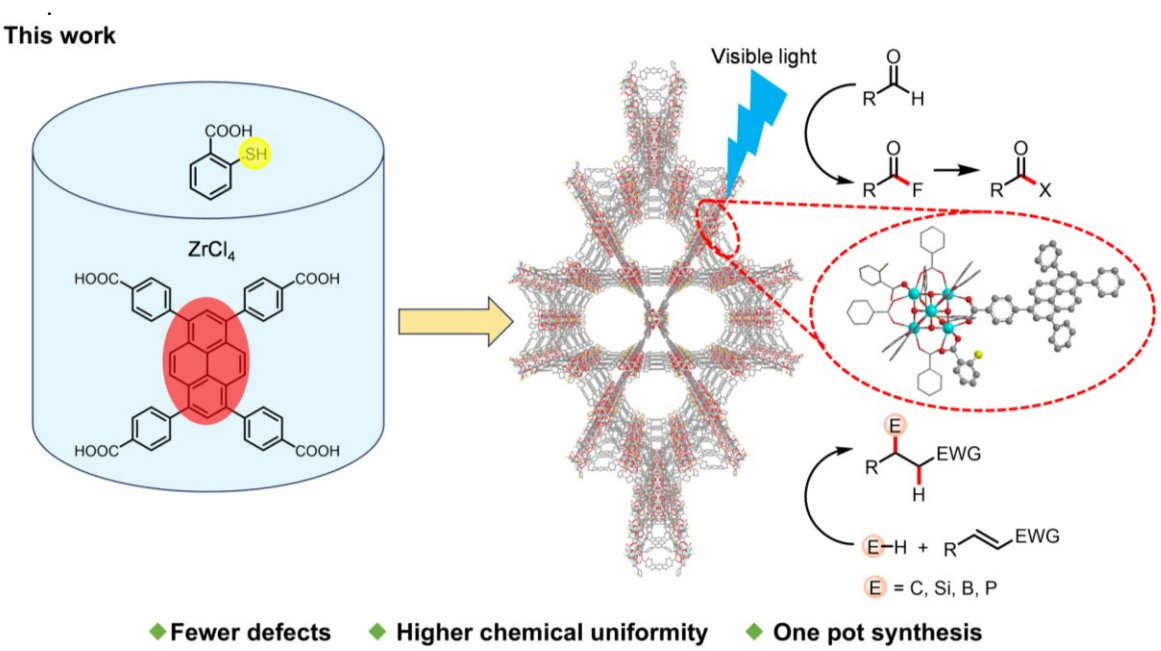
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Keywords: *Modulator, Bifunctional*

Pursuing both structural uniformity/crystallinity and functional complexity is a long-term goal in functional materials engineering. Often, efforts to enhance one attribute may compromise the other. Herein, we report an elaborate strategy of “integrating catalytic center into modulator”, which enables the one-pot synthesis of a bi-functional metal-organic framework (MOF), Zr-TBAPy-TSA (TBAPy = 1,3,6,8-tetrakis(p-benzoic acid)pyrene; TSA = o-thiosalicylic acid). TSA serves as both a modulator for MOF preparation and a catalytic center. Zr-TBAPy-TSA is distinguished by its highly uniform and crystalline structure, as evidenced by detailed characterizations including single-crystal X-ray diffraction. Additionally, Zr-TBAPy-TSA incorporating both photosensitizer and thiol active centers showcases superior catalytic performance in the activation of element-H bonds (elements include C, B, Si, P). Due to its less defective structure, extra high turnover numbers of up to 14200 and good catalyst recyclability are obtained



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DESIGN OF CHIRAL POROUS BIO-HYBRID MATERIALS AS CATALYSTS FOR CO_2 CONVERSION

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Metal Organic Frameworks (MOFs) are used for various applications including gas storage/separation, catalysis, biomedicine etc… [1]. In recent years, significant attention has been focused on reducing their environmental impact by prioritizing using safer solvents or reaction media, sustainable and non-toxic metal ions, and biocompatible organic linkers derived from biomolecules or biomass. Biomolecules such as amino acids and peptides are attractive building blocks to design MOFs, commonly known as bioMOFs, which still represent only a marginal fraction of 3D MOFs discovered so far [2]. The cycloaddition of CO_2 to epoxides to form cyclic carbonates (CAs) is a promising approach for CO_2 conversion, offering efficient resource utilization and 100% atom economy, which finds applications in manufacturing various fine chemicals. Although a large variety of MOF catalysts have been proposed for the CO2 cycloaddition to epoxides under ambient conditions, they generally operate with a high amount of homogeneous halide co-catalyst [3]. In this project, we have synthesized MOF-based nanocomposites and bioMOFs following different strategies in solution. Their chemical/thermal stability, homochirality, Lewis/ Brønsted acid-base properties, and CO2 adsorption properties are currently characterized by coupling multiple advanced characterization techniques. The catalytic performance of these materials is also evaluated for the CO2 cycloaddition to epoxides. Our objective is to develop a series of chemically stable MOF-based heterogeneous catalysts for CO2 cycloaddition to epoxides that can operate under ambient and eco-compatible solvent-free conditions and with a minimal amount of co-catalyst. Moreover, this project also aims to evaluate the promises of these materials as asymmetric catalysts for synthesizing enantiomerically pure or enantio-enriched CAs.

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UiO-67 AS A HETEROGENOUS CATALYST FOR THE HYDROBORATION OF CARBONYL COMPOUNDS

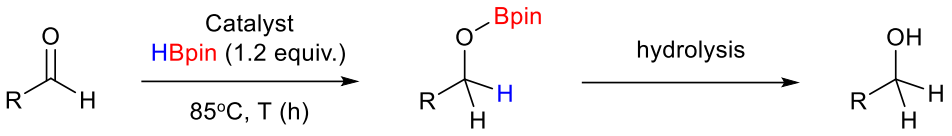
Paige R. Hawkins,[a] Chris S. Hawes,[a] and Peter D. Matthews[a]

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Keywords: *Catalysis, hydroboration, Lewis acidic*

Catalytic reduction of carbonyl compounds plays a pivotal role across many branches of chemical sciences, transforming simple molecules into highly valuable and practical chemical assets.[1,2] Traditionally, such transformations have relied heavily on homogenous systems containing precious metal catalysts, which are often scarce, expensive and difficult to recycle.[3-5] As a result, there is growing interest in the development of more sustainable, abundant, and metal-free alternatives to activate these compounds without losing reactivity and reducing costs.[6] One approach involves hydroboration, offering a more selective route to reduce carbonyl compounds. Although it is commonly performed under homogenous conditions, it can tailored to function effectively in heterogenous systems, overcoming the limitations associated with same-phase reactions.



Scheme 1: Hydroboration of aldehydes using HBpin.

In this research, we explore the Lewis acidic UiO-67 as a heterogenous catalyst for the reduction of a broad scope of aromatic aldehydes using pinacolborane (Scheme 1). High conversions (>90%) are observed across a range of substrates under relatively mild conditions, whilst maintaining crystallinity throughout. In addition to smaller model substrates, this work also explores bulkier aldehydes containing both electron-withdrawing and donating substituents to assess how electronic effects influence conversion and reactivity.

Ultimately, this study contributes to a broader understanding of how a well-known metal-organic framework (MOF) can act as an efficient catalyst for the selective reduction of a large scope of aldehydes, and how its pore size and shape affect this activity. Analysis of the electronic and steric effects reveals a clear relationship between the framework and substrate, giving valuable insights as to how other similar molecules may react on a larger scale. Importantly, the MOF retains its structure under the reaction conditions, making it a promising platform for scaled-up transformations on an industrial level.

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EFFICIENT STRATEGY TO CREATE HIGH-DENSITY INTRINSIC CARBON DEFECTS IN METAL-FREE CARBON ELECTROCATALYSTS FOR CO2 ELECTROREDUCTION INTO CO

Ryuji Takada,[a] Koji Miyake,[a] Yoshiaki Uchida,[a] and Norikazu Nishiyama[a]

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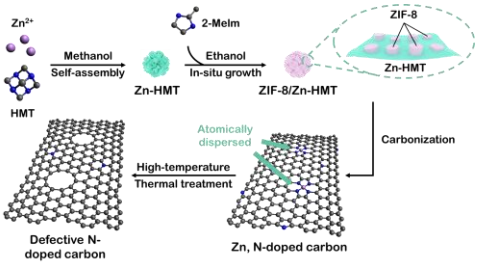
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Keywords: *CO_2 electroreduction reaction, metal-free electrocatalyst, intrinsic carbon defect*

Carbon dioxide electrochemical reduction reaction (CO_2RR) driven by renewable energy is considered as a promising approach to achieve carbon neutrality. CO_2RR into carbon monoxide (CO) has been highly attracted because CO serves as a key feedstock for C2+ chemicals. In this regard, various metal-based electrocatalysts have been developed to achieve high CO selectivity through CO_2RR. However, these metal-based catalysts prevent the large-scale application of CO_2RR due to their high cost and poor durability. Compared with metal-based catalysts, carbon materials offer advantages such as low cost and high durability[1].

Recently, some studies have suggested that introducing intrinsic carbon defects into carbon matrix can also enhance catalytic activity for various electrochemical reactions. Therefore, developing an efficient strategy to create intrinsic carbon defects offers great potential in the design of highly active carbon materials for electrochemical reactions. In particular, the N-dopant removal strategy, which means pyrolytic N removal from the N-doped carbon materials at a high temperature, has been widely utilized to generate the intrinsic carbon defects. However, the role of intrinsic carbon defects has received little attention. Moreover, it is still challenging to efficiently introduce high-density intrinsic carbon defects into carbon matrix.

In this study, we provide an effective method to synthesize metal-free carbon materials with abundant intrinsic carbon defects for selectively enhanced CO_2RR into CO. Inspired by single-atom catalysts, Zn, N-doped carbon material derived from carbonized MOF was used as a precursor of defective carbon because the sequential processes of the evaporation of atomically dispersed Zn and the removal of pyridinic N at a pore edge are expected to create abundant intrinsic carbon defects (**Scheme 1**).



Scheme 1. The schematic illustration for the preparation of MOFs and defective N-doped carbons.

First, ZIF-8/Zn-HMT as a precursor of Zn, N-doped carbon material was synthesized according to previous research[2]. Zn-HMT, which is the zinc coordination polymer with HMT ligands, is considered an excellent template for growing different MOF. Zn-HMT is often employed as a self-sacrificed precursor or template, and the carbonization of Zn-HMT leads to N-rich carbon materials, which are important to create intrinsic carbon defects by the removal of N-dopants. Applying Zn-HMT as templates, ZIF-8/Zn-HMT was prepared by heteroepitaxial growing ZIF-8 on the templates with the reaction between in-situ released Zn ions from Zn-HMT and added 2-MeIm. Adding 2-MeIm can further increase the N contents of derivative carbons. Next, Zn, N doped carbon material was obtained by carbonization of ZIF-8/Zn-HMT at 900 °C for 2 h under an N_2 atmosphere. Additional thermal treatment was performed on as-prepared Zn, N doped carbon material to create high-density intrinsic carbon defects. The optimized catalysts showed a high plateau FE_{CO} over 90.0% under the potential range from -0.6 V to -0.9 V vs. RHE (**Figure 1**). The optimized catalyst is one of the best metal-free carbon electrocatalysts reported recently toward CO_2RR into CO in an aqueous solution.

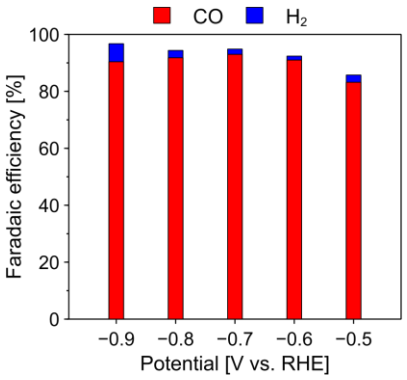


Figure 1. Faradaic efficiency of gas products on optimized catalyst at different applied potentials in a CO_2-saturated 0.1 M $KHCO_3$ solution.

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POST-SYNTHETIC METALATION OF AL-PMOF FOR ENHANCED VISIBLE-LIGHT CO_2 PHOTOCONVERSION

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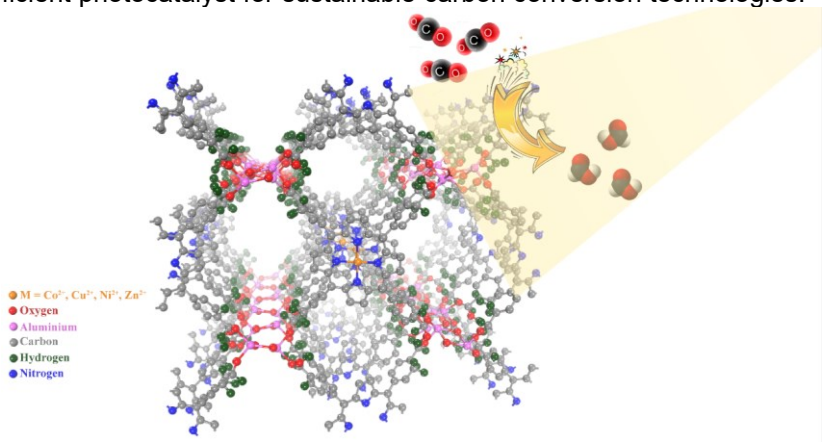
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Keywords: *Porphyrin-based MOF, CO_2 Photoreduction, Post-synthetic modification, Visible-light photocatalysis, Aluminum-based MOF*

The challenge of efficient CO_2 photocatalytic reduction to produce useful fuels persists because current photocatalysts encounter three main obstacles: restricted light absorption and insufficient charge separation together with poor electron transfer capabilities [1]. In this matter, aluminum-based porphyrin MOFs demonstrate great potential as photocatalysts under visible light because of their tunable structures and visible-light activity. Nevertheless, modest photocatalytic activity and fast electron-hole recombination remain plagues for pristine Al-PMOF. This study explores and compares the photocatalytic efficiency of Al-PMOF by incorporation of four non-noble metals (Co^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+})[2] under visible light irradiation, with a particular emphasis on formic acid production to address this critical gap, aiming to improve charge separation and catalytic performance[3]. Among the tested materials, Al-PMOF(Co) exhibited the highest photoactivity, and through systematic variation of the Co loading (0.25–15 wt.%), has been identified an incorporation level of 8 wt.% that maximizes photocatalytic performance while preserving the structural integrity of the MOF. The photocatalytic activity of Al-PMOF(Co) 8 wt.% (22.5 $\mu mol \cdot g^{-1} \cdot h^{-1}$) was 1.6-fold higher compared to pristine Al-PMOF. Through providing important insights into the electronic structure changes upon cobalt incorporation, Density Functional Theory (DFT) calculations validated the experimental results and clarified the mechanistic pathway of enhanced CO_2 photoreduction through bandgap narrowing and improved charge carrier dynamics. The reusability and stability of the material with the highest activity was examined through three different tests. These results highlight the role of cobalt incorporation in enhancing charge separation and improving CO_2 photoreduction. This work provides valuable insights into the design of efficient photocatalyst for sustainable carbon conversion technologies.



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ONE β-DIKETIMINATE ZINC MOF WITH CATALYTIC ACTIVITIES TOWARDS RING-OPENING POLYMERIZATION AND CROSS-COUPLING REACTIONS

Yahong Li, Liang zhang and Yafei Li

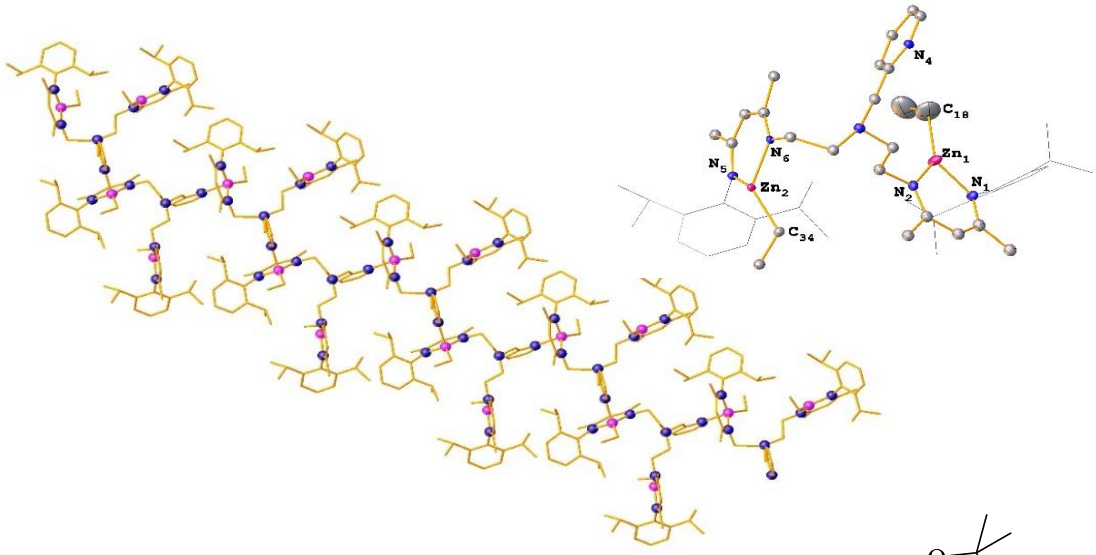
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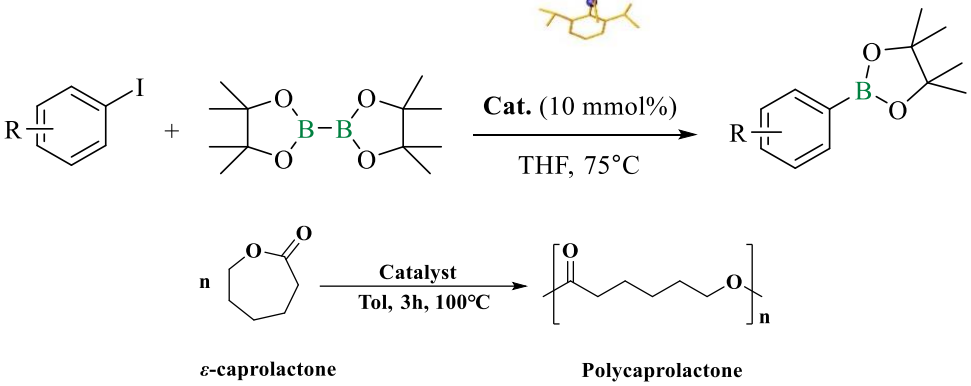
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Keywords: *Zinc, β-diketiminate, ring-opening polymerization, cross-coupling, aryl iodides*

Owing to low toxicity, wide availability, good biocompatibility, and low price of zinc, zinc-containing complexes have become increasingly important in many fields[1,2]. In this work, one zinc complex $[LZn_2Et_2]_n$ (**1**) was synthesized by reacting bis(β-diketiminate) ligand N^1-(4-((2,6-diisopropylphenyl) imino)pent-2-en-2-yl)-N^2-(2-((4-((2,6-diisopropylphenyl)imino)pent-2-en-2-yl)amino)ethyl)-N^2-(pyridin-2-ylmethyl)ethane-1,2-diamine (H_2L) with $ZnEt_2$. X-ray single-crystal diffraction analysis indicated that compound **1** displays a novel one-dimensional chain structure. Compound **1** exhibits high catalytic activities toward ring-opening polymerization of ε-caprolactone and cross-coupling reactions between aryl iodides and B_2Pin_2 (B_2Pin_2 = 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bis(1,3,2-dioxa-borolane)).

(a) (b)





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UNDERSTANDING THE ROLE OF CLUSTER DIMENSIONALITY IN NI-BASED METAL-ORGANIC FRAMEWORKS ON THEIR ACTIVITY IN OXYGEN EVOLUTION REACTION

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Keywords: *Ni-MOFs, cluster dimensionality, oxygen evolution reaction, oxohydroxide, disorder.*

The oxygen evolution reaction (OER) is a critical process in energy storage and hydrogen production. Metal-Organic Frameworks (MOFs) have emerged as promising OER catalysts [1], but their catalytic performance varies significantly with the dimensionality of the inorganic clusters, a factor that remains insufficiently understood and requires further investigation. In this study, two Ni-MOFs with chain (Ni-MOF-74) and layer (Ni-BDC)-type inorganic secondary building blocks were synthesized via a precursor-sacrifice approach [2], in which $Ni(OH)_2$, initially prepared through electrodeposition, serves as a precursor (**Figure 1a**). In situ Raman spectroscopy and ex situ X-ray techniques confirmed the pre-catalyst nature of the Ni-based materials, which transform into β-NiOOH with varying levels of disorder depending on the dimensionality of the inorganic secondary building units. Notably, the 2D loosely packed octahedral layer clusters in Ni-BDC promote greater disorder in β-NiOOH compared with chain (1D) clusters in Ni-MOF-74 and dense octahedral layer in $Ni(OH)_2$ as reported by the I_b/I_s ratio obtained from Raman bands of active phase, which enhances OER catalytic activity [3]. This improvement is evidenced by low overpotentials of 158 ± 7 mV at 10 mA/cm^2 and 216 ± 10 mV at 100 mA/cm^2, with a Tafel slope of 37.4 ± 2 mV/dec for Ni-BDC compared to other samples. Furthermore, the Ni-BDC catalyst exhibited a good stability, maintaining consistent performance over 100 hours at a current density of 100 mA/cm^2, making it one of the best Metal-Organic frameworks OER electrocatalysts to date. This study is among the first to establish a direct correlation between the structural properties of Ni-MOFs, the degree of disorder in the active MOF-derived (β-NiOOH) phase and its catalytic activity (**Figure 1b**). These findings provide valuable insights into the rational design of highly active and stable Metal-Organic Frameworks for future OER applications.

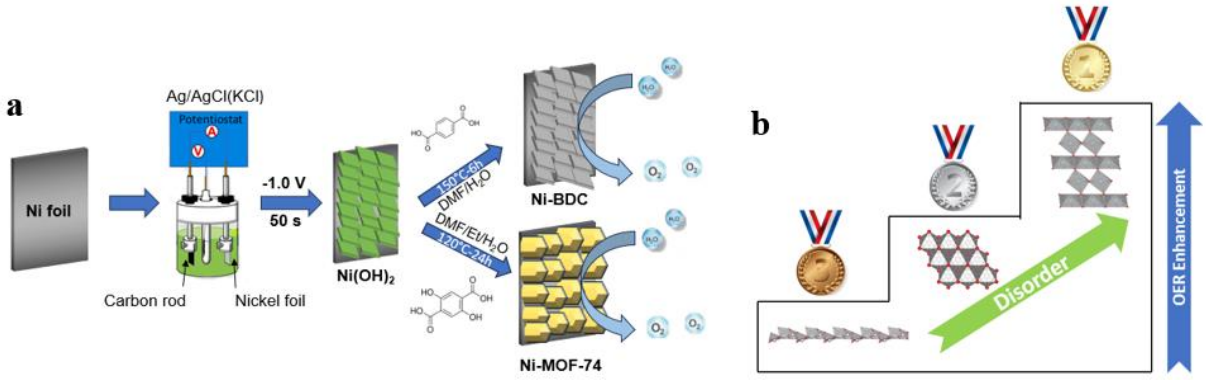


Figure 1: **(a)** Materials synthesis procedures and **(b)** correlation between the structural properties of Ni-MOFs, the degree of disorder in the active MOF-derived (β-NiOOH) phase and its catalytic activity.

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OXIDATIVE DEGRADATION OF POLYETHYLENE GLYCOL PROMOTED BY METAL–ORGANIC FRAMEWORKS

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Keywords: *Oxidative degradation, Polyethylene glycol, Catalyst*

Polyethylene glycol (PEG) is a water-soluble synthetic polymer widely used in industries such as pharmaceuticals, cosmetics, and biotechnology, thanks to its biocompatibility and low toxicity. Although PEG is generally considered safe and environmentally friendly, it can persist in aquatic and soil environments, raising concerns about its long-term impact as a pollutant. Current approaches to degrading PEG often rely on harsh chemicals, such as halogenated reagents[1], which are neither sustainable nor environmentally desirable.

In light of these concerns, our group has been working to develop a degradation method that does not require the use of harsh reagents. We turned our attention to metal–organic frameworks (MOFs), inspired by two key facts. First, that PEG is known to spontaneously insert into the coordination channels of MOFs in its molten state[2], and second, that open metal sites within MOFs have previously been reported to catalyze thermal degradation of polymers[3]. These distinctive features suggest that MOFs could serve as versatile and effective platforms for promoting polymer degradation reactions more broadly.

In this work, we utilized a one-dimensional nanochannel MOF featuring redox-active open metal sites within the channels to fully explore the catalytic potential of MOFs. When PEG chains are melted, they can enter the coordination channels and come into contact with the open metal sites. Upon heating the PEG with MOF powder in air, a degradation reaction occurred, and the resulting products included oligomers and shorter polymer chains which can be degraded readily in natural environment.

To determine whether degradation occurs within the coordination channels, we carried out a pre-insertion of PEG, ensuring the polymer was embedded within the coordination channels prior to the degradation process. This resulted in greater degradation than the simple heating method, indicating that the open metal sites within the pores act as active catalytic centers. In contrast, a one-dimensional nanochannel MOF lacking open metal sites showed significantly less degradation using the pre-insertion method. This comparison underscores the key role of open metal sites and highlights how MOF channel design influences reactivity. Overall, our findings demonstrate that MOF coordination channels can serve as confined environments for the oxidative degradation of polymer chains—a function not previously reported.

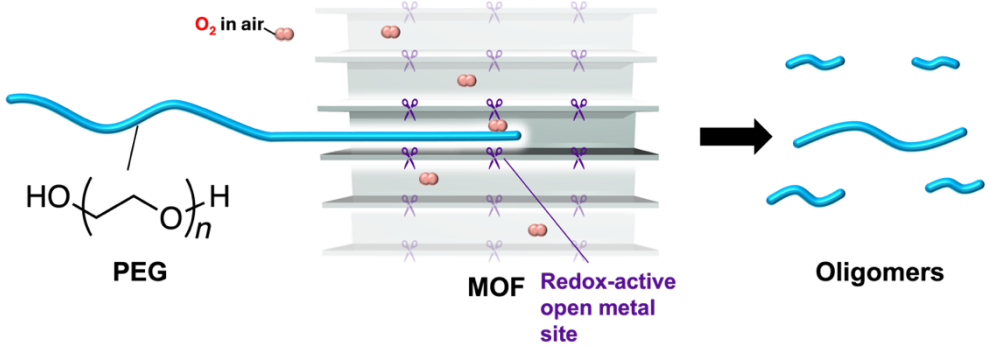


Figure 1: Schematic of the oxidative degradation of PEG promoted by the open metal site of MOF.

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HALOGEN-DRIVEN MODULATION OF IRIDIUM-FUNCTIONALIZED WATER-STABLE METAL–ORGANIC FRAMEWORKS FOR EFFECTIVE OXYGEN EVOLUTION REACTION

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Keywords: *Zirconium-based MOF, halogen, iridium, electrocatalysis*

Oxygen evolution reaction (OER) plays an important role in proton exchange membrane water electrolysis (PEMWE), however, due to the sluggish four-electron transfer process, OER is the rate-determining step in PEMWE. Therefore, the use of an electrocatalyst is necessary. And Iridium-based materials show excellent electrocatalytic activity for the reaction in acidic electrolytes. Nevertheless, the limited surface area of bulk iridium-based materials hinders the utilization of internal active sites. Through post-synthetic modification, high-density and highly addressable iridium active units can be incorporated within a water-stable metal–organic framework (MOF), UiO-66, enabling appealing performance for OER.[1] Moreover, halogen atoms could cause an electronic reconfiguration and modulate the electronic structure of iridium-based electrocatalysts for accelerating the reaction kinetics process.[2][3] We thus reasoned that abundant and well-dispersed halogen atoms neighboring iridium catalytic sites immobilized in the highly porous UiO-66 framework should be promising electrocatalysts for OER.

In this study, a series of UiO-66 analog, UiO-66-X (X = Cl, Br, I, H), are synthesized via different halogen-functionalized or non-functionalized terephthalate linkers,[4] and the spatially dispersed iridium catalytic sites are post-synthetically immobilized on the nodes of these UiO-66-X (see Figure 1).[1] The porosity, crystallinity, and iridium loading were characterized. The electrocatalytic performance of the resulting iridium-functionalized UiO-66-X is probed in 0.1 M $HClO_4$, and the effect of halogen species on OER process is further studied. Linear sweep voltammetry (LSV) reveals that Ir-UiO-66-Cl exhibits the current density approximately two times higher than that of Ir-UiO-66. Findings here shed light on the use of halogen atoms for modulating the local environment of the catalytic sites on the framework, suggesting that such material design could be further applied in various electrocatalytic systems.

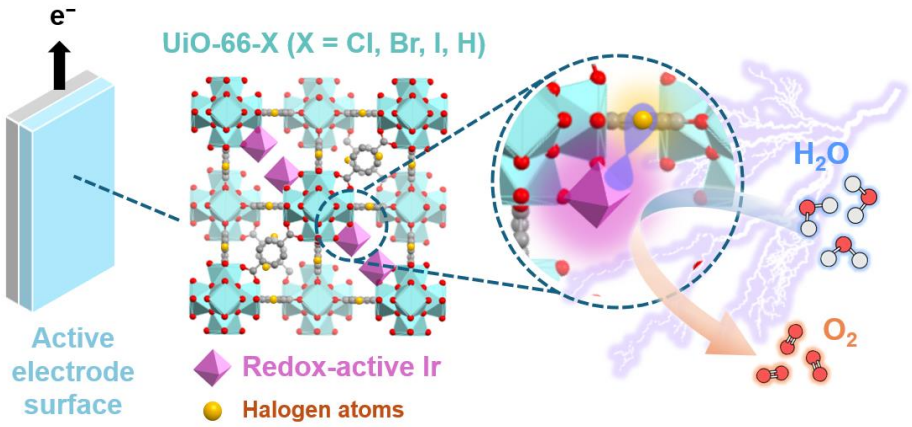


Figure 1. Schematic representation for the halogen atoms modulating the electronic structure of iridium catalytic sites immobilized in the UiO-66 structure and facilitating the OER.

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LIGAND FUNCTIONALIZATION AND MOFS SYNTHESIS FOR THEIR USE IN TUNEABLE GREEN CATALYSIS AND GAS SENSING

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Keywords: *Conductive MOFs, ligand functionalization, gas sensing, green catalysis.*

The increasing demand for sustainable alternatives to fossil-based chemicals and the growing concern about greenhouse gas emission are indicative of the urgent need for advanced materials capable of addressing these environmental challenges. Metal-organic framework materials (MOFs), with their tunable porosity, high surface area, and structural versatility, have emerged as promising candidates for catalysis and gas sensing. More concretely, triphenylene-based MOFs are gaining attention due to their inherent stability and potential for functionalization [1,2].

Functionalizing ligands with specific chemical groups, such as amines or hydroxyls, is a key strategy to enhance the performance of the resulting MOFs in terms of gas adsorption capacity, selectivity to specific gases and catalytic activity. This allows creating active sites within the MOF, allowing for stronger and more selective interactions with target gas molecules [3,] such as carbon dioxide (CO_2) and methane (CH_4). Furthermore, functionalization can also improve the overall stability of MOFs, making them less prone to degradation under environmental conditions.

This work reports the synthesis and characterization of hexaaminotriphenylene ligands through Buchwald–Hartwig coupling, as well as the formation of triphenylene derivatives via Suzuki–Miyaura cross-coupling reactions to introduce amine and hydroxyls functionalities [3,4]. These ligands have been used to construct MOFs using nickel, cooper and palladium metal salts as coordination nodes with high porosity and crystalline structures. Additionally, we are developing novel ligands based on trinaphthylene cores, expanding the diversity of polyaromatic scaffolds for MOF design [4,5]. These MOFs, thanks to their unique structure, have enabled the immobilization of catalytically active metal centers, including cooper, palladium and nickel, inside the framework. The resulting MOF-based catalysts demonstrate high activity and selectivity in Suzuki–Miyaura coupling reactions conducted in Natural Deep Eutectic Solvents (NADES), offering a sustainable approach to catalytic transformations. Furthermore, these MOFs have been successfully used as gas sensors for the detection of CO_2 and CH_4, the two main greenhouse gases.

In this presentation, we will describe the ligand synthesis and MOFs formation and characterization and we will discuss the relation between the catalytic and gas sensing properties and the ligand functionalization.

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TAILORED METAL-ORGANIC FRAMEWORK AND DERIVED MATERIALS FOR ADVANCED ENERGY CONVERSION AND STORAGE

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Keywords: *electrocatalysis, water splitting, zinc-air battery, superbattery*

The increasing demand for sustainable energy solutions has driven extensive research into the development of functional materials for energy storage and catalysis.[1-2] In this abstract, a series of innovative approaches to design and synthesize advanced metal-organic frameworks (MOFs) and MOF-derived materials with tailored structures and multifunctional properties is presented. As an advanced multifunctional electrocatalyst, a trimetallic Fe–Co–Ni MOF was synthesized via a layer-by-layer (LbL) reductive electrosynthesis method, yielding an epitaxially grown trilayer MOF architecture with outstanding trifunctional electrocatalytic activities towards the hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and oxygen reduction reaction (ORR), supported by density functional theory (DFT) calculations.[3] The Fe–Co–Ni MOF also demonstrated remarkable stability and superior performance in Zn–air batteries, surpassing that of commercial benchmarks, alongside notable supercapacitive properties. Building upon these breakthroughs, a MOF-derived Fe_2O_3/C composite integrated with N-doped reduced graphene oxide (rGO) demonstrated excellent bifunctional electrocatalytic performance, achieving a low potential gap (ΔE) of 0.88 V between OER and ORR in alkaline media, making it an excellent material for zinc-air battery cathodes.[4] Additionally, a partially transformed Ni-MOF-based hybrid material demonstrated enhanced electrochemical properties in alkaline battery configurations.[4] In another approach, a one-pot co-synthesis method was employed to develop a water-stable dual Ni/Co-MOF-reduced graphene oxide (rGO) nanocomposite, which exhibited superior capacitive behavior.[5] Furthermore, an Fe-doped zeolitic imidazolate framework-8 (ZIF-8) was composited with graphene oxide to fabricate a dual metal oxide/N-doped rGO (DMO–NrGO) heterostructure, delivering an almost unprecedented voltage window of 1.95 V in aqueous superbatteries alongside outstanding energy and power characteristics.[6] Collectively, these findings underscore the versatility of MOFs and their derivatives as platforms for the development of high-performance electrocatalysts and energy storage devices. The structure–property relationships elucidated in these works provide critical insights for the future design of multifunctional MOF-based materials for applications in catalysis, batteries, supercapacitors, and beyond.

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SHAPING OF METAL-ORGANIC FRAMEWORK BASED COATINGS FOR HYDROGEN PRODUCTION BY PHOTOCATALYTIC OVERALL WATER SPLITTING

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Keywords: *Metal-Organic Frameworks (MOF), photocatalysis, overall water splitting, coating*

Hydrogen (H_2) green production through photocatalytic water dissociation into H_2 and O_2 is currently one of the most attractive processes for hydrogen generation, particularly due to its intrinsic sustainable nature.[1] In this landscape, Metal-Organic Frameworks (MOF) have bloomed over the last years as promising catalyst candidates for the hydrogen and oxygen evolution reactions (HER and OER, respectively), showing very good conversion yields.[2] Non-noble MOF-based catalysts are particularly interesting and the MOF2H2 project appears as a game changer in the sustainable production of hydrogen from water through photocatalytic overall water splitting (OWS).[3]

Nonetheless, MOFs are powdered materials and in real life devices, coated films of the photoactive material are often required.[4] Stable films deposition can be achieved using different approaches, usually drop casting, spin-coating, spray pyrolysis and screen printing, and even if bulk MOF thin films can be formed, the film mechanical stability and its adhesion to the substrate can be easily compromised under the working conditions. To circumvent these limitations, binders are commonly used, often being from polymeric or inorganic nature. While for electrocatalytic overall water splitting polymer binders such as Nafion can often be found,[5] for light-driven photocatalytic OWS inorganic binders have shown to be particularly efficiency for larger panels shaping.[6]

In this communication, we will present our ongoing work on the shaping process of MOF-based catalyst films for light driven H_2 production, as part of the MOF2H2 project. The binders' selection and film optimization will be discussed and our most recent advances in large film shaping, and characterization will be highlighted.

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Acknowledgments:

The European Union under the Grant Agreement #101084131 (MOF2H2 project) is acknowledged for funding.

Fe-BASED METAL-ORGANIC FRAMEWORKS FOR PHOTOCATALYTIC AMMONIA SYNTHESIS

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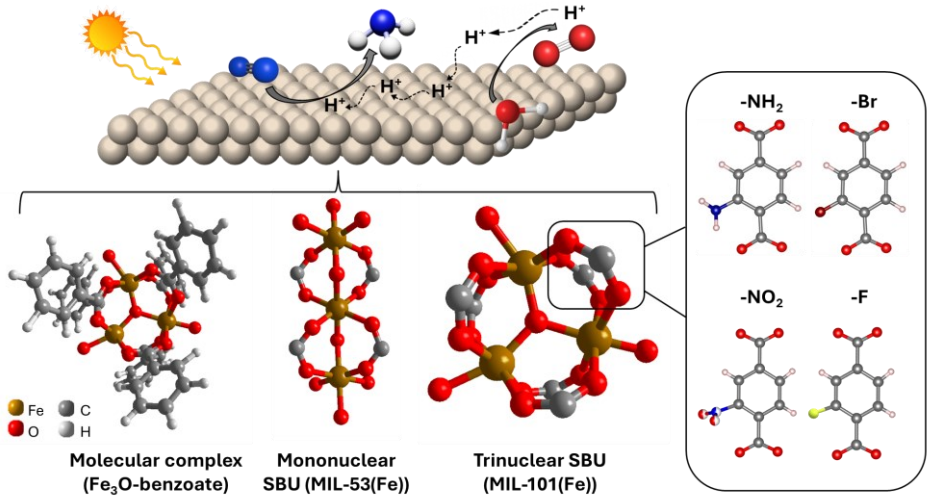
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Keywords: *Photocatalysis, Ammonia synthesis, Metal-organic frameworks*

Photocatalytic ammonia (NH_3) synthesis using Fe-based MOFs offers a sustainable alternative to thermo- and electro-catalytic routes, proceeding without external energy input and relying solely on light, nitrogen, and water [1-4]. However, the mechanistic understanding of charge separation dynamics and the structure-activity relationship remains limited.

In this work, MIL-101(Fe), composed of $Fe_3(\mu_3\text{-}O)OH(H_2O)_2$ clusters and modified dicarboxylate linkers, is used as a platform to introduce functional groups (–NH_2, –Br, –NO_2, –F) and investigate their influence on catalytic performance. Ligand tuning enables a systematic investigation of the interplay between activity, electronic structure, Lewis acidity of Fe, and N_2 adsorption capacity. Time-resolved infrared and visible transient absorption spectroscopy reveal distinct lifetimes of photoinduced charge-separated states following partial ligand dissociation from the Fe-oxo node, as recently reported for pristine MIL-101(Fe) [5].

To highlight the importance of the trinuclear oxo-bridged secondary building unit (SBU) present in MIL-101(Fe), we compare its performance to a molecular analogue (Fe_3O-benzoate) and a MOF featuring a mononuclear SBU (MIL-53(Fe)). Experimental and computational studies demonstrate the crucial role of the central oxygen atom in promoting delocalized electronic states and efficient redox shuttling within the trinuclear SBU, underscoring its function as a unique catalytic motif capable of facilitating both water oxidation and N_2 reduction.



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FACILE SYNTHESIS OF NANOPARTICLE@POLYMER@Zr-MOF CORE–SHELL NANOHYBRIDS FOR ELECTROCHEMICAL SENSING OF Pb(II) IONS

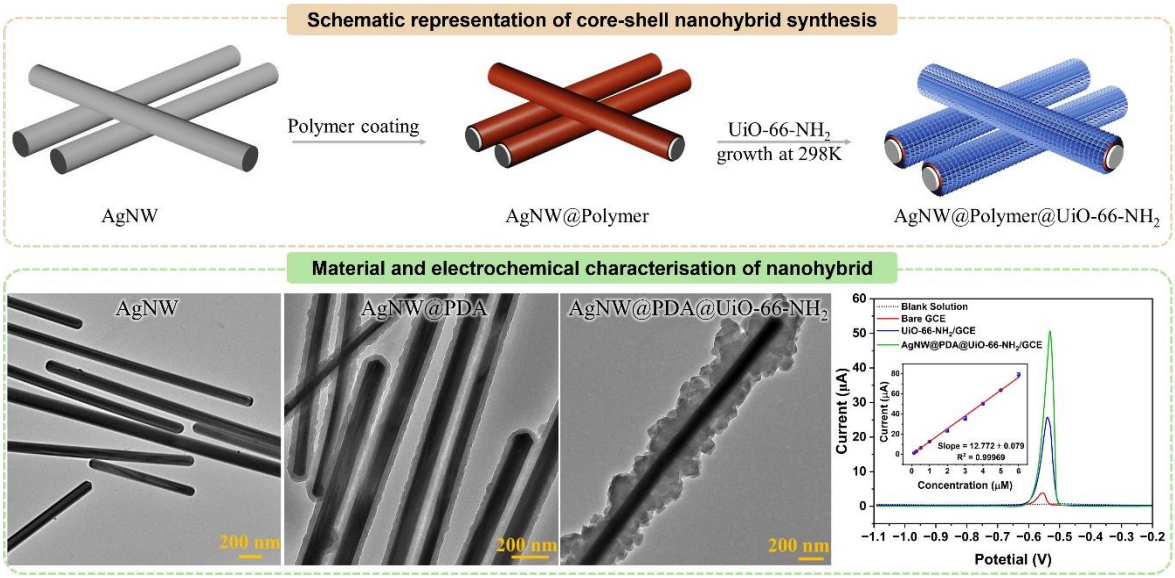
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Keywords: *UiO-66-NH_2, Core-shell nanohybrid, Electrochemical sensing, Heavy metal ion detection*

The synthesis of nanoparticle@zirconium (Zr) based core-shell hybrid is challenging due to aggregation of nanoparticles in MOF synthesis medium, often caused by thermal and salt-induced charge screening[1],[2]. Herein, we present an optimised room-temperature synthesis route for a well-defined core-shell structure of silver nanowire@polymer@UiO-66-NH_2 with a single nanoparticle as the core. The well-defined nanohybrid was obtained by optimizing the reaction system through a systematic study of key parameters, including the flow rate of organic linker addition, linker concentration, and the type of polymer coating, to control the core-shell morphology. The results indicate that increasing the flow rate of organic linker addition at a fixed concentration leads to the formation of more free MOF along with the core-shell nanohybrid. A similar trend was observed when the linker concentration was increased at a fixed optimised flow rate. This behaviour can be attributed to rapid MOF nucleation driven by the rising bulk linker concentration of the reaction system, which exceeds the optimum linker concentration for the formation of the core-shell nanohybrid. Next, different types of intermediate polymer coatings with functional groups such as amine, catechol (from polydopamine-PDA), hydroxyl and carboxyl (from carboxymethyl cellulose-CMC), and amide (from polyacrylamide-PAM)-promote metal ion chelation and facilitate the heterogeneous nucleation of MOF around the nanoparticles, possibly due to a reduction in interfacial energy, resulting in the formation of a defined core-shell nanohybrid[3]. The versatility of the developed synthesis route was further demonstrated by employing 2D and 3D-nanoparticles as cores, which led to the formation of uniform core-shell nanohybrids under optimised reaction conditions. Furthermore, the as-synthesised AgNW@PDA@UiO-66-NH_2 nanohybrid was employed as an electrode material for the electrochemical sensing of Pb(II) ions in water via differential pulse anodic stripping voltammetry (DPASV). By optimizing the deposition time, deposition potential, and concentration, the nanohybrid-modified GCE exhibited a limit of detection (LOD) of 0.5 nM, a limit of quantification (LOQ) of 1.56 nM, and a sensitivity of 12.8 μA/μM, demonstrating its high potential for trace-level heavy metal ion detection.



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ISOMERIC CYANO-VINYLENE-LINKED COVALENT ORGANIC FRAMEWORKS AND THEIR IMPACT ON PHOTOCATALYTIC HYDROGEN EVOLUTION

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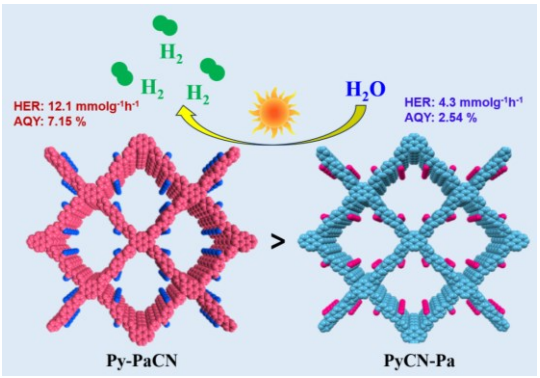
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Keywords: *Covalent organic frameworks; Cyano-vinylene linkage; Isomerism; photocatalysis; hydrogen generation.*

The global energy demand is rapidly growing, and at the same time, the essential energy resources are gradually decreasing with time.[1] Furthermore, the widespread usage of fossil fuels has resulted in pollution and climate change, raising serious environmental issues. Consequently, the sustainable production of clean fuel from renewable energy sources has received global attention. In this regard, hydrogen (H_2) has been considered a clean fuel and an environment-friendly alternative to fossil fuels, with potential utility as fuel in vehicles or in fuel cells for energy generation.Recent studies have shown that rational design of framework materials composed of donor-acceptor components can promote enhanced H_2 generation from water.[2,3] In this context, covalent-organic frameworks (COFs) offer significant advantages owing to their broad visible light absorption, efficient charge separation tunable pore size, and functionality making them an ideal candidates for photocatalytic hydrogen production application. Encouraged by the potential utility of COFs, we sought to develop functionalized Isomeric cyano-vinylene-linked frameworks and investigated their structural impact on hydrogen production from water. The synthesis, characterization, and photocatalytic investigation of D-A functionalized COFs for generating clean fuel will be presented.[4]



Scheme: Photocatalytic hydrogen production catalysed by the Isomeric cyano-vinylene-linked functionalized Covalent organic framework.

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SYNERGISTIC ADSORPTION AND PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE BY Mn-DOPED-ZIF-67@ZEOLITE-X HYBRID MATERIALS

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Keywords: *Mn-doped ZIF-67, Zeolite-X composite, water remediation, Methylene blue degradation*

Zeolitic imidazole framework ZIF-67 has attracted significant interest in dye removal applications owing to their high surface area and tunable pore structures[1]. Nonetheless, their practical applications are constrained by its structural instability, metal leaching, and limited active sites[2]. To overcome these challenges, we synthesized a series of hybrid materials combining ZIF-67 with Zeolite X and a further doping with manganese to enhance redox activity[3]. Four different materials were synthesized: ZIF-67, ZIF-67@Zeolite-X composite, Mn-doped ZIF-67, and Mn-doped ZIF-67@Zeolite-X composite. The comprehensive characterization performed using X-ray diffraction, scanning electron microscopy, Brunauer–Emmett–Teller surface area analysis, and UV–Visible diffuse reflectance spectroscopy confirmed the successful formation of hybrid structures, and an enhancement of the visible-light absorption capabilities associated to the Mn doping.

Our results showed that the Mn-doped ZIF-67@Zeolite X composite exhibited superior methylene blue removal efficiency through a synergistic adsorption and photocatalytic mechanism. The introduction of Zeolite X notably enhanced the structural stability of ZIF-67, substantially reducing cobalt leaching and thus ensuring long-term catalytic reusability. Mn doping further increased the photocatalytic activity by extending visible-light absorption, leading to improved degradation performance.

This study highlights the effectiveness of MOF–zeolite integration coupled with metal doping strategies to simultaneously achieve high adsorption capacity, efficient photodegradation, and enhanced stability. These findings offer valuable insights for designing robust hybrid materials tailored for sustainable water purification and wastewater treatment processes.

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EFFECT OF COPPER MODIFICATION ON PCN-222 PROPERTIES

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Keywords: *CO_2 photoconversion, Cu modification, MOFs*

Metal–organic frameworks (MOFs) are a class of crystalline materials formed by the coordination of metal ions or clusters with organic ligands, resulting in highly porous structures with exceptionally large surface areas. Their tunable pore sizes and adjustable chemical functionalities enable a wide range of applications, including gas storage and separation, catalysis, sensing, and drug delivery. Additionally, the unique properties of MOFs make them promising candidates for environmental remediation and energy storage solutions, addressing several contemporary technological and ecological challenges. Enhancing the activity of MOFs can be achieved through a variety of strategies that are often employed in combination. One common approach is post-synthetic modification, where functional groups are introduced to the framework after synthesis, thereby improving catalytic performance, selectivity, and adsorption properties. In parallel, defect engineering is used to intentionally create structural defects - such as under-coordinated sites - that serve as additional active centers. Altering the metal centers or modifying the organic ligands through metal doping further tunes the electronic and structural characteristics of the MOFs, leading to enhanced reactivity. Additionally, controlling the morphology and reducing the particle size by optimizing synthesis conditions increases the active surface area, which in turn boosts overall efficiency. Finally, the formation of composite and hybrid systems by integrating MOFs with other materials like metal nanoparticles, metal oxides, or carbon-based materials can induce synergistic effects that significantly improve their performance in various applications.

In this study, a series of PCN-222-based photocatalysts were successfully synthesized using a post-synthetic Cu^{2+} modification method, achieving photocatalytic activity under ultraviolet and visible light. With the help of transmission electron microscopy, the formation of hexagonal pores due to the fusion of Zr-SBU (secondary building units) with porphyrin was observed in detail for the first time. The mechanism of Cu^{2+} coupling with porphyrins in metal-organic structures (MOFs) and on the surface of MOFs in the form of oxides was studied in detail. The most active photocatalyst PCN-222 (Cu75) showed excellent performance in the photoreduction of CO_2 to HCOOH, achieving a conversion factor of 92.8 μmol g^{-1} h^{-1} and a quantum yield of 1.58% at 400 nm. The band edge levels of the components in the obtained materials were determined using first-principles calculations. The mechanism for excitation and photoconversion of CO_2 to HCOOH was proposed and confirmed using $^{13}CO_2$. The novel and rapid approach introduced in this study is a significant step toward efficient production of clean energy.

This research is supported by the Polish National Science Centre (Grant No. NCN 2021/41/B/ST4/00849).

HETEROSTRUCTURE NANOCATALYST BASED ON CE-MOF AND MOS_2 FOR VISIBLE-LIGHT-DRIVEN CO_2 REDUCTION TO ETHANOL

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Keywords: *Metal-Organic Framework, Heterostructure, Photocatalysis, CO_2 Reduction.*

The process of photocatalytic CO_2 reduction into value-added fuels and chemicals remains a highly promising avenue in the realm of renewable energy generation.[1] However, inadequate product selectivity, low yields of multi-carbon products, and fast recombination of electron-hole pairs are the main challenges for the practical implementation of photocatalysts.[2] In this study, we introduce a novel approach for utilizing the electrostatically self-assembled Ce-MOF and MoS_2 nanosheet-based heterostructure, referred to as Ce-MOF_MoS_2 NS for catalytic conversion of CO_2. Visible-light-driven CO_2 reduction by Ce-MOF_MoS_2 NS depicts a high yield of ethanol (1947 µmol/g in 18 hours) with a remarkable selectivity of 93.6 % in water (Fig. 1). The proximity of Ce-MOF and MoS_2 nanosheet facilitates the enhanced charge separation by creating a shorter electron transfer pathway from MoS_2 to the catalytically active low-lying 4f-orbitals of Ce^{4+}.[3] This electron migration route has been confirmed by the ultrafast transient absorption measurement, Kelvin probe force microscopy (KPFM), electron paramagnetic resonance spectroscopy, time-dependent density functional theory calculations, and photoelectrochemical measurements.[4,5] The facile electron transfer from MoS_2 to Ce^{4+} and the existence of two CO_2 molecules near the defect site in Ce-MOF enables the C–C coupling, thereby leading to ethanol formation. Furthermore, in situ diffuse reflectance FTIR analysis has been performed to deduce the probable mechanistic pathway for CO_2 reduction over Ce-MOF_MoS_2 NS. Overall, these findings highlight the rational design of a MOF-based photocatalyst for the efficient conversion of CO_2 to sustainable chemicals.

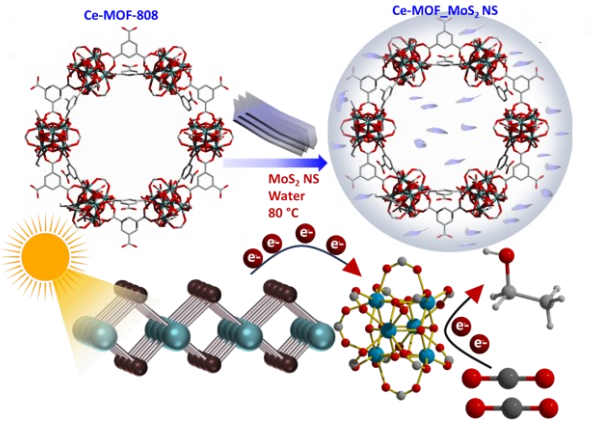


Fig. 1 Schematic representation of developing Ce-MOF_MoS_2 NS towards visible-light-driven CO_2 reduction for ethanol formation.

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A NOVEL BIOCOMPATIBLE IRON–*N*-ACETYLASPARTIC ACID MOF FOR PHOSPHATE SEQUESTRATION: TOWARD ORAL THERAPIES FOR CKD PATIENTS

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Keywords: metal-organic framework, phosphate sequestering, biocompatibility, iron MOF, gut-restricted therapy, CKD

Hyperphosphatemia, characterized by elevated serum phosphate levels, is a common and life-threatening complication in patients with chronic kidney disease (CKD). Current phosphate binders often suffer from limited efficacy, poor tolerability, and high pill burden, underscoring the need for safer and more effective oral therapies. Metal–organic frameworks (MOFs), with their tunable porosity, high surface area, and chemical versatility, offer a promising platform for targeted ion sequestration in biomedical applications. In this study, we report the synthesis and characterization of a novel biocompatible MOF based on iron and N-acetylaspartic acid (Fe–NAA MOF), designed for selective phosphate binding under gastrointestinal (GI)-relevant conditions as a potential oral therapeutic for managing hyperphosphatemia in CKD patients.

The Fe–NAA MOF was synthesized via a one-pot solvothermal method using $FeCl_3$ and N-acetylaspartic acid in aqueous media. The structure was confirmed by powder X-ray diffraction (PXRD), while thermal and aqueous stability were assessed using thermogravimetric analysis (TGA) and Brunauer–Emmett–Teller (BET) surface area measurements. Phosphate binding performance was evaluated across a range of pH values simulating the GI tract (pH 2–7.5), revealing high binding capacity (250–300 mg/g) and selectivity in the presence of competing ions such as chloride, sodium, calcium, and magnesium.

To assess biocompatibility, the Fe–NAA MOF was formulated in capsules and orally administered with feed to a 5/6 nephrectomized porcine model simulating CKD conditions. The dosing regimen was 1.5-2.0 g/day (administered twice daily) over a 90-day period. Systemic inflammatory markers were monitored to evaluate tolerability. Serum white blood cell (WBC) counts remained stable (Day 1: 11.77 × 10^9/L; Day 89: 11.01 × 10^9/L), and C-reactive protein (CRP) levels stayed within physiological limits (Day 1: 0.5 mg/L; Day 89: 0.4 mg/L), indicating no acute immune activation or systemic inflammation. Serum electrolyte levels—including sodium, calcium, magnesium, and chloride—also remained within normal physiological ranges throughout the dosing period, further supporting the material's biocompatibility. Further studies are in progress in healthy and 5/6-neprectomized SD rats.

This work highlights the feasibility of leveraging iron-based MOFs for biomedical ion sequestration and lays the foundation for further development of gut-restricted therapies for CKD-related complications.

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POST-SYNTHETIC IMMOBILIZATION OF ENZYMES INTO ZIF-8 PRESERVES STABILITY AND ACTIVITY

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Keywords: *Enzyme stabilization, Metal–organic frameworks (MOFs), Protein–MOF interaction,ZIF-8 infiltration,Biocatalysis.*

Enzymes are biological catalysts that accelerate chemical reactions in living organisms, playing a crucial role in various physiological processes. Targeted delivery of enzymes is a promising area of research for treating diverse diseases; however, their intrinsic fragility low thermal stability, limited pH tolerance, and susceptibility to denaturation in organic solvents remains a critical barrier. Encapsulation of biomacromolecules in metal−organic frameworks (MOFs) has emerged as a promising strategy to preserve biological functionality under harsh conditions, but conventional one-pot encapsulation often compromises enzymatic activity.
Here, we demonstrate that employing enzyme infiltration instead of one-pot encapsulation within zeolitic imidazolate framework-8 (ZIF-8) preserves the catalytic potential of enzymes under a variety of stress conditions. Comparative activity assays revealed that one-pot encapsulation led to 100% loss of activity across the enzymes tested, while infiltration maintained >90% of their native activity. Spectroscopic characterization (FTIR and CD analysis) confirmed that ZIF-8 precursors induced conformational changes during in-situ encapsulation, causing irreversible denaturation, whereas infiltration retained the secondary structure of the enzymes.Furthermore, stability tests demonstrated that infiltrated enzymes retained up to 85% activity after exposure to elevated temperatures (60 °C), retained >80% activity.
Our findings highlight that minimizing direct interactions between ZIF-8 precursors and enzymes through infiltration prevents structural deformation and allows enzymes to maintain their native conformation and catalytic efficiency. This mild, biocompatible strategy offers a powerful route for engineering robust biocatalysts and holds significant promise for applications in industrial biocatalysis, biosensing, and therapeutic enzyme delivery.

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COPPER RELEASE BY MOF-74(Cu) IN PHYSIOLOGICAL MEDIA, AN IN VITRO AND IN VIVO STUDY

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Keywords: MOF-74*, copper release, copper biodistribution*

Low concentrations of copper in the brain have been linked to neurodegenerative diseases. This defect impairs the body's ability to distribute copper properly throughout the body. Consequently, the brain and other parts of the body do not receive sufficient copper, which instead accumulates in the small intestine and kidneys. Therefore, the administration of this metal is recommended as a treatment to reduce neuronal deterioration and prevent disease progression.[1] In this context, advances in the application of innovative systems for the delivery of Cu(II) could provide new strategies with the potential to significantly improve the treatment of diseases.[2]

MOF-74 is a well-known family of MOFs with a wide variety of divalent metal cations coordinated to the 2,5-dioxide terephthalate (DOT) ligand, and it is typically characterised by its open metallic sites. However, its low chemical stability towards water significantly limits any plausible industrial application for this Cu(II)-based MOF. This apparent disadvantage is explored for potential clinical applications. This work investigate the gradual decomposition of MOF-74(Cu) in a physiological environment, keeping in mind that released copper distribute throughout the body, including brain.

The kinetics of Cu(II) release from MOF-74(Cu) were evaluated in vitro using the dialysis membrane diffusion technique. The in vitro Cu(II) release profiles from MOF-74(Cu) were assessed in phosphate buffer at a physiological pH of 7.2.

Release profile data were fitted to mathematical models to understand the kinetics of Cu(II) release from MOF-74(Cu). The Cu(II) release data from MOF-74(Cu) was best fitted to the zero-order kinetic model.

For the study of the biodistribution of MOF-74(Cu), in vivo experiments were carried out in male Wistar rats. Considering the total copper content, the total mass of MOF-74(Cu) necessary to administer doses D1 (39.75 mg kg^{-1}) and D2 (79.5 mg kg^{-1}) of Cu(II) was calculated. It was found that doses of 312 mg kg^{-1} and 156 mg kg^{-1} per body weight of the rat caused high toxicity and weight loss, respectively, as indicators of disrupted homeostasis. A dose of 79.5 mg kg^{-1} body weight did not produce either of these harmful effects.

The *in-vivo* study where the compartmentalization of copper in different relevant tissues was carried out[3], representing an interesting and novel pharmacological alternative to neurodegenerative diseases, since the risk of accumulation and intoxication by copper in the main detoxification organ, the liver, is considerably reduced while a slight increase of copper in the brain is required.

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STRUCTURING FUNCTION: MOF–POLYMER COMPOSITES FOR CUSTOMIZABLE THERAPEUTIC APPLICATIONS

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Keywords: *MOF–polymer composites, Drug delivery systems, Tissue engineering, Multifunctional materials, Material design*

Platforms for advanced therapeutic applications increasingly demand materials that combine tailored functionality with defined mechanical properties and application-specific shapes. One promising strategy to address these demands is the integration of (multi)functional components into biocompatible polymer matrices. In this context, metal-organic frameworks (MOFs) have emerged as attractive candidates due to their modularity, high porosity, and tunable properties, while polymers offer flexibility, processability, and the ability to act as reservoirs, support structures, and performance enhancers. Herein, we demonstrate how MOF–polymer composites can unite the best of both worlds to create systems with tailorable properties for specific therapeutic scenarios. Across three recent studies, we explore how MOF type and functionality, polymer matrix, drug cargo, shaping method, and composite design can be systematically varied to engineer materials for specific therapeutic scenarios. In the first approach, melt electrowriting (MEW) was used to fabricate microfibrous scaffolds from polycaprolactone, a biodegradable polyester known for its robustness and cytocompatibility. Incorporation of NH_2-MIL-88B(Fe), decorated with silver/silver chloride, yielded scaffolds with antibacterial activity, MRI visibility, and immune compatibility. MEW enabled precise architectural control, while the MOF served as a functional filler and potential drug carrier, opening pathways for localized therapeutic delivery.[1] In a second strategy, the MOF ZIF-8(Zn) was loaded with Thioflavin T and embedded in an alginate hydrogel, creating soft, processable materials with pH-triggered release behaviour suitable for wound and tumour environments. Sodium alginate, a naturally derived, biocompatible, and clinically established polysaccharide, ensured mild processing and biomedical relevance. Structural integrity and release profiles were maintained, and varying incorporation methods enabled tuning of drug release, highlighting the versatility of MOF-hydrogel systems for implant coatings and topical delivery.[2] Lastly, ZIF-8(Zn) was used to encapsulate both 5-fluorouracil and bromelain, further underlining its multifunctionality. Embedding the drug-loaded MOFs into alginate once more enabled translation into application-relevant formats for skin-related therapies. The concept was also extended to other MOFs such as UiO-66(Zr) and MIL-100(Fe), demonstrating adaptability to different cargos and chemistries.[3]
Together, these studies showcase a flexible therapeutic platform approach in which MOFs function as active, multifunctional components, and composite properties can be tailored through informed material selection and design.

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PURIFYING AIR FROM PATHOGENIC FUNGAL SPORES USING METAL-ORGANIC FRAMEWORKS@POLYSOLFUNE BEADS IN FOOD STORAGE

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Keywords: *MOFs, air filtration, antifungal activity, polysulfone composites, food storage*

The increasing incidence of postharvest fungal infections, particularly by *Penicillium expansum* and *Botrytis cinerea*, poses a major threat to global food security and storage sustainability. Current strategies based primarily on chemical fungicides present increasing challenges due to the development of fungal resistance and chemical residue issues. Here we report metal organic framework@polysolfulone composite (MOF@PSF) beads for air filtration from relevant pathogenic fungal spores at the postharvest stage.[1]

MOFs based on essential metals such as zinc and copper, including HKUST-1,ZIF-8 and and Zn(II)/Cu(II)-bipyrazolate frameworks (e.g., ZnBPZ, $ZnMe_4BPZPh$, $CuNH_2BPZ$) known for their properties and previous applications, were investigated. Composite beads were prepared by the phase inversion method and characterized for their structure and porosity, highlighting the retention of crystallinity and porosity of MOFs incorporated into the polymer matrix.

The *in vitro* antifungal activity of these MOFs and composite beads was evaluated against several fungal species responsible for rapid fruit spoilage. The results showed significant inhibition of mycelial growth for HKUST-1 and ZIF-8 against most of the fungal strains tested. The MOF@PSF beads retained high porosity, and demonstrated strong antifungal effects via multiple mechanisms, including reactive oxygen species (ROS) production, and inhibition of spore germination. Further investigations explored the mechanisms of antifungal action, including effects on cell wall and membrane integrity and ROS production in hyphal cells.

A custom-built dual-chamber filtration prototype,(Figure) designed to simulate food storage conditions, confirmed the effective removal of airborne fungal spores by the MOF@PSF filters. The system significantly reduced fungal growth and cross-contamination, offering a chemical-free and reusable approach to improve postharvest fungal infection. These results underline the potential of MOF@PSF beads as sustainable air filtration materials for food safety and environmental applications.

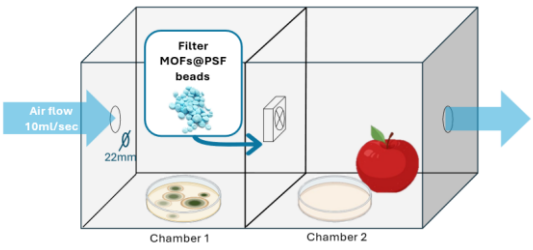


Figure. Experimental setup of the dual-chamber prototype used for air purification tests

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NUMERICAL ANALYSIS OF KEY FACTORS IN DRUG ENCAPSULATION OF CYCLODEXTRIN-BASED METAL–ORGANIC FRAMEWORKS WITH AMPHIPHILIC NANOPORES

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Keywords: *Cyclodextrin, Drug Delivery System, Drug Encapsulation, Numerical Analysis*

Introduction

Metal–Organic Frameworks (MOFs) are porous materials with high potential in drug delivery systems (DDS) due to their large surface area, tunable pore structures, and modifiability. Cyclodextrin-based MOFs (CD-MOFs) have attracted attention for their excellent biocompatibility and unique amphiphilic pore structure, allowing for the encapsulation of both hydrophilic and hydrophobic drugs [1]. However, the key factors influencing drug encapsulation in these systems remain unclear. In this study, we performed molecular simulations on 26 types of anticancer drugs with varying hydrophobicity and molecular weight to evaluate their encapsulation behavior in CD-MOFs. Multiple regression analysis was also conducted to identify the molecular properties most strongly associated with drug loading.

Simulation Method

To consider the presence of ethanol as a solvent in the simulations, a two-step simulation approach was employed. Canonical Monte Carlo (CMC) simulations were conducted to evaluate the chemical potentials of 5-fluorouracil (5FU) and ethanol in a simulated solution phase. The Widom insertion method was employed, wherein μ was calculated from the energy change associated with the insertion of a virtual molecule. The obtained chemical potential of 5FU was then used in grand canonical Monte Carlo (GCMC) simulations. Interatomic interactions in both simulations were modeled using the Lennard–Jones (LJ) potential and Coulombic interactions. Simulations were performed at a temperature of 298 K, and the encapsulation amount of the drug at constant chemical potential was evaluated. The hydrophobic pores of the CD-MOF were defined as a spherical region with a radius of 0.5 nm. Ensemble averaging was applied to calculate the number of drug molecules encapsulated per unit cell. The drug molecules used were selected from an anticancer drug database.

Results and Discussion

The chemical potential of 5FU calculated by the Widom insertion method was −4826.02 K. The calculated loded amount with calculated fugacity was 128.84 mg-drug/g-MOF. This was closer to the experimental result of 143.0 mg-drug/g-MOF. Therefore, the Widom insertion method more accurately reflects experimental conditions. Due to the computational cost of applying CMC simulations to all drugs, a fixed chemical potential of −4826.02 K was adopted for all GCMC simulations.

From the multiple regression analysis, total loaded amount was negatively correlated with molecular weight and LogP, suggesting that increased steric bulk and hydrophobicity reduce loading efficiency. LogP is the logarithm of a compound's partition coefficient between octanol and water and reflects hydrophobicity. In contrast, the presence of halogens and benzene rings positively influenced loading, likely due to enhanced interactions with the MOF framework. For hydrophobic pores specifically, carbon chains and benzene rings contributed positively to encapsulation. Molecular shape, characterized by bounding box dimensions, also played a role. The elongated molecules with smaller width and greater length showed better encapsulation efficiency. Compact 3D structures, such as Cabazitaxel, hindered the encapsulation into pore, whereas linear molecules like Capecitabine were more easily encapsulated.

Conclusion

In this study, the chemical potentials were calculated using CMC simulations, enabling GCMC simulations that account for the presence of solvent. Encapsulation simulations were performed for 26 different drug molecules, and the loaded amount in each type of pore were quantified. The simulation results were generalized through multiple regression analysis. Based on the obtained regression coefficients, we successfully quantified the physicochemical properties of drug molecules that contribute to the encapsulation mechanism in CD-MOFs.

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ROLE OF STRUCTURAL DEFECTS IN MOF ON DRUG LOADING

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Keywords: *Defect engineering, UiO-66, Drug delivery system*

Introduction

Metal–organic frameworks (MOFs) are porous crystals formed by self-assembly of metal ions and organic ligands. MOFs have shown promise as carriers for drug delivery system (DDS) to deliver drugs to the site of disease. Easy functionalization is one of the advantages of MOFs. One of the functionalization methods is defect engineering, in which metal ions and/or organic ligands are defective. Defects in MOFs result in an increase in the pore size and a change of the hydrophilicity and hydrophobicity in the pores [1]. These factors should have the potential to improve the drug-lading capacity in DDS. However, the effect of defects on drug-loading capacity is still known. This study focused on the defective UiO-66 to investigate the effect of defect on drug-loading capacity. For this purpose, this study specifically examined the size ratio of MOF pores to drug molecules and the number of sites of hydrogen bonding.

Experiments

This study used three different UiO-66, which was composed of zirconium ions and terephthalic acid (BDC). UiO-66 was synthesized by the solvothermal method. Defective UiO-66 was synthesized using a controlled secondary building unit (SBU) approach. The SBU precursor was synthesized in advance and reacted with BDC linker at room temperature. UiO-66_TCI was purchased from Tokyo Chemical Industry (TCI). The structural defects in MOFs were evaluated by TGA and XRD measurements. 5-fluorouracil (5FU) and curcumin (CCM) were selected as model drugs. These drugs have different molecular weights and number of hydrogen bond site. The amount of drug loaded into MOFs was calculated from HPLC measurement. We investigated the effect of defects with MOFs on drug-loading capacity of MOFs.

Results and discussion

Defect ratio was calculated from the TGA profiles [2]. The defect ratio was larger in the order of UiO-66, Defective UiO-66, and UiO-66_TCI. The low angle XRD peaks suggested the presence of metal cluster defects in Defective UiO-66 and UiO-66_TCI. The amount of 5FU loading gradually decreased as the defect ratio of MOF increased. Meanwhile, the trend of the loading amount of CCM was converse to that of 5FU. These trends were suggested to be determined by the balance between the size ratio of pore to drug sizes and the number of OH group of zirconium cluster with MOFs involved in hydrogen bonding.

Conclusion

In this study, the effects of defects with UiO-66 on the drug-loading capacity were investigated. It was revealed that the effects of defects varied with type of drug. Defects in MOFs have the potential to improve selectivity and loading capacity for specific drug molecules.

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ENVIRONMENTAL HAZARD TESTING OF METAL-PHENOLIC NETWORKS USING AQUATIC ORGANISMS

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Keywords: *metal-phenolic networks, ecotoxicity, aquatic toxicity, heavy metals*

The mining industry and wastewater treatment processes need effective metal remediation and recovery technologies to promote environmental safety and the circular economy. One actively studied group of novel adsorbents is metal-phenolic networks (MPNs), synthetic materials in which plant-based polyphenol linkers coordinate with metal ions to form a 3D structure. Coating MPNs on nanoparticle cores increases specific surface area and, consequently, also their adsorption capacity [9]. In this study, the environmental effects of MPN nanoparticles (MPN NPs) are investigated systematically, following an exposure-scenario -based approach to inform the design and development of MPN NPs as heavy metal adsorbents.

MPN NPs of gold core, tannic acid (TA) as phenolic linker, and either iron, cobalt, nickel, or chromium as coordinating metal were synthesised freshly prior to each test. Biocompatibility was first tested using microorganisms [1], which were exposed to MPN NPs in MQ water for 2 h or 24 h, and subsequently, growth on a nutrient agar was used as an indicator of microbial viability. None of the tested MPN NPs (Fe-TA@Au, Co-TA@Au, Ni-TA@Au) showed toxicity at 50 mg/L against bacteria (*Escherichia coli, Staphylococcus aureus*) or microalgae (*Raphidocelis subcapitata*). The effects of the MPN NP components (i.e., TA and metals) were also tested to detect effects of possible degradation of MPN NPs. After 2 h exposure, TA, $FeCl_3$, $Co(NO_3)_2$, and $NiCl_2$ showed no toxicity at 1000 mg/L, 200 mg/L, 700 mg/L, and 700 mg/L, respectively, against *E. coli* and *S. aureus*. These concentrations were about two orders of magnitude higher than the levels of TA and metals in MPN NPs, indicating that MPN decomposition would pose no hazard to aquatic prokaryotic microbial communities. Similarly, TA and $FeCl_3$ did not affect algal viability after 2 or 24-h exposure at the concentrations present in MPN NPs. However, Co^{2+} and Ni^{2+} salts exerted an algicidal effect at as low as 7 mg/L. While the algicidal concentrations of Co^{2+} and Ni^{2+} were higher than the levels of Co or Ni in MPN NPs, the results suggest that freshwater algae could be affected by the degraded Co- or Ni-based MPNs. After 24 h exposure, the bactericidal concentrations of Fe^{3+}, Co^{2+}, and Ni^{2+} salts were still at least an order of magnitude higher than the metal levels in MPN NPs, indicating that MPN decomposition would not affect aquatic microorganisms during 24 h. Also, the tests with the marine non-pathogenic bacterium *Aliivibrio fischeri* (EN ISO 11348-3:2008) indicated that none of the MPN NPs inhibited the natural bioluminescence of the bacteria, while pure metal salts and TA had <10% inhibiting effects. This confirms the reduced toxicity of complexed metals (i.e., coordinated in MPNs) and thus, their improved biocompatibility compared to single components.

Biocompatibility of MPN NPs was further tested with an OECD Test No. 201: Freshwater Alga and Cyanobacteria, Growth Inhibition Test, where *R. subcapitata* was exposed to MPN NPs (50 mg/l) for 72 h under illumination and constant shaking. Taken together, among the tested MPN NPs, Fe-TA-based MPN appears as the most promising candidate for environmental applications of heavy metal adsorption.

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FROM STRUCTURE TO FUNCTION: TUNING MIL-101(Fe) PLATFORMS FOR ANTI-INFLAMMATORY AGENTS DELIVERY

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Keywords: *Fe-based metal-organic frameworks, nanocarriers, adsorption, drug-controlled release, anti-inflammatory activity*

Migraine, one of the neurological conditions, affects approximately 15% of the global population. It is characterized by intense headaches accompanied by nausea, vomiting, and heightened sensitivity to light.[1] The mechanism of migraine remains unclear, but it may involve inflammation. In recent years, scientists have focused on various therapies based on combinations of nonsteroidal anti-inflammatory drugs with substances of natural origin, which selectively inhibit cyclooxygenase 1 and 2 (COX1 and COX2). Unfortunately, these medications often suffer from poor water solubility, uncontrolled release, and numerous adverse side effects. To overcome these limitations, advanced drug delivery systems are being developed. Metal-organic frameworks, with highly customizable features such as size, pore structure, shape, and surface properties, offer significant capability as biological agent platforms to meet specific therapeutic needs. These materials can be engineered to possess stimulus-responsive drug release.[2]

Our study aims to evaluate the potential of the MIL-101(Fe) materials synthesized under various conditions as carriers for sodium naproxen or ketoprofen combined with curcumin to maximize the efficacy of migraine treatment. Such advanced delivery systems will be safer and more compatible with human physiology.

The solvothermal synthesis of materials was carried out at a temperature range of 90-120 ºC for 24 h in *N,N*-dimethylformamide. Iron(III) chloride and terephthalic acid were applied as a metal precursor and a linker, respectively. The samples were characterized in detail using X-ray diffraction, low-temperature nitrogen adsorption/desorption, thermogravimetric analysis, infrared spectroscopy, and scanning electron microscopy. The cytotoxicity of MIL-101(Fe) materials was evaluated through the WST−1 colorimetric assay. The adsorption of biological agents (naproxen sodium, ketoprofen, and curcumin) was conducted for 2 hours at RT. Subsequently, the release processes were carried out in phosphate buffers, simulating intestinal (pH 6.8) and saliva (pH 7.4) fluids at 37.0 ºC. The potential of MIL-101(Fe) materials with adsorbed naproxen sodium/ketoprofen and curcumin to inhibit cyclooxygenases (COX-1 and COX-2) was also tested.

The synthetic conditions of MIL-101(Fe) materials strongly influenced their textural parameters, morphology, sorption capacity, and anti-inflammatory activity. All MIL-101(Fe) carriers had a typical microporous structure, which is indicated by the nitrogen adsorption-desorption isotherm of type I. The material obtained at 120 ºC exhibited the highest specific surface area (1492 m^2/g) and pore volume (1.12 cm^3/g) among all synthesized carriers. The particles' shapes were spherical or octahedral. The samples were characterized by low cytotoxicity. Cell viability remained high even at the concentration of 200 µg/ml. The MIL-101(Fe) materials demonstrated high sorption capacities towards naproxen sodium (140-470 mg/g), ketoprofen (80-209 mg/g), and curcumin (42-167 mg/g). The differences were associated with better solubility of naproxen sodium (200 mg/ml) and ketoprofen (9.9 mg/ml) compared to curcumin (0.31 µg/ml), and the type of interactions between the active substances and the MIL-101(Fe) surfaces. The study showed that the pH of the environment and the intrinsic porosity of carriers significantly affect the naproxen sodium, ketoprofen, and curcumin release. Biological agents-loaded platforms inhibited COX-1 and COX-2 enzymatic activity, with the most potent effect observed for the MIL-101(Fe) sample obtained at 120 °C. The anti-inflammatory activity was further confirmed by suppressed IL-6 secretion under LPS stimulation.

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STUDY OF THE FLEXIBILITY OF A MULTITARGET DRUG CARRIER AND HIS DRUG CAPTURE AND DELIVERY

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Keywords: *SMOF, drug-delivery, flexible crystal structure…*

The great potential of porous metal-organic materials (MOFs) has led to a large number of studies in various applications over the last decade. Among the wide variety of such compounds are the family of SMOFs (supramolecular metal-organic frameworks).[1] Herein, we present a SMOF **CuNaph** formed by a heptameric copper-adenine $[Cu_7(\mu\text{-adeninato})_6(\mu_3\text{-OH})_6(\mu\text{-OH}_2)_6]^{2+}$ entity and a dicarboxylate counterion (2,6-naphthalendicarboxylate anion). These structural units are linked by supramolecular interactions such as hydrogen-bonds and $\pi-\pi$ stackings. The supramolecular network established by these interactions is flexible enough to allow a rearrangement of the structure when the water solvent molecules are removed or when we introduce new molecules into its pores, showing a structural breathing effect depending on the filling of the pores.

Addressing drug loading and release applications, our research group has already demonstrated the efficacy of these materials for the controlled released of anti-cancer drugs such as 4/5-ASA, allopurinol and 5FU.[2] This finding underlines the importance of research in this area and highlights the importance of using suitable materials to release drug molecules. However, there are still some issues such as drug rapid release, non-specific distribution, degradation or limited efficacy that must be addressed. In this sense, it is mandatory to get an insight on how these molecules interact with the drug carrier. In the present study, we have carried out an exhaustive single crystal diffraction study of the molecular interactions that 5Fu and cis-Pt drugs establishes with this SMOF, Figure 1. In addition, it has been possible to load these two drugs simultaneously and to study their release kinetics in comparison with single drug loaded samples. These results must be understood as the first steps in the search of multi-drug carriers for multitarget therapeutic approaches.

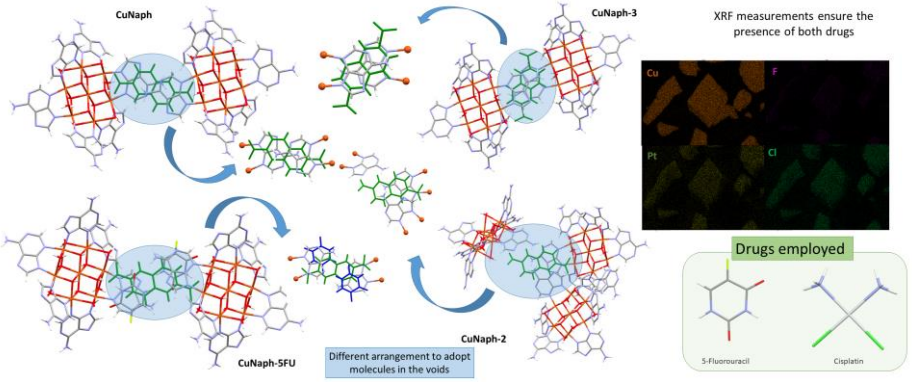


Figure 1.- Structural flexibility arising from the supramolecular interactions between the heptanuclear entities and the dicarboxylate anion altogether with SEM-EDX images showing the evidence of the 5FU and cisplatin loading.

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APPLICATION OF BIOASSAYS FOR GUIDING THE DESIGN OF EFFICIENT AND SAFE METAL PHENOLIC NETWORK NANOCOMPOSITES

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Keywords: *safe-by-design, nanocomposites, metal-phenolic networks, bioassays, metals*

The design of novel nano-based materials should aim to maximize functionality while ensuring material safety. To date, there exists a relatively comprehensive body of knowledge concerning the relationship between physicochemical properties and the biological effects of nanomaterials.[1,2] Here, the strategy to utilize toxicity data as a feedback loop for guiding the design of eco-safe and efficient nanocomposite materials for tomorrow's circular economy is discussed, illustrated through a case study of metal-phenolic network nanocomposites (MPN NCs). MPN NCs are a novel class of sorbent materials, consisting of plant-based chelators – polyphenols and metals- coordinated with polyphenolic linkers, and coated on a nanoparticulate core. MPN NCs show promise for toxic metal adsorption and recovery due to their extraordinarily high surface area, tunable pore size in the polyphenolic matrix, and adjustable surface properties. Fast and facile environmental toxicity tests were employed to screen the eco-safety of MPN NCs with varying compositions (tannic acid moiety and coordination metals such as Fe, Ni, Co, or Cr). The tests included biocidal assays with bacteria, protozoa, and algae, as well as measuring sublethal endpoints such as inhibition of algal growth in freshwater and bioluminescence of marine bacteria *Vibrio fischeri*. Human health-relevant effects were tested in differentiated macrophages *in vitro*. Additionally, the same biotests were applied to confirm the functionality of the safe MPN NCs as adsorbents of toxic metal ions (e.g., Cu and Zn). All MPN NCs were demonstrated to mitigate the heavy metal toxicity as indicated by the increase of half-effective concentration (EC_{50}) of heavy metals in the presence of MPN NCs in the bioassays. The composition of the MPN NC determined its efficiency in metal toxicity mitigation. Measurement of sub-lethal endpoints, such as oxidative stress and bioavailable heavy metal quantification with recombinant bacteria, enabled elucidation of the mode of action of the MPN NCs in reducing metal toxicity, for instance, by sorbing metal ions through decreasing their bioavailability and mitigating oxidative stress. The proposed bioassay-based approach aids in identifying characteristics of MPN NCs for safe and effective applications.

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SURFACE FUNCTIONALITY IN NANOCOFS DRIVES ENHANCED CELLULAR UPTAKE IN LUNG CANCER CELLS

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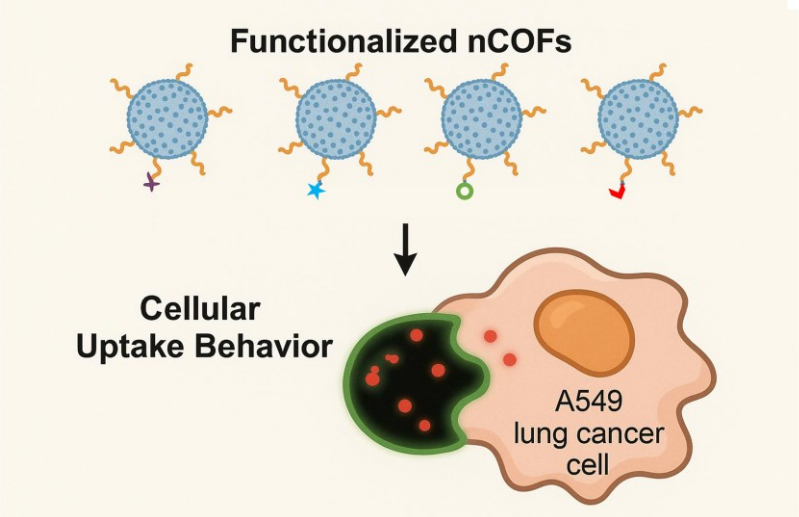
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Keywords: *Covalent organic frameworks, drug-delivery, cellular internalization*

Conventional research on covalent organic frameworks (COFs) has prioritized their drug-loading capacity and controlled release for drug delivery nanoplatforms, their structure-property-cellular internalization mechanisms remain underexplored.[1] In this study, we demonstrate that subtle functional group variations in nanoCOFs (nCOFs) critically govern their surface chemistry and subsequent cellular uptake behavior. To isolate functionality as the sole variable, we synthesized biocompatible imine-linked isoreticular nCOFs with identical backbones, uniform particle sizes (75–80 nm), and consistent spherical morphologies. Additionally, surface modification with *Pluronic-F127* ensured enhanced colloidal stability in cell culture and phosphate buffer saline media over extended periods. Moreover, the conjugation of Cyanine-5 (Cy5) dye with pristine nCOFs (Cy5@nCOF) and *Pluronic-F127* modified nCOFs (F127@Cy5@nCOFs) facilitated the visualization of cellular internalization using confocal laser scanning microscopy tracking. The findings demonstrated notable variations in the internalization efficiency of nCOFs in A549 lung cancer cells, which could be directly linked to their surface chemistry. The study evaluated four distinct tethered functional groups on isoreticular, spherical COF nanostructures with controlled particle size distribution. These insights advance the rational design of COF-based platforms, enabling precise tuning for targeted drug delivery, biosensing, or theragnostic applications through strategic functional group selection.



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METAL-ORGANIC FRAMEWORK-COATED GLASS VIALS AS NOVEL ANALYTICAL DEVICE FOR MINIATURIZED BIOANALYSIS OF HUMAN URINE

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Keywords: *UiO-66(Zr)-abdc, microextraction*, *analytical device, bioanalysis, antidepressants.*

Metal-organic frameworks (MOFs) possess remarkable properties, including permanent porosity, the highest surface areas described up to date, ultralow density, and outstanding thermal and chemical stability, while being highly versatile materials prone to targeted design. From the perspective of bioanalysis, their ability to trap target compounds even when present at very low concentrations in biofluids is a recent feature demonstrated, particularly when integrating MOFs onto certain analytical devices (mostly fibers and thin film membranes). The integration of MOFs as thin films onto glass vials has been recently described as useful for environmental analysis, demonstrating an enhancement in the analytical performance over that of conventional methods [1]. Clearly, their use into the bioanalytical field needs to be proven. In this study, a thin film formed by the UiO-66(*Zr*)-abdc MOF was grown onto the inner surface of glass vials. These MOF-coated vials were used in bioanalysis for the microextraction of a panel of antidepressants and their metabolites present in human urine, all in combination with LC-MS/MS. The MOF-based devices demonstrated high extraction efficiency and significant preconcentration capacity for the target analytes. Adsorption and desorption processes were evaluated through kinetic studies, showing uptake values of up to 80% for compounds such as duloxetine, with desorption occurring in just a few minutes. A full extraction–desorption cycle was completed in less than 15 minutes, with detection limits down to 0.50 μg L^{-1} in human urine samples. In addition to its analytical efficiency, the device proved to be highly reusable: as an application of a simple washing followed by drying restored its performance without loss of efficiency. The results demonstrate the material's excellent performance and its potential to be involved in therapeutic monitoring.

Acknowledgments

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A SELF-ACTIVATING MOF-BASED CANCER VACCINE (ARK-CAN002) INDUCES DENDRITIC CELL ACTIVATION AND PREVENTS RECURRENCE OF COLORECTAL CANCER IN PRECLINICAL MODELS

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Keywords: *Metal-organic frameworks; Cancer vaccines; Dendritic cell activation; photodynamic therapy; Reactive oxygen species*

Metal-organic frameworks (MOFs) have emerged as a cutting-edge platform for next-generation cancer therapeutics. In this study, we developed ARK-CAN002, a porphyrin-based MOF engineered to exert both photodynamic therapy (PDT) and immune activation for the treatment of colorectal cancer (CRC), without the need for additional immunotherapeutic agents. Upon light irradiation, ARK-CAN002 efficiently generates reactive oxygen species (ROS), inducing localized tumor cell death and the subsequent release of tumor-associated antigens. Remarkably, ARK-CAN002 itself directly promotes the activation and maturation of dendritic cells (DCs), thereby transforming the tumor site into an in-situ cancer vaccine. This unique property of ARK-CAN002 enables a robust and systemic anti-tumor immune response, overcoming tumor-induced immunosuppression. In extensive *in vitro* and *in vivo* studies, ARK-CAN002 treatment not only significantly inhibited primary tumor growth but also led to complete prevention of tumor recurrence in all treated subjects, demonstrating a 100% success rate in recurrence suppression. These findings highlight the potential of ARK-CAN002 as a novel, self-activating cancer vaccine platform that synergistically combines photodynamic therapy with intrinsic immune stimulation, providing a highly effective and durable strategy for CRC treatment without the need for additional immune-modulating agents.

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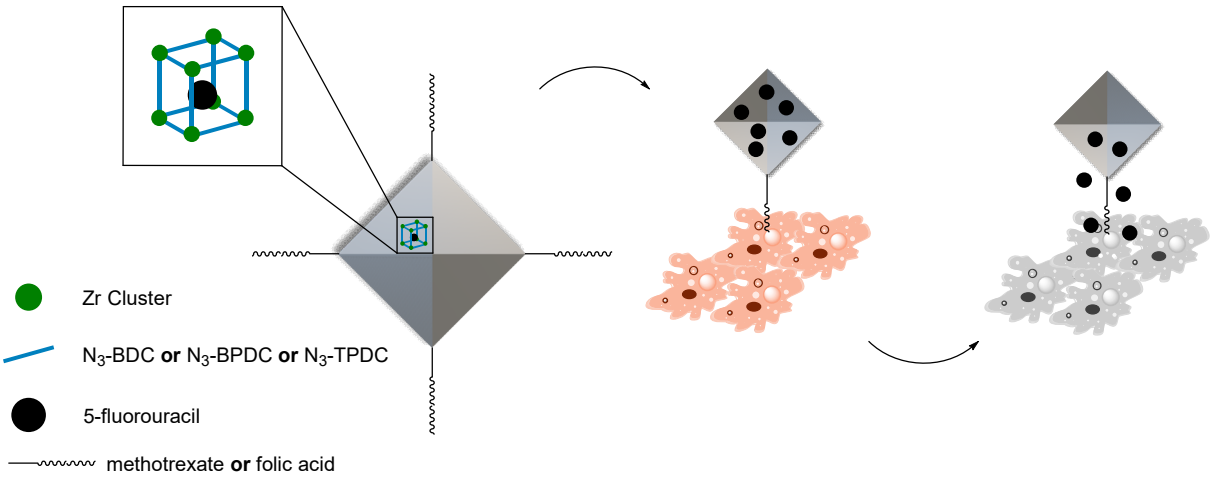
Dual-Targeting UiO-MOFs: Functionalization with Cytotoxic Tumor-Targeting Ligands and Controlled Fluorouracil Release

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Keywords: *drug delivery, folic acid, methotrexate, fluorouracil, cancer, dual-targeting*

The development of metal-organic frameworks (MOFs) functionalized with tumor-targeting ligands and loaded with chemotherapeutic agents offers innovative dual-targeting strategy for combating cancer in a precise and effective manner.[1] This project aims to combine intrinsic cytotoxic tumor-targeting ligands on UiO-MOFs with the controlled release of 5-FU. For this purpose, the surface of UiO-66/67/68-N_3 is covalently functionalized with folic acid via Click chemistry as it is selectively taken up by cancer cells that overexpress folate receptors like HeLa through the reduced folate carrier (RFC). Similarly, the surfaces of these MOFs are functionalized with methotrexate (MTX), a cytotoxic antifolate that is taken up via the same RFC pathway,[2] to compare their tumor-targeting capabilities and cytotoxic properties. Additionally, all functionalized MOFs are further loaded with the antiproliferative fluorouracil (5-FU) and tested for drug release and enhanced cytotoxicity against cancer cells. The functionalization processes and drug loading are characterized using techniques such as PXRD, IR and qNMR spectroscopy, TGA, and physisorption as well as their biological activity and specificity toward cancer cells will be investigated. This work highlights the potential of functionalized MOFs as dual targeting systems for specific delivery and controlled release of chemotherapeutic agents.



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Elucidation of drug adsorption mechanism of Metal-organic frameworks by electric field application and DFT simulation

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Keywords: *Adsorption mechanism, Drug delivery systems, electric field, DFT, UiO-66*

Introduction

In recent years, metal-organic frameworks (MOFs) have gained attention as drug carriers in drug delivery systems. Our previous studies have reported that the adsorption performance in liquid phase adsorption depends on the balance of intermolecular interactions.[1] Therefore, we verified whether the loading capacity changes by changing the balance by applying an electric field. The drug loading experiments were conducted using various drugs, MOFs, and solvents in both with- and without-electric field conditions. Furthermore, the changes in interactions were evaluated by DFT simulation.

Experiments

5-fluorouracil (5FU, 130.08 g/mol), acetaminophen (AAP, 151.16 g/mol), and ibuprofen (IBU, 206.28 g/mol) were selected as model drugs with different molecular weights. UiO-66, UiO-66-NH_2 and UiO-66-NO_2 were chosen as MOF. Water and DMF were selected as the solvent. The concentration conditions for drug loading experiments were set as follows: 5FU concentration was 1.5 g/L with a MOF to drug mass ratio of 2:3, AAP concentration was 6 g/L with a MOF to drug mass ratio of 1:6, and IBU concentration was 10 mg/L with a MOF to drug mass ratio of 100:1. The prepared solution was stirred for 1 hour to allow the drug to be adsorbed. In the electric field application system, two carbon plates were placed 2 cm from the bottom of the container, separated by 4 cm, and a voltage of 1 V was applied. The drug loading amount was calculated based on TG/DTA measurements.

Results and Discussion

It was observed that the drug loading amount tended to increase/decrease by the application of the electric field depending on the combination of solvent and MOF. In the case of UiO-66-NO_2, the loading amount increased significantly in water solvent, while it decreased in DMF solvent. In the case of UiO-66-NH_2, the loading amount did not change in water solvent, although it slightly increased in DMF solvent. This would be because the electric field applied biased the charge within the molecule to alter the balance of various interactions. Especially, hydrogen bonds, π-π interactions, and electrostatic interactions were mainly important intermolecular forces for adsorption. Therefore, we focused on the relationship between these interactions and molecular structure. The functional groups added to the ligands of UiO-66 influenced hydrogen bonding and electrostatic interactions. Both the solvents, water and DMF, were highly polar, mainly affecting hydrogen bonds and electrostatic interactions due to their molecular structures. In terms of differences depending on the type of drug, the smaller drug molecule size had more significant effect on the loading amount. In addition, we performed DFT simulations to quantitatively evaluate the changes in interactions due to the application of an electric field. In the presentation, we will show the detailed results of DFT simulations.

Conclusion

This study performed loading experiments using various combinations of MOFs, drugs, and solvents in both with- and without-electric field conditions. Additionally, we evaluated the changes in interactions by DFT simulation. By applying an electric field, the balance of various interactions changed due to the polarization of each molecule and the induced dipole moment, resulting in the different trend of the drug loading amount. Based on the polarity of the solvent and MOF, it can be expected that the drug loading capacity can be improved by applying an electric field. The findings in this study should contribute to greatly improve the DDS carrier ability of MOFs.

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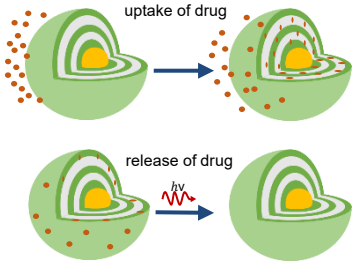
DESIGN AND OTIMIZATION OF UIO-66 COATED GOLD NANOPARTICLES FOR DRUG DELIVERY

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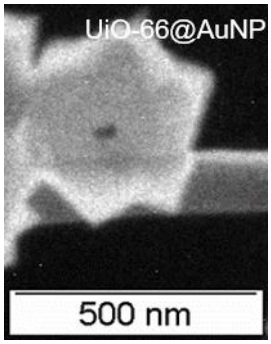
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Keywords: *drug delivery, hybridmaterial, UiO-66, gold nanoparticle*



Precise and targeted drug delivery is crucial for improving the treatment of diseases such as cancer while minimizing adverse side promising material for drug delivery due to its stability, large surface area, and low toxicity.[1] This study explores an advanced drug delivery platform that integrates a gold nanoparticle core with a UiO-66 shell, creating a dual-functional system with both imaging and therapeutic capabilities.

The gold core enhances the system's functionality in two key ways. First, gold nanoparticles serve as excellent contrast agents for imaging techniques like computed tomography (CT) and photoacoustic imaging.[2] This capability ensures precise localization of the delivery system within the body, reducing the risk of off-target effects. Second, the gold core acts as a photothermal agent. While spherical gold nanoparticles are also capable of generating heat under radiation, gold nanorods could offer better control and enhanced photothermal efficiency due to their tunable optical properties. Gold nanorods exhibit strong absorption in the near-infrared (NIR) range, which enables deeper tissue penetration with minimal interference from biological components.[3] NIR irradiation generates localized heat, which could trigger drug release from the UiO-66 shell.



The design of this system is guided by the hypothesis that optimizing the MOF shell's thickness and thermal conductivity can enhance its performance. The shell's thickness is expected to influence drug loading capacity and the rate of diffusion during heat-triggered release, while thermal conductivity is hypothesized to impact the efficiency of heat transfer for controlled drug release. By fine-tuning these parameters, the system aims to achieve an effective balance between functionality, biocompatibility, and structural stability.

In summary, this dual-functional nanoparticle system offers a novel approach to drug delivery by combining imaging precision with heat-activated release. This innovation holds significant potential for advancing targeted therapies in oncology and other medical fields.

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BIOCOMPATIBILITY AND STABILITY OF MFM-300(AL) IN CYANOBACTERIAL CULTURES

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Keywords: *MOFs, cyanobacteria*

Metal-organic frameworks (MOFs) are porous materials comprised of metal ions or clusters, and organic ligands [1]. The structure of MOFs can be adjusted by modifying the metal cation, linkers, and through post-synthetic modifications [2]. Recently, MOFs have been employed within microalgal cultures to either enhance cellular performance and growth, or to eradicate harmful strains. For instance, researchers have demonstrated that incorporating a CO_2 adsorbing MOF can nearly double photosynthetic efficiency and as a result CO_2 fixation in a green alga, *Chlorella pyrenoidosa,* culture [3]. However, to utilise MOFs for enhancing microalgal culture growth, it is crucial to understand how the cells react to the presence of MOFs in their culture. In this study, the impact of various concentrations of MFM-300 (Al), a MOF known for its ability to adsorb CO_2, NO_2, and SO_2, [4, 5] on a culture of *Synechococcus sp. PCC 7002* was examined. Cell growth and photosynthetic performance in the presence of MFM-300(Al) were compared to a control culture without MOF. Results revealed that the cells could grow normally in the presence of up to 1mM MFM-300(Al). Additionally, the impact of the cyanobacteria culture on the MOF structure was investigated. The results indicate that the MOF starts to degrade when the photosynthetic activity of cyanobacteria causes the pH of the cultures to exceed 8.5. This study provides valuable insights into the influence of MOFs on cyanobacteria cells and their effects on growth and photosynthetic performance. Furthermore, it provides information on the stability of MOFs in culture media and highlights the impact of the growth condition of cells such as its pH on the integrity of MOFs. These findings underscore the need to study the interaction between MOFs and living organisms, prior to their integration into future applications.

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IN SITU ELECTROCHEMICAL DEPOSITION OF COMPACT METAL-ORGANIC FRAMEWORK THIN FILMS FOR HIGH-RESOLUTION X-RAY IMAGING

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Keywords: *X-ray, imaging, MOFs, thin films.*

X-ray imaging scintillators have gained substantial attention in many sectors like medical radiography, security inspection, and high-energy physics, which is due to their ability to convert high-energy radiation photons into low-energy visible photons, facilitating detailed inspection of internal structures in complex devices and organisms. For practical applications, X-ray imaging scintillator screens need to combine high sensitivity with exceptional spatial resolution to capture fine imaging details. Therefore, innovative techniques using continuous screens composed of pure scintillation materials are needed to achieve high spatial resolution and cost efficiency X-ray imaging technologies.

Here, we present a versatile approach based on in situ electrochemical-directed synthesis for the growth of uniform polycrystalline metal-organic framework (MOF) thin films that are customized for X-ray imaging. Using electrochemical process, continuous MOF thin films were successfully grown using lanthanides as the metal clusters and ditopic linkers as the organic linker. In this study, RE = Tb^{3+} and Eu^{3+} were used as the metal ion centers, and (fumaric acid [fum], terephthalic acid [BDC], and biphenyl-4,4'-dicarboxylic acid [BPDC]) as the organic linkers. These selections enabled the fabrication of the intended luminescent MOFs (RE-MOFs,). These RE-MOFs synthesized using hydrothermal method have an **fcu** topology and their remarkable luminescence properties of lanthanide metal ions, coupled with their high atomic number, put them as promising materials for the conversion of high-energy X-ray photons into lower-energy visible photons. The deliberate incorporation of lanthanide metal ions as central constituents within MOFs facilitates the effective absorption of X-ray energy, leading to the excitation of these ions and their direct luminescence. Furthermore, due to the close proximity between the metal center and the linker molecules within the framework, the liberated electron-hole pairs can recombine on the linkers, resulting in the excitation of the organic linkers. Also, the energy transfer from the linker to the metal center increases the luminous efficiency of the metal center, thereby increasing the comprehensive RL efficiency of the RE-MOFs.

Notably, among the various MOFs examined, the Tb-BDC-**fcu**-MOF exhibited the strongest RL intensity and revealed excellent performing material that enable ultrahigh-resolution X-ray imaging. Using in-situ electrochemical route, thin films with thicknesses ranging from 1-40 µm were grown by controlling the growth duration. The films exhibited homogeneity and continuity of densely packed structures with small grain sizes and smaller light spots, suggesting a reduced light scattering effect. Remarkably, this MOF thin film surpassed most reported organic and inorganic scintillators, achieving an X-ray imaging resolution of 32-line pairs per millimeter, a resolution at least 2–3 times superior to that of commercial screens available in the X-ray imaging marketplace.[1] Interestingly, this method notably provides minimized light scattering and simplified scalability for large-scale production. These discoveries hold significant promise and could potentially establish these RE-MOF thin films as efficient scintillators for advanced X-ray imaging applications.

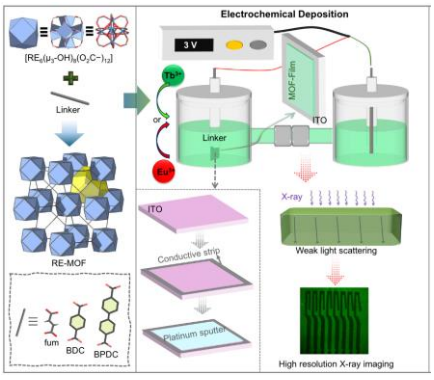


Figure 1. Illustration of the MOF structures and the tailored synthesis of RE-MOF thin films for high-resolution X-ray imaging

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ZINC-BASED HIGHLY POROUS MOF FOR HIGHLY SENSITIVE AND SELE SENSING OF FE^{3+} IONS AND ORGANOARSENIC IN ENVIRONMENTAL WATER, FOOD, AND VEGETABLE SAMPLES IN AQUEOUS MEDIUM WITH THEORETICAL REVELATION

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Abstract

Metal−organic frameworks are a class of attractive materials for fluorescent sensing. Improvement of hydrolytic stability, sensitivity, and selectivity of function is the key to advancing the application of fluorescent MOFs in aqueous media.[1] In this study, we demonstrated the synthesis of a Zn^{2+} based robust (water and pH =2–12 stable) luminescent microporous MOF, for the selective sensing of the Fe^{3+} ions and hazardous organoarsenic feed additive Roxarsone (Rox) in an aqueous medium. The sensing of these analytes occurs with remarkable rapidity (~5 seconds), and the calculated limits of detection (LOD) for Fe^{3+} ions and Rox are determined to be 22.5 ppb and 24.9 ppb, respectively.[2] The identification of these analytes was further elucidated through a solid, solution-based, cost-effective paper strip methodology, which demonstrates triphasic identification capabilities. The sensor exhibits reusability without a significant compromise in its detection efficiency. The sensing merits of MOF motivated us to synthesize a composite of MOF@Aagar_Gel composite, which manifested colorimetric detection capabilities for these specific analytes. Comprehensive experimental investigations indicated that the mechanisms potentially responsible for the detection of Fe^{3+} ions and Rox are fluorescence resonance energy transfer (FRET) and Photoinduced electron transfer (PET). This sensing mechanism is additionally corroborated by theoretical study and excited lifetime measurement. The anti-interference ability and recyclability along with the pH stability gave these MOF high potential to be used as practical sensors toward Fe^{3+} ions and Rox in water as a greenest medium.

Keywords**:** Zn based coordination polymer; Fe^{3+} sensing; Rox sensing; theoretical investigation

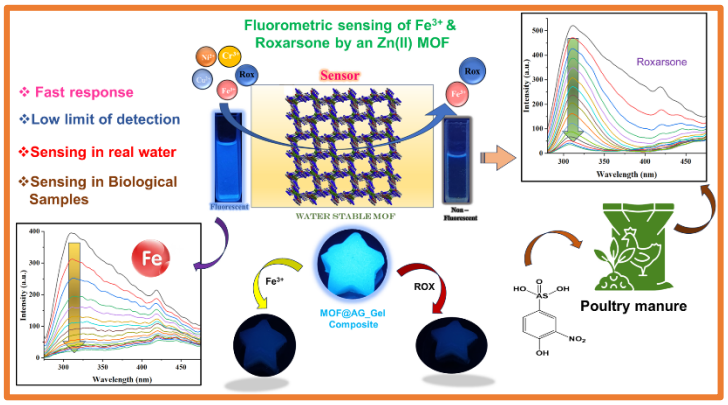


Figure 1. Graphical presentation of detection of Fe^{3+} ions and Roxarsone molecules

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METAL-ORGANIC FRAMEWORK (MOF) GLASS COMPOSITE FOR MINERAL RECOVERY FROM SEAWATER

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Keywords: *MOF glass, composite, ion exchangeable materials, sorption study, mineral recovery*

Access to clean and sufficient water is one of the most urgent challenges facing humanity. While oceans cover 71% of Earth's surface, only a tiny fraction of freshwater, just 0.03%, is directly used for drinking or agriculture. Desalination, which turns seawater into drinkable water, offers hope but comes with a hefty price tag. One way to bring down the cost of desalination is by turning a problem into a solution, recovering valuable minerals from seawater in the process. Seawater and brine are rich in critical elements like lithium (Li) and magnesium (Mg), which are in growing demand for technologies like batteries and renewable energy systems. Recovering these minerals not only helps make desalination more economical but also addresses the looming global shortage of key resources like lithium and uranium. However, current desalination technologies rely heavily on polymer-based membranes and ion exchange resins. These materials often fall short due to issues like poor heat resistance, limited selectivity for specific ions, and short operational lifespans.

Recently, we have developed a breakthrough material: a hybrid made by combining metal-organic framework (MOF) glass with traditional oxide glass. This new composite brings together the best of both worlds, the stability and moldability of traditional glass with the high porosity and selectivity of MOFs. The result is a tough, versatile material that can target and remove specific minerals from seawater with high efficiency. In tests, our hybrid glass outperformed existing commercial materials, showing excellent performance in removing lithium and magnesium ions, two of the most critical elements for both industry and health. To prove its effectiveness in real-world conditions, we tested seawater samples from the Red Sea (Saudi Arabia), the Mediterranean Sea (Spain), and the Baltic Sea (Denmark). The results were consistently strong across all locations, demonstrating that this material can be reliably used in different marine environments. What's more, the hybrid can be shaped into self-standing membranes, making it suitable for large-scale desalination systems. This opens the door to cleaner, more affordable water and sustainable mineral recovery from the same process.

In short, this innovative material offers a dual benefit: it softens seawater while capturing valuable resources, helping us tackle two global challenges at once, water scarcity and mineral shortages.

Zr-MOF / BIOCHAR OR / CLAY COMPOSITE MATERIALS FOR THE REMOVAL OF PHARMACEUTICALS FROM AQUEOUS MEDIA

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Keywords: *biocompatible MOFs*, Zr-MOFs, MOF composites, removal of pharmaceuticals

Pharmaceutical and pesticide pollutants are of growing environmental concern and there is a need to develop new materials for their efficient removal from aqueous media. Zirconium-based metal–organic frameworks (Zr-MOFs) have emerged as promising materials for environmental remediation due to their exceptional chemical and thermal stability, particularly under aqueous conditions. In this study, three well-known biocompatible Zr-MOFs, particularly UiO-66, UiO-66-NH_2, and MOF-801, were selected because of their structural robustness and porosity, and subsequently employed in the construction of a series of composite materials. Thus, the synthesis of Zr-MOF / Cyprus Bamboo biochar (10%) and Zr-MOF / Bentonite Clay (10 %) shall be discussed. The synthesized materials were characterized with a series of techniques and evaluated for their capability to sorb selected pharmaceutical pollutants commonly detected in wastewater, specifically ibuprofen, diclofenac, and sulfamethoxazole. The results demonstrate the potential of these Zr-MOF-based composite materials as effective and sustainable adsorbents for the removal of emerging contaminants from aqueous environments.

Acknowledgement:

This work was conducted in the frame of the project, entitled “Integrated Approaches at Local Scale for Enhancing Water Reuse Efficiency and Sustainable Soil Fertilization from Wastewater’s Recovered Nutrients”, acronym ‘CIRQUA”, Grant agreement No. 2321, Call 2023 Section 1 Management of Water IA, which is part of the PRIMA programme supported by the European Union. The PRIMA programme is supported under Horizon 2020, the European Union’s Framework Programme for Research and Innovation. This content reflects only the authors’ view. The PRIMA Foundation is not responsible for any use that may be made of the information it contains.

IMPACT OF THE CRYSTAL STRUCTURE OF M-CAT-1 MOFs ON THEIR CHEMORESISTIVE GAS SENSING PROPERTIES

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Keywords: *Conductive MOFs, Crystal Structure, Gas Sensors, Chemoresistance, Gas-MOF interactions*

Triphenylene-derivative based MOFs present some of the highest electrical conductivities within the field of conductive MOFs.[1] The benefit of having light porous materials with excellent electrical conductivity properties makes these MOFs suitable for a large field of applications, such as supercapacitors, batteries and chemoresistive gas sensors. However, research aimed at understanding their crystalline structure and the possible charge transport mechanisms is essential to understand how these materials work and their suitability for potential applications.

We have synthesized highly conductive M-CAT-1 MOFs using the 2,3,6,7,10,11-hexahydroxytriphenylene ligand with metal salts of Co, Ni, Cu and Zn. By optimizing the synthesis conditions, we have obtained single crystals of these MOFs which show a diversity in crystal structure for the different M-CAT-1 MOFs (from these, only the crystal structure of Co-CAT-1 crystal has been reported [2]). Furthermore, by performing PXRD under controlled conditions of temperature and humidity we have been able to study the effect of these parameters on the crystal structure of the MOFs. We have measured the electrical conduction of these materials under different gas atmospheres, and we have observed chemoresistive responses that make these materials suitable for gas sensing. Figure 1 (right) shows the chemoresistance response in the presence of different concentrations of CH_4.

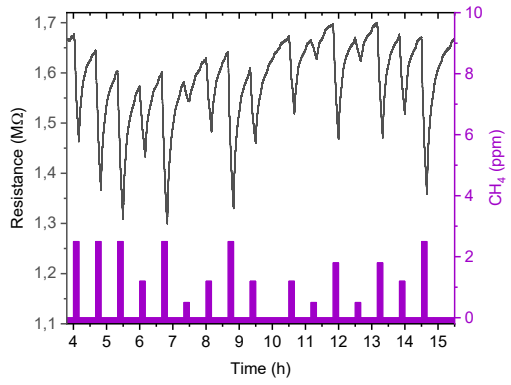


Figure 1. Resistance variation of Ni-CAT-1 MOF when exposed to pulses of varying CH_4 gas concentrations.

In this work, we will report the obtained crystallographic structure of the various M-CAT-1 as well as their electrical responses to two of the main greenhouse gases, CH_4 and CO_2. We will provide insight on how the gases interact with the MOF structure and we will discuss the observed chemoresistance.

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FUNCTIONALIZATION OF NANOFIBERS WITH METAL-ORGANIC FRAMEWORKS FOR CBRNs PROTECTION; NANO-SHIELD PROJECT

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Keywords: *Metal-Organic Frameworks, Hybrid Nanofibers, CBRN protection, antimicrobial, VOCs adsorbent*

Chemical, biological, radiological and nuclear threats (CBRN) are among the key risks for European safety. Their outbreak is often very rapid, with devastating consequences for military and civil victims. The CBRN risks are associated with advances in research worldwide.

The main objective of NANO-SHIELD project is the design and development of new products for the elimination of bacteria, viruses (biological protection), chemicals from the air (non-specific catalysis or specific toxic molecule elimination) and layer blocking radiation (including nuclear). Specifically, our contribution has been focused on developing nanofibers by needle-based electrospinning dopped with metal-organic frameworks and inorganic particles to provide protection against CBRNs. Metal-organic frameworks (MOFs) are materials that have been used in combination with nanofibers demonstrating the possibility to obtain hybrid materials with antimicrobial, chemical and radiation protection.[1,2,3] Their porosity, metal presence and tuneability provide different functionality to the polymer nanofiber that acts as a support.

During the project different polymer systems, synthetic and biobased polymers, have been used and were mixed with commercially available (MOFs; ZiF-8, UiO-66-NH_2 and HKUST, $AgNO_3$ or CuO among others). The electrospinning (Figure 1) parameters have been optimized, and different loaded concentrations of particles have been investigated. The potential of the obtained nanofibers was analyzed for antimicrobial and antivirus tests. Moreover, the nanofibers have been proved as adsorbents for volatile organic compounds such as toluene.

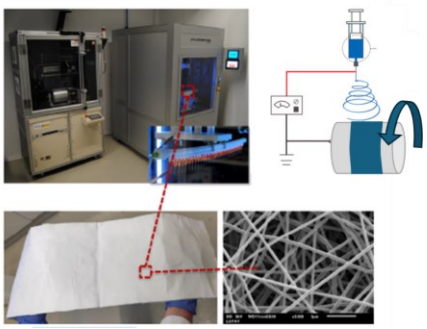


Figure 1. Leitat Electrospinning equipment

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DEGRADATION OF GLYPHOSATE TO BENIGN N-FORMYL GLYCINE USING MOF-808 NANOCRYSTALS

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Keywords: *glyphosate degradation, heterogeneous catalysis, nMOF-808.*

Glyphosate (N-phosphonomethyl glycine, GPh) is an industrial herbicide used worldwide in modern agricultural practices. With the growing concerns regarding cumulative environmental and health effects, pathways for catalytic GPh degradation to benign products are becoming a pressing societal need. This report demonstrates that MOF-808[1] with different crystal sizes can be employed as an efficient heterogeneous catalyst for the complete degradation of GPh at room temperature (Fig. 1)[2]. Importantly, this degradation releases N-formyl glycine to the environment, which is an innocuous chemical, especially when compared to more common GPh degradation products.

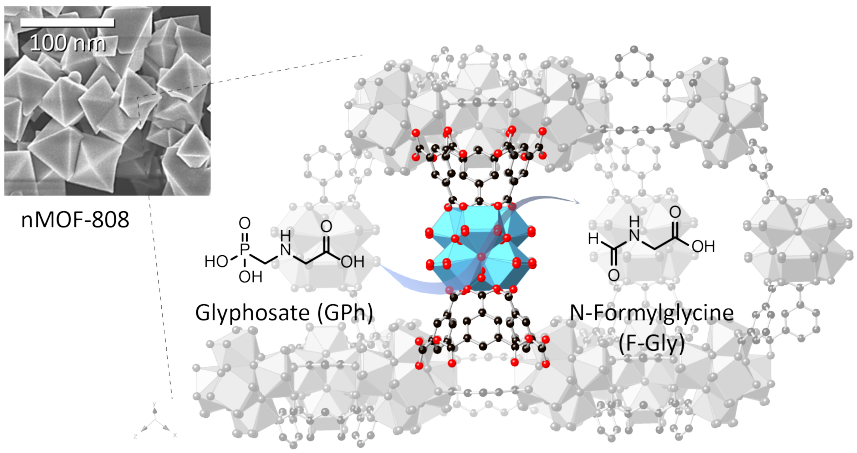


Fig. 1. Schematic representation of GPh degradation catalyzed by nMOF-808.

Nanocrystalline MOF-808 (nMOF-808)[3] exhibits enhanced reactivity than larger MOF-808 crystals, attributed to the higher coordination of hydroxyl and water molecules to the secondary building units (SBU) as determined using a range of X-ray absorption spectroscopy (XAS) techniques. These studies indicate that the crystal size-dependency in GPh degradation is related to structural modifications on coordinative unsaturated Zr sites promoting the fast exchange of weakly bonded ligands. Taken together, this study demonstrates that GPh degradation can be optimized through ligand field tuning in MOFs, which can help improve overall efficiency of the catalysts.

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SHAPING Co-BTC: STRUCTURE–FUNCTION INSIGHTS INTO TETRACYCLINE REMOVAL FROM WATER

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Keywords: *cobalt-based MOFs, particle shape, solvothermal synthesis, antibiotic adsorption, catalytic oxidation*

The growing presence of pharmaceutical residues, particularly antibiotics, in aquatic environments poses a serious threat to ecosystems and public health. Among them, tetracycline is one of the most frequently detected contaminants and is widely used as a model compound for evaluating the efficiency of emerging adsorbent materials in wastewater treatment.[1] Co-BTC, a cobalt-based MOF, features a high density of reactive cobalt sites and surface carboxyl groups, making it a promising candidate for pollutant removal.[2] Although nominally composed of cobalt ions and trimesate linkers derived from 1,3,5-benzenetricarboxylic acid, its coordination environment is often more complex. Solvent molecules such as dimethylformamide (DMF) and water can coordinate to the metal centers during synthesis, influencing connectivity and framework packing. This can affect the network topology, leading to framework interpenetration, compact structural arrangement, and the presence of narrow micropores. However, the abundance of accessible cobalt sites and surface carboxyl groups supports strong interactions with polar contaminants, highlighting the need for morphology-dependent evaluation of functional performance.

In this work, Co-BTC materials were synthesized solvothermally using either cobalt(II,III) oxide or cobalt(II) nitrate as the metal source, and trimesic acid as the linker. Two solvent systems were investigated: water/DMF/ethanol and ethylene glycol/ethanol. The resulting materials were thoroughly characterized using X-ray diffraction, scanning electron microscopy with energy-dispersive X-ray analysis, Fourier-transform infrared spectroscopy, X-ray photoelectron analysis, and nitrogen adsorption/desorption measurements. Subsequently, Co-BTC samples were tested for tetracycline removal from water through adsorption and catalytic oxidation.

The choice of metal precursor and solvent system had a pronounced effect on particle morphology. Three morphologically distinct Co-BTC materials were obtained: crystalline spherulites (aggregates of rod-like crystals) synthesized from Co_3O_4 in water/DMF/ethanol, and square-sectioned rods and amorphous smooth spheres formed from $Co(NO_3)_2$ in water/DMF/ethanol and ethylene glycol/ethanol, respectively. Crystalline samples exhibited low surface areas (8–34 m^2/g), while the amorphous spheres demonstrated a significantly higher surface area (344 m^2/g). Morphology, crystallinity, and textural parameters were found to strongly influence sorption efficiency and overall tetracycline removal. In the adsorption process, drug sorption efficiency reached ~40–60% after 1 h. Extending the adsorption time to 6 h and the addition of H_2O_2 further enhanced tetracycline removal to ~80–90%. Although the salt-derived materials (rods and spheres) exhibited higher initial adsorption capacity, stability studies revealed significant phase transitions and cobalt leaching upon reuse. In contrast, Co-BTC spherulites synthesized from cobalt oxide showed superior structural integrity and reusability. The results indicate surface complexation between cobalt sites and tetracycline, while the enhanced performance in the presence of H_2O_2 supports the involvement of oxidative mechanisms and a Fenton-like reaction.

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ENHANCED CO_2 ADSORPTION EFFICIENCY IN AMINE-MODIFIED MIL-101(Cr)

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Keywords: *CO_2 Capture, Metal-Organic Frameworks (MOFs), Amine Impregnation*

The buildup of CO_2 from fossil fuel consumption is a key contributor to climate change. While aqueous amine solvents are widely used for CO_2 capture, they come with issues such as high energy requirements and corrosion. As a result, porous adsorbents, especially Metal-Organic Frameworks (MOFs), are being investigated as more efficient alternatives due to their high surface area and pore volume.[1] Modifying MOFs with amines further improves their CO_2 capture performance, offering a promising solution to these challenges.[2] To explore the effects of hydrocarbon chain length, amino group content, and the type of amine (primary or secondary), ethylenediamine (EN), diethylenetriamine (DETA), triethylenetetramine (TETA), and tetraethylenepentamine (TEPA) were impregnated onto a dried MOF using a wet impregnation method (**Figure 1**).

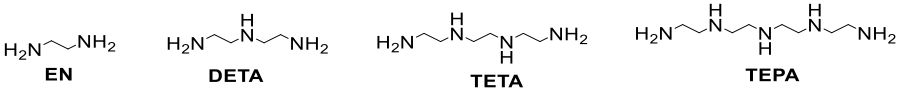


Figure 1. Structure of impregnated amines on MIL-101(Cr)

The mixture was agitated, heated to evaporate the solvent, and then dried in an oven overnight. The modified MOFs were characterized through Powder X-ray diffraction (PXRD) and nitrogen adsorption/desorption isotherms to determine surface area and pore volume. CO_2 adsorption isotherms were measured at low pressure and temperatures of 0, 30 and 60ºC. The selectivity of CO_2 over N_2 was determined from the adsorption isotherms of both gases measured at 30 °C, followed by analysis using the IAST method. Finally, it was analyzed the H_2O adsorption at 25ºC.

PXRD of MIL-101(Cr) impregnated with amines reduces peak intensities, indicating decreased crystallinity due to distortion of the framework by bulky amine groups. However, the persistence of key peaks confirms that the core MIL-101(Cr) structure remains intact. The BET surface area results showed a decrease ranging from 18% to 38% after modifying MIL-101(Cr) with amines. However, the pore size distribution determined by DFT analysis indicated that neither the pore size nor pore accessibility was significantly altered, ruling out physical pore blockage as the main reason for the surface area reduction. **Figure 2** shows the CO_2 adsorption isotherms at 0 °C, revealing that all amine-modified samples exhibited improved CO_2 uptake compared to the unmodified MOF.

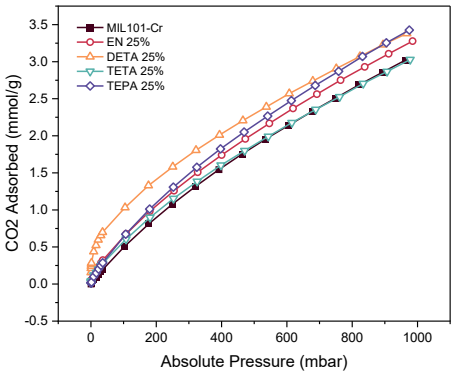


Figure 2. CO_2 adsorption in amine-modified MIL101-Cr at 0ºC

The highest capacity was observed for TEPA and DETA, reaching 3.43 and 3.38 mmol/g, respectively. This enhancement is attributed to new interactions between the amine-functionalized MOF surface and CO_2, such as the formation of carbamic acid, as confirmed by DRIFTS spectroscopy. These findings are consistent with the isosteric heat of adsorption values, calculated using the Clausius-Clapeyron equation, which were around 30 kJ/mol, indicating a combination of physisorption and chemisorption. Also, the amine modifications improved the selectivity for CO_2 over N_2 and reduced water uptake, determined by water adsorption isotherms measured at 25 °C.

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GREENHOUSE GASES CAPTURE BY MICRO/MESOPOROUS MOFs: AN *IN SITU* POWDER X-RAY DIFFRACTION INVESTIGATION

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Keywords: *in situ powder diffraction, adsorption, greenhouse gases*

The multifaceted phenomenon of global warming, which is one of the current environmental issues[1], is primarily due to the constant increase of greenhouse gases (GHGs) concentration in the atmosphere. Carbon dioxide (CO_2) and nitrous oxide (N_2O) are two of the most concerning GHGs: despite its *ca.* 1000 times lower concentration, the latter possesses a 273 times higher global warming potential on a 100-year scale, as well as an ozone-depleting effect[2].

A promising approach to decrease GHGs atmospheric concentration, until new technologies are implemented to reduce their emissions of anthropic origin, is physisorption on porous solids. Metal-organic frameworks (MOFs) appear feasible candidates in this applicative context. In the recent past, NU-1000-PhTz[3], obtained *via* Solvent Assisted Ligand Incorporation from NU-1000[4], was studied as an adsorbent for CO_2 and N_2O, revealing an intriguing temperature-modulated selectivity. To rationalize this occurrence we recurred to high-resolution powder X-ray diffraction (HR-PXRD) at the beamline ID22 of ESRF[5], *in situ* dosing the two gases on NU-1000-PhTz and, for comparison, NU-1000, in the 0-3 bar pressure range at 253, 273 and 298 K. An extensive data treatment showed the substantial rigidity of the two frameworks in the investigated conditions and allowed access to the salient crystallochemical features underneath the performance of the two MOFs: primary adsorption sites, host-guest (side-on or end-on) interactions and local modifications of the linker cooperating to adsorption. Quantification of the adsorbate, hence depiction of PXRD-derived isotherms, was also feasible, enabling extraction of thermodynamic information.

Overall, this study concurs to demonstrate the great potential and versatility of *in situ* PXRD to disclose otherwise not accessible structural details concurring to rationalize the functional behaviour of porous materials. Besides enriching the actual case of study, the crystallochemical features disclosed by *in situ* PXRD are of relevance in the investigation of new-generation materials with the same applicative aim.

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EFFICIENT SEPARATION OF SMALL GAS MOLECULES USING CAU-23 MEMBRANES

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Keywords: *Metal-organic framework, Gas separation*

Metal-organic frameworks (MOFs) are porous crystalline materials constructed from metal nodes and organic linkers. Their high surface areas, tunable pore structures, and chemical versatility make them promising candidates for applications such as gas storage, sensing, drug delivery, catalysis, and gas separation.[1] In this work, we fabricated CAU-23 membranes on *α*-Al_2O_3 substrates via a secondary growth method for gas separation applications. CAU-23[2] is an aluminum-based MOF featuring one-dimensional channels along the *b*-axis with a pore-limiting diameter of 6.1 Å (Figure 1), making it suitable for the selective separation of small gas molecules. We studied the effects of synthesis conditions on membrane morphology and compared different activation strategies for their influence on gas transport performance. The resulting membranes were evaluated for the separation of H_2, CO_2, N_2, and CH_4, and showed promising selectivity in CO_2/N_2 and CO_2/CH_4 separations, highlighting the potential of CAU-23 membranes in energy-efficient gas separation technologies.

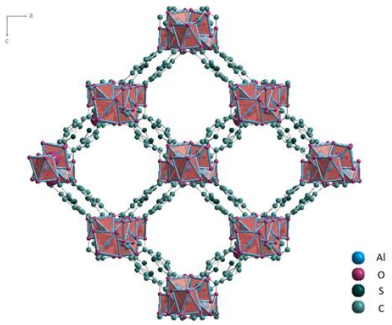


Figure 1. Crystal structure of CAU-23.

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LANTHANOID METAL-ORGANIC FRAMEWORKS AS SENSORS FOR POLLUTANTS IN WATER

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Keywords: *lanthanoid, rare earth, metal-organic frameworks, sensors*

Rapid industrial and technological development leads to the release of a large amount of organic and inorganic pollutants in waters, which has irreversible negative consequences on the biochemical processes of living organisms[1]. In recent years, lanthanoid metal-organic frameworks (Ln-MOFs) have been proven as effective luminescent sensors for pollutants in water due to their unique optical properties, high selectivity and sensitivity, short response time and high reproducibility of results[2]. For MOFs as luminescence-based chemosensors, several pathways have been examined to elucidate the interaction with foreign species, but luminescence continues to be the most preferred and relatively easiest mechanism to interpret. The key parameters to estimate any chemical sensor include sensitivity, selectivity, response time, stability of the material, and reusability of the probe. Detectability makes luminescence more attractive than light absorption since it is more sensitive and even small numbers of photons can be detected using photon-counting techniques, even in the absence of a large background signal.

In the current study an investigation based on combining different organic linkers with lanthanoid ions having emission in the visible part of the spectrum is presented. The applied hydrothermal and solvothermal syntheses lead to a variety of structures. Characterization of the structures, investigation of the stability in water and their sensitivity to various inorganic ions, organic molecules and antibiotics demonstrates their potential as sensor materials. The behavior of the samples in media with different acidity was studied showing the working pH range of the materials. The luminescence intensity of the samples is monitored in the presence of different concentration of quenchers (Figure 1). The collected data were plotted and Stern-Volmer curves were obtained with different linear and non-linear fits, suggesting different quenching mechanisms.

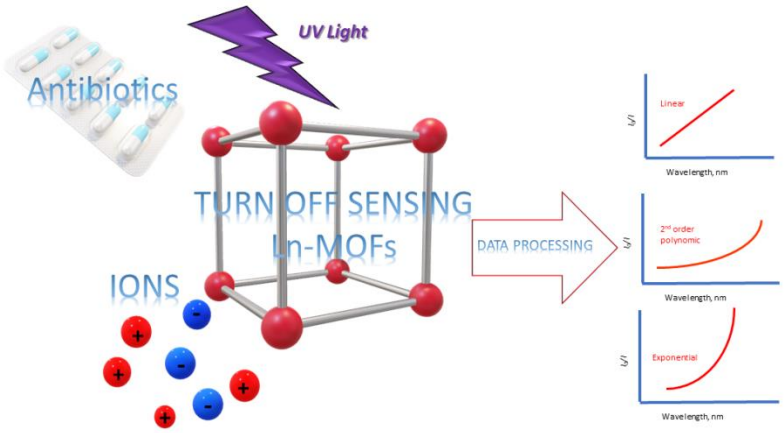


Figure 1. Ln-MOFs sensing.

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EFFICIENT AND EFFECTIVE REMOVAL OF TOLUENE FROM AQUEOUS SOLUTION USING MIL-100(Fe)

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Keywords: *VOCs, adsorption, water treatment.*

Water pollution, a pressing environmental issue that arises from the uncontrolled release of wastewater from the vast industrial and municipal sectors[1] has escalated due to the burgeoning human population. Volatile organic compounds (VOCs) are chemical complexes based on aromatic and hydrocarbon structures.[2] VOCs are highly persistent in the environment and are classified as harmful and toxic pollutants. VOCs participate in atmospheric photochemical reactions that promote ozone formation,[3] due to their usually being found in the vapor phase. The main concern is the lack of monitoring of VOCs in water systems. The family of VOC aromatics (benzene, toluene, and xylenes) are the most persistent in water.[4] Specifically, toluene is a widely known raw material for diverse solvents, inks, and adhesives applications.[5] Toluene molecules have displayed high toxicity for human health, even at low concentrations.[6] Thus, developing methodologies to remove toluene from the water matrix is necessary. Adsorbents such as zeolites[7] and activated carbon[8] have been employed to remove VOCs from water, but they have been demonstrated to be ineffective. As an alternative, Metal–Organic Frameworks (MOFs) are crystal materials formed of metal ion centers linked by organic ligands.[9] They are highly porous and structurally stable, making them excellent adsorbents for removing pollutants from water. The MIL-100(Fe) was employed for the remediation of toluene-contaminated water. The MIL-100(Fe) samples synthesized for this work exhibit high thermal (300 °C) and chemical (pH range 2–10) stability. Adsorption kinetics and isotherms were fitted to the Elovich and Temkin models. The pH of the aqueous sample containing Toluene impacted the adsorption capacity of MIL-100(Fe) through modulation of the MOF ζ potential. As a result, we concluded that MIL-100(Fe) is most effective at adsorbing toluene in the 6–10 pH range, a finding that underscores its potential in water treatment. The maximum Langmuir adsorption capacity of 318.48 mg g^{-1} was determined. MIL-100(Fe) showed excellent adsorption–desorption performance and stability; hence, it can be used repeatedly without losing toluene adsorption capacity. FT-IR spectra suggest that π–π interactions serve a crucial role during toluene adsorption, further confirming the effectiveness of MIL-100 (Fe) in water treatment.

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COLORIMETRIC IDENTIFICATION OF COLORLESS ACID VAPORS USING A METAL-ORGANIC FRAMEWORK-BASED SENSOR

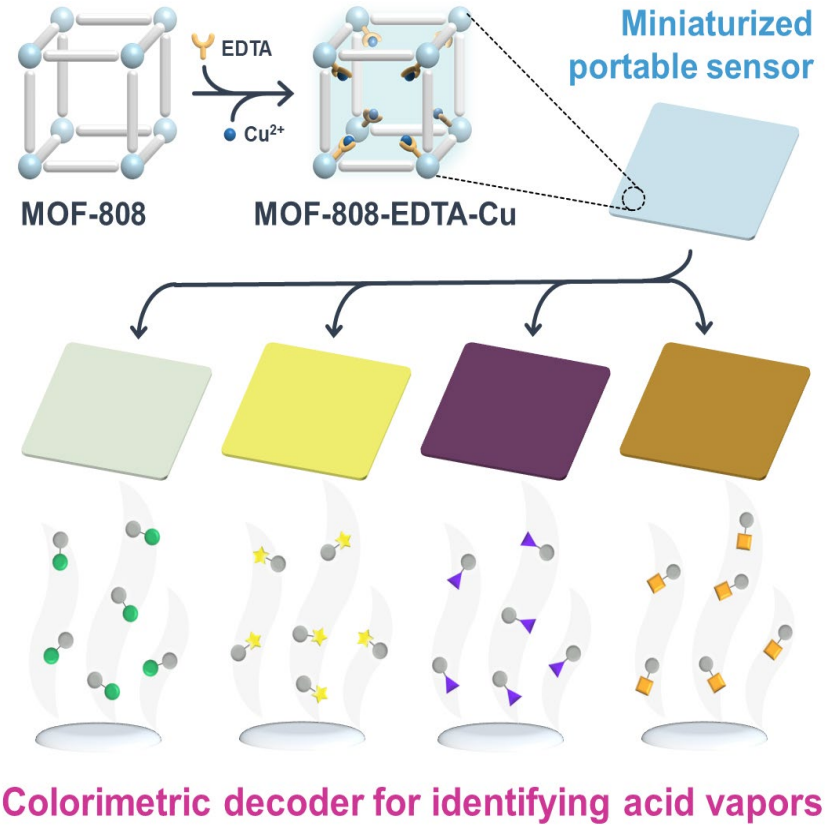
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Keywords: *Metal-organic frameworks, Acid vapor sensor, Colorimetric decoder*

The identification of hazardous acid vapors is vital for safety and emergency response, especially for proper evacuation and first aid. However, current studies face challenges in differentiating between various acid vapors, as many studies are still in their early stages. In this study, we propose a novel on-site monitorable acid vapor decoder, MOF-808-EDTA-Cu, integrating the robust MOF-808 with Cu-EDTA. This serves as a proton-triggered colorimetric decoder to translate the anionic component of corrosive acids into a visible color. Specifically, the sensor exhibits a significant cyan-to-yellow shift when exposed to HCl vapor and can visually differentiate between various acid vapors such as HF, HBr, HI through distinctive color variations. Moreover, the compatibility of the MOF-based sensor with multiple metal ions with atomic-level dispersion expands its discrimination range, enabling the identification of six different colorless acid vapors within a single sensor domain. Furthermore, by incorporating a flexible polymer, the MOF-808-EDTA-Cu was successfully processed into a portable miniaturized acid sensor with distinct color changes easily monitored by the naked eye and camera sensors. This provides practical validation for its use as a sensor capable of continuous 24-hour one-site monitoring in the real world.



DEVELOPMENT OF MOFs BASED ADSORBENTS FOR THE SELECTIVE CAPTURE OF VOLATILE ORGANIC COMPOUNDS EMITTED BY EGYPTIAN MUMMIES' BALMS

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Keywords: *MOFs, adsorption, VOCs, mummies, Ancient Egypt*

Air quality in museums is a major concern as it has a direct impact on the preservation of cultural heritage (CH). Indoor museum pollution mainly arises from the emission of volatile organic compounds (VOCs) released by various museum objects, and accumulating in their showcases. Mummies' balms, a mixture of various natural substances, can emit continuously, a few hundreds of chemically different VOCs, including monoterpenes, carbonyl compounds, aromatics and alkanes [1]. Conventional adsorbents are poorly selective in storage museum conditions with relative humidities (RH) found in between 40-80%. This challenge can be addressed through the development of novel chemically stable adsorbents. In the past few years, Metal-organic frameworks (MOFs) have shown a high performance for the selective adsorption of a large variety of VOCs under humid ambient conditions [2]. Moreover, such MOFs could be also processed in the form of monoliths, tablets and membranes that could be inserted at the vicinity of artefacts in the showcase[3]. Such shaped MOFs were shown to present a high adsorption capacity and selectivity towards different VOCs (acetic acid) and a very high chemical stability under humid ambient conditions. However, the co-adsorption properties of such MOFs were rarely explored while the competitive adsorption of different COVs by MOFs may be expected under the real conditions of the application, namely under exposure of VOCs emitted by mummies. This project aims to develop efficient MOFs based adsorbents for the capture of VOCs emitted by different Egyptian mummies under humid ambient conditions and evaluate their adsorption efficiency in real conditions of the application. A prerequisite will be the complete characterization of VOCs emitted by various Egyptian mummies' balms with known molecular compositions. This study will focus on optimizing a novel adsorbent suitable not only to capture selectively VOCs emitted from ancient mummies' balms, but also a wider range of VOCs emitted from CH objects.

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HIGHLY EFFICIENT REMOVAL OF PERFLUOROOCTANOIC ACID (PFOA) FROM WATER USING ZIRCONIUM TEREPHTHALATE (UIO-66) GEL

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Keywords: *Water purification, MOF gel, PFAS, adsorption*

Perfluoroalkyl substances (PFAS), including perfluorooctanoic acid (PFOA), are persistent environmental pollutants that pose significant challenges to ensuring safe drinking water. In this study, we explore the application of novel metal–organic framework (MOF) gels as potential membrane materials for water purification and provide an in-depth analysis of their structural attributes and efficiency in removing PFOA [1].

In detail, we investigated zirconium-terephthalate (UiO-66) gels as scalable, high-performance platforms for pollutant removal, environmental remediation, and wastewater treatment. Leveraging the intrinsic porosity and chemical tunability of UiO-66 powders, we synthesized a colloidal UiO-66 gel via a modulated sol–gel route, yielding ~20 nm nanocrystallites that self-assemble into a hierarchical, defect-rich network with excellent mechanical integrity.

Comprehensive structural characterization by powder X-ray diffraction (PXRD) and transmission electron microscopy (TEM) confirmed retention of the UiO-66 framework in gel form. Bright-field TEM revealed discrete spherical nanoparticles with a narrow size distribution (20 nm), while selected area electron diffraction (SAED) confirmed a nanocrystalline architecture. High-angle annular dark-field STEM (HAADF-STEM) images further indicated an interconnected network of meso- and macropores, arising from the colloidal assembly of MOF nanoparticles. Quantitative analysis of HAADF contrast indicated evenly dispersed Zr oxoclusters throughout the UiO-66 gel matrix. Energy-dispersive X-ray spectroscopy (STEM-EDS) elemental maps of Zr and O confirmed framework integrity and uniform elemental distribution; after PFOA uptake, identical SAED patterns and unaltered pore morphology demonstrated structural robustness upon pollutant.

UiO-66 gel's affinity for PFOA was quantified by ^19F NMR: a single-cycle treatment of PFOA-contaminated water (2.37 mM initial concentration) achieved 96.2 ± 0.2 % removal, reducing residual PFOA to below 0.1 mM. Solid-state NMR and STEM-EDS elemental mapping demonstrated uniform PFOA uptake throughout the gel matrix and coordination of fluorinated moieties to zirconium oxoclusters.

To assess real-world applicability, the UiO-66 gel was processed into a flexible membrane by simple deposition onto filter paper. Gravity-driven ultrafiltration of three sequential 6 mL PFOA feed fractions yielded harvesting efficiencies above 93.5 %, with negligible pressure requirements and rapid throughput. These results underscore the gel's potential for low-energy water treatment and point-of-use remediation, where easy handling, membrane formability, and high pollutant-binding capacity are critical.

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MOF-IMPRINTED POLYMERS FOR WATER DECONTAMINATION OF DYE POLLUTANTS

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Keywords: *ZIF-8, MIL-100(Fe), dye pollutant capture, molecular imprinted polymer.*

The use of water-compatible molecularly imprinted polymers for the removal of contaminants is under current research. These materials can provide highly efficient, robust, inexpensive, and reusable matrixes for secure capture, without generating degradation byproducts that can potentially be more harmful than the parent compound. However, focusing on major-concern dye pollutants, just a few reports of imprinted polymers are available. The main problem facing their preparation is that most dyes used as templates are degraded during the polymerization, thus affecting the cavity formation. In this context, we have prepared new functional materials incorporating nano-sized MOFs with proved capacity at dye absorption, into a polymeric matrix compatible with the packing for wastewater treatment procedures.[1] To maximize the interaction at the interface between both materials, MOFs were included into the methacrylamide polymer using the molecular imprinting technique. We characterized the solid materials including textural properties and tested the capturing ability of the imprinted composites on capturing various dyes. The most relevant results (some of them depicted in Figure 1) show that in comparison with pristine ZIF-8 samples, ZIF-8@MIP shows lower N_2 adsorption, due to the change of porosity caused by the polymeric cover that surrounds the ZIF-8 nanoparticles (the non-imprinted material, NIP, shows no N_2 adsorption). Notably, the inclusion of ZIF-8 led to a sharp improvement in the absorption capacity for Nile Blue (NB), thiazine- (Methylene Blue, MB, Azure A, AZ) and triphenylmethane- (Methyl Violet, MV) pollutants. Conversely, both ZIF-8@MIP and NIP have no capture ability towards anionic azo dyes (Methyl Red, MR and Methyl Orange, MO), in contrast with the ZIF-8 itself. On the other hand, MIL-100(Fe)@MIP showed much better capturing ability for the azo dye MO, outperforming both NIP and notably the pristine MIL-100(Fe).

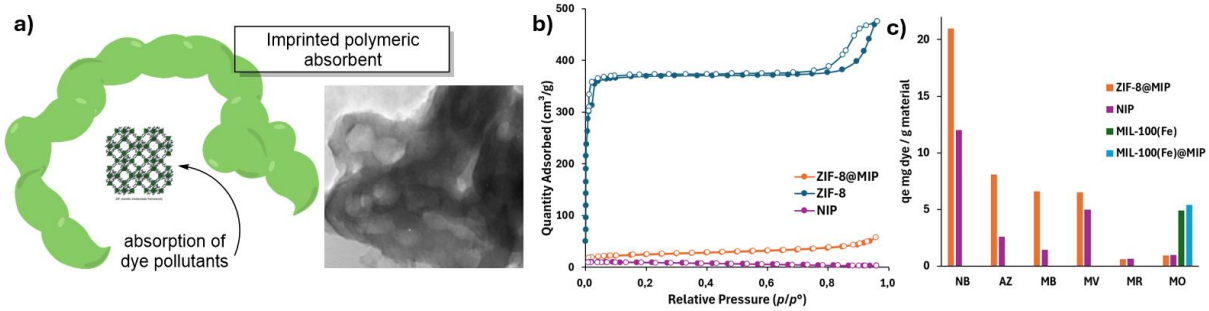


Figure 1. a) Schematic representation and SEM image of the designed material ZIF-8@MIP, incorporating the imprinted ZIF-8 into a methacrylamide polymeric matrix. b) Compared textural properties of the ZIF-8@MIP composite with the pristine ZIF-8 and the non-imprinted polymer, NIP. c) Selected results of dye pollutant capture (of Nile Blue, NB, Azure A, AZ, Methylene Blue, MB, Methyl Violet, MVm Methyl Red, MR and Methyl Orange, MO) for ZIF-8@MIP compared to NIP. For MIL-100(Fe), capture of MO by both the composite and the pristine MOF are compared.

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MIXED-LIGAND STRATEGY FOR PREPARATION OF MOF MEMBRANE FOR GAS SEPARATION

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Keywords: *Metal-organic frameworks, gas separation, CO_2/N_2 separation, in-situ growth method, mixed-ligand strategy*

Metal-organic frameworks (MOFs) are porous materials with significant potential for molecular separations. These remarkable structures consist of metal ions and organic linkers, resulting in a wide variety of pore sizes and structural diversity. Many MOFs have been found to hold exceptional potential for a wide range of applications, including separation, adsorption, and catalysis. For instance, MOF-303 demonstrates excellent gas separation performance. However, most MOFs are limited by the complex steps required to grow dense membranes. Only a few, such as MIL-160, possess the ability to undergo in-situ growth. In this study, I aim to combine the ligands of MOF-303 and MIL-160—namely H_3PDC and FDCA—to create a dense MOF membrane that addresses the shortcomings of both materials. This mixed-ligand MOF offers a significant advantage by simplifying the process, thus paving the way for scalability and potential commercialization.

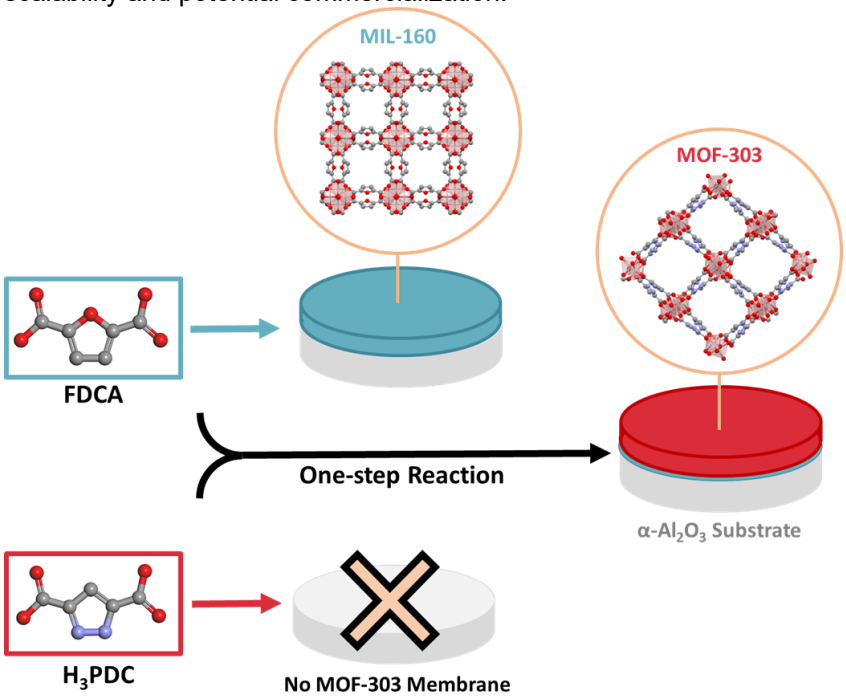


Figure 1. Illustration of mixed-ligand strategy to fabricate MOF-303 membrane via in-situ growth (MIL-160 is acted as seed layer)

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LANTHANIDE-DECORATED METAL–ORGANIC FRAMEWORKS WITH ENHANCED OPTICAL PROPERTIES FOR SENSING ORGANIC POLLUTANT

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Keywords: *Contaminants, Detection, MOFs, Lanthanides, Fluorescence, Antibiotics.*

In recent years, the serious problems derived from the presence of organic contaminants in waters, has led to the use of new porous materials for their detection and capture.[1] In this context, Metal-Organic Frameworks (MOFs) have emerged as ideal materials due to their high permanent porosity, stability and crystallinity. Furthermore, their great chemical versatility, including the possibility for post-synthetic modification, offers large advantages over other traditional porous materials, such as zeolites or activated carbon.[2] Zirconium(IV)-based MOFs have been especially investigated for applications related to molecules capture, due to their great chemical and thermal stability. Moreover, the similarity in the physicochemical properties between zirconium and hafnium atoms opens the possibility of study the synthesis of isostructural hafnium(IV)-based MOFs. Further expanding their potential, these stable materials could be modified with lanthanide(III) ions, to exploit their inherent and unique fluorescence properties and use them for optical detection of certain organic molecules.[3] In this project, zirconium(IV) and hafnium(IV) MOFs —MOF-808 and MIP-206— were synthesized, functionalized with lanthanide(III) ions, and thoroughly characterized using different techniques. Finally, the ability of these materials to detect amoxicillin and chloramphenicol antibiotics in water was evaluated, demonstrating their potential for environmental applications.

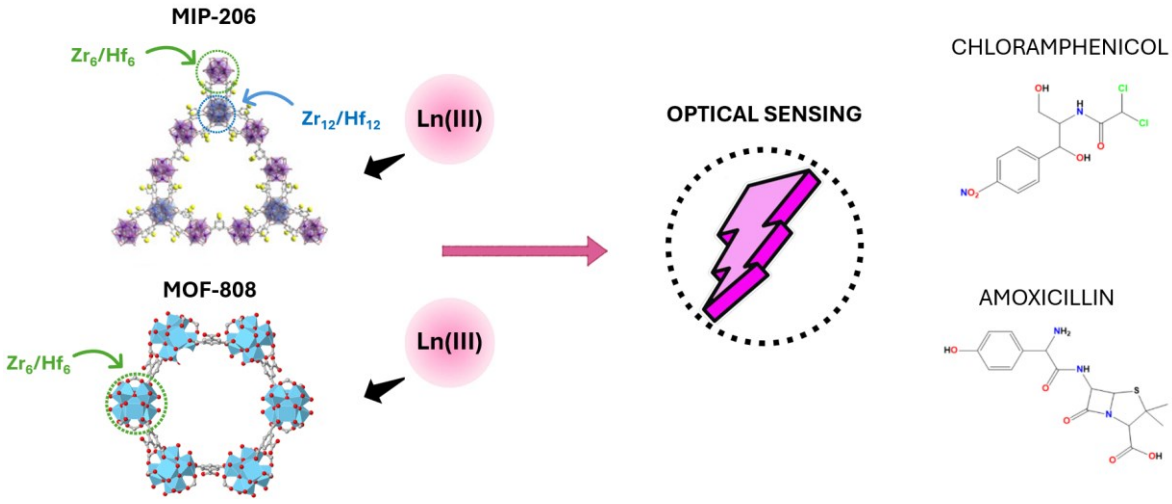


Figure 1. Representation of the inorganic M_6O_8 (M=Zr or Hf) clusters in MIP-206 and MOF-808 and the lanthanide functionalization for optical sensing of antibiotics.

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DETECTING NITRITE IN WATER USING Rh6G@UiO-66-NH2 AND UiO-66-NH2 MICROFLUIDIC PAPER-BASED ANALYTICAL DEVICES

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Keywords: *Metal organic frameworks, nutrient detection, microfluidic paper-based analytical devices*

Traditional methods of detecting nutrients in coastal waters involves laboratory testing which can be limited cost and availability of transport. Sensors that can be deployed on site alternatively provide real-time, actionable data but can be restricted by their need for highly trained individuals and their cost.[1] Microfluidic paper-based analytical devices (µPADs) offer a low-energy and user-friendly solution, which are also easy to fabricate and are made of inexpensive materials.

The ability to rationally design metal organic frameworks (MOFs) for specific analytes enhances their capability for sensing and detection. Therefore, the integration of MOFs with µPADs offers several advantages, like improved sensitivity and selectivity. However, most research has focused on detecting heavy metals and biological targets like glucose, rather than nutrients especially NO_2^- in coastal waters.[2]

Rhodamine 6G (Rh6G) encapsulated into well-known water stable UiO-66-NH_2 was identified as a possible candidate for integration into a µPAD.[3] After successfully replicating the synthesis of the Rh6G@UiO-66-NH_2, the ability of the dye@MOF as a sensor for NO_2^- was then established in solution, as shown in Fig. 1. However, expressing a fluorescence intensity ratio did not always mitigate the other ion's interference effects as discussed in the literature. Further challenges emerged when investigating the response of Rh6G@UiO-66-NH_2 grafted onto filter paper, as the dye@MOF appeared to detach from the paper surface as displayed in Figure 2. The focus of this research has since shifted to grafting UiO-66-NH_2 onto filter paper using an alternative method, resulting in positive results when exposed to water.

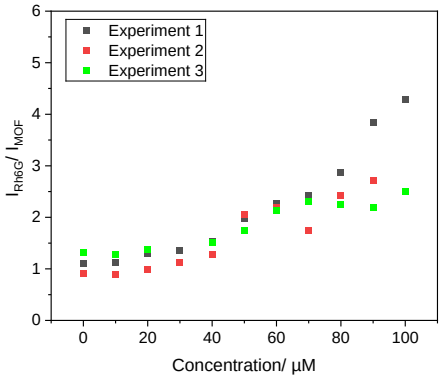


Figure 1 The trend of fluorescence intensity ratio I_{Rh6G}/I_{MOF} of Rh6G@UiO-66-NH_2 in solution with changing nitrite concentration.

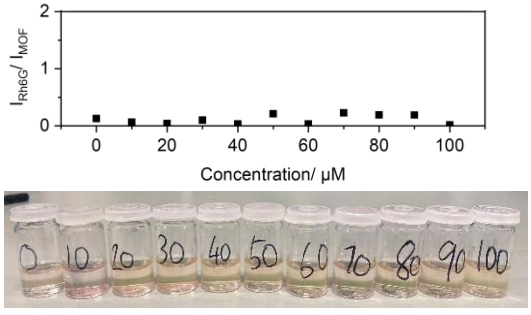


Figure 2 (Top) The trend of fluorescence intensity ratio I_{Rh6G}/I_{MOF} of Rh6G@UiO-66-NH_2 grafted onto filter paper with changing nitrite concentration. (Bottom) Detection solutions after exposure to Rh6G@UiO-66-NH_2 on filter paper.

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METAL-ORGANIC FRAMEWORKS FOR THE CAPTURE OF CHLORINATED VOLATILE ORGANIC COMPOUNDS: A CASE STUDY ON PERCHLOROETHYLENE

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Keywords: *perchloroethylene, adsorption, capture, trace levels, MOFs, simulations*

Chlorinated volatile organic compounds (VOCs), particularly perchloroethylene (PCE), are major indoor air pollutants posing serious risks to human health and well-being. While general exposure levels in the population remain low (< 0.001 ppm), significantly higher concentrations are found in dry-cleaning facilities (up to 400 ppm), and even at home (up to 40 ppm) due to secondary emissions through workers exhalation.[1,2] The widespread presence of PCE and its associated health risks, combined with tightening regulatory standards, highlight the urgent need for efficient and sustainable adsorbents for indoor air purification.[1]

In this study, we evaluated the PCE sorption performance of several MOFs. Gravimetric sorption isotherms recorded at 303 K across a broad concentration range (1–400 ppm) demonstrated the superior low-concentration performance of CAU-11(Al), alongside DUT-4(Al), Cu-NH_2-TPTC, and various UiO-66(Ce) derivatives (Figure 1). The remarkable uptake capacity of CAU-11(Al) at trace levels stems from its strong affinity toward PCE, supported by periodic DFT calculations. At higher concentrations, representative of industrial settings, DUT-4(Al) and Cu-NH_2-TPTC also exhibited promising sorption capacities.
Beyond adsorption performance, structural stability and regenerability were assessed. CAU-11(Al) retained its structural integrity and enabled partial desorption upon heating, while DUT-4(Al) showed fully reversible PCE uptake. Notably, CAU-11(Al) exhibited outstanding moisture resistance, maintaining high performance under elevated relative humidity, an essential requirement for real-world indoor applications.

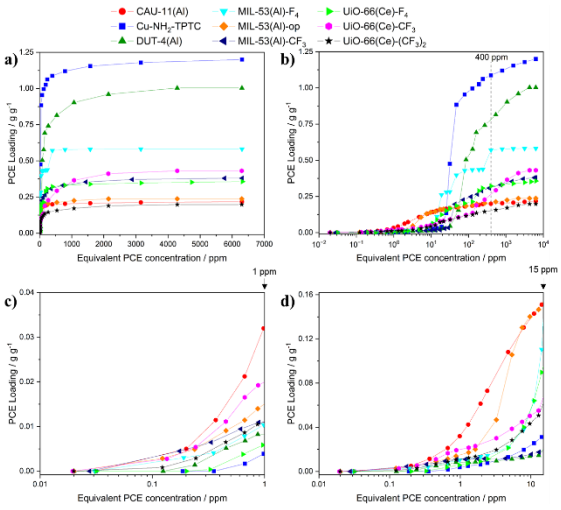


Figure 1. Gravimetric PCE adsorption isotherms recorded at 303 K in the full range of PCE concentration for CAU-11(Al), Cu-NH_2-TPTC, DUT-4(Al), MIL-53(Al)-F_4, MIL-53(Al)-op, MIL-53(Al)-CF_3, UiO-66(Ce)-F_4, UiO-66(Ce)-CF_3, and UiO-66(Ce)-$(CF_3)_2$: **a)** linear and **b)** semi-logarithmic scale plots. Zoom of **Figure 1b** for PCE concentration below **c)** 1 ppm and **d)** 15 ppm.

Altogether, these findings underscore the potential of MOFs, particularly CAU-11(Al), as efficient, robust, and environmentally friendly materials for mitigating PCE pollution in indoor environments. Their ability to operate across a wide concentration range makes them strong candidates for integration into next-generation air purification systems.

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MOF-808 MEMBRANES FOR APPLICATIONS IN MOLECULAR SEPARATIONS

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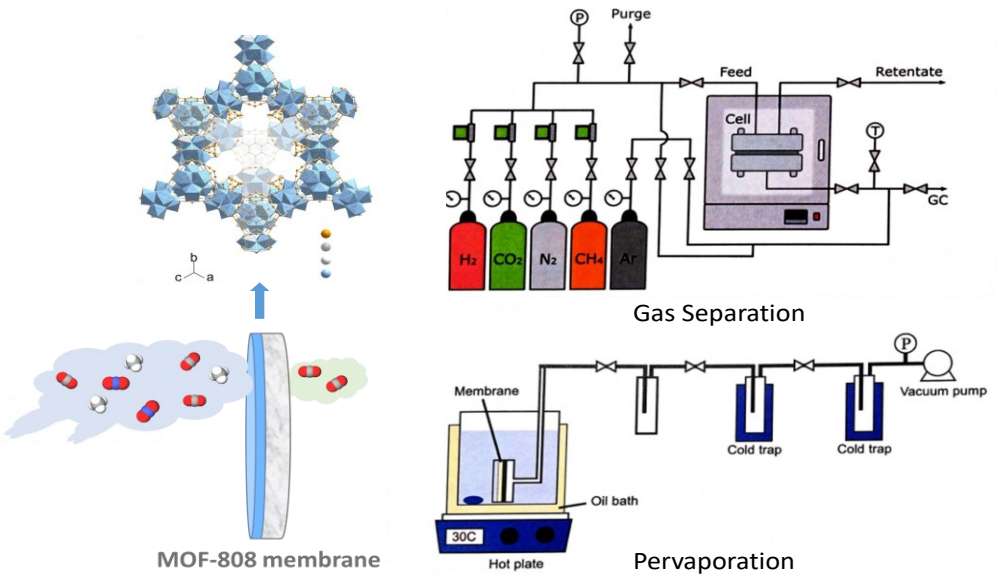
Keywords: *MOF-808, green process, gas separation, pervaporation*

Metal-organic frameworks (MOFs) are crystalline porous materials composed of metal nodes and organic linkers, known for their high surface area, tunable pore structures, and design flexibility. Compared to traditional porous materials, MOFs offer superior tunability and have been widely applied in gas adsorption, storage, and separation processes, as well as pervaporation[1].

This study focuses on MOF-808, a zirconium-based MOF featuring a three-dimensional pore structure, chosen for its potential in both gas separation and pervaporation. A low-defect MOF-808 membrane was successfully synthesized on an alumina substrate using a seeded growth method, employing a green chemistry approach with water and formic acid as solvents[2].

For gas separation, the membrane was tested using H_2, N_2, CH_4, and CO_2 under a 2-bar feed pressure. Permeation parameters were calculated based on downstream pressure measurements. The results demonstrated moderate gas selectivity, although some membrane defects were observed to limit performance. In the pervaporation process, a feed solution (typically 90wt% alcohol) was applied to one side of the membrane, while the permeate side was maintained under vacuum (0.01 torr) at temperatures between 313 K. After a 1-hour equilibration, vapors were collected over 2 hours using liquid nitrogen for performance analysis.

The green synthesis method used in this study replaces the conventionally toxic DMF solvent with an environmentally friendly system, aligning with sustainable development goals. Overall, the MOF-808 membrane exhibited promising performance in both gas separation and water removal via pervaporation. Future work will focus on further reducing membrane defects and optimizing synthesis conditions to enhance efficiency, supporting broader applications in environmental and energy-related separations.



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Defect Engineering of MOF-808 Incorporated in Mixed Matrix Membranes for CO_2 Capture

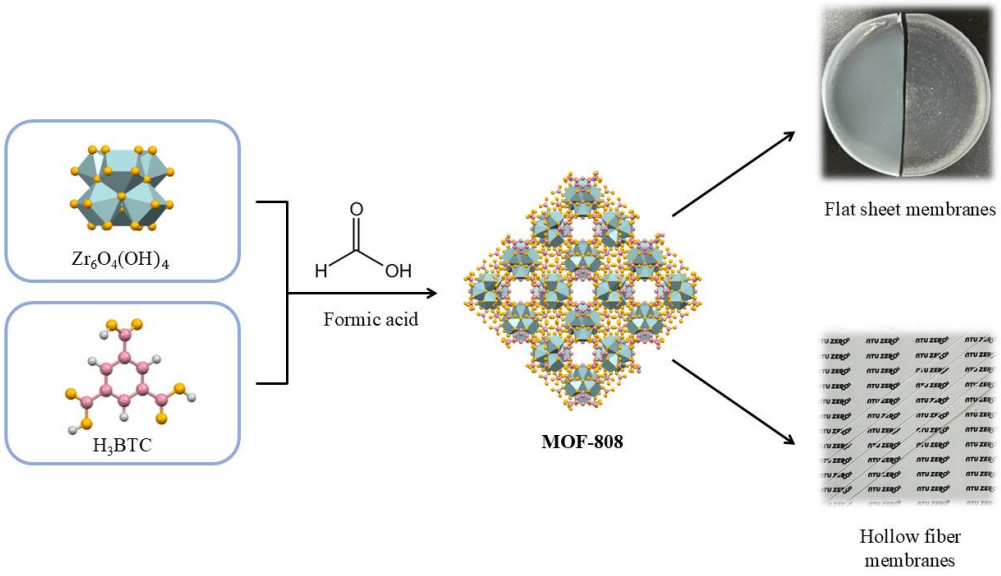
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Keywords: *MOF-808, modulator, CO_2/N_2 separation, green process*

Carbon capture has emerged as a critical strategy in mitigating the escalating threat of global warming. Mixed matrix membranes (MMMs) incorporating metal-organic frameworks (MOFs) have attracted considerable attention due to their superior gas separation performance. Among various MOFs, MOF-808 is particularly notable for its exceptional stability and environmentally synthesis process. In this study, MOF-808 was synthesized with varying modulator loadings, which significantly influenced its structural properties. A drying-free method was employed to incorporate MOF-808 into a Pebax polymer matrix, ensuring uniform dispersion. The incorporation of MOF-808 into the Pebax matrix enhanced CO_2 permeability and CO_2/N_2 selectivity, achieving values of 142 Barrer and 77, respectively. Additionally, the membranes can be processed via dip-coating, enabling scalable module fabrication. This technique allows the formation of uniform thin-film layers on hollow fiber supports, facilitating industrial application. Notably, the fabrication process avoided toxic solvents, presenting a sustainable approach for developing high-performance MMMs for efficient CO_2 capture.



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EXPLORING IMINE-BASED COVALENT ORGANIC FRAMEWORKS (COFS) FOR ENHANCED BISPHENOL A ULTRASONIC REMOVAL: A COMPARATIVE STUDY

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Keywords: *COFs, adsorption, BPA, microplastics, mechanism*

The extensive presence of endocrine-disrupting chemicals (EDCs) in water bodies, such as Bisphenol A (BPA), has raised significant concerns due to their high toxicity. Even trace BPA concentrations (below 1 μg m^{-3}) can adversely affect human reproductive and endocrine systems [1].

This work explores two imine-based COFs (COF-1 and COF-2) synthesized with a common linker (DHTA), while the second linker was varied to examine the impact of pore size and structure on the BPA adsorption performance. The XRD and FTIR techniques confirmed the synthesis of both COFs and the exceptional structural stability of COF-1 and COF-2 across a broad pH range of 2-12. The maximum adsorption capacities of BPA obtained for COF-1 and COF-2 were 2022.0 mg g^{-1} and 2074.8 mg g^{-1}, respectively, which are higher than those reported in the literature [2]. Here, a comprehensive analysis of the possible adsorption mechanism was proposed, following the kinetic, isotherm, and spectroscopic analyses. Therefore, the experimental data was well-fitted by the PSO model, IPD, and Dubinin-Radushkevich model, suggesting that COF-1 and COF-2 exhibit similar adsorption mechanisms with a higher adsorption capacity of COF-2. This means that the higher aromatic ring content of COF-2 enhances the π-π interaction, and the appropriate pore size facilitates the higher adsorption capacity compared to COF-1. Also, spectroscopical analysis demonstrates that Van der Waals forces, π-π interactions, and physical interactions, where C, N, and O play crucial roles, drive the adsorption process of BPA. In addition, the regeneration of the adsorbents was evaluated over five cycles using methanol as eluent. This study underscores the synthesis of two imine-based COFs as promising candidates for environmental remediation, addressing a pressing global environmental concern.

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CHEMIRESISTIVE SENSING CAPABILITIES OF 2D π-CONJUGATED COBALT-BASED METAL–ORGANIC FRAMEWORKS

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Keywords: *metal–organic frameworks, triphenylene, nanorods, gas sensor, chemiresistive sensing*

2D conductive metal-organic frameworks (MOFs) are becoming popular for sensing applications as they possess high surface area, porosity, and intrinsic electrical conductivity [1,2]. Among these, MOFs constructed from hexahydroxytriphenylene (HHTP) ligands can be advantageous for chemiresistive sensing due to their structural and electronic features; however, their practical implementation in this field is still in its early stages and has not been fully explored [3].

In this context, we present the synthesis and comprehensive characterization of a cobalt-based MOF (Co-HHTP MOF, structure shown in Fig.1), synthesized through a simple solvothermal method at lower working temperature. Structural and morphological studies confirmed the formation of a crystalline framework with nanorod-like surface morphology. Nitrogen adsorption-desorption measurements revealed a specific surface area of ≈80 m²/g, indicating significant porosity favourable for gas adsorption. Co-HHTP MOF are being explored as room-temperature chemiresistive sensors for greenhouse gases (in particular CH_4 and CO_2) as well as various volatile organic compounds, where gas detection relies mainly on measurable changes in electrical resistance of MOFs upon exposure to these analytes. Our studies will focus on evaluating the sensing capabilities of these 2D π-conjugated MOFs, including key parameters such as selectivity, sensitivity, and stability. In addition, the influence of water vapor on sensor performance will be thoroughly examined to assess its practical applicability.

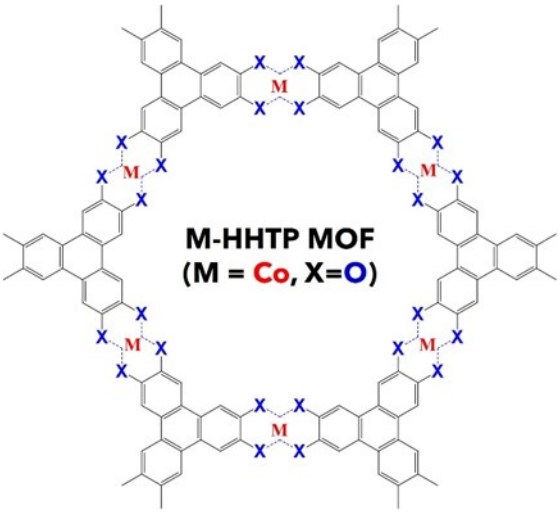


Fig.1: Structure of Co-HHTP MOF.

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INTERACTION OF H2S WITH A BI(III)-BASED MOF: POLYSULPHIDE FORMATION AND THE EFFECT ON THE FLUORESCENCE

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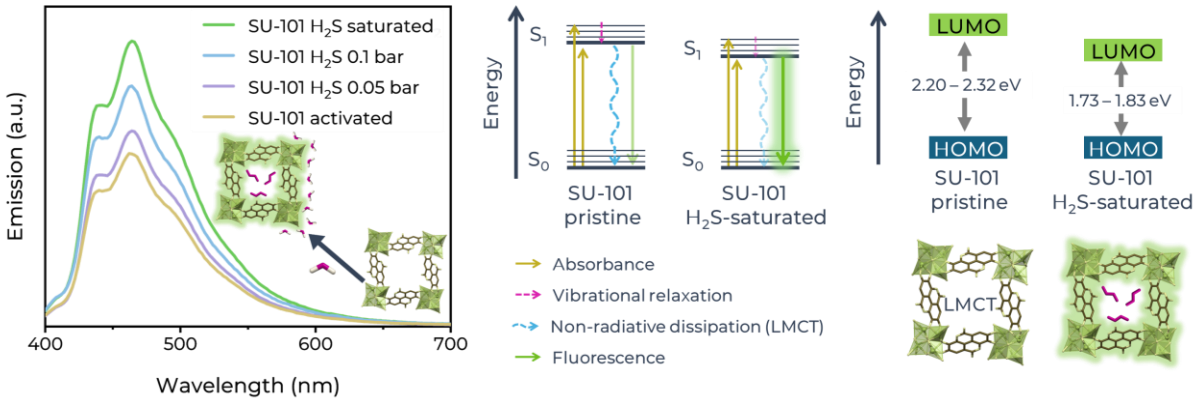
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Keywords: *MOFs, SU-101, H_2S, Fluorescence sensing, Polysulfide formation, H_2S adsorption*

Hydrogen sulfide (H_2S) is a highly toxic chemical that at low concentrations can irritate the eyes and respiratory tract, but at high levels can cause unconsciousness and respiratory arrest.[1] Its effective detection is essential for environmental monitoring and human health protection.

In this work, we demonstrate the use of a Bi(III)-based metal-organic framework (MOF), SU-101, as a selective and efficient fluorescence-based sensor for H_2S detection.[2] The detection mechanism is based on the formation of polysulfide species within the MOF structure, which leads to the modulation of the electronic structure of the material causing a significant increase of the fluorescence intensity. Time resolved photoluminescence (TRPL) measurements show an increase in the fluorescence lifetime after H_2S adsorption. Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) confirmed the formation of Sn^{2-} and S_4^{2-} species after exposure to H_2S at different pressures (0.05, 0.1 and 1 bar). This chemical transformation induces the rigidification of the framework, and a blockage in the ligand-metal charge transfer (LMCT) process that generates the fluorescence of SU-101 and enhances the radiative emission.[3] Furthermore, density functional theory (DFT) theoretical simulations validated the energetic stability of the polysulfide species within SU-101. Additionally, by UV-vis spectroscopy, the HOMO-LUMO energy gaps of the pristine and H_2S-saturated material were estimated by the Tauc method, obtaining a decrease after H_2S adsorption and supporting the idea of electronic restructuring causing the observed turn-on.[4]

These findings position SU-101 as a promising candidate for practical H_2S detection applications, combining high selectivity, chemical stability and efficient fluorescence response.



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SELECTIVE TRACE BROMIDE ION REMOVAL FROM CHLORIDE ION-DOMINATED SOLUTIONS USING DEFECTIVE ZR-BASED METAL-ORGANIC FRAMEWORKS

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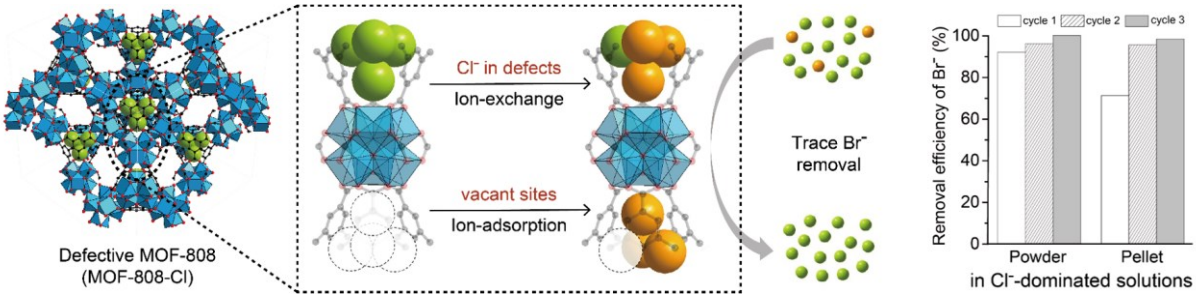
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Keywords: *bromide ion removal, defect site, metal-organic framework, ion-exchange, ion-adsorption, chloride ion, trace pollutant*

The removal of bromide ion (Br^-) in water is an important issue as it can generate bromate (BrO_3^-) and brominated disinfection by-products (DBPs), which are toxic, carcinogenic, and corrosive in nature. Several processes such as membrane, electrochemical, and adsorption methods can be used to remove Br^- from water. Nevertheless, these methods encounter substantial challenges when deployed in chloride-dominated contexts, which are prevalent in industries requiring high-purity salts. Particularly in water chlorination, the electrolysis of saltwater can result in bromate formation even with trace Br^- ions, thus potentially resulting in serious public health risks in drinking water. The primary difficulty in the removal of Br^- from Cl^--dominated condition is that the chemical and physical properties of both ions become less distinct in high concentration of competing ions.

In this study, we showed that the open acidic sites on the secondary building units (SBU) in a defective Zr-based MOF-808 (MOF-808-Cl) selectively remove the trace Br^- in the presence of higher concentration of Cl^- using different degree of electrostatic interaction induced by their own polarizability. Its structure and counter-ion position were characterized using single crystal X-ray diffraction and a compositional analysis. The efficacy of MOF-808-Cl in removing Br^- was evaluated using ion chromatography (IC). The powder and pelletized MOF samples were tested for Br^- removal efficiency in both immersion and penetration systems. The Br^- removal was carried out with the mixed mechanism of ion-exchange and -adsorption which contributions were estimated to be about 70% and 30%, respectively. The Br^- was successfully removed when the concentration of Cl^- is even 100 times higher than that of Br^-. This result shows the potential of MOF-808-Cl for industrial applications requiring trace ion removal, also providing insights for future research on selective ion removal in competitive environment [1].



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SYNERGISTIC INTEGRATION OF MXENE, BENTONITE, AND MOF-303 FOR HIGH-PERFORMANCE INTERFACIAL SOLAR STEAM GENERATION

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Keywords: *Metal-organic framework; MOF-303; MXene; freestanding MXene membrane; solar steam generation.*

Interfacial solar steam generation (ISSG) has emerged as a promising approach for sustainable water purification.[1] However, the development of efficient, robust, and scalable membrane materials remains a key challenge. MXenes, a class of two-dimensional transition metal carbides and nitrides, have attracted considerable attention due to their excellent photothermal conversion and hydrophilic properties. Yet, issues such as oxidation susceptibility and mechanical fragility limit their practical use in freestanding membrane applications. In this study, we developed a freestanding composite membrane composed of Ti3C2Tx MXene, extracted bentonite (EB), and MOF-303(fine) (figure 1), designed to synergistically enhance photothermal efficiency, structural integrity, and water transport. EB provided mechanical reinforcement and oxidation resistance, enabling substrate-free operation. MOF-303(fine), a microporous aluminum-based metal-organic framework, was incorporated to reduce the evaporation enthalpy of water through nanoconfinement effects. Comprehensive structural and thermal analyses confirmed that the optimized membrane maintained a well-aligned, layered architecture and significantly reduced the energy required for water vaporization. Under one sun irradiation, the MXene/EB/MOF-303(fine) membrane achieved a high water evaporation flux of 3.43 kg m-2 h-1 and an energy conversion efficiency of 159%, outperforming both MXene-only and previously reported composite systems. The membrane also demonstrated excellent stability over multiple cycles and effectively desalinated seawater to meet WHO drinking water standards. These results underscore the potential of the MXene/EB/MOF-303(fine) membrane as a scalable and efficient platform for solar-driven water purification, offering an integrated solution to address the photothermal, mechanical, and functional challenges of ISSG technologies.

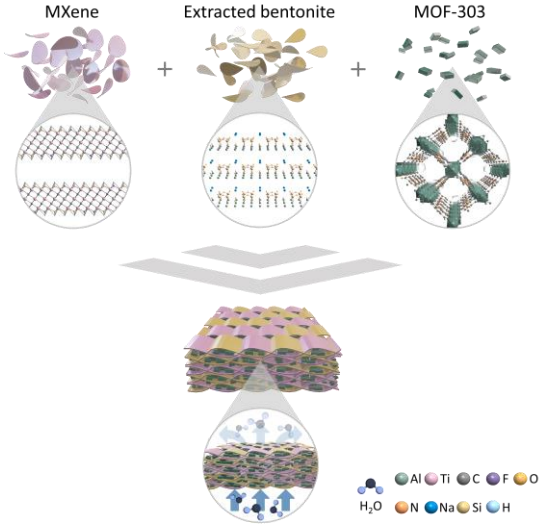


Figure 1. Schematic illustration of the formation of the MXene/EB/MOF-303 membrane through the assembly of MXene nanosheets, EB nanosheets, and MOF-303.

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CONSTRUCTING POLYCRYSTALLINE MOF MEMBRANES WITH SOLUTION-DIFFUSION MASS TRANSFER VIA DEFECT FILLING

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Keywords: *MOF, ionic liquid, defect filling, membrane separation, H_2 purification*

Polycrystalline metal-organic framework (MOF) membranes possess well-ordered molecular sieving channels, enabling precise molecular separation. However, the uncontrolled formation of non-selective intergranular defects during MOF membrane growth significantly limits separation efficiency. Especially, under high-pressure operating conditions, these defects serve as the origin of irreversible structural degradation, further compromising the performance and stability of polycrystalline MOF membranes[1]. We propose a strategy to fill intergranular defects in polycrystalline MOF membranes using ionic liquids (ILs). This method involves the in-situ growth of polycrystalline MOF membranes in the presence of ILs, facilitating the formation of mixed matrix membranes (MMMs) composed of a rigid polycrystalline MOF matrix integrated with flexible IL fillers confined within intergranular defects (IL@MOF). The fabricated IL@MOF membranes exhibit reversed CO_2/H_2 separation, a challenging achievement given that smaller H_2 molecules typically demonstrate higher permeance in MOF membranes.

Hydrogen purification membranes can significantly reduce energy consumption if preferential separation of CO_2 is achieved, allowing high-pressure H_2 to be retained as the product (Fig 1). To evaluate the impact of different ILs on separation performance, ILs with varying molecular sizes were encapsulated into polycrystalline MOF membranes. The results revealed that the IL molecules preferentially occupied intergranular defects rather than the intrinsic MOF cavities. The incorporated ILs exhibited strong affinity toward CO_2 molecules, facilitating their dissolution and selective transport while effectively impeding the permeation of other gases. MOF channels offer rapid transport pathways for CO_2 molecules.

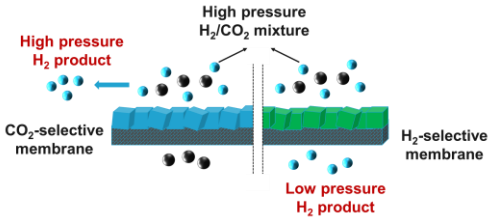


Fig 1. Comparison of CO_2-selective and H_2-selective membrane for H_2 purification

Traditional MMMs consist of a polymer matrix and porous fillers, where molecular transport is primarily governed by the solution-diffusion mechanism of the polymer. However, these MMMs often suffer from the inherent limitations of the polymer matrix, such as plasticization under high-pressure operating conditions[2]. The fabricated IL@MOF membrane exhibits mass transport behavior similar to that of traditional MMMs, despite employing a polycrystalline MOF as the matrix. This transport mechanism effectively ensures membrane stability under harsh operating conditions. By preparing polycrystalline MOF membranes with varying pore sizes, all types of IL@MOF membranes showed a transition from a molecular sieving mechanism to a solution–diffusion-based transport mechanism, enabling reverse selective separation of CO_2 over H_2. At a high pressure of 8 bar, the membranes achieve a CO_2/H_2 separation selectivity of up to 15. Moreover, they demonstrate excellent thermal stability, retaining a selectivity of 10 at an elevated temperature of 100 °C. The broad applicability of this strategy offers a novel solution to the challenging task of CO_2/H_2 membrane separation.

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MOFs AND TIO_2-BASED COMPOSITES FOR ADSORPTION AND PHOTODEGRADATION OF EMERGING POLLUTANTS

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Keywords: *TiO_2, composites, photodegradation, pollutants, remediation*

The combination of a photocatalyst, such as TiO_2, with a metal-organic framework (MOF) form composites with synergic properties. The resulting MOF@TiO_2 composite can capture and further break down target molecules of interest. This way, it is possible to remove emerging pollutants from environmental water samples in a two-steps process: by using MOFs as sorbents followed by the degradation through light irradiation of the contaminants using TiO_2 as catalyst.

This work introduces a new generation of MOF@TiO_2 composites synthesized through a straightforward solvothermal approach. The selection of the MOFs (CAU-10-NH_2, MIL-53(*Al*), and CIM-100(*Al*)), are all aluminum(III)-based, is based on (i) the low toxicity of the metal (useful if intending environmental remediation), (ii) adequate surface area and porosity, and (iii) water stability. Both, the neat materials (MOFs and TiO_2) and the resulting composites (CAU-10-NH_2@TiO_2, MIL-53(*Al*)@TiO_2, and CIM-100(*Al*)@TiO_2), were thoroughly characterized to evaluate intrinsic properties of each component and the synergies upon their combination.

The neat materials and the composites were evaluated for the removal of a group of specific emerging pollutants (parabens, benzophenones and UV filters) from environmental waters. Four different pollutants (methylene blue, propylparaben, benzophenone, and triclosan) were selected as model analytes to evaluate the photodegradation capacity of the composites. The determination and subsequent degradation were carried out using a high-performance liquid chromatograph coupled to a diode array detector (HPLC-DAD). This technique, unlike those commonly used to study photodegradation processes, allows the simultaneous monitoring of the degradation process of a mixture of analytes, mimicking real environmental scenarios where multicomponent contaminants are present.

Acknowledgements

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NOVEL HIERARCHICAL MOFS FOR BALANCED VOLUMETRIC AND GRAVIMETRIC H_2 AND CH_4 STORAGE

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The ongoing energy transition plans have driven the search for alternative energy sources that are both efficient and environmentally sustainable. Among the various options, the use of biomethane is favored, while hydrogen is considered a promising energy carrier. However, significant technological challenges remain, particularly in developing safe and high-performance storage systems that meet the required capacity and kinetics. Metal-organic frameworks (MOFs) are extensively studied for their use in a broad range of sorption applications due to their fascinating structural characteristics. The concept of reticular synthesis, which is the process of assembling predesigned rigid molecular building blocks into predetermined ordered structures, is rapidly growing. However, its full potential toward the rational design of MOFs relies on the availability of highly connected building blocks. In this respect, building blocks with connectivity greater than 12 are highly desirable but extremely rare.

Herein, we report the discovery of **novel 18-connected**, trigonal prismatic, **ternary building blocks (tbb's)** and their assembly into a series of unique MOFs, denoted as **Fe-tbb-MOF-x (x: 1, 2, 3),** while post-metallation experiments led to two more analogues, namely **Al-tbb-MOF-1** and the bimetallic **Fe/Ni-tbb-MOF-2.** These MOFs exhibit hierarchical micro- and mesoporosity with ultrahigh BET areas (4,263-4,847 $m^2\ g^{-1}$) and pore volumes (1.95-2.29 $cm^3\ g^{-1}$) as confirmed by Ar sorption isotherms at 87K.

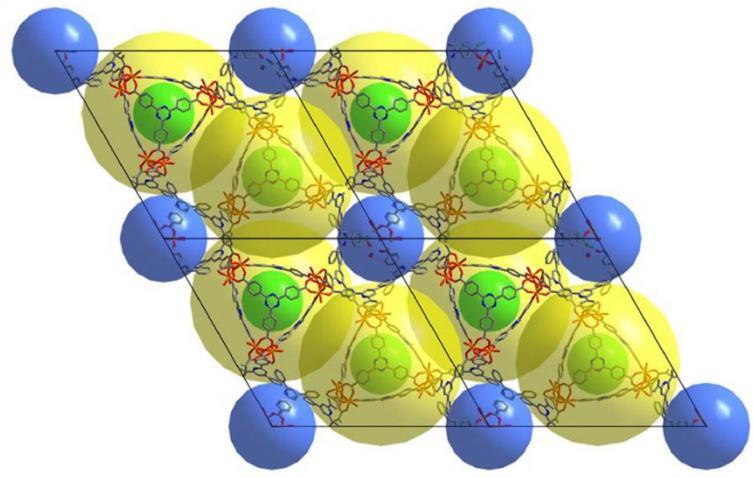


Figure 1. Structure of Fe-tbb-MOF-1 showing the interconnected cages with hierarchical porosity (green cages: 0.8 x 1.6 nm, blue cages: 1.6 nm, green cages 3.0 nm)

Systematic high pressure adsorption measurements showed that the materials also demonstrate well-balanced high gravimetric and volumetric deliverable capacities for cryoadsorptive H_2 storage under temperature/pressure swing conditions (11.6 wt %/41.4 g L^{-1}, 77 K/100 bar–160 K/5 bar), as well as CH_4 storage at near ambient temperatures (367 mg g^{-1}/160 cm^3 STP cm^{-3}, 5-100 bar at 298 K. The results place these materials among the top performing MOFs. Indicative H_2 isotherms

recorded at 77K are illustrated in Figure 2, while the corresponding total and deliverable amounts are given in Table 1.

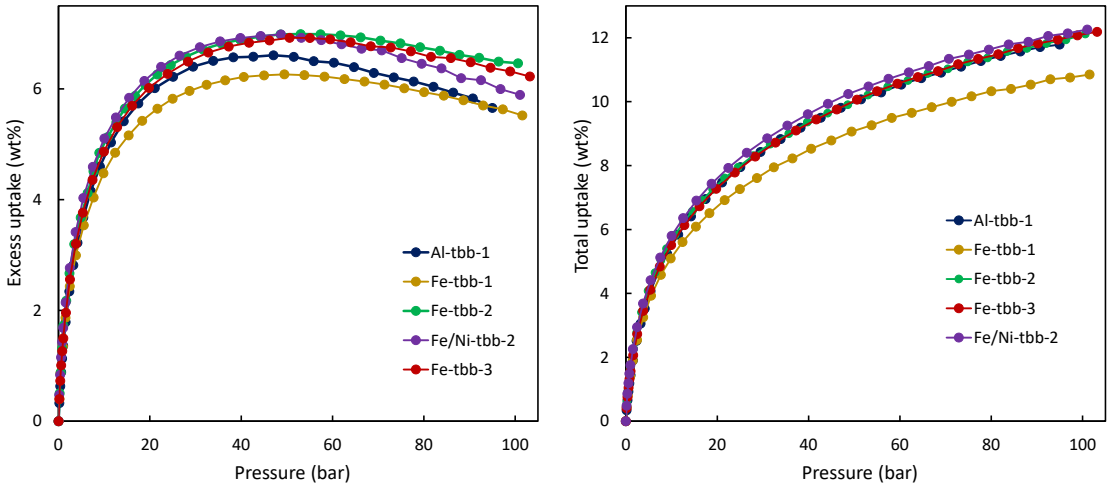


Figure 2. H_2 excess (left) and total (right) gravimetric uptake at 77K for the new M-tbb-MOF-x family of MOFs

Table 1. Total H_2 gravimetric / volumetric uptakes and the corresponding working capacity under pressure/temperature swing conditions

	Al-tbb-MOF-1		Fe-tbb-MOF-1		Fe-tbb-MOF-2		Fe-tbb-MOF-3		Fe/Ni-tbb-MOF-2	
	wt%	g/L	wt%	g/L	wt%	g/L	wt%	g/L	wt%	g/L
77K 100 bar	12.0	40.8	10.8	37.8	12.1	42.9	12.1	43.0	12.2	43.5
160K 5 bar	0.5	1.4	0.4	1.3	0.5	1.5	0.4	1.4	0.5	1.6
Working Capacitiy	11.5	39.4	10.4	36.5	11.6	41.4	11.7	41.6	11.7	41.9

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6th European Conference on Metal Organic Frameworks and Porous Polymers

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4	**Len Barbour** Unravelling transient porosity: structural and thermodynamic insights into flexible porous materials
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