Young Scientist Symposium

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EuroMOF25

20-21 September 2025

Heraklion Crete, Greece

ABSTRACT BOOK

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Welcome to the Young Scientist Symposium of EuroMOF2025!

It is our great pleasure to welcome you to the vibrant city of Heraklion for one and a half days filled with exciting science and inspiring exchange.

This year's program features 20 talks, more than 115 posters, and participants joining us from 30 different countries—a testament to the diversity and strength of our community.

In this book of abstracts, you will find the details that showcase the breadth of research being presented. We hope it will guide you as you navigate the sessions, discover new ideas, and connect with fellow scientists.

We wish you stimulating discussions, fruitful collaborations, and plenty of opportunities to enjoy both the spectacular science and the lively atmosphere of EuroMOF2025.

With warm regards,
Alexandra, Andrea, Emmanuel, Giasemi, Ken, Manuel, Romy, and Sven

CONFERENCE CHAIRS

Dr. Romy L. Ettlinger

TUM Junior research group leader

Chair of Inorganic and Metal-Organic Chemistry, Technical University of Munich

Prof. Sven M.J. Rogge

Associate research professor

Center for Molecular Modeling, Ghent University

Cultural and Conference Center · Heraklion, Greece

20th–21st September, 2025

PROGRAM SATURDAY – 20th September, 2025

13:00-13:45	**Registration Young Scientist Symposium**	
Chair: Romy L. Ettlinger		
13:45-14:00	Opening of the Young Scientist Symposium	
14:00-14:40	From Exciton to Formate: Radical Pathways in Porphyrin-Based MOFs	Bettina Baumgartner
14:40-15:00	Ordering Bent and Straight Dicarboxylate Linkers in an fcu Zirconium Metal-Organic Framework	Grace Farmer
15:00-15:20	Phenomena based on Redox-conductive Metal-Organic Framework	Amol Kumar
15:20-15:40	**Coffee break**	
Chair: Giasemi Angeli		
15:40-16:00	Machine Learned Potential for High-Throughput Phonon Calculations of Metal-Organic Frameworks	Prathami Divakar Kamath
16:00-16:20	Tuning the Crystallinity of a Metal–Organic Coordination Network at the Liquid–Solid Interface	Antonino Cucinotta
16:20-16:40	Thermally Stable Binary Hybrid Organic-Inorganic Perovskite Glasses	Arad Lang
16:40-17:00	Carbon Capture from Natural Gas Flue Emissions and Air via (Bi)Carbonate Formation in a Cyclodextrin-Based Metal-Organic Framework	Alexandra Lim
17:00-17:40	Plenary discussion	
17:40-...	**Poster party + social event**	

PROGRAM SUNDAY – 21st September 2025

08:30-09:00	**Open Exchange – Start of Day 2**	
Chair: Sven M. J. Rogge		
09:00-09:40	Metal-Organic Polyhedra: Porous Nanoparticles with Molecular Reactivity	Arnau Carné-Sánchez
09:40-10:00	Structuring Function: MOF–Polymer Composites For Customizable Therapeutic Applications	Sarah Dummert
10:00-10:20	From Weak to Wow: Fluorescence Modulation by Metal Centres For SO_2 Detection in the MFM-300(M) Family	Valeria B. López-Cervantes
10:20-10:40	**Coffee break**	
Chair: Andrea Laybourn		
10:40-11:00	Excision of Organic Macrocycles from Covalent Organic Frameworks via Clip-Off Chemistry	Jorge Albalad
11:00-11:20	Modelling Elusive Order-Disorder Phase Transitions in Metal–Organic Frameworks	Thomas Nicholas
11:20-11:40	Disclosing the Photocatalytic Properties of Ce-UiO-66 Based on Perfluorocarboxylic Acid Linkers: Experimental and Theoretical Insights	Diletta Morelli Venturi
11:40-12:00	Electrical Characterization of a Large-Area Single-Layer of Cu_3BHT 2D Conjugated Coordination Polymer	Sandra Martínez Estévez
12:00-12:10	Group picture Young Scientist Symposium	
12:10-14:00	**Lunch break + poster session**	
Chair: Emmanuel Klontzas		
14:00-14:40	Plenary discussion	
14:40-15:00	Sustainable Dynamic Solvent System (DSS) Unraveling Flexibility of Pyrazolate MOFs With Winerack Topology	Leonid Shupletsov
15:00-15:20	Exploring The Synthesis Of High Nuclearity Cluster-Based Metal–Organic Frameworks Using Early Lanthanoids	Micaela Richezzi
15:20-15:40	HKUST-1 and CPO-27 Decorated With Graphene Oxide: Shaped Composite Beads With Improved Hydrolytic Stability And Enhanced CO_2 Adsorption	Yassine Khadiri
15:40-16:00	**Coffee break**	
Chair: Manuel Souto Salom		
16:00-16:20	Resource Recovery Using Porous Composite Materials	Theresa Bloehs
16:20-16:40	Gas Adsorption Meets Deep Learning	Antonios Sarikas
16:40-17:00	How Powerful is Ligand Engineering in Enhancing MOF Performance?	Zheao Huang
17:00-17:10	Closing of the Young Scientist Symposium	

INVITED PRESENTATIONS

FROM EXCITON TO FORMATE: RADICAL PATHWAYS IN PORPHYRIN-BASED MOFS

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Keywords: *photoactive MOFs, artificial photosynthesis, porphyrin, charge transfer mechanism, CO2*

Artificial photosynthesis offers a promising route toward sustainable energy solutions, but achieving precise control and a deep understanding of the underlying photochemical processes remains a significant hurdle. Metal-organic frameworks (MOFs), particularly those featuring photoresponsive porphyrin linkers, have emerged as compelling materials due to their modular architectures and large internal surface areas. In this work, we explore the photoreduction of CO_2 within the Zr-based porphyrinic MOF, PCN-223, using an array of complementary spectroscopic techniques.

While prior models suggest that photoinduced electron transfer from the porphyrin to the Zr_6-oxo nodes initiates catalysis at the cluster site,[1–3] our results challenge this narrative. Using X-ray absorption spectroscopy (XAS), electron paramagnetic resonance (EPR), UV-visible absorption, transient absorption, and Fourier-transform infrared (FTIR) spectroscopy, we find no evidence for the formation of Zr^{3+} under illumination. Instead, light excitation triggers the emergence of an organic radical species within the porphyrin network itself.

Spectroscopic signatures indicate that a symmetry-breaking radical pair ($P•^+/P•^-$) forms between closely packed porphyrin units, facilitated by strong excitonic interactions. The sacrificial donor triethanolamine (TEOA) preferentially quenches the oxidized porphyrin ($P•^+$), leaving the reduced species ($P•^-$) to drive CO_2-to-formate conversion. FTIR spectra confirm the production of $HCOO^-$ and show that the radical state is stabilized under illumination in the presence of TEOA.

These findings revise the current understanding of MOF-based photocatalysis by shifting the focus from the inorganic node to linker-centered charge transfer. Our study underscores the critical role of linker arrangement, radical stabilization, and electronic structure in facilitating efficient photoreactions within MOFs. This mechanistic insight paves the way for designing next-generation photocatalysts that harness cooperative linker behavior akin to natural photosynthetic systems.

References

[1] H.-Q. Xu, J. Hu, D. Wang, Z. Li, Q. Zhang, Y. Luo, S.-H. Yu, H.-L. Jiang. *J. Am. Chem. Soc.* **2015**, *137*, 13440-13443.

[2] Z. Jin, D. Liu, X. Liu, P. Chen, D. Chen, H. Xing, X. Liu. *Inorg. Chem.* **2024**, *63*, 1499-1506.

[3] Y. Benseghir, A. Solé-Daura, D. R. Cairnie, A. L. Robinson, M. Duguet, P. Mialane, P. Gairola, M. Gomez-Mingot, M. Fontecave, D. Iovan, B. Bonnett, A. J. Morris, A. Dolbecq, C. Mellot-Draznieks. *J. Mater. Chem. A* **2022**, *10*, 18103-18115.

METAL-ORGANIC POLYHEDRA: POROUS NANOPARTICLES WITH MOLECULAR REACTIVITY

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Keywords: *Metal-Organic Polyhedra, Metal-Organic Cage, Self-assembly, Porous Materials …*

Metal-Organic Polyhedra (MOPs) represent the ultimate strategy to downsize hybrid porous materials below 5 nm.[1] At this dimension, MOPs uniquely combine properties typically associated with discrete molecules (e.g., solubility and stoichiometric reactivity), reticular porous materials (e.g., permanent porosity and tunable cavities), and ultra-small inorganic nanoparticles (e.g., high surface density of reactive sites). In this talk, I will present how we have combined these unique features to develop MOPs as molecular nanoscopic platforms—or “molecular nanoparticles”—which can be functionalized through covalent and coordination chemistry to achieve targeted properties and applications, such as tunable solubility, biofunctionalization, and molecular transport/separation.[2] In addition, I will show how the precise knowledge of the number and position of reactive groups decorating the surface of MOPs can be leveraged to predict their self-assembly behavior upon reaction with additional metal ions and organic molecules, giving rise to complex crystalline architectures and soft porous materials such as gels and aerogels.[4,5] Finally, I will discuss the use of MOPs to transfer designed porosity across different physical states, including liquids.[6]

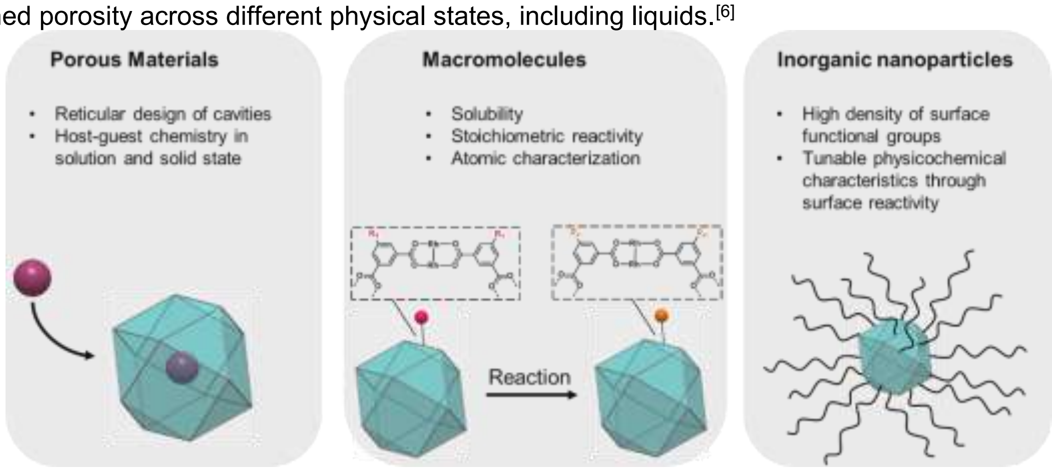

Figure 1. Illutration showing the conceptualization of MOPs as porous materials, macromolecules and inorganic nanoparticles.

References

[1] D. J. Tranchemontagne, Z. Ni, M. O'Keeffe, O. M. Yaghi. Coordination Polymers. *Angew. Chem. Int Ed.* **2008**, 47, 5136-5147.

[2] J. Albalad, L. Hernández-López, A. Carné-Sánchez, Daniel Maspoch. *Chem. Commun.* **2022**, 58, 2443-2454.

[3] A. Khobotov-Bakishev, L. Hernández-López, C. von Baeckmann, J. Albalad, A. Carné-Sánchez, D. Maspoch. *Adv. Sci.* **2022**, 9, 2104753.

[4] L. Hernández-López, A. Khobotov-Bakishev, A. Cortés-Martínez, Ed. Garrido-Ribó, P. Samanta, S. Royuela, F. Zamora, D. Maspoch, A. Carné-Sánchez. *J. Am. Chem. Soc.* **2025**, 147, 16560-16567.

[5] C. von Baeckmann, J. Martínez-Esaín, J. A. Suárez del Pino, L. Meng, J. Garcia-Masferrer, J. Faraudo, J. Sort, A. Carné-Sánchez, D. Maspoch. *J. Am. Chem. Soc.* **2024**, 146, 7159-7164.

ORAL PRESENTATIONS

ORDERING BENT AND STRAIGHT DICARBOXYLATE LINKERS IN AN FCU ZIRCONIUM METAL-ORGANIC FRAMEWORK

Grace S. G. Farmer[a], Daniel J. Cheney[a], Khai-Nghi Truong[b], Nusik Gedikoglu[a], Bhupendra P. Mali[a], Datta Markad[a], Frédéric Blanc[a], Alexandros P. Katsoulidis[a], and Matthew J. Rosseinsky[a]

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Keywords: *Zirconium MOFs, multicomponent, high-throughout synthesis, structural transformation*

Zirconium metal-organic frameworks (Zr-MOFs) are attractive for an array of applications owing to their high stability and structural diversity. The ordered arrangement of multiple linkers with different lengths and geometries within one framework offers the precise tailoring of the porous and structural properties of a MOF. The geometry of the dicarboxylic acid linker has a distinct effect on the connectivity of the resulting zirconium framework for single linker frameworks.[1] Incorporation of multiple linkers can therefore produce new cages and windows that are inaccessible by a single linker, resulting in materials with enhanced performance in adsorption and separation. However, the addition of the extra linker in the chemical synthesis system makes the exploration challenging. Therefore, we implement high throughput synthesis (HTS) methods to systematically screen chemical spaces for the discovery of new multicomponent Zr-MOFs *via* a one-step synthesis. The HTS workflow facilitates the systematic variance of the ratio of the two linkers, the amount of modulator, and the ratio of the linkers to the metal source.[2]

Here, we explore the combination of straight 1,4-benzene dicarboxylic acid (BDC) and bent 2,5-thiophenedicarboxylic acid (TDC) (Figure 1a,b). A new two-linker **fcu** Zr-MOF decorated by ordered straight and bent linkers, was discovered *via* a one-pot HTS route. This is the first **fcu** Zr-MOF containing TDC as a linker affording the distortion of the tetrahedral and octahedral cages, compared to UiO-66, with characteristically new shapes. The new MOF demonstrated the efficient separation of *n*-hexane/benzene/cyclohexane. Furthermore, the framework exhibits a chemically controllable dynamic unbinding and subsequent rebinding of the bent linker, without destroying or changing the composition of the framework (Figure 1c). This structural transformation was explored with electron diffraction and solid-state magic angle spinning (MAS) NMR, alongside structural refinement of the powder x-ray diffraction. Thus, the development of new multicomponent MOFs can be delivered by the efficient exploration of large chemical spaces by HTS yielding structural motifs and reactivity patterns beyond those envisaged from the structures of single linker MOFs.[3]

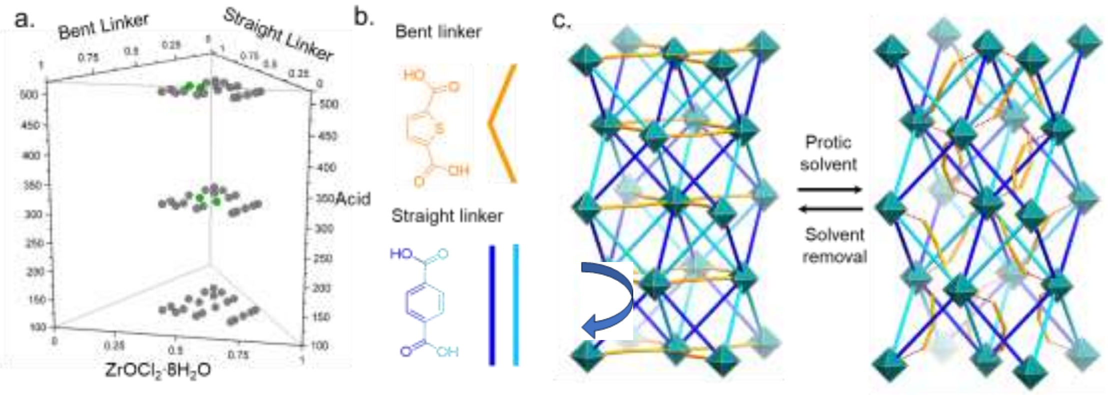

Figure 1 (a) The explored chemical space, (b) the studied linkers, and (c) the structural transformation of the new MOF. $[Zr_6(O)_4(OH)_4]^{12+}$ clusters are depicted by teal Zr_6 octahedrons.

References:
[1] Guillerm, V. & Maspoch, D. 2019, Journal of the American Chemical Society, 141, 16517-16538
[2] Tollitt, A., Rosseinsky M., 2021, Angewandte Chemie International Edition 4, 1-17
[3] Farmer G., Rosseinsky M., 2025, Under review at Journal of the American Chemical Society

PHENOMENA BASED ON REDOX-CONDUCTIVE METAL ORGANIC FRAMEWORK

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Keywords: *MOF, Thin Films, Spectroclectrochemistry, Cyclic voltammetry, Redox hopping*

The development of redox-conductive metal–organic frameworks (MOFs) has opened new avenues for applications in energy storage, electronics, and catalysis.[1] To address fundamental questions surrounding diffusional electron hopping and redox conductivity, a series of isoreticular MOFs were synthesized using redox-active diimide-based linkers XDIs (X = PM (pyromellitic), N (naphthalene), or P (perylene); DI = diimide). These MOFs were grown as crystalline thin films on conductive fluorine-doped tin oxide (FTO) substrates.

Due to the distinct redox characteristics of each linker, the resulting Zn-XDI MOFs were evaluated for their electrochromic properties, with some demonstrating record-high coloration efficiency.[2] Additionally, mixed-linker MOFs comprising statistically distributed PMDI and NDI units were constructed. In these materials, two distinct electron transport mechanisms were observed: diffusional hopping between linkers of the same type and thermodynamically driven electron transfer between dissimilar linkers, introducing a second, energetically favorable transport pathway.[3] MOFs also show significant promise in photoelectrochemical (PEC) applications, particularly in supporting high photovoltages. When used to modify semiconductor surfaces, MOFs enhance PEC performance by facilitating efficient interfacial charge transfer. These hybrid photocathodes leverage the light-harvesting capabilities of semiconductors to drive redox reactions at reduced energy input, while the MOF layer contributes tunable active sites and ensures long-term stability. Herein, we explore this charge transport process on a model photocathode consisting semiconductors (SCs) that are coated with Zn-NDI MOF as surface overlayer.

References

[1] J. Li, A. Kumar, B. A. Johnson, S. Ott, *Nat. Commun.* **2023**, *14*, 4388.
[2] A. Kumar, J. Li, A. K. Inge, S. Ott, *ACS Nano* **2023**, *17*, 21595-21603.
[3] J. Li, A. Kumar, S. Ott, *Journal of the American Chemical Society* **2024**, *146*, 12000-12010.

MACHINE LEARNED POTENTIAL FOR HIGH-THROUGHPUT PHONON CALCULATIONS OF METAL-ORGANIC FRAMEWORKS

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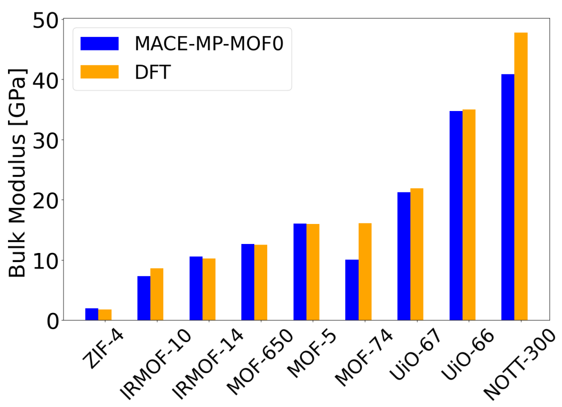
Keywords: *Machine Learning Potentials (MLP), phonons, quasi-harmonic, high-throughput screening*

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.



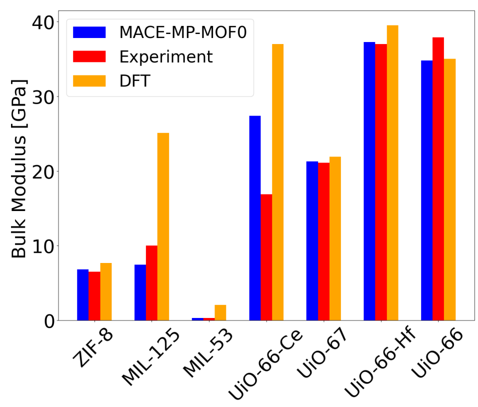


Figure 1. Bulk modulus predictions with MACE-MP-MOF0 for well-known MOFs in literature which are diverse in chemistry and topology, as compared to a) only DFT and b) DFT and Experiments

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

TUNING THE CRYSTALLINITY OF A METAL–ORGANIC COORDINATION NETWORK AT THE LIQUID–SOLID INTERFACE

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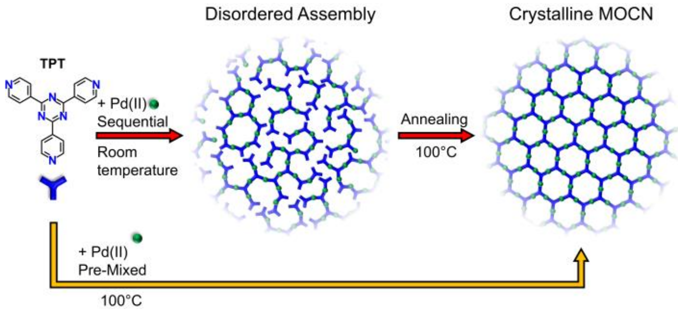
Keywords: *MOCN, STM, Porosity, Crystallinity.*

Metal–organic coordination networks (MOCNs) are surface-supported single-layered metal-organic frameworks (MOFs) analogs. Surface confinement promotes low coordination numbers, and the presence of coordinatively unsaturated metal sites, combined with unique electronic and magnetic properties, renders them promising candidates for use in solution-based heterogeneous applications. The bottom-up synthesis of such surface-supported MOCNs requires a rigorous design by utilizing two-dimensional (2D) crystal engineering. However, a comprehensive description of the factors governing their synthesis at the liquid-solid interface is still missing, resulting in only a few reported examples.

Scanning probe microscopy (SPM) is emerging as a space-resolved, non-invasive technique, for the characterization of MOFs and MOCNs at the molecular level. Atomic force microscopy (AFM) is routinely employed to characterize microscopic features of MOF surfaces, while molecular resolution studies of surface-supported porous MOCNs have been carried out through ultra-high vacuum scanning tunneling microscopy (UHV-STM). In a pioneering work, Kitagawa et al. showed AFM at the solid-liquid interface to be suitable for the investigation of MOF surfaces with molecular resolution, providing insights into guest adsorption and release and delamination processes[1]. We used STM at the liquid-solid interface to study, at the molecular scale, the chiral phases in a surface-supported MOCN containing prochiral hydrogen-bonded supramolecular building blocks[2].

In the work presented here, we report on the molecular resolution SPM characterization of a porous MOCN formed at the liquid-solid interface under ambient conditions, solely stabilized by metal coordination.[3] Starting from the ligand 2,4,6-tri(4-pyridyl)-1,3,5-triazine (**TPT**) compact self-assembly on highly-oriented pyrolytic graphite (HOPG), the *in-situ* addition of a Pd(II) salt solution leads to the formation of a single-layered porous, albeit amorphous assembly. A temperature-driven disorder-to-order transition leading to a porous MOCN honeycomb is observed when an annealing step is introduced after the metal addition in this sequential synthesis protocol. An analogous crystalline MOCN is obtained by pre-mixing the reactants in a different solvent at high temperatures.



*Schematic illustration of the two synthetic protocols presented in this work for the fabrication of the porous **TPT-Pd(II)** MOCN.*

Possible growth pathways are discussed on the basis of the different morphologies observed in samples fabricated using the two synthesis methods. Additionally, the porosity of the MOCN is examined by adding a guest molecule. This study paves the way for the investigation at the nanometer scale of analogous systems at the liquid-solid interface, targeting insights concerning their synthesis, crystallinity, temperature effect, concentration effect, and porosity.

References

[1] N. Hosono, S. Kitagawa, et al. *Nat. Chem.*, **2019**, 11, 109–116

[2] A. Cucinotta, S. De Feyter, et al. *J. Am. Chem. Soc.*, **2023**, 145, 1194–1205

[3] A. Cucinotta, S. De Feyter, et al. *J. Am. Chem. Soc.*, **2025**, 147, 7682–7693

THERMALLY STABLE BINARY HYBRID ORGANIC-INORGANIC PEROVSKITE GLASSES

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Keywords: *Hybrid glasses, Hybrid perovskites, Thermal stability, Physical properties.*

Two-dimensional hybrid organic-inorganic perovskites (2D-HOIPs) have recently garnered significant attention for their potential integration into next-generation optoelectronic applications. Their chemical diversity and straightforward synthesis, together with band gap tunability and enhanced stability, make them promising candidates to replace their three-dimensional counterparts as active materials in photovoltaics, light emitters, and photodetectors.[1,2] Recent studies have revealed that 2D-HOIPs with the chemical formula $(RNH_3)2MX_4$ (where R is a bulky organic moiety, M is a divalent metal cation, and X is a halide) can undergo melting — a reversible solid-liquid transition — upon heating.[3,4] Furthermore, by carefully engineering the organic cation, the cooling-induced crystallisation can be suppressed, resulting in a glassy (amorphous) state.[5,6] However, these so-called "HOIP glasses" exhibit thermal instability, reverting to their thermodynamically stable crystalline form upon mild heating or even at room temperature over a time span of hours to days.[7]

In this work, we address the thermal instability of HOIP glasses through melt alloying, a technique we recently demonstrated to apply to meltable 2D-HOIP systems.[8] Binary HOIP glasses were synthesized by blending powders of two glass-forming 2D-HOIPs: $(S\text{-}NEA)_2PbBr_4$ (where S-NEA = (S)-(−)-1-(1-naphthyl)ethylamine)[9] and $(MIPA)_2PbI_4$ (where MIPA = methyl-iodopropylamine).[10] Melt-quenching these blends resulted in the formation of glassy phases. The glass transition temperatures, optical band gap, and mechanical hardness of these glasses were found to depend on the blend composition. Most notably, the binary glasses exhibited complete thermal stability, with no recrystallisation observed even after one month of storage at room temperature.

References

[1] K. Zheng, T. Pullerits, *J Phys Chem Lett* **2019**, *10*, 5881.
[2] L. Mao, C. C. Stoumpos, M. G. Kanatzidis, *J Am Chem Soc* **2019**, *141*, 1171.
[3] D. B. Mitzi, D. R. Medeiros, P. W. DeHaven, *Chemistry of Materials* **2002**, *14*, 2839.
[4] T. Li, W. A. Dunlap-Shohl, Q. Han, D. B. Mitzi, *Chemistry of Materials* **2017**, *29*, 6200.
[5] A. Singh, D. B. Mitzi, *Nat Rev Mater* **2025**.
[6] C. Ye, L. N. McHugh, C. Chen, S. E. Dutton, T. D. Bennett, *Angewandte Chemie International Edition* **2023**, *62*.
[7] A. Singh, D. B. Mitzi, *ACS Mater Lett* **2022**, *4*, 1840.
[8] A. Lang, C. Chen, C. Ye, L. N. McHugh, X. W. Chua, S. D. Stranks, S. E. Dutton, T. D. Bennett, *J Am Chem Soc* **2024**.
[9] A. Singh, M. K. Jana, D. B. Mitzi, *Advanced Materials* **2021**, *33*.
[10] W. Wang, C. D. Liu, C. C. Fan, X. Bin Fu, C. Q. Jing, M. L. Jin, Y. M. You, W. Zhang, *J Am Chem Soc* **2024**, *146*, 9272.

CARBON CAPTURE FROM NATURAL GAS FLUE EMISSIONS AND AIR VIA (Bi)CARBONATE FORMATION IN A CYCLODEXTRIN-BASED METAL-ORGANIC FRAMEWORK

S. Alexandra Lim,[a,‡] Mary E. Zick,[a,‡] Jaehwan Kim,[a] Benjamin J. Rhodes,[b] Joharimanitra Randrianandraina,[c] Tristan A. Pitt,[a] Ronald T. Jerozal,[a] Jung Hoon Lee,[c] Alexander C. Forse,[b] Phillip J. Milner[a,*]

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Keywords: *carbon capture, metal-organic frameworks, cyclodextrin, direct air capture, NGCC flue gas emissions*

Carbon capture and utilization or sequestration (CCUS) from industrial point sources and direct air capture (DAC) are both necessary to curb the rising atmospheric levels of CO_2. Amine scrubbers, the current leading carbon capture technology, suffer from poor oxidative and thermal stability, limiting their long-term cycling stability under oxygen-rich streams such as air and the emissions from natural gas combined cycle (NGCC) power plants. Herein, we demonstrate that the hydroxide-based cyclodextrin metal-organic framework (CD-MOF) Rb_2CO_3 CD-MOF ST possesses high CO_2 capacities from dry dilute streams at low temperatures and humid streams at elevated temperatures. Additionally, it displays good thermal, oxidative, and cycling stabilities and selective CO_2 capture under mixed gas conditions in dynamic breakthrough experiments. Unexpectedly, under dry, hot conditions, a shift in the CO_2 adsorption mechanism—from reversibly formed bicarbonate to irreversibly formed carbonate—is observed, as supported by gas sorption and spectroscopic studies (**Figure 1**). This mechanistic switch, akin to urea formation in amine-functionalized sorbents, has not been previously reported in a hydroxide-based material and sheds new light on the interplay between bicarbonate and carbonate species during CO_2 capture. Our findings provide valuable insight for the design of next-generation materials containing oxygen-based nucleophiles for carbon capture applications.

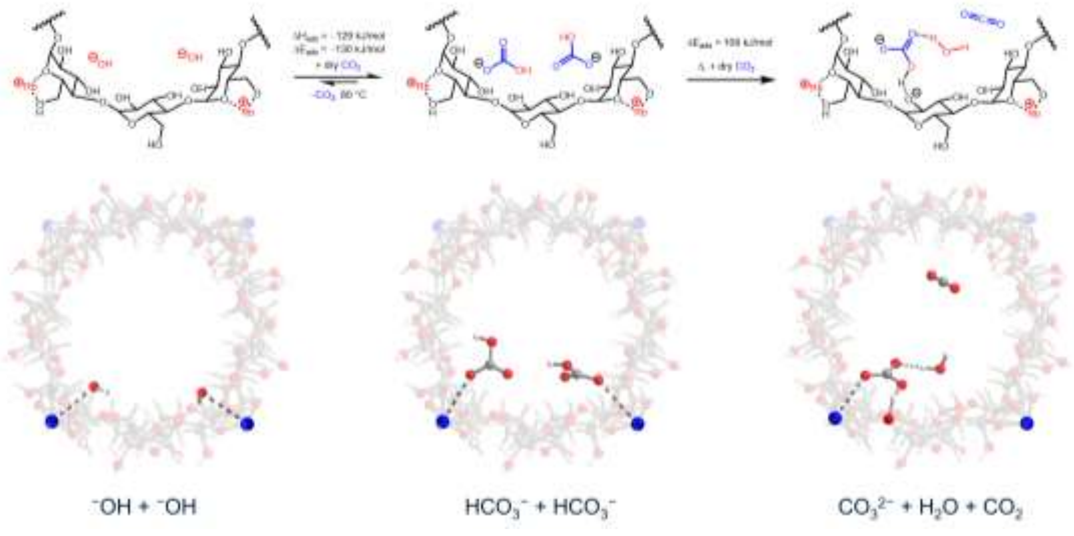

Figure 1. Proposed mechanistic switch from HCO_3^- at low temperatures to CO_3^{2-} at high temperatures under CO_2 flow in Rb_2CO_3 CD-MOF ST (top) and corresponding DFT-calculated structures of a single pore (bottom). Blue, red, grey, and white spheres correspond to rubidium, oxygen, carbon, and hydrogen atoms, respectively.

References

[1] J. S.A. Carneiro, G. Innocenti, G, J. H. Moon, Y. Guta, L. Proaño, C. Sievers, M. A. Sakwa-Novak, E.W. Ping, C. W. Jones. Angew Chem Int Ed **2023**, 62 (24).

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.

References

[1] Salma Mansi, Sarah Dummert, Geoffrey J. Topping, Mian Zahid Hussain, Carolin Rickert, Kilian M. A. Mueller, Tim Kratky, Angela Casini, Franz Schilling, Roland A. Fischer, Oliver Lieleg, and Petra Mela *Adv. Funct. Mater.* **2024**, 34, 2304907.

[2] Sarah V. Dummert, Sylvia Dörschmidt, Theresa Bloehs, Katia Rodewald, Mian Zahid Hussain, Julien Warnan, Roland A. Fischer, Angela Casini*, and Romy Ettlinger, *under review*.

[3] Sarah V. Dummert, Theresa Bloehs, Roland A. Fischer, Angela Casini, and Romy Ettlinger, *manuscript in preparation.*

FROM WEAK TO WOW: FLUORESCENCE MODULATION BY METAL CENTRES FOR SO_2 DETECTION IN THE MFM-300(M) FAMILY

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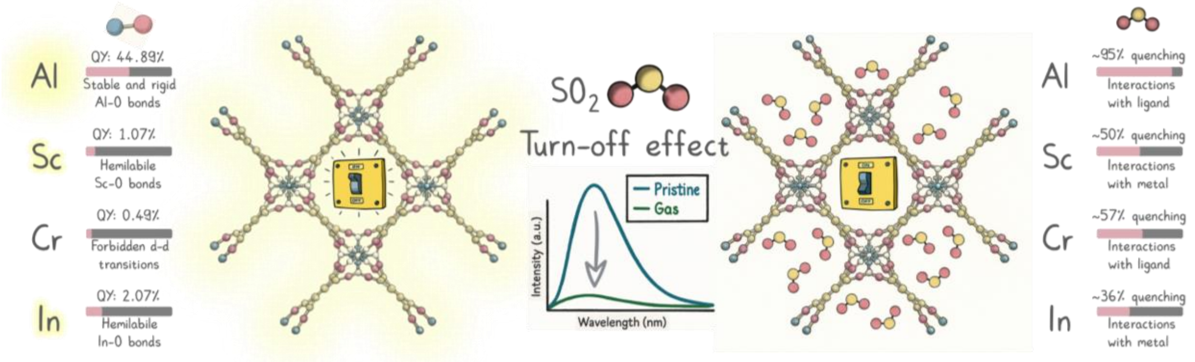
Keywords: *SO_2, fluorescence detection, fluorescence quenching, MFM-300(M)*

Sulphur dioxide (SO_2) is a colourless, pungent-smelling gas, classified as a critical pollutant for human health.[1] Detecting SO_2 quickly, selectively and reversibly remains a key challenge in sensor development, given the corrosive nature of the gas and its impact on the environment and human health even at low concentrations. Fluorescence detection emerges as an attractive strategy due to its high sensitivity, short response times and the possibility of integration into portable optical platforms. In this context, MOFs offer unique advantages due to their tunable porosity and their ability to modify the optical response through structural design.[2]

In the present work, the MFM-300(M) family (M = Al(III), Sc(III), Cr(III), In(III))[3] is explored as a model system to study how the metal centre can modulate the fluorescent properties and their response to SO_2, allowing correlations between structure, electronic properties and gas-material interaction to be established. Revealing that the origin of the fluorescence in these materials is ligand-centred. MFM-300(Al) exhibits the highest fluorescence quantum yield (44.89%) and the most pronounced quenching upon exposure to SO_2, which can be attributed to localised interactions between the gas and the μ_2-OH ligands, carboxyl groups and the aromatic rings of the ligand. In contrast, MFM-300(Sc) and MFM-300(In) show moderate quenching, associated with charge transfer processes facilitated by the presence of semi-open metal sites, while MFM-300(Cr) exhibits intrinsically weak emission due to spin-forbidden $d \rightarrow d$ transitions. The time-resolved photoluminescence spectra (TRPL) of MFM-300(Al) show a drastic reduction in the lifetimes (from 3.7 to 1.1 ns), indicating a dynamic quenching mechanism. Tauc analysis of HOMO–LUMO gaps suggests that quenching occurs without global bandgap redistribution, but a localised perturbation of the electronic environment. DFT, ELF and adsorption energies calculations reveal that the interaction with SO_2 occurs by physisorption, generating localised electronic distortions in the ligand (Al) or around the metal (Sc, In), thus modulating the deactivation pathways of the excited state. With a detection limit of 51 ppm in suspension and selectivity towards CO_2 and H_2O, MFM-300(Al) is positioned as a promising detector.



References

[1] J. R. Balmes, J. M. Fine and D. Sheppard, *Am. Rev. Respir. Dis.*, **1987**, 136, 1117–1121.

[2] Tingting Wu, Xiang-jing Gao, Fayuan Ge and He-gen Zheng, *CrystEngComm*, **2022**, 24, 7881–7901.

[3] S. Yang, J. Sun, A. J. Ramirez-Cuesta, S. K. Callear, W. I. F. David, D. P. Anderson, R. Newby, A. J. Blake, J. E. Parker, C. C. Tang and M. Schröder, *Nat. Chem.*, **2012**, 4, 887–894.

EXCISION OF ORGANIC MACROCYCLES FROM COVALENT ORGANIC FRAMEWORKS VIA CLIP-OFF CHEMISTRY

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Keywords: *Clip-off Chemistry, Covalent Organic Frameworks (COFs), Macrocycles, Bond Breaking*

Synthetic organic chemistry has consistently focused on the design and creation of new molecules to benefit society, with the development of innovative synthetic methodologies and reactions enabling us to rethink how molecules can be synthesized. Traditionally, the synthesis of small organic molecules has been approached through stepwise processes that involve reactions between simpler precursors, but such methods struggle to find optimal pathways when dealing with the synthesis of structural materials with elevated degrees of freedom, such as organic macrocycles, cages, catenanes or complex polymers.

Here, we propose a paradigm shift in the synthesis of functional organic molecules. We report an advance in the synthesis of new organic molecules based on the approach "Clip-off Chemistry",[1] whereby it is possible to selectively excise molecules from ordered, extended organic structures, namely covalent organic frameworks (COFs). COFs are crystalline materials that extend in two and three dimensions, and can be viewed as embodiments not only of the original building blocks used to assemble them but, more crucially to our strategy, as sources of macrocycles, cages, catenanes, or polymers that spontaneously form during their assembly.[2] A selective bond-breaking step in specific positions throughout the framework liberates these subunits, achieving excellent selectivity and yields.

In this communication, we show the utility of this "*solid-to-molecule*" approach towards the synthesis of functional organic macrocycles, circumventing traditional challenges in their synthesis, such as low selectivity, poor yields, side-products, or the need for complex purification steps.[3] Through Clip-off Chemistry, macrocycles, which require stringent control to avoid side products such as linear oligomers or smaller rings, can be synthesized selectively and in gram scale. Specifically, we report the synthesis of nine hexagonal polyamide- and polyimide-linked macrocycles, with peripheral aldehyde and carboxylic acid groups. Moreover, we demonstrate that our excision synthesis strategy can be coupled with isoreticular chemistry to rationally tune both the size and functionality of the synthesized macrocycles, enabling the synthesis of macrocycles with progressively larger ring sizes, including 114-, 138- and 162-atom rings, as well as the incorporation of functional groups such as fluorine.

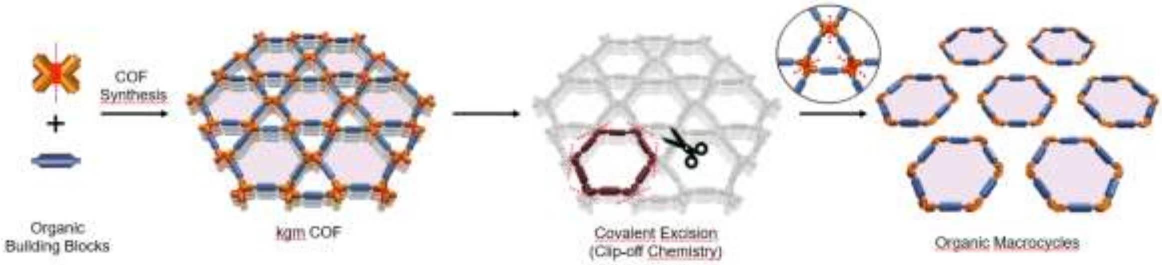

Figure 1. Schematic of the Clip-off Chemistry synthesis of organic macrocycles from excision of a COF.

References
1 Yang, Y.; Broto-Ribas, A.; Ortín-Rubio, B.; Imaz, I.; Gándara, F.; Carné-Sánchez, A.; Guillerm, V.; Jurado, S.; Busqué, F.; Juanhuix, J.; Maspoch, D. *Angew. Chem. Int. Ed.* **2022**, 61, e202111228.
2 Lohse, M. S.; Bein, T. *Adv. Funct. Mater.* **2018**, 28, 1705553.
3 Sánchez-Naya, R.; Cavalieri, J. P., Albalad, J.; Cortés-Martínez, A.; Wang, K.; Espinosa, C.; Parella, T.; Fiori, S.; Ribas, E.; Mugarza, A.; Ribas, X.; Faraudo, J.; Yaghi, O.M.; Imaz, I.; Maspoch, D. *Science* **2025**, *Accepted Manuscript 18/04/2025 (open access Chemrxiv version: 10.26434/chemrxiv-2024-5vb65.*

MODELLING ELUSIVE ORDER–DISORDER PHASE TRANSITIONS IN METAL–ORGANIC FRAMEWORKS

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Keywords: *order-disorder transitions, molecular simulation, machine-learning, total scattering*

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.

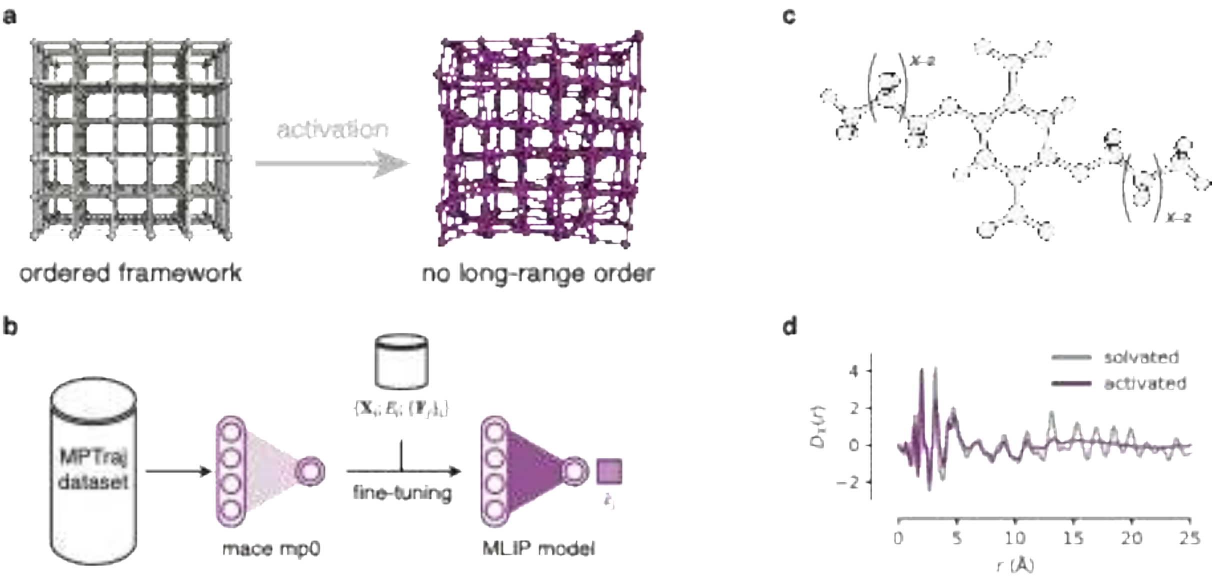

Figure 1. **Overview of this study. a**, Schematic illustration of an order–disorder transition in a MOF. **b**, MOF-5 derivatives investigated in this work with varying alkyl chain lengths on the BDC linker. **c**, Workflow illustrating the use of foundational MLIP models[5] to efficiently train accurate, 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.

References

[1] T. D. Bennett, A. K. Cheetham, *Acc. Chem. Res.* **2014**, 47, 1555–1562
[2] M. T. Wharmby, S. Henke, *et al.*, *Angew. Chem., Int. Ed.* **2015**, 54, 6447–6451
[3] K. W. Chapman, G. J. Halder, P. J. Chupas, *J. Am. Chem. Soc.* **2009**, 48, 17546–17547
[4] T. D. Bennett, FX Coudert, S. L. James, A. I. Cooper, *Nat. Mater.* **2021**, 20, 1179–1187
[5] I. Batatia, D. P. Kovacs, G. Simm *et al.*, *Adv. Neural Inf. Process. Syst.* **2022**, 35, 11423
[6] R. Pallach, J. Keupp, K. Terlinden *et al.*, *Nat. Commun.* **2021**, 12, 4097

DISCLOSING THE PHOTOCATALYTIC PROPERTIES OF Ce-UiO-66 BASED ON PERFLUOROCARBOXYLIC ACID LINKERS: EXPERIMENTAL AND THEORETICAL INSIGHTS

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Keywords: *Cerium MOFs, Redox chemistry, Photocatalysis*

Cerium-based metal-organic frameworks (MOFs) are attracting increasing interest due to the similar framework topologies with zirconium MOFs and the redox properties of Ce(IV). Thus, the structural stability of Zr-MOFs and the potential catalytic activity are combined in Ce(IV)-MOFs. In particular, the photocatalytic reactions have been studied in detail, which are initiated by a ligand-to-metal charge transfer (LMCT) from the linkers to the Ce(IV) centers. [1] Various ligands have been employed and recently also the use of perfluorinated linkers have been reported. The presence of the dipole in the C-F bond, coupled with the high electronegativity and low electrical polarizability of fluorine can produce a variety of properties, including specific adsorption sites for polar molecules.[2]

Herein, we report a facile room temperature synthesis and structural characterization of new Ce(IV)-MOFs with UiO-66 structure using two perfluorinated alkyl linkers, namely tetrafluorosuccinic (H_2TFS) and octafluoroadipic (H_2OFA) acids, wich resulted in the formation of $[Ce_6O_4(OH)_4(TFS)_6]\cdot 10H_2O$ and *CeOFA* $[Ce_6O_4(OH)_4(OFA)_6]$ $7H_2O$, denoted CeTFS and CeOFA, respectively. The frameworks contain hexanuclear $Ce_6O_4(OH)_4^{12+}$ clusters, which are linked by the dicarboxylate ions, thus exhibiting the same **fcu** topology as observed in MOF-801 and UiO-66. [3]

The crystallization of CeTFS and CeOFA was studied in situ using the SynRAC reaction cell at the European Synchrotron Radiation Facility (France). EXAFS and quasi-simultaneous X-ray diffraction were performed during the crystallization of the material. In particular, the conversion of the cerium ammonium nitrate in water to the final product was observed for both for both CeTFS and CeOFA. In the case of CeTFS, the kinetics of formation is fast with the complete conversion of CAN in water to the final product within 5 minutes. In contrast, the reaction rate for CeOFA was significantly slower, with the final product content reaching approximately 80% after 15 minutes.

The electronic structure of these MOFs was studied by DFT calculations to gain insight into the density of states structure and band gaps of 2.8 and 2.9 eV were determined, for CeTFS and CeOFA, respectively. The catalytic properties of the Ce-MOFs were demonstrated using the degradation of methyl orange (MO) dye as a model reaction. The photocatalytic tests were carried out both under UV light irradiation and without UV light irradiation (thermal conditions) under different pH conditions.[3]

References

[1] J. Gosch, D. Morelli Venturi, et al., *Inorg. Chem.,* **2023**, *62*, 5176.

[2] D. Morelli Venturi, F. Costantino, *RSC Adv.,* **2023**, *13*, 29215.

[3] D. Morelli Venturi, M.S. Notari, et al., *Chem. Eur. J.*, **2024**, 30, e202400433

ELECTRICAL CHARACTERIZATION OF A LARGE-AREA SINGLE-LAYER OF Cu_3BHT 2D CONJUGATED COORDINATION POLYMER

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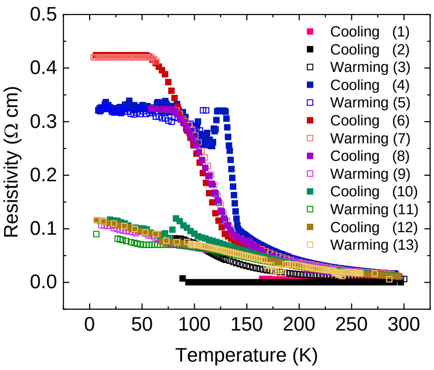
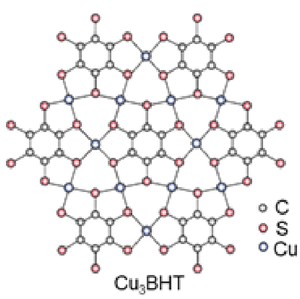
Keywords: 2D *c-MOF, electrical resistivity.*

Two-dimensional conjugated metal-organic frameworks (2D c-MOFs) are formed by the coordination of metal centers and planar organic conjugated building blocks. The modular nature of 2D c-MOFs make them highly advantageous for realizing materials with extensive tunability of their electrical and optical properties. In this contribution, I will discuss the synthesis and electrical characterization of a large-area, single-layer Cu_3BHT 2D MOF. The Cu_3BHT layer was synthesized at the water surface using the Langmuir-Blodgett technique and subsequently transferred onto SiO_2/Si substrates with pre-patterned electrical contacts. Electrical measurements displayed ohmic behavior across areas as large as ~1 cm². Cooling and heating cycles revealed hysteresis in the electrical response, indicating the formation of different current pathways as the samples underwent structural and chemical changes during the temperature sweeps. This hysteresis diminished after several cycles, with the conductivity stabilizing into an exponential temperature dependence, suggesting a tunnelling process governed the conduction mechanism in these polycrystalline single-layer Cu_3BHT samples[1].





Reference

[1] S. M. Estévez, et al., *Adv. Func. Mater*. **2009**, 2416717.

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.

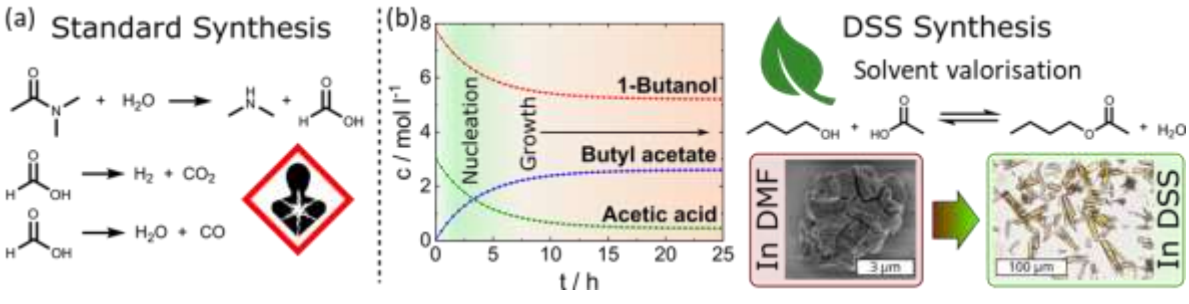

Figure 1. Comparison of standard DMF and DSS synthesis of [Ni(bdp)]n.

References
[1] (a) M. Shu et al., Cryst. Growth Des., 2006, 6, 1890–1896. (b) J. P. Zhang, et al., Angew. Chemie - Int. Ed., 2007, 46, 889–892. (c) H. J. Choi, et al., J. Am. Chem. Soc., 2008, 130, 7848–7850. (d) E. Buchner, Berichte der Dtsch. Chem. Gesellschaft, 1889, 22, 2165–2167.
[2] (a) M. Maliuta, et al., Dalt. Trans., 2023, 52, 2816–2824. (b) S. Ehrling, et al., Trends Chem., 2021, 3, 291–304. (c) L. Abylgazina, et al., Front. Chem., 2021, 9, 1–10. (d) I. Senkovska, et al., Adv. Mater. Adv. Mater. 2025, 2414724.
[3] (a) V. Colombo *et al*., *J. Am. Chem. Soc.*, 2012, 134, 12830–12843. (b) S. Galli *et al*., *Chem. Mater.*, 2010, 22, 1664–1672.

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.

References

[1] D.-X. Xue, A. J. Cairns, et al. *J. Am. Chem. Soc.* **2013**, 135 (20), 7660-7667.

[2] J. P. Vizuet, M. L. Mortensen, et al. *J. Am. Chem. Soc.* **2021**, 143 (43), 17995-18000.

[3] G. Skorupskii, M. Dinca, *J. Am. Chem. Soc.* **2020**, 142 (15), 6920-6924.

[4] S. E. Henkelis, D. J. Vogel, et al. ACS Appl. Mater. Interfaces 2021, 13 (47), 56337-56347.

HKUST-1 AND CPO-27 DECORATED WITH GRAPHENE OXIDE: SHAPED COMPOSITE BEADS WITH IMPROVED HYDROLYTIC STABILITY AND ENHANCED CO_2 ADSORPTION

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Keywords: *HKUST-1, CPO-27, Graphene oxide, Beads, Hydrolytic stability, CO_2 adsorption*

Metal-Organic Frameworks (MOFs) are highly porous and crystalline materials that have garnered interest in fields like catalysis, energy storage, and gas sorption since their emergence in the 2000s. However, their industrial application has been limited by processing challenges and low chemical and thermal stability [1]. To mitigate issues like porosity loss and crystallinity damage from physical shaping methods, researchers propose using chemical shaping through the integration of MOFs with biopolymers such as chitosan (CS) and alginate (Alg). This approach allows for the creation of various shaped composite materials while maintaining the properties of MOFs [2].

Typically, shaping MOFs through combination with a polymer occurs using either *in-situ* or *ex-situ* growth (direct mixing) strategies. However, the simplicity, uniform distribution of MOFs within the polymer matrix, and enhanced interactions between the polymer and MOFs often favor the *in-situ* method over the *ex-situ* approach. In our works, we examined the effects of chitosan and alginate biopolymers on the textural properties of HKUST-1, shaped into CS@HKUST-1 and Alg@HKUST-1 beads through an *in-situ* growth strategy under mild conditions. The results reveal that the chitosan matrix is more suitable for growing HKUST-1 crystals at room temperature, leading to composite beads with specific surface areas (S_{BET}) up to 923 $m^2.g^{-1}$. To address the weak water stability of HKUST-1, graphene oxide was blended with chitosan and the MOF precursors, resulting in ternary composite beads (Fig. 1.b) with high crystallinity and porosity (879 $m^2.g^{-1}$), and improved structural stability in water (up to 48 hours, compared to less than 24 hours for the pristine MOF) [3]. Furthermore, to assess the viability of this approach, we also developed CS@CPO-27-Co binary and ternary composites, resulting in robust beads with high crystallinity and specific surface areas exceeding 500 $m^2.g^{-1}$ [4]. The as prepared CS@HKUST-1 and CS@CPO-27-Co (Fig.1.a.b) were tested for the CO_2 capture, were they showed adsorption capacities of 2.60 and 3.10 $mmol.g^{-1}$, respectively at 298 K.

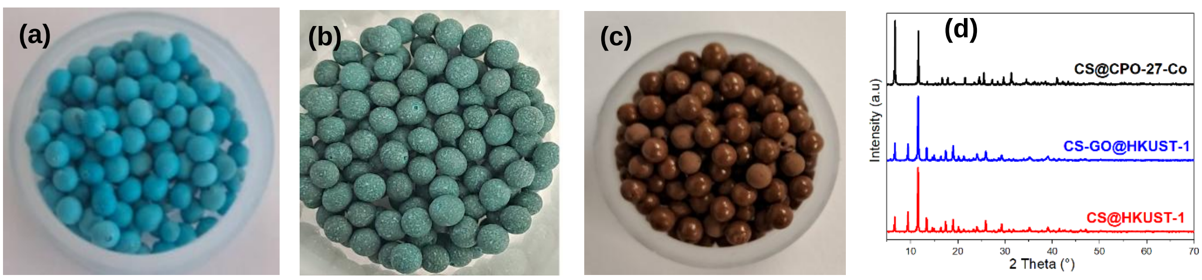

Fig. 1. The as-prepared CS@HKUST-1 (a), CS-Go@HKUST-1 (b), and CS@CPO-27-Co (c) beads, and their corresponding PXRD patterns (d).

References

[1] A. Wright, et al., Nat. Mater., pp. 1–10, Aug. **2024**, doi: 10.1038/s41563-024-01947-4.

[2] A. Balakrishnan et al.,Mater. Adv., vol. 4, no. 23, pp. 5920–5947, **2023**, doi: 10.1039/D3MA00413A.

[3] Y. Khadiri et al., Mater. Today Sustain., vol. 28, p. 100998, Dec. **2024**, doi: 10.1016/j.mtsust.2024.100998.

[4] Y. Khadiri et al., Chem. Commun., vol. 60, no. 60, pp. 7717–7720, Jul. **2024**, doi: 10.1039/D4CC02082K.

RESOURCE RECOVERY USING POROUS COMPOSITE MATERIALS

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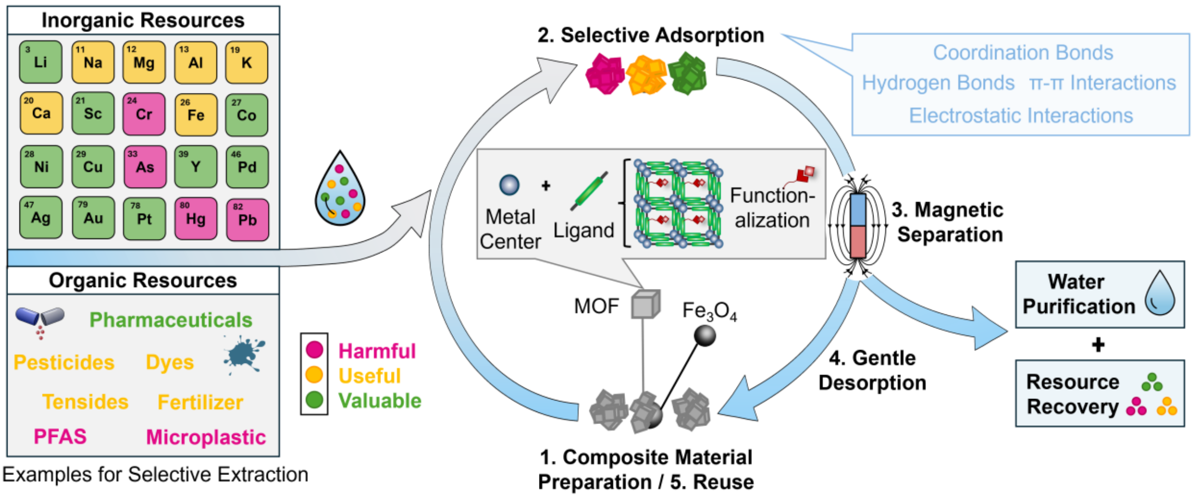
Keywords: *Metal-organic frameworks, Fe_3O_4 composites, resource recovery from water*

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.

References

[1] United Nations Department of Economic and Social Affairs: Sustainable Development Goal 6: https://sdgs.un.org/goals/goal6 (accessed: 17.04.2025)

[2] S. Dutta, R. Fernández de Luis, J. Goscianska, A. Demessence, R. L. Ettlinger, S. Wuttke, *Adv. Funct. Mater.* **2024**, 34, 2304790.

[3] M. Mon, R. Bruno, J. Ferrando-Soria, D. Armentano, E. Pardo, *J. Mater. Chem. A*, **2018**, 6, 4912-4947

[4] T. Bloehs, R. L. Ettlinger, *Manuscript in preparation.*

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.

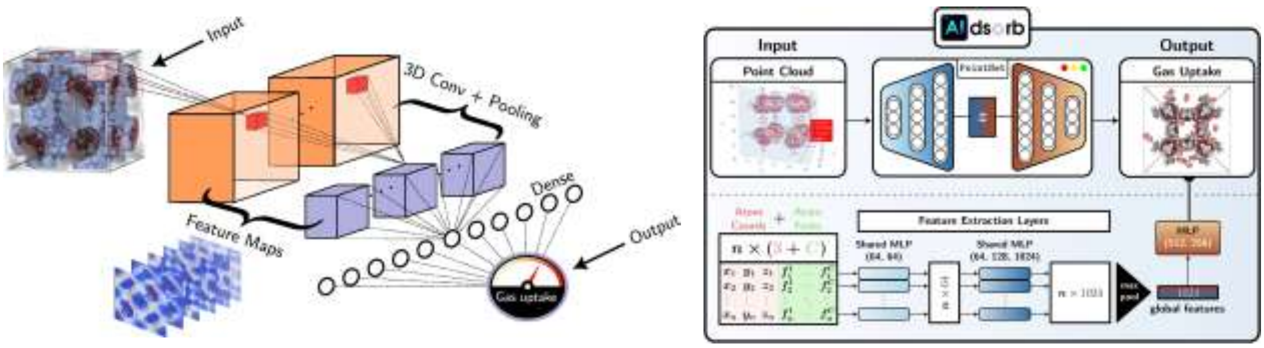

Figure 1: *Deep learning frameworks to predict gas adsorption properties of MOFs using voxelized PES (left) and point clouds (right).*

References

[1] A. P. Sarikas, K. Gkagkas, G. E. Froudakis. *Scientific Reports.* **2024**, 14, 2242.

[2] A. P. Sarikas, K. Gkagkas, G. E. Froudakis. *Scientific Reports.* **2024**, 14, 27360.

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.

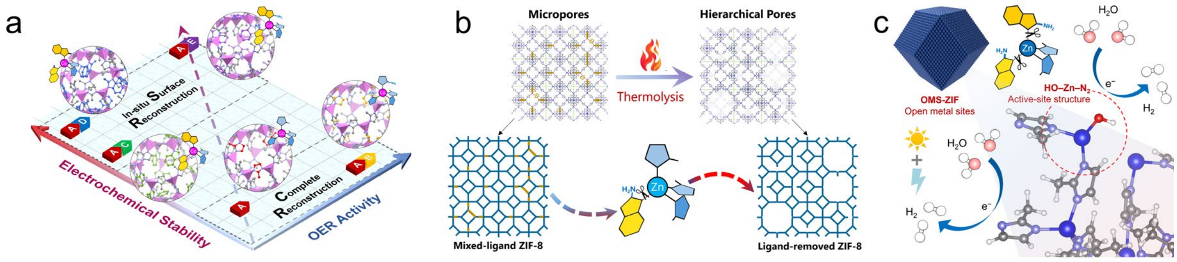

Figure: Schematic diagram of the mixed-ligand strategy (a) [1], selective ligand removal strategy (b) [2] and open metal sites (c) [3] for the ZIF frameworks.

References

[1] Z. Huang, Z. Wang, H. Rabl, S. Naghdi, Q. Zhou, S. Schwarz, D. H. Apaydin, Y. Yu, D. Eder. *Nat. Commun.* **2024**, 15, 9393.

[2] Z. Huang, J. Rath, Q. Zhou, A. Cherevan, S. Naghdi, D. Eder. *Small*, **2024**, 20, 2307981.

[3] Z. Huang, Z. Wang, Q. Zhou, H. Rabl, S. Naghdi, Z. Yang, D. Eder. *Angew. Chem. Int. Ed.* **2024**, **n/a**, e202419913.

POSTER PRESENTATIONS

CAN WE DEVELOP MOFS BASED ON METAL-PHOSPHIDES?

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Keywords: *metal-phosphides, metal-organic frameworks, electron diffraction*

Metal-phosphides (MPs) have attracted the interest of the research community the last sixty years.[1] Their structurally properties have been broadly studied and from the 1990s the field has exploded due to their catalytic properties *e.g.* electrocatalysis.[2] Since 2015, MPs have been incorporated on MOFs for the development of composite materials exhibiting significant catalytic properties.[3] Apart from the outstanding properties of the composites, those exhibit the following drawbacks: a) decreased porosity, b) harsh conditions for the development of them, and c) eventually leaching as the MPs are not chemically stabilized on the MOFs.

Considering the aforementioned drawbacks, we have managed to develop synthetic protocols where the MPs are part of the SBU of the MOFs. In the present work, for the first time are presented the examples of this class of combination, where the formation of P-bridges is taking place in aerobic conditions, leading to novel multi-component MOFs. The structures of the materials have been thoroughly determined by the use of X-ray and Electron Diffraction[4]. Stability and gas adsorption studies have been performed for the aforementioned materials and it has been proved to enhance stability.

References

[1] J. M. Léger *Physica B* **1993**,190 ,84-91.

[2] Y. Liu, A. J. McCue, D. Li, *ACS Catalysis* **2021**, 11, 9102-9127.

[3] S. Chen, H. Jang, J. Wang, Q. Qin, X. Liu, J. Cho, *J. Mater. Chem. A* **2020**, 8, 2099-2104.

[4] T. Yang, T. Willhammar, H. Xu, X. Zou, Zh. Huang, *Nature Protocols* **2022**, 17, 2389-2413.

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NANO-SPRINGE ENRICHED HIERARCHICAL POROUS MOP/COF HYBRID AEROGEL: EFFICIENT RECOVERY OF GOLD FROM ELECTRONIC WASTE

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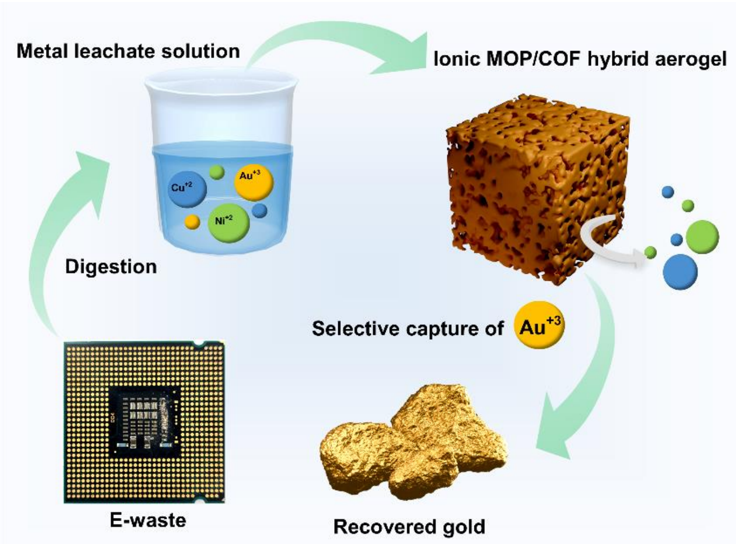
Keywords: *E-waste, Gold, MOP, Aerogel, COF*

Abstract: 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.



References:

[1] Majumder, D.; Fajal, S.; Shirolkar, M.; Torris, A.; Banyla, Y.; Biswas, K.; Rasaily, S. and Ghsoh, S.K. Nano-Springe Enriched Hierarchical Porous MOP/COF Hybrid Aerogel: Efficient Recovery of Gold from Electronic Waste. *Angew. Chem. Int. Ed.* **2024,** e202419830.

https://doi.org/10.1002/anie.202419830.

References

[1] S. R. Batten, S. M. Neville, D. R.Turner Coordination Polymers. Design, Analysis and Application RSC Publishing, Cambridge, **2009**.

[2] E. Quartapelle-Procopio, F Linares, et al. *Angew. Chem. Int Ed.* **2010**, 46, 1-5.

APPLICATIONS OF NH_2-MIL-125-BASED MATERIALS FOR PHOTOCATALYSIS

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Keywords: *MOFs, NH_2-MIL-125 (Ti), photocatalysis*

NH_2-MIL-125 (Ti) is a titanium-based metal–organic framework characterized by its robust, porous crystalline structure and enhanced photoactivity. Constructed from titanium-oxo clusters coordinated with 2-aminoterephthalic acid, the framework integrates amino functional groups that not only stabilize the structure but also narrow the band gap, extending light absorption into the visible spectrum. These structural and electronic features underpin its effectiveness in a range of applications, notably in photocatalysis for the degradation of organic pollutants, CO_2 reduction, and hydrogen generation. Additionally, the high surface area and small pore environment of NH_2-MIL-125 (Ti) make it a promising candidate for gas storage, separation, and sensing technologies.

In this research, two series of NH_2-MIL-125 (Ti) based materials were obtained. The first is in the form of TiO_2 nanotube thin films, which are decorated with NH_2-MIL-125 (Ti/Co). The second series contains NH_2-MIL-125 (Ti/M) derived materials, M=Co, Ni, Cu formed by thermal treatment of the material - obtain highly porous TiO_2 particles doped with Ni, Co and Co oxides. The obtained hybrids show high activity in photo- or photoelectrocatalitic production of hydrogen with simultaneous degradation of seawater contaminants (phenol or 5-fluorouracil), as well as in CO_2 photoreduction under UV-Vis irradiation. It is worth noting that, the materials were tested with water samples taken from the Baltic Sea, the Mediterranean Sea and the Atlantic Ocean reflecting natural environmental conditions. Characterization of prepared materials, including action spectra analysis, UV-Vis and PL spectroscopy, FTIR, XRD, XPS as well as BET surface analysis and CO_2 sorption analysis, allowed for the correlation of the properties of the obtained materials with their activity and the explanation of the photocatalytic mechanism.

This work was founded by the Polish National Science Centre within the scope of PRELUDIUM project No. 2023/49/N/ST5/01046 “New composites of modified TiO2 NTs with nano-MOFs for photoconversion CO_2 to solar fuels”

TOWARDS GREENER REFRIGERANTS: SIMULATING ADSORPTION REFRIGERATION IN RIGID METAL ORGANIC FRAMEWORKS

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Keywords: *Computational, Simulations, MOFs, Adsorption, Refrigerants*

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. We calculate a colossal isothermal entropy change of 417.20 ± 134 J K^{-1} kg^{-1} upon the adsorption of carbon dioxide, under 4 bars of pressure, which is highly competitive with current refrigerants. Based on their mechanical stability and barocaloric performance, we show that rigid MOFs are viable candidates for the next generation of greener refrigerants.

References

[1] D. C. Savitha *et al*., *Int. J. Sustain. Energy*, **2022**, 41, 235.
[2] S. Szczesniak *et al*., *Energies*, **2022**, 15, 5999.
[3] C. Cazorla, *Appl. Phys. Rev*., **2019**, 6, 041316.
[4] G. Falchetta *et al*., *Nat. Comms*., **2024**, 15, 7874.
[5] J. García-Ben *et al*., *Chem. Mater*, **2022**, 34, 3322.
[6] M. Alhamami *et al*., *Materials*, **2014**, 7, 3198.
[7] M. Gelpi *et al*., *Adv. Mater.*, **2023**, 36, 2310499.

STUDY OF MOFS (METAL-ORGANIC FRAMEWORKS) FOR H/D/T ISOTOPIC SEPARATION

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Keywords: *MOFs, hydrogen, isotopes, separation*

The tritium content of some waste from CEA's activities (CEA stands for Commissariat à l'Energie Atomique et aux énergies alternatives) makes it incompatible with the environment and must therefore be separated from the rest to decontaminate the light elements. To accomplish this separation, zeolites are currently used in CEA. Those materials are reported in the literature as the benchmark for this application, particularly some chabazites[1].

To find an alternative to zeolites with improved performance (i.e. selectivity and capacity), Metal-Organic Frameworks (MOFs) are considered as promising candidates. They are highly versatile in terms of applications, thanks to their diverse structures and their various physicochemical properties, which can be finely tuned and on purpose.

Among the various separation mechanisms, two are typical for hydrogen isotope separation ($H_2/D_2/T_2$). The first, known as 'Kinetic Quantum Sieving' (KQS)[2], is based on kinetic separation induced by confinement in small pores with diameters close to those of H2 and its isotopes. The second, 'Chemical Affinity Quantum Sieving' (CAQS)[3], enables isotopic separation thanks to different chemical affinities between the adsorbent and the adsorbate, particularly on strong adsorption sites such as Open Metal Sites (OMS). As part of this collaborative project between IMAP, CEA Valduc and ICB, we are relying on these two separation mechanisms to guide our choices to find high-performance MOFs combining both high selectivity and adsorption capacity.

In parallel, some preselected MOFs (covering various chemical and structural features) will undergo radiation tests to assess their stability under beta radiation from the tritium present in small quantities in the gas mixture to be treated. These tests will mimic a representative environment of real-life conditions, which is an essential criterion to select the most appropriate sorbent for this application.

Thus, this presentation will introduce the work developed within the frame of this project, the various aspects of hydrogen isotope separation, and provide an overview on benchmark sorbents for hydrogen isotopic separation, including some reported MOFs. Finally, to gain a better understanding of the improvements and comparative performance of our system, the results of the radiation resistance study, as well as the separation and sorption experiments carried out during this work, will be compared to the best-performing sorbents reported so far.

References

[1] I. Bezverkhyy, et al. *ACS Applied Materials & Interfaces*, **2022**, 14.47, 52738-52744.

[2] Q. Yan, J.Wang, L. Zhang, et al. *Nat. Commun*, **2023**, 14, 4189.

[3] I. Weinrauch, I. Savchenko, D. Denysenko et al. *Nat. Commun*., **2017**, 8, 14496.

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) are emerging as promising materials for gas storage, catalysis, and energy applications due to their low atomic weight and high structural tunability [1,2]. In this study, we explore the synthesis of Li-MOFs using alkynyl, aryloxide, and carboxylate-based ligands, each directing the formation of 3D framework architectures with distinct structural features (Figure 1). A series of synthetic approaches was employed to probe the impact of ligand type and reaction conditions on framework dimensionality, crystallinity, and stability. Lithium acetylide frameworks were synthesized under inert conditions using Schlenk techniques, while aryloxide-based MOFs were obtained via solvothermal reactions with lithium bis(trimethylsilyl)amide (LiHMDS). Additionally, ultramicroporous 3D structures were formed by reacting LiOH with quinoline-carboxylate ligands in mixed solvents. The resulting materials were characterized by powder X-ray diffraction (PXRD), single-crystal XRD (SXRD), FTIR, and NMR spectroscopy. While gas sorption experiments were not conducted for the alkynyl- and aryloxide-based MOFs, computational modeling suggests the lithium acetylide framework offers high gas storage potential. Meanwhile, CO_2 adsorption isotherms at 293 K indicate decent surface areas in carboxylate-based Li-MOFs, underscoring their relevance for gas capture applications. These results demonstrate how ligand functionality and coordination environments steer the construction of ultralight Li-MOFs, offering structural diversity and functional potential for future energy and environmental applications.

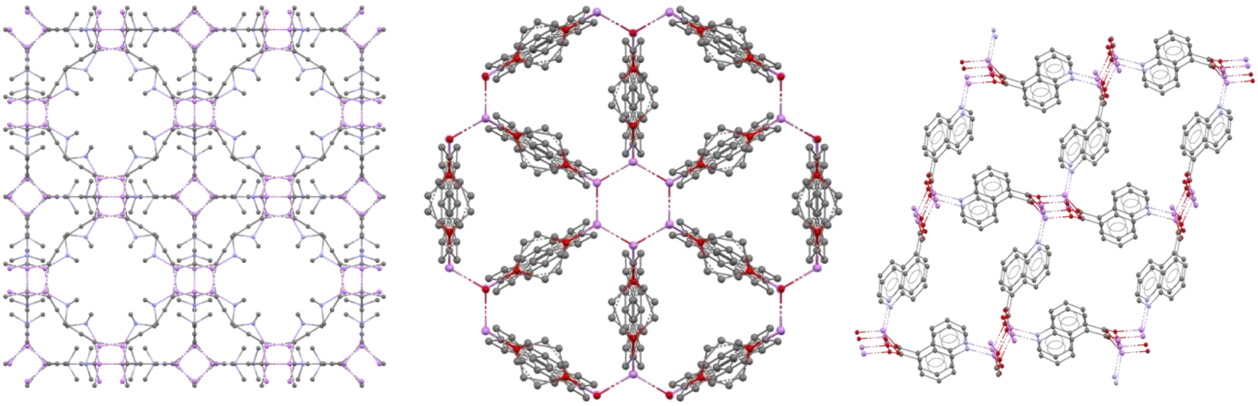

Fig. 1 3D Lithium MOFs using alkynyl, aryloxide and carboxylate - based linkers (left to right). Element colours: C = grey, Li = pink, O= red, N = purple

REFERENCES

[1] B. F. Abrahams, A. D. Dharma, M. J. Grannas, T. A. Hudson, H. E. Maynard-Casely, G. R. Oliver, R. Robson and K. F. White, Inorg Chem, 2014, 53, 4956–4969.

[2] D. Pugh, E. Ashworth, K. Robertson, L. C. Delmas, A. J. P. White, P. N. Horton, G. J. Tizzard, S. J. Coles, P. D. Lickiss and R. P. Davies, Cryst Growth Des, 2019, 19, 487–497.

AMINO ACID FUNCTIONALIZED MOF-808 FOR CO_2 CAPTURE: UNRAVELING THE HOST-GUEST INTERACTION VIA INS SPECTROSCOPY AND DFT CALCULATIONS

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Keywords: Solid *adsorbents, greenhouse gases, inelastic neutron scattering, decorated MOFs*

In recent years, the exploration of different materials and technologies for carbon dioxide (CO_2) capture has gained substantial attention in pursuit of sustainable and efficient methods to mitigate anthropogenic CO_2 emissions. The concentration of CO_2 in the atmosphere was 421 parts per million (ppm) until 2022[1], which is an alarming figure considering that this concentration was 280 ppm at the onset of the Industrial Revolution and the safe level is 350 ppm[2]. The combustion of fossil fuels, such as coal, oil, and natural gas, for energy production is a major source of anthropogenic CO_2 emissions. It is the primary cause of climate change and the greenhouse gas effect[3]. Currently, there are two routes to reduce CO_2 emissions. The first one is direct air capture (DAC) and sequestration[4], and the second one is the reduction of CO_2 emissions from stationary and mobile sources after combustion when the concentration of CO_2 is between 10 and 15%. An appropriate adsorbent with good kinetics, selectivity at trace concentrations, and uptake would make DAC a hands-on methodology to address this global issue[5]. MOFs are promissory solid adsorbents for DAC in terms of selectivity, production costs, and CO_2 uptake that, with a convenient assembly of the building blocks, it could reach adsorption capacities and selectivity features not typically found in traditional CO_2 solid porous adsorbents obtained as a result of unique affinity towards CO_2 molecule. MOF-808 is composed of zirconium metal nodes and trimesic acid as the organic linker. These components form its periodic structure with a characteristic pore of 14 Å. The aim of this work was to functionalize the pore of MOF-808 by employing a post-synthesis procedure with the amino acid Lysine (Lys^{+1}) to enhance carbon dioxide (CO_2) capture. It was observed a noticeable enhancement in adsorption for the MOF-808@Lys^{+1} compared to the bare one, particularly within the pressure range relevant for industrial applications. The adsorption mechanism between the CO_2 and the functionalized MOFs was unraveled through inelastic neutron scattering (INS) spectroscopy and DFT calculations. The results indicated that the adsorption mechanism is governed by chemisorption processes where the CO_2 forms carbamic acid with the lateral amine present in the lysine.

References

[1] National Oceanic and Atmospheric Administration. Carbon dioxide now more than 50% higher than pre-industrial levels.

[2] C. Pettinari and A. Tombesi, MRS Energy Sustain. **2020,** 7, E35.

[3] K.O. Yoro and M.O. Daramola, Advances in Carbon Capture, Woodhead Publishing, 3-28, **2020.**

[4] C. Beuttler, L. Charles, J. Wurzbacher, Front. Clim. **2019**, 1, 469555.

[5] O. Shekhah, Y. Belmabkhout, Z. Chen, V. Guillerm, A. Cairns, K. Adil, M. Ed-daoudi, Nat. Commun. **2014**, 5, 1-7.

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.

References

[1] M. Kalaj, S.M. Cohen. *ACS Cent. Sci*. **2020**, 6 (7), 1046-1057.

[2] B. Lerma-Berlanga, C.R. Ganivet, N. Almora-Barrios, R. Vismara, J.A.R. Navarro, S. Tatay, N.M. Padial, C. Martí-Gastaldo. *Angew. Chem. Int. Ed*. **2022**, 61 (41), e202208139.

[3] B. Lerma-Berlanga, N.M. Padial, M. Galbiati, I. Brotons-Alcázar, J. Albero, H. García, A. Forment-Aliaga, C.R. Ganivet, C. Martí-Gastaldo. *Adv. Funct. Mater*. **2023**, 33, 2302246.

[4] G. Gómez-Tenés, P. Gimeno-Fonquernie, A. Misturini, C. Chinchilla-Garzón, V. Carratalá, L. Cisneros, C. Martí-Gastaldo. *Chem. Commun*. **2024**, 60, 12977.

[5] G. Gómez-Tenés, N. Almora-Barrios, S. Tatay, N.M. Padial, C. Martí-Gastaldo. *To be submitted*.

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.

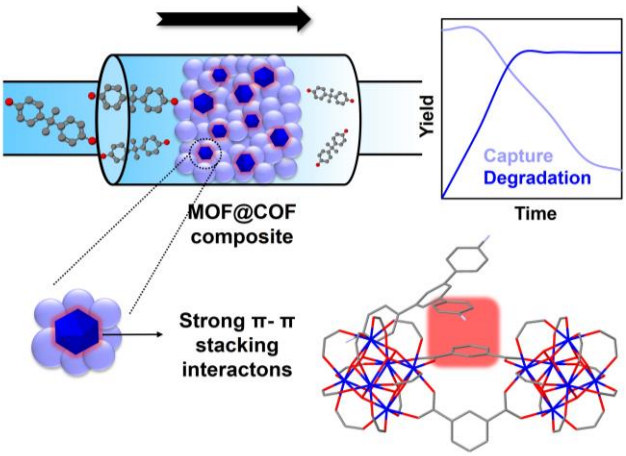

Figure 1. Depiction of the dual role of the FeMOF@COF composite and the nature of its interfacial interactions.

References

[1] F. Ahmadijokani, A. Ghaffarkhah, H. Molavi, S. Dutta, Y. Lu, S. Wuttke, M. Kamkar, O. J. Rojas, M. Arjmand, *Adv. Funct. Mater.*, **2023**, 34, 2305527.

[2] L. Garzón-Tovar, J. Pérez-Carvajal, A. Yazdi, J. Hernández-Muñoz, P. Tarazona, I. Imaz, F. Zamora and D. Maspoch, *Angew. Chem. Int. Ed.*, **2019**, 58, 9512–9516.

[3] I. del Castillo-Velilla, C. Castillo-Blas, T. D. Bennett, B. Cuadrado-Benavent, F. Zamora, A. E. Platero-Prats and C. Montoro, *Submitted*, **2025**.

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.

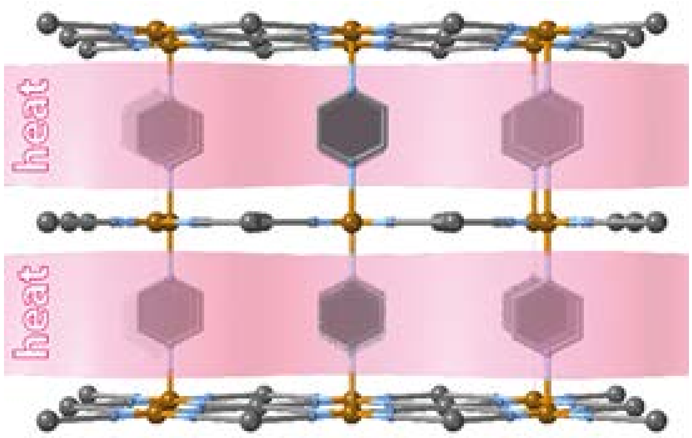

Figure 1. Thermal defect generation in [Fe(pz)x{Pt(CN) showcasing the thermal removal of the pillaring pz linkers, water molecules in the pores and pz disorder have been removed for clarity.

References

[1] S. Tatay et al. Nat. Commun. **2023**, 14, 6962.

[2] V. Niel, J.M. Martinez-Agudo, M.C. Muñoz, A.B. Gaspar, J.A. Real. Inorg. Chem. **2001**, 40, 3838-3839.

RAPID FORMATION OF VINYLENE-LINKED COVALENT ORGANIC FRAMEWORKS

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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.

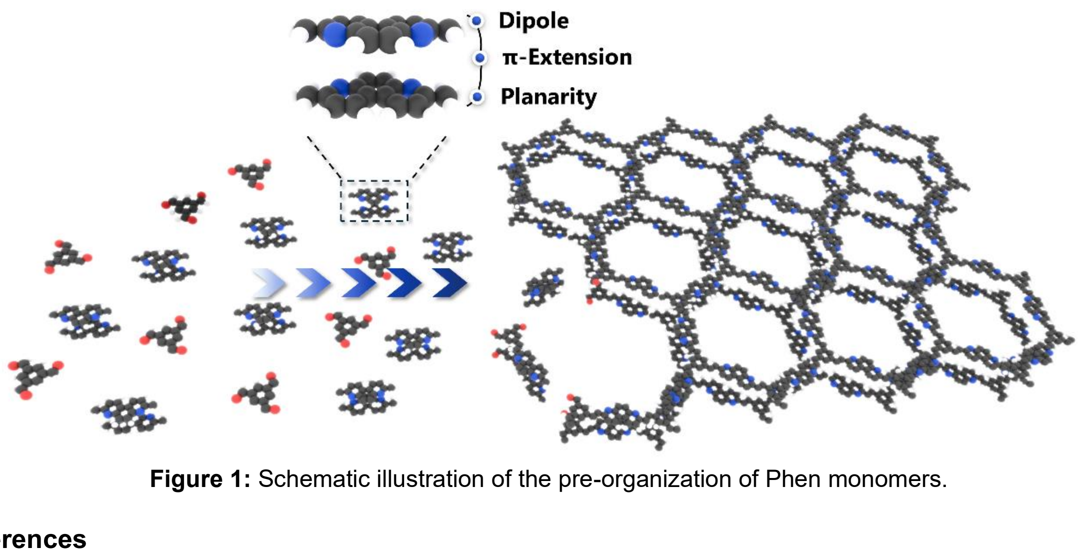

Figure 1: Schematic illustration of the pre-organization of Phen monomers.

References
[1] X. Li, Mater. *Chem. Front.* **2021**, *5*, 2931-2949.
[2] T. Prieto, C. Ponte, R. Guntermann, D. D. Medina, L. M. Salonen, *Chem. Eur. J.* **2024**, *30*, e202401344.
[3] C. Ponte, T. Prieto, A. L. Magano, A. Moya, K. Strutyński, L. Estévez, S. P. S. Fernandes, I. Misa, M. Sardo, L. Rodriguez-Lorenzo, O. Lebedev, Yu. V. Kolen'ko, M. Melle-Franco, R. Mas-Ballesté, L. M. Salonen, *Chem Mater.* **2025**, *37*, 1923-1934.

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.

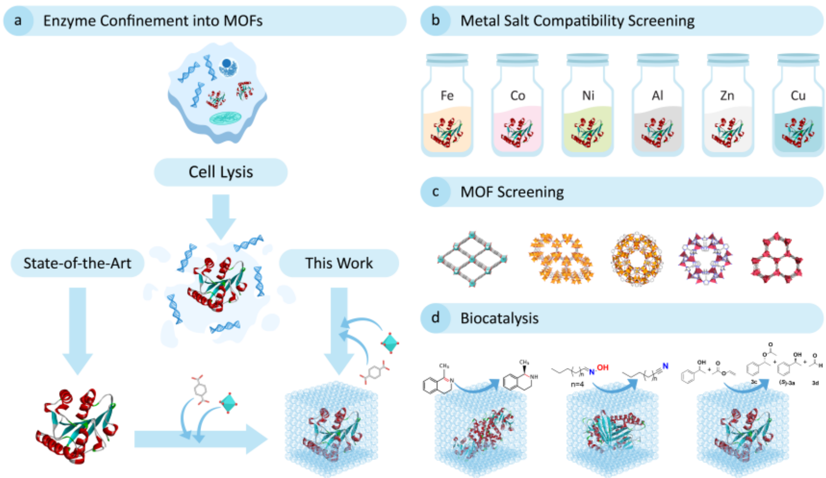

Figure 1. State-of-the-art and overview of the work.

[1] K. Y. Wang, J. Zhang, Y. C. Hsu, et al. *Chem. Soc. Rev.* **2023**, 123, 9, 5347–5420.

[2] J. Yang, O. Zaremba, J. Andreo, H. Gröger, S. Wuttke, *ACS Nano* **2025**. DOI: 10.1021/acsnano.4c18266.

PHOTO/THERMAL ACTIVE METAL-ORGANIC FRAMEWORKS: STRUCTURAL TRANSFORMATIONS AND REACTION KINETICS

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Keywords: *Metal-Organic Frameworks, Photo/Thermal, Structural Transformations, Reaction Kinetics*

Reversible switching processes are ubiquitous in nature and include examples of fascinating physicochemical phenomena involving various stimuli such as temperature, photons, protons, electrons, solvents, and pressure[1]. In this talk, I will present our recent research on the structural transformations and reaction kinetics on photo/thermal active metal-organic frameworks (MOFs)[2]. For the structural transformations, the reversible control of both topology and partial interpenetration in photo/thermal-active MOFs have been realized through solid-state [2+2] cycloaddition and ring-opening reactions (Fig. 1). And for the reaction kinetics research, a series of multivariate MOFs (MOFs) [3] were synthesized and characterized by laser scanning confocal microscopy (LSCM) on the corresponding MOF crystals, which showed distinct reaction behaviours coming from their different combinations of organic linkers. At last, I will present the applications in photo-induced mechanical motion of these MOFs.

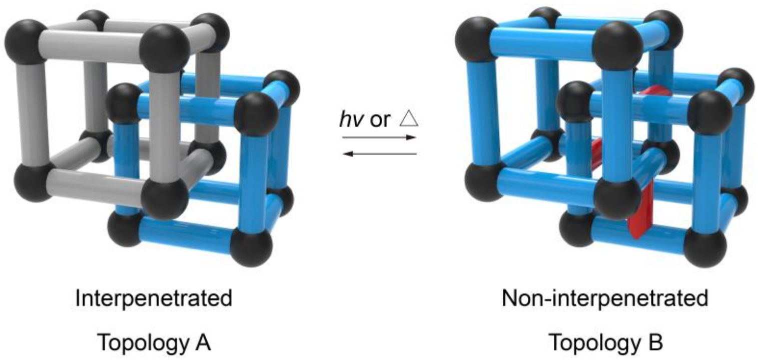

Figure 1. Structural transformations through a photo/thermal active metal-organic framework.

References

[1] A. McConnell, C. Wood, P. Neelakandan, J. Nitschke. Stimuli-responsive metal-ligand assemblies. *Chem. Rev.* **2015**, 115:7729-7793.

[2] M. Wang,Y. Deng, Y. Hong, J. Gu, Y. Cao, Q. Liu, P. Braunstein, J. Lang, In situ observation of a stepwise [2 + 2] photocycloaddition process using fluorescence spectroscopy, Nat. Commun. **2023**, 14, 7766.

[3] H. Deng, C. J. Doonan, H. Furukawa, R. B. Ferreira, J. Towne, C. B. Knobler, B. Wang, O. M. Yaghi, Multiple functional groups of varying ratios in metal-organic frameworks, *Science* **2010**, 327, 846-850.

LUMINESCENT METAL-ORGANIC FRAMEWORKS AS AN EFFECTIVE ALTERNATIVE FOR HEAVY METAL DETECTION IN AQUEOUS ENVIRONMENT

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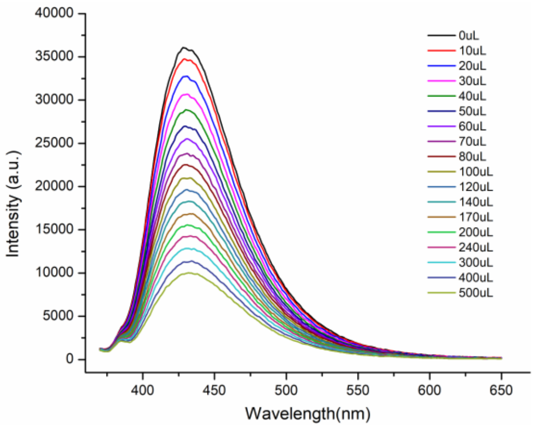
Keywords: *fluorescent MOF, heavy metal ions, detection, wastewater treatment*

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 $CuCl_2$ ($\lambda_{exc} = 340$ nm).

The research project was supported by the Greece 2.0, Recovery and Resilience Fund financed by the European Union -Next Generation EU and is part of the Action "Research - Create - Innovate" (ID 16971)

References

[1] C. Lai, Z. Wang, L. Qin, Y. Fu, B. Li, M. Zhang, S. Liu, L. Li, H. Yi, X. Liu et al., *Coordination Chemistry Reviews*, **2021**, 427, 213565.

[2] M. Babazadeh, R. Hosseinzadeh-Khanmiri, J. Abolhasani, E. Ghorbani-Kalhor, *RSC Advances*, **2015**, 5, 19884–19892.

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.

GAS SEPARATION AND VOLATILE ORGANIC COMPOUNDS DETECTION PROPERTIES OF A NOVEL CU-BASED FLEXIBLE METAL-ORGANIC FRAMEWORK

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Keywords: Metal-Organic Frameworks, flexibility, gas adsorption, CO_2 capture, VOCs detection

The large-scale burning of fossil fuels underway from the industrial revolution is resulting in CO_2 record levels. Aside from CO_2, the primary greenhouse gas, volatile organic compounds (VOCs) are acerbating the actual environmental problem. According to the VOC Solvents Emissions Directive 1999/13/EC from the European Union it is necessary to control the VOCs level, particularly indoor. In the continuous search of new materials able to interact with CO_2 and VOCs, Metal-Organic Frameworks (MOFs) have emerged as an outstanding class in CO_2 adsorption and VOC detection. Particularly, Cu-based MOFs with coordinatively unsaturated sites, are considered one of the most appealing class of MOFs due to their facility to interact with these gases[1,2]. In this work, a novel MOF named GR-MOF-26 based on copper and the combination of the 5-amino-2,4,6-triiodoisophthalic acid (H_2atiip) and the 4,4'-bipyridyl (bipy) ligands is reported.

This material exhibits a selectivity for CO_2 adsorption over CH_4 at both low and high pressure (Figure 1). The potential interactions of the CO_2 with the framework were evaluated by single crystal X-ray diffraction (SC-XRD) studies employing the isoelectronic CS_2 molecule. Further, SC-XRD also demonstrated that GR-MOF-26 is able to reversibly change its structure upon the exposition to different VOCs, that in combination with the color changes associated to the structure flexibility, open a new way for the development of VOCs detectors. In particular, a colorimetric device based on GR-MOF-26 able to detect the presence of MeOH, EtOH, ^{i}PrOH, AcN and THF is currently under developing in our group.

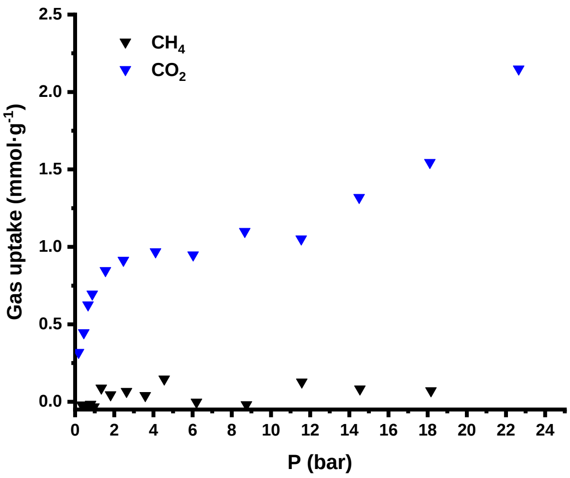

Figure 1: CH_4 and CO_2 sorption isotherms of GR-MOF-26.

Acknowledgements

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References

[1] H. Li, L. Li, R.-B. Lin, W. Zhou, Z. Zhang, S. Xiang, B. Chen, Porous Metal-Organic Frameworks for Gas Storage and Separation: Status and Challenges. *EnergyChem* **2019**, *1* (1), 100006.

[2] P. Hajivand, J. Carolus Jansen, E. Pardo, D. Armentano, T.F. Mastropietro, A. Azadmehr, Application of Metal-Organic Frameworks for Sensing of VOCs and Other Volatile Biomarkers. *Coord. Chem. Rev.* **2024**, *501*, 215558.

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), known for their crystalline porosity and customizable chemistry, hold significant potential in gas storage, molecular separation, and environmental cleanup applications [1]. This research utilizes a multi-scale computational approach to investigate the adsorption behavior of perfluorooctanoic acid (PFOA) on pristine MOF-808 and its iron-functionalized variant (Fe-MOF-808). Structural characterization will be used to pinpoint favorable adsorption sites, while atomistic-level simulations - specifically Density Functional Theory (DFT) and Molecular Dynamics (MD) - will provide detailed insights into the interactions between PFOA and the MOF surfaces. Thermodynamic parameters, including adsorption enthalpies and equilibrium constants, will be calculated using Grand Canonical Monte Carlo (GCMC) simulations. The study will critically evaluate the impact of iron functionalization on adsorption capacity and interaction dynamics, aiming to clarify its effect on enhancing pollutant affinity. This comparative investigation is expected to support the rational development of MOFs tailored for environmental remediation, particularly in the selective capture of emerging contaminants.

References

[1] E. Loukopoulos, S. Marugán-Benito, D. Raptis, E. Tylianakis, G. E. Froudakis, A. Mavrandonakis, A .E. Platero-Prats, *Advanced Functional Materials*, **2024**, 34, 2409932.

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.

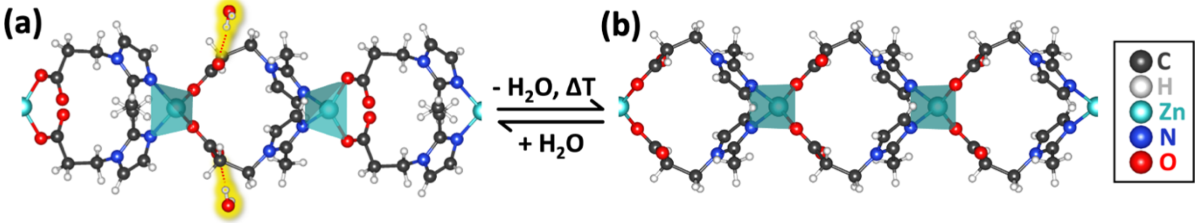

Figure 1. Single polymer strand of (**a**) hydrated GUT-2 where the H_2O molecules (highlighted in yellow) inside the pores can be removed in a reversible reaction by thermal treatment to produce (**b**) its activated form. Exposure to humid air restores the original, hydrated crystal structure.

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 ($\approx 2\times10^{-6}$ K^{-1}), reflecting the rigidity imposed by strong covalent bonding. In contrast, moderate expansion ($\approx 6\times10^{-6}$ K^{-1}), is observed along the hydrogen-bonded direction, while the highest thermal expansion coefficient ($\approx 9\times10^{-6}$ 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.

References

[1] S.R. Balestra, R. Bueno-Perez, S. Hamad, D. Dubbeldam, A.R. Ruiz-Salvador, S. Calero. *Chem. Mater.* **2016**, 28, 8296-8304.

[2] K. Kodolitsch, A. Torvisco, T. Kamencek, M. Mazaj, E. Zojer, C. Slugovc. *Eur. J. Inorg. Chem.* **2025**.

[3] N. Strasser, B. Schrode, A. Torvisco, S. John, B. Kunert, B. Bitschnau, F.P. Lindner, C. Slugovc, E. Zojer, R. Resel. *ArXiv:2504.05189*, **2025**.

ELUDICATING THE IMPACT OF THE SYNTHESIS METHODE ON THE STRUCTURAL FLEXIBILITY OF MIL-88 A (FE) DURING WATER HARVESTING

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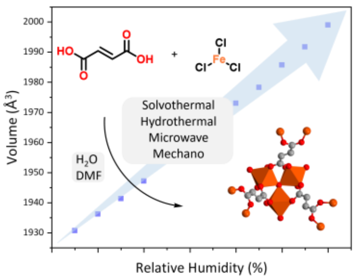
Keywords: *flexible MOF, swelling, water harvesting, adsorption, in situ PXRD*

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.

References

[1] Krause, S., Milić, J.V. *Commun. Chem.* 6, **2023**, 151.
[2] C. Mellot-Draznieks, C. Serre, S. Surble, N. Audebrand, G. Ferey, J. Am. Chem. Soc. **2005**, 127(46), 16273–16278.
[3] C. Serre, F. Millange, S. Surble, G. Ferey, *Angew. Chem Int Ed*. **2004**, 43(46), 6285–6289.
[4] T. Chalati, P. Horcajada, R. Gref, P. Couvreur and C. Serre, *J. Mater. Chem*., **2011**, 21, 2220.

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 structural collapse can cause gradual degradation of performance over time, it is clear that a fundamental understanding of structure-to-mechanical-property relationships are of crucial importance for virtually any practical application of MOFs.

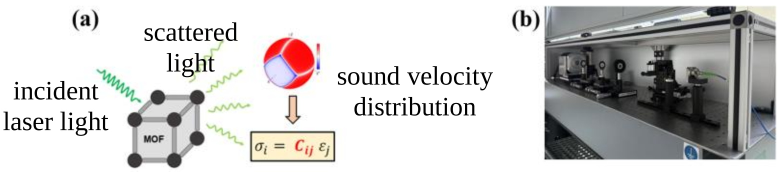

Figure 1. Measurement principle in Brillouin experiments to determine the full elastic tensors (a). Single-stage spectrometer in combination with birefringent Rayleigh filer for fast acquisition times of Brillouin spectra (b).

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 1a. 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]. Based on the excellent agreement between our measurements and simulations and the speedup of the later by the use of MLIPs by orders of magnitude, we currently extend the range of investigated materials to obtain a full understanding of the thermoelastic properties of MOFs. Eventually, we will extend our studies to elevated temperatures and pressures and to the study of dynamic and time-dependent processes in MOFs.

References

[1] I. E. Collings et al. J. Appl. Phys. 126, 181101, **2019**.

[2] I. Kabakova et al. Nat Rev Methods Primers 4, 8, **2024**

[3] JC. Tan et al. PRL 108, 095502, **2012**

[4] S. Wieser et al. npj Comput Mater 10, 18, **2024**

[5] F. P. Lindner et al. J. Phys. Chem. Lett. 16, 1213-1220, **2025**

DYNAMIC BREATHING BEHAVIOUR OF THE TITANIUM-BASED METAL-ORGANIC FRAMEWORK NTU-9 UPON ADSORPTION OF WATER AND ORGANIC SOLVENTS

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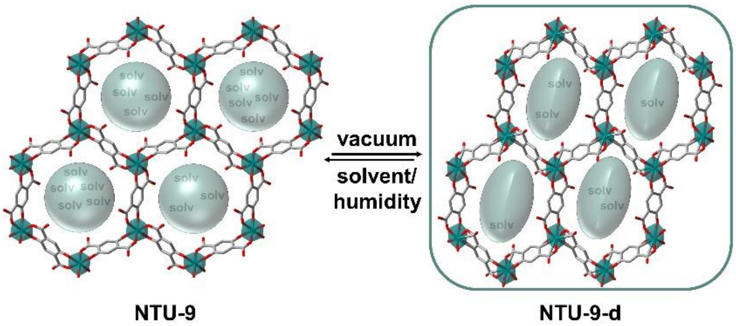
Keywords: *titanium MOF, flexible MOF, stimuli-responsive MOF, breathing behaviour, in situ PXRD*

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]

References
[1] K. Barthelet, J. Marrot, D. Riou and G. Férey, *Angew. Chem. Int. Ed.*, **2002**, 41, 281-284.
[2] J. Gao, J. Miao, P.-Z. Li, W. Y. Teng, L. Yang, Y. Zhao, Bin Liu and Q. Zhang, *Chem. Commun.*, **2014**, 50, 3786-3788.
[3] S. Yu, Y. Xiao, Z. Liu, J.-M. Lyu, Y.-L. Wang, Z.-Y. Hu, Y. Li, M. Sun, L.-H. Chen and B.-L. Su, *Chem. Commun.*, **2023**, 59, 1801-1804.
[4] J. E. Knapp, B. Ortín-Rubio, F. Heck, K. Gjorgjevikj A. Sleptsova, S. Krause, S. Bette, B. V. Lotsch, *submitted*.

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.

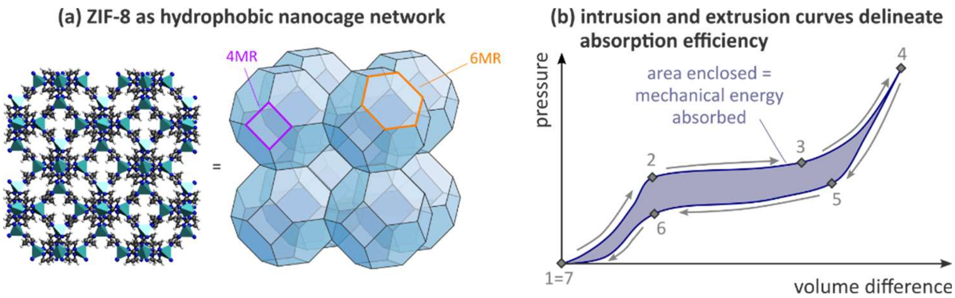

Fig. 1: *(a) ZIF-8 structure of Zn^{2+} nodes and methylimidazolate linkers; (b) Forced liquid intrusion/extrusion cycle and associated energy dissipation. Intrusion occurs between points 2&3 and extrusion between points 5&6.[1]*

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.

References

[1] Y. Sun, S. M. J. Rogge, A. Lamaire, S. Vandenbrande, J. Wieme, C. R. Siviour, V. Van Speybroeck, J.-C. Tan, Nat. Mater. 2021, 20 (7), 1015-1023.

[2] S. Vandenhaute, M. Cools-Ceuppens, S. DeKeyser, T. Verstraelen, V. Van Speybroeck, npj Comput. Mater. 2023, 9 (1), 1–8.

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

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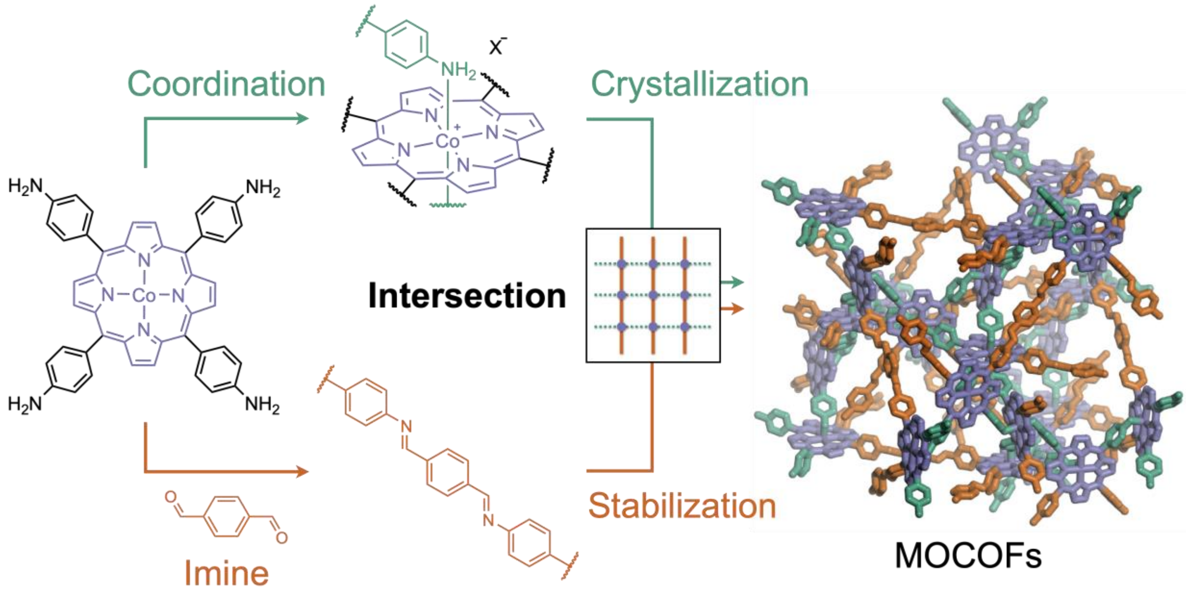
Keywords: *MOFs, COFs, crystallization, chemical stability, topology*

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.



Reference

[1] O. M. Yaghi, *J. Am. Chem. Soc.* **2016**, *138*, 15507–15509.

[2] K. Endo,* S. Canossa, F. Heck, D. M. Proserpio, M. S. Istek, F. Stemmler, J. van Slageren, S. Hartmann, A. Hartschuh, B. V. Lotsch,* *Nat. Synth.* **2025**, DOI: 10.1038/s44160-024-00719-x.

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.

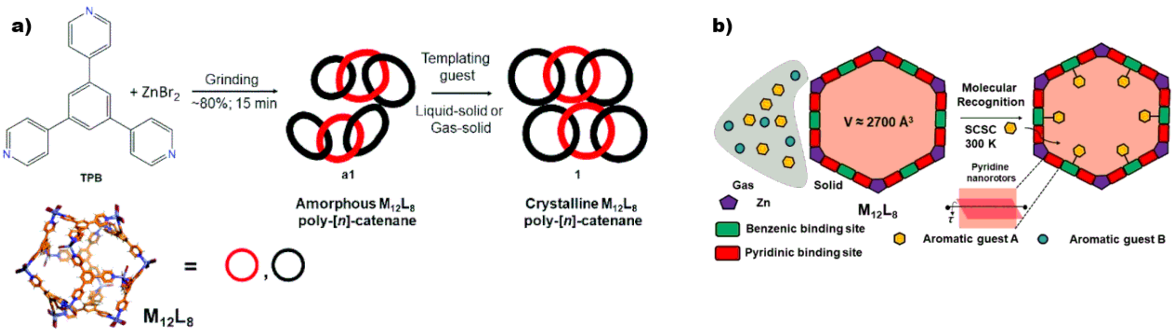

Figure 1: a) Synthesis and amorphous-to-crystalline transformation of $M_{12}L_8$ PC-MOC; b) Molecular recognition in **1** in a gas-solid reaction by means of a SC-SC process.

References

[1] A. Famulari, J. Martí-Rujas*, Angew. Chem. Int. Ed.* **2024**, *63*, e202407626.

[2] J. F. Stoddart, *Chem. Soc. Rev.* **2009**, *38*, 1802–1820.

[3] A. Famulari, J. Martí-Rujas, *Crystal Growth & Design* **2022**, *22* (7), 4494-4502.

[4] J. Martí-Rujas, S. Elli, A. Zanotti, A. Famulari, F. Castiglione, *Chem. Eur. J.* **2023**, *29*, e202302025.

[5] S. Elli, A. Famulari, J. Martí-Rujas, *ChemPlusChem* **2024**, *89*, e202400332.

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.

- [1] S. Wieser and E. Zojer. *npj Comput. Mater.* **2024**, Vol., 10-18
- [2] N. Strasser, S. Wieser, and E.Zojer. *Int. J. Mol. Sci.* **2024**, Vol., 25-3023
- [3] L. Legenstein, L. Reicht, S. Wieser, M. Simoncelli, E. Zojer. *npj Comput. Mater.* **2025**, Vol., 11-29
- [4] S. Wieser, T. Kamencek, J. P. Dürholt, R. Schmid, N. Bedoya-Martínez, E. Zojer. *Advanced Theory and Simulations.* **2021**, Vol., 4-2000211
- [5] S. Wieser, T. Kamencek, R. Schmid, N. Bedoya-Martínez, and E. Zojer. *Nanomaterials.* **2022**, Vol., 12-2142

LUMINESCENT METAL-ORGANIC FRAMEWORKS AS MULTI-FUNCTIONAL MATERIALS FOR WATER REMEDIATION: SETTING UP BEST PRACTISES

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Keywords: *persistent organic pollutants, sensing, luminescence, statistically robust protocol*

Over the past decades, the amount of persistent organic pollutants (POPs) of anthropic origin in wastewater-treatment-plant influents and effluents and in natural water bodies[1] has steadily increased. This occurrence demonstrates the inadequacy of conventional wastewater treatment technologies for an efficient removal of POPs, which can severely affect living organisms and the environment even at very low concentration.

Luminescent metal-organic frameworks (LMOFs) appear promising candidates for the detection and removal of water pollutants. Nonetheless, a robust and reliable investigation methodology has still to be implemented. To foster an overcoming of this limitation, we selected the polymorphic LMOFs NU-1000[2] and NU-901[3] as cases of study to propose a statistically validated sensing protocol to detect exemplary POPs belonging to the class of pharmaceuticals, namely: diclofenac sodium (DCF), ibuprofen sodium (IBU), paracetamol (PAR), fluoxetine (FXT) and acetylsalicylic acid (ACA). To monitor NU-1000 and NU-901 fluorescence emission as a function of POP chemical nature and concentration, replicates were executed for each experiment, and the effect of sensor dilution was explored. This systematic approach, underestimated in the relevant literature, enabled us to identify POP/LMOF systems with an apparently promising *but* unreproducible behaviour, or whose encouraging signal change, erroneously attributable to the POP alone, was the result of opposite contributions of POP and dilution. Application of statistical tests[4] to those POP/LMOF systems with a robust behaviour disclosed that, under ambient conditions and in the concentration range 0-9.5 μM, NU-1000 selectively detects DCF over IBU, PAR, FXT and ACA, while NU-901 shows reliable results only with DCF and PAR. A mathematical modelling of LMOFs fluorescence intensity variation as a function of the concentration of DCF (NU-1000) or DCF and PAR (NU-901) showed that quantification of these pollutants, besides detection, can be successfully attained, concomitantly allowing the disclosure of kinetical aspects (in the form of binding constant[5]), and an estimation of the limit of detection. Finally, expanding the scope with the adoption of a more complex aqueous matrix proves the importance of confirming the appealing performance observed in ideal conditions by testing a more realistic environment.

This apparently basic-science work does go beyond the state of the art in the title applicative context, demonstrating that the adoption of best practises, assessing the role of typically disregarded variables and relying on statistical and mathematical modelling, is an essential asset. The resulting systematic protocol is of undoubted relevance to sketch out future studies on porous materials intended for the same application.

Ministero dell'Università e della Ricerca

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References

[1] M. Patel, *Chem. Rev.* **2019**, 119, 3510-3673.

[2] J. E. Mondloch et al. *J. Am. Chem. Soc.* **2013**, 135, 10294-10297.

[3] S. J. Garibay et al. *Cryst. Eng. Comm.* **2018**, 20, 7066-7070.

[4] D. C. Howell, Statistical methods for Psychology (ch. 12), Wadsworth Cengage Learning, **2009**.

[5] J. Li et al. *Sensors and Actuators B* **2018**, 268, 446-455.

TUNING ELECTRICAL CONDUCTIVITY IN ONE-DIMENSIONAL 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 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. Moreover, by altering the halide ion from Cl^-, Br^- to I^-, the π-stacking geometry can be tuned. Employing numerous characterization techniques, we will demonstrate how the electrical conductivity correlates to the π-stacking geometry in the three **PMC-3-X**.

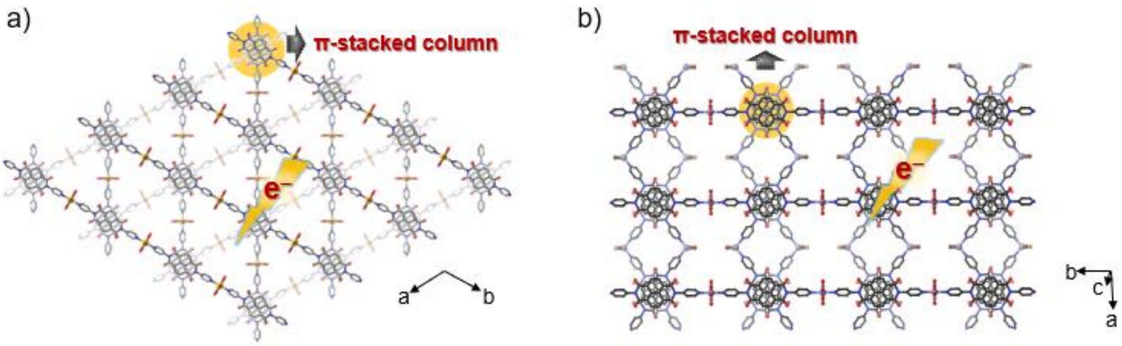

Fig. 1 Crystal structure of a) **PMC-1** and b) **PMC-3-Br** .

References

[1] L. S. Xie, G. Skorupskii, M. Dinca, *Chem. Rev*. **2020**, 120, 8536−8580.

[2] L. Qu, H. Iguchi, S. Takaishi, F. Habib, C. F. Leong, D. M. D’Alessandro, T. Yoshida, H. Abe, E. Nishibori, M. Yamashita, *J. Am. Chem. Soc.* **2019**, 141, 6802−6806.

ALKALI-RESISTANT MOFS WITH ION CONDUCTIVITY FOR ALKALINE ANION EXCHANGE MEMBRANE APPLICATIONS

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Keywords: *Alkali-resistant MOF, Ion conducting MOF, Alkaline anion exchange membranes, CoTBT*

Metal-organic frameworks (MOFs) represent an attractive choice for alkaline anion exchange membrane (AAEM) fuel cells [1] due to their innate electrical insulating characteristics, adaptable ion-conduction pathways, and suitability for processing [2]. In this study, we investigate the MOF CoTBT (TBT = 4,4'-thiobisbenzenethiol), a 2D anionic framework synthesised according to the previous report [3]. The structure consists of negatively charged layers and interlayer cations originating from the ionic liquid used during synthesis.

CoTBT demonstrates excellent chemical stability, maintaining its crystallinity upon exposure to 20 M alkaline solution for at least five days [3], in addition to superior electrochemical stability. This behaviour is likely related to the strong Co^{2+}-S coordination bonds and the possible stabilising role of hydrophobic interlayer species. Despite its relatively low BET surface area, CoTBT exhibits appreciable ion conductivity in both its pristine (as-synthesised) and alkali-treated forms.

Humidity-dependent conductivity measurements revealed a strong sensitivity to moisture, suggesting that water-mediated proton or hydroxide transport plays a significant role in conduction. This behaviour is consistent with the Grotthuss-type mechanism involving hydrogen bonding with surface-adsorbed water. Additionally, differences in the ion conductivity among the pristine CoTBT and its alkali-treated analogues (CoTBT-NaOH and CoTBT-KOH) were observed under identical conditions. I will discuss the origin in these variations, which may be attributed to the interplay between the type of interlayer cations, their hydration behaviour, and ion mobility after alkali treatment.

This study highlights the potential of CoTBT as a chemically robust and intrinsically ion-conductive MOF for AAEM applications. The findings underline the importance of tuning ionic species and hydration behaviour alongside MOF design to achieve high performance in applications, such as fuel cell membranes.

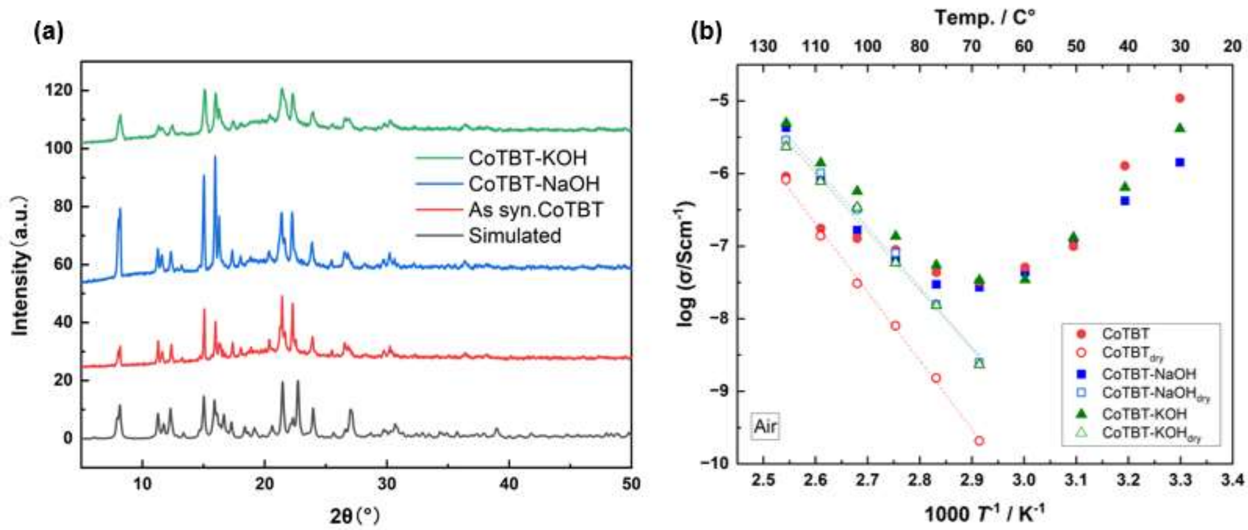

Fig. 1 *(a) PXRD patterns of CoTBT, CoTBT-NaOH, and CoTBT-KOH. Alkali-treated samples were soaked in 20M solutions for 5 days.*

(b) Ionic conductivity of the samples under dry and humid conditions (pH_2O = 0.025 bar) as a function of temperature.

References:

[1] M.-M. Titirici and P. Á. Szilágyi. *Mater. Adv.* **2022**, 3(24), 8815-8829.

[2] S. Hérou, P. Kasongo-Ntumba, A. Prakash Periasamy, J. King, M. McVea, S. Doszczeczko, A. Bushby, A. B. Jorge Sobrido, M.-M. Titirici, and P. Á. Szilágyi, *Sci. Rep*. **2024**, 14, #14529.

[3] Q. Hou, L.-J. Chen, J. He. *Chem. Commun*. **2023**, 59(46), 7072-7075.

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.

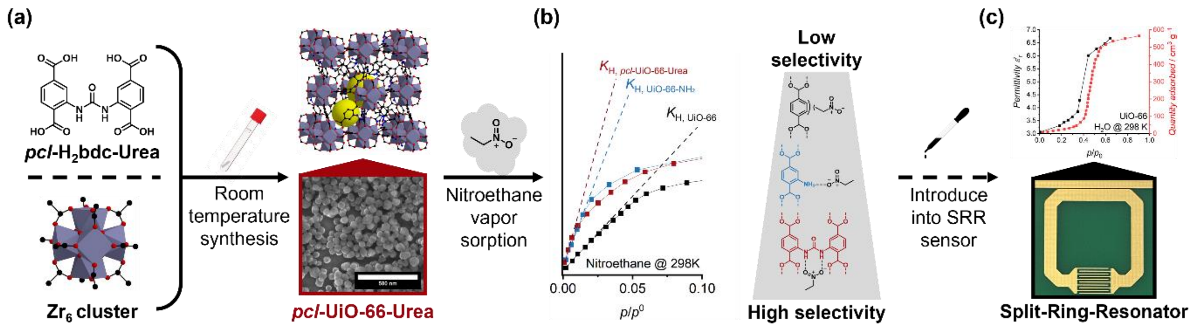

Fig. 1: Synthesis of *pcl*-UiO-66-Urea MOF through a room temperature approach **(a)**, determination of nitro compound selectivity through nitroethane vapor sorption and Henry constant K_H evaluation **(b)** and planned introduction into SRR sensor with exemplary measurement reproducing a water vapor sorption isotherm using UiO-66 **(c)**.

References

[1] S. Dai, C. Simms, I. Dovgaliuk, G. Patriarche, A. Tissot, T. N. Parac-Vogt, C. Serre, *Chem. Mater.* **2021**, *33*, 7057.

[2] T. Reinecke, J.-G. Walter, T. Kobelt, A. Ahrens, T. Scheper, S. Zimmermann, *J. Sens. Sens. Syst.* **2018**, *7*, 101.

TAILORING LOW-CERIUM BIMETALLIC MOFS TOWARDS A SUSTAINABLE OXYGEN EVOLUTION REACTION

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Keywords: *MOF-808, CPO-27, water splitting, OER, cerium-doped materials*

As of 2025, approximately 90% of hydrogen produced is "grey", deriving from fossil fuels through steam reforming and coal gasification processes,[1] contributing significantly to CO_2 emissions.

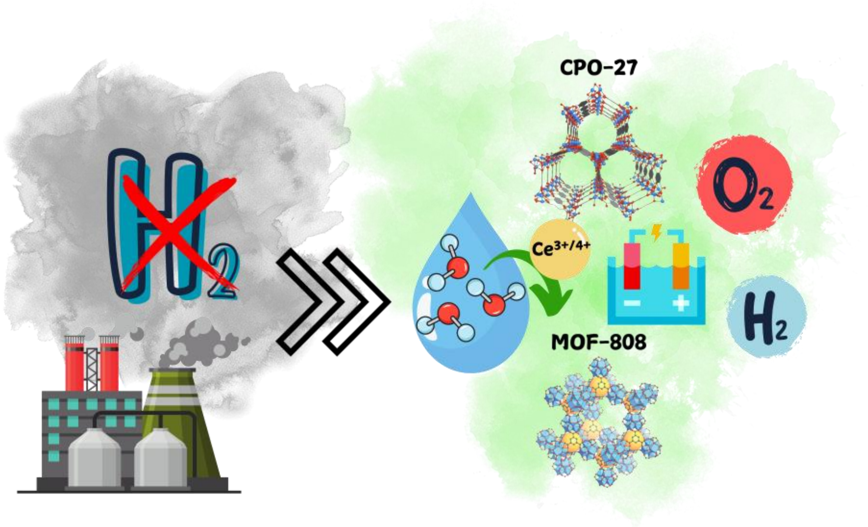
Electrochemical water oxidation represents a viable alternative; however, challenges such as cost, durability, and stability of the overall process and catalysts, require further optimization.

Metal Organic Frameworks (MOFs) have recently attracted significant attention for their potential in water-splitting applications, particularly as catalysts for the oxygen evolution reaction (OER), demonstrating competitive performances compared to other materials. Nonetheless, OER is often conducted under highly alkaline conditions, in which many MOFs are prone to rapid degradation, leading to diminished activity and limited operational lifespan.[2]

In this study, bimetallic MOF-808 and CPO-27 doped with Ce(IV) and Ce(III) respectively, have been prepared via a green, water-based synthesis under mild conditions, and characterized by XRD, ICP-MS, SEM-EDS, FT-IR, TGA and porosimetry. These analyses suggested comprehensive insights into their crystallinity, microporous nature, crystal morphology and cerium content.

X-ray absorption spectroscopy (XAS) experiments at the European Synchrotron Radiation Facility (ESRF) provided valuable information regarding metallic nodes coordination sphere and MOFs stability in basic solutions, simulating OER operating conditions.

Cyclic voltammetry and polarization curve analyses, in addition, indicate promising electrocatalytic activity and low overpotentials. Future investigations will focus on quantifying the electrochemically active surface area (ECSA) and constructing Tafel plots with the aim of elucidating the mechanisms underlying the observed performance and guiding the development of efficient MOF-based catalysts for OER.



References

[1] R. Roy, G. Antonini, et al. *Int. J. Hydrogen Energy* **2025**, 116, 200-210

[2] C, Wang, Y. Feng, et al. *ACS Cayalysis* **2021**, 11, 6750-7612

ESTABLISHING MATERIAL-TRANSFERABLE DESIGN RULES FOR DEFECTIVE METAL-ORGANIC FRAMEWORKS AND METAL HALIDE PEROVSKITES THROUGH STRAIN ENGINEERING

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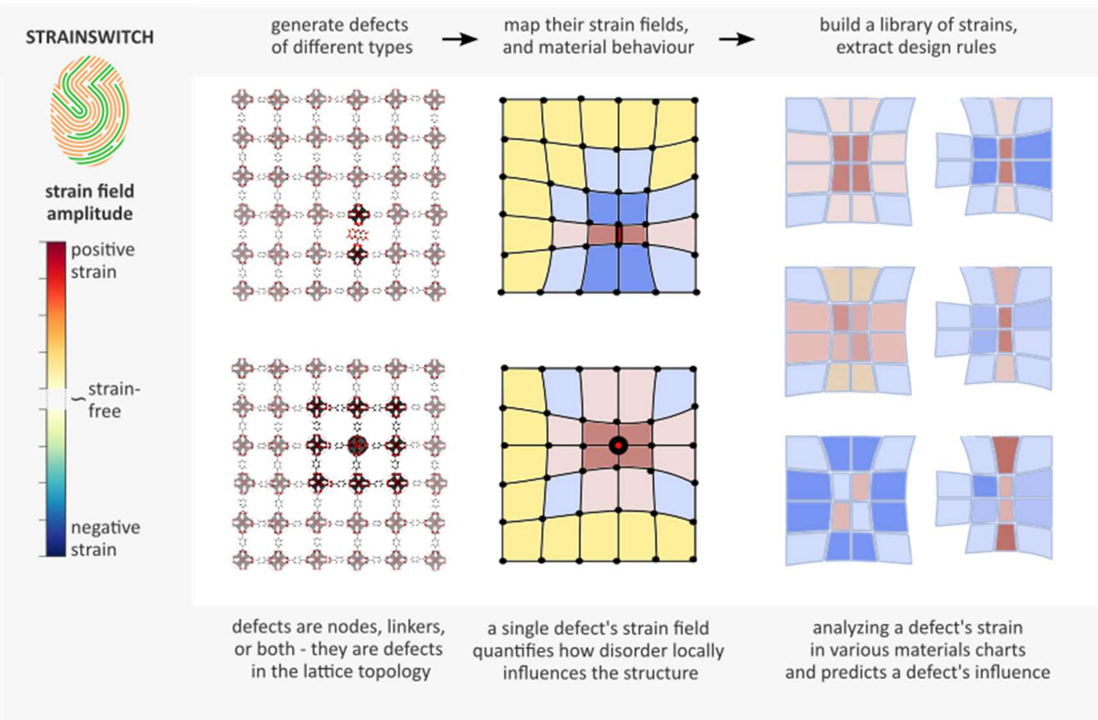
Keywords: *Strain engineering, disorder, materials chemistry, phase stability, design rules*

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].

[1] S.M.J. Rogge, S. Borgmans, and V. Van Speybroeck, *Matter* **2023**, 6, 1435-1462.
[2] S. Vandenhaute, *et al.*, *npj Comput Mater.* **2023**, 9, 19.
[3] N. Clovin, S.M.J. Rogge, *in preparation,* **2025**

TAILORING ACTINIDE PRECIPITATION IN COMPLEX ORGANIC MEDIA

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Keywords: *Precipitation, Actinide, Coordination Polymers*

The reprocessing steps of uranium oxide (UOx) in the French nuclear fuel cycle consist in two consecutive processes, PUREX (Plutonium Uranium Reduction Extraction) and MIMAS (Micronized MASter blend). While these processes come up with good purity and yields, they also present several drawbacks[1], e.g. the high number of steps, the management of primary and secondary effluents, the risk of plutonium proliferation or even the use of toxic compounds such as hydrazine. In this regard, several reprocessing alternatives are being considered[1, 2]. The chemical co-precipitation of U, Pu or their analogues has been widely investigated[3, 4]. However, very few studies report the co-precipitation directly in the organic phase. This study focuses on the development of a selective actinide precipitation (U and Th) from a loaded organic phase (Extractant = TBP or mono-amide). This work is therefore devoted to the synthesis of various actinide-MOFs and the subsequent annealing step in order to form suitable actinide oxide precursors (Figure 1).

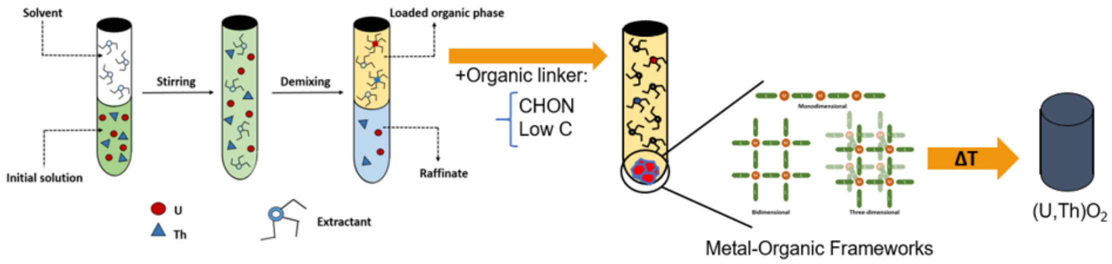

Figure 1: Schematic diagram of experimental method

The precipitation time and the amount of organic linker are key parameters in the precipitation of actinides, enabling control over U and Th yields. The materials obtained exhibit a range of morphologies. The associated diffraction patterns are similar and do not display any structures that have been recorded in the literature. (Figure 2)

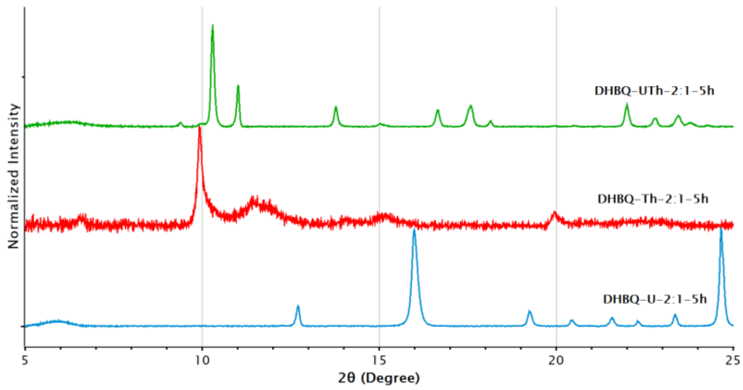

Figure 2: X-Ray diffraction patterns of U, Th and UTh powders precipitated with a 2:1 molar ratio of organic linker and for 5 hours

References

[1] *Status and Trends in Spent Fuel Reprocessing*; TECDOC Series; INTERNATIONAL ATOMIC ENERGY AGENCY: Vienna, 1999.

[2] Colledge, H. *et al.* A Review of Alternative Finishing Options for Uranium/Plutonium and Minor Actinide Nitrate Products from Thermal and Fast Reactor Fuels Reprocessing. *Progress in Nuclear Energy*, **2023**, *165*, 104903.

[3] Collins, E. D. *et al. Evaluation of Co-Precipitation Processes for the Synthesis of Mixed-Oxide Fuel Feedstock Materials*; ORNL/TM-2011/164, 1024695; 2011; p ORNL/TM-2011/164, 1024695.

[4] Hibert, N. *et al.* Coprecipitation of Actinide Peroxide Salts in the U–Th and U–Pu Systems and Their Thermal Decomposition. *Dalton Trans.*, **2022**, *51* (34), 12928–12942.

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.

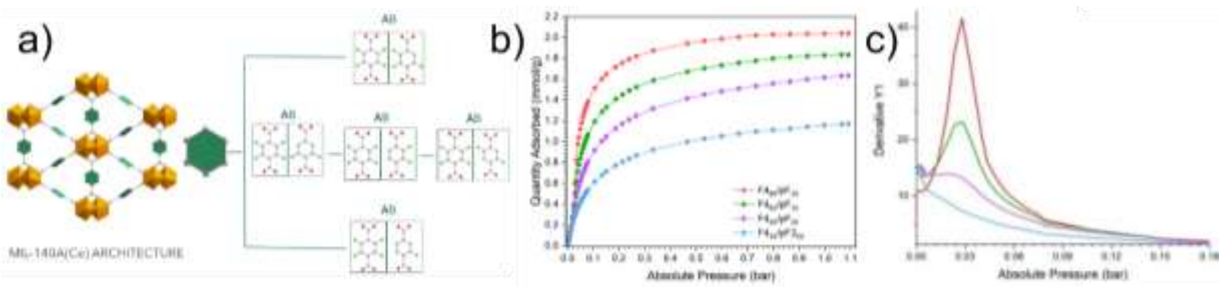

Figure 1. Mixed-linker F4:F*x*_MIL-140A(Ce) a); CO_2 adsorption isotherms of F4:*p*F2_MIL-140A(Ce) at different F4/*p*F2-BDC ratios b); first derivative of CO_2 adsorption isotherms c).

References
[1] S. J. Lee; S. G. Telfer *Angew Chem Int Ed* **2023**, *62*.
[2] M. Cavallo, *et al. J. Mater. Chem. A* **2023**, *11*.
[3] F. Nerli, *et al.* https://doi.org/10.26434/chemrxiv-2024-00bk3-v2.

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.

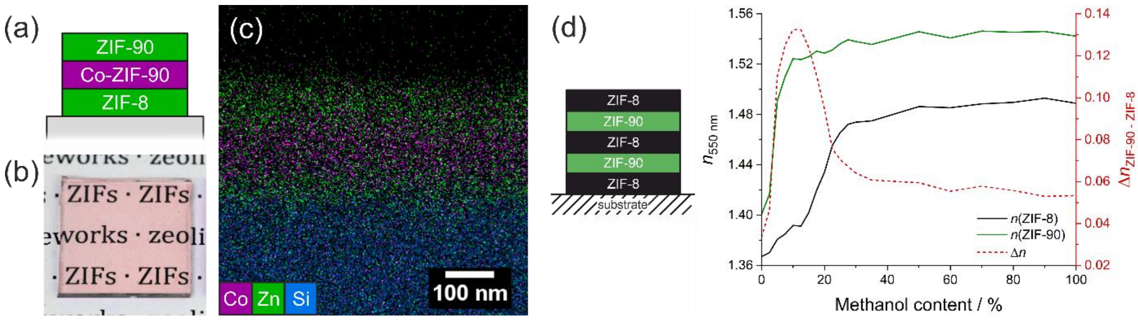

Fig. 1: (a) scheme of the mixed ZIF stack, (b) photograph of the stack fabricated on glass, (c) EDX mapping of a cross-section. (d) Scheme of the alternating ZIF-8/ZIF-90 layers and the resulting refractive index switch with differing methanol vapor content.

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.

References

[1] N. C. Keppler, J. Fricke, A. Schaate, A. Hannebauer, K. D. J. Hindricks, S. Zailskas, P. Behrens, *Cryst. Growth Des.* **2022**, 22, 7008.
[2] N. C. Keppler, L. Steinbach, J. Fricke, A. Hannebauer, E. Rohloff, A. Schaate, P. Behrens, "Adsorption-induced optical modulation in ZIF thin film stacks with distinct order for photonic crystal applications", *revised manuscript submitted to ACS Applied Materials & Interfaces,* April **2025**.
[3] N. C. Keppler, K. D. J. Hindricks, P. Behrens, *RSC Adv.* **2022**, 12, 5807.
[4] L. Zheng, N. Keppler, H. Zhang, P. Behrens, B. Roth, *Adv. Mater. Technol.* **2022**, 7, 2200395.

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.

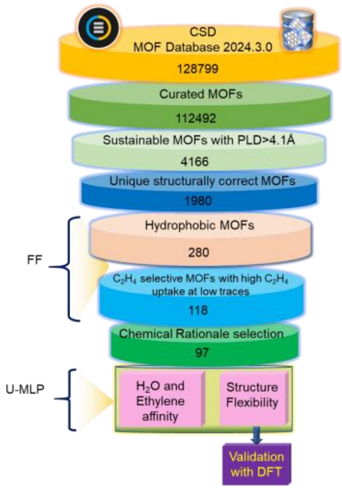

Figure 1: Schematic workflow of an FF/U-MLP/DFT strategy applied to find the most promising MOF candidates for the selective capture of ethylene over water

References

[1] S. Takamoto, C. Shinagawa, D. Motoki, K. Nakago, W. Li, I. Kurata, T. Watanabe, Y. Yayama, H. Iriguchi, Y. Asano, T. Onodera, T. Ishii, T. Kudo, H. Ono, R. Sawada, R. Ishitani, M. Ong, T. Yamaguchi, T. Kataoka, A. Hayashi, N. Charoenphakdee, T. Ibuka, *Nat. Commun*. **2022**, 13, 2991.

[2] Matlantis (https://matlantis.com/), software as a service style material discovery tool.

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.

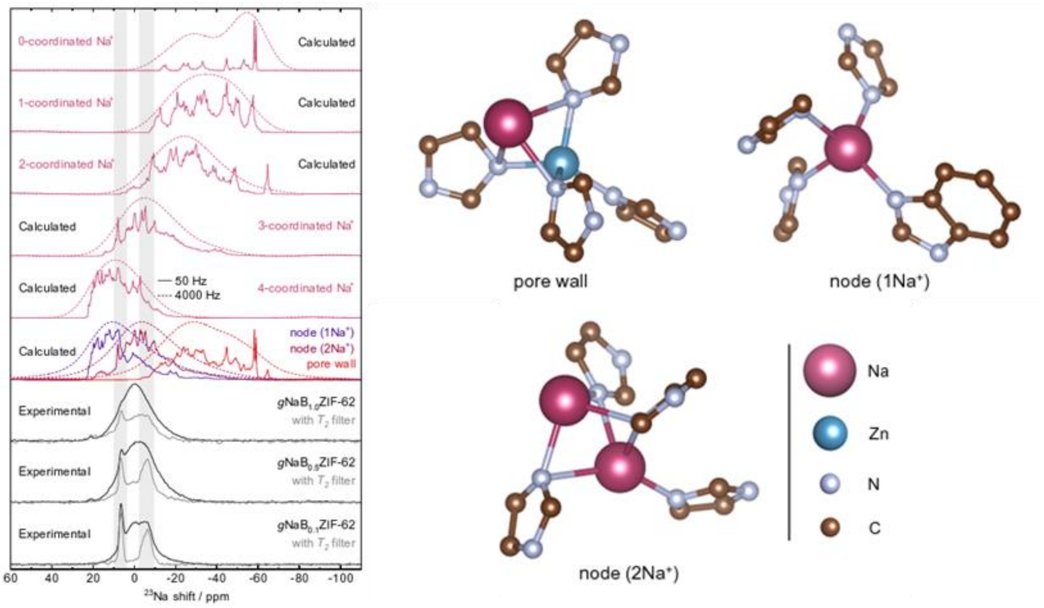

Figure 1 (Adapted from Figure 4 of [1]). NMR and DFT analysis of structural changes during vitrification. Predicted 23Na NMR spectra of Na+ sites in DFT-simulated gNaBxZIF-62 structures, categorised by Na+ occupation in the gNaBxZIF-62 and N–Na+ coordination number. Experimental 23Na NMR (20.0T, 20 kHz 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.

References

[1] P. Kolodzeiski, et al. Sodium-Ion-Modified Zeolitic Imidazolate Framework Glasses. ChemRXiv. **2025**.

ELECTROCHEMICAL DEPOSITION OF HKUST-1 POLYCRYSTALLINE FILMS AS TRIBO-POSITIVE MATERIAL FOR ROBUST TRIBOELECTRIC ENERGY HARVESTERS

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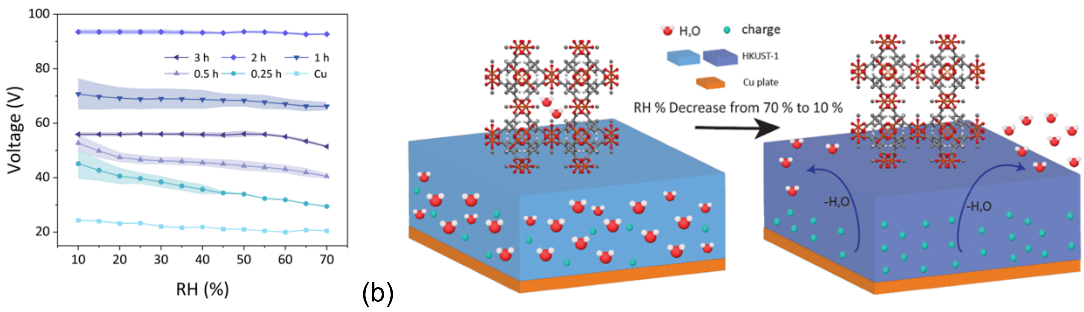
Keywords: *Metal-organic framework, Electrochemical deposition, Triboelectric nanogenerator, HKUST-1 crystalline film*

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.



(a) (b)

Figure 1: Humidity test across levels from 70% to 10%: a) Output Voltage, b) Proposed Mechanism – [ref.X]. Unpublished data.

Reference:

[X] C. Jin and J.C. Tan, Manuscript in preparation (2025).

[1] Choi, Y. S., et al. *Adv Energy Mater.* **2021**, *11* (7), 2003802.

[2] Slater, B.; Tan, J.-C. *Chem Sci* **2024**, *15* (26), 10056-10064.

[3] Khandelwal, G., et al. *Adv Energy Mater.* **2019**, *9* (14), 1803581.

[4] Khandelwal, G., et al. *J Mater Chem A* **2020**, *8* (34), 17817-17825.

[5] Babu, A.; Bochu, L., et al. *ACS Sustain Chem Eng* **2023**, *11* (47), 16806-16817.

POLYMORPHISM-DRIVEN TOPOLOGY TUNING IN PURE AND MIXED-PHASE NI(II)-BASED METAL–ORGANIC FRAMEWORKS

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Keywords: *Polymorphism, Metal-Organic Framework, Topology*

Polymorphism refers to the phenomenon where a single chemical compound can crystallize into two or multiple structural arrangements, each exhibiting unique physical properties despite identical molecular composition.[1] In the context of porous materials, polymorphism leads to structural variations, such as differing pore geometries and surface characteristics, all derived from the same chemical constituents. This concept has gained increasing attention in the study of metal−organic frameworks (MOFs) in the past few years.[2] However, researchers have focused primarily on the pure phases of polymorphic MOFs, while intermediate-phase and mixed-phase structures have been largely overlooked due to their structural complexity and the challenges associated with controlling their synthesis.

In our work, we revisit the polymorphism of Ni-BDC-DABCO MOF. In addition to the well-known pure-phase polymorphs with square (*sql*) and Kagome (*kgm*) topologies,[3] we investigate mixed-phase MOFs by various structural and gas adsorption analysis techniques, giving access to structure−property relationships. Furthermore, systematic study of the synthesis conditions allows us to unravel key parameters determining the phase composition in these mixed-phase MOFs.

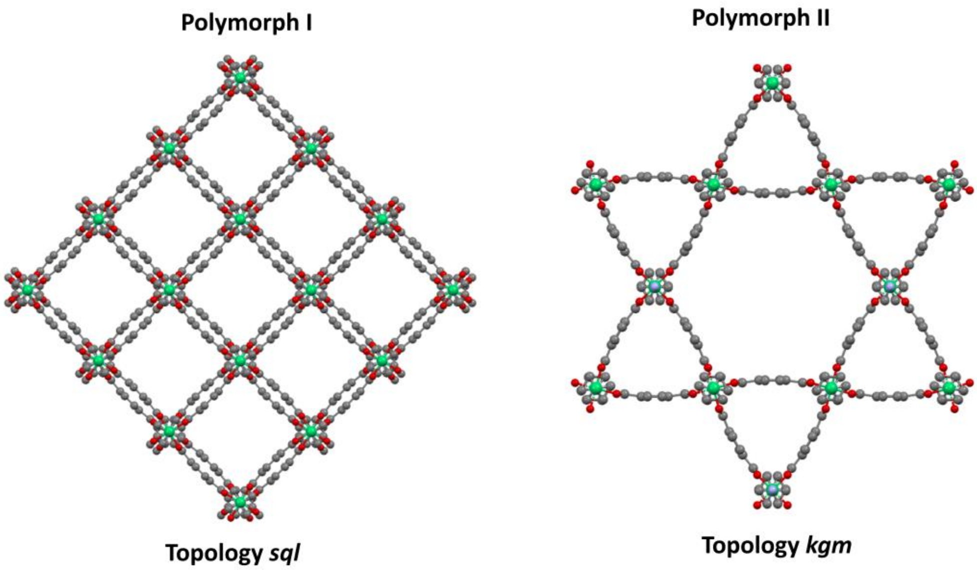

Figure 1. Two polymorphs of Ni-BDC-DABCO MOF representing *sql* and *kgm* topologies.

References

[1] J. P. Brog, C. L. Chanez, A. Crochet, K. M. Fromm, RSC Adv., **2013**, 3, 16905-16931.

[2] C. Ma, L. Zheng, G. Wang, J. Guo, L. Li, Q. He, Y. Chen, H. Zhang, Aggregate, **2022**, 3, e145.

[3] K. Zhou, S. Chaemchuen, Z. Wu, F. Verpoort, Microporous Mesoporous Mater., **2017**, 239, 28-33.

PHOTOINDUCED GUEST RELEASE USING WERNER CLATHRATES

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Keywords: *Werner clathrates, photodimerization, guest release*

Guest-release materials have potential applications in many fields including medical, food and material chemistry. If the guest release can be controlled by external stimuli, more advanced release materials could be developed.[1] Among the different types of stimuli, a light stimulus has significant advantages due to easy control of movement and conformation, rapid responsiveness, and no requirement of additional chemical components.[2]

In this work, we synthesized the photoactive ligand-coordinated Werner clathrates with different types of guest molecules. All clathrates exhibited a similar porous structure with isolated cavities including guest molecules. The photo-induced guest release properties will be discussed.

References

[1] J. Liang, Y. B. Zulkifli, S. Choy, Y. Li, M. Gao, B. Kong, J. Yun, K. Liang, *Environ. Sci. Technol.* **2020**, 54, 11356-11364.

[2] S. Yamada, N. Uematsu, K. Yamashita, *J. Am. Chem. Soc.* **2007**, 129, 12100-12101.

SYNTHESIS OF A FLEXIBLE CALCIUM COORDINATION POLYMER FOR THE DEVELOPMENT OF COORDINATION POLYMER GLASSES

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Keywords: *flexible coordination polymer, light metal cation, phase transition*

Recently, coordination polymer (CP) liquids/glasses have garnered significant attention due to their absence of grain boundary and high processability.[1,2] We previously reported that the flexible copper CP crystal was transformed into glass by a melt-quenching method and the obtained copper CP glass showed kinetic gas selectivity.[2] In terms of the metal cation for CP liquid/glasses, existing research primarily focused on heavy metal cations, while CP liquid/glasses with light metal cations are relatively scarce. Considering that calcium cation offers several advantages, including biocompatibility, affordability, and abundance, this study focused on calcium CP liquid/glasses and we synthesized new flexible 1D calcium CP using flexible components. The phase transition behavior will be discussed.

References

[1] T. D. Bennett, S. Horike, *Nat. Rev. Mater.* **2018**, 3, 431-440.

[2] X. Zheng, M. Kato, Y. Uemura, I. Yagi, K. Takahashi, S. I. Noro, T. Nakamura, *Inorg. Chem.* **2023**, 62, 1257-1263.

ANION-EXCHANGEABLE DEFECTIVE UiO-66 FOR NITRATE REMOVAL IN WATER

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Keywords: *metal-organic framework, nitrate removal, defective UiO-66, anion exchange*

Nitrate anion is a potential water pollutant because many human activities such as industries and agriculture produce excessive nitrate.[1,2] High concentrations of nitrate anion in water could harm the environment and endanger human health if consumed. Therefore, processing or removing the nitrate anion from water is necessary, and physical removal methods such as adsorption and ion exchange are frequently used due to their effectiveness and simplicity in the process. Metal-organic frameworks (MOFs) are hybrid organic-inorganic polymers with high porosity and structural tunability, which attract much attention for contaminant separation. Recently, we found that the anion-exchangeable defective UiO-66 showed nitrate removal by an anion exchange (Figure).[3] To our knowledge, the anion-exchangeable properties of UiO-66 type MOFs study are very rare. In this study, we report on the synthesis of the UiO-66 derivative, the defective structure, and the nitrate removal properties in water.

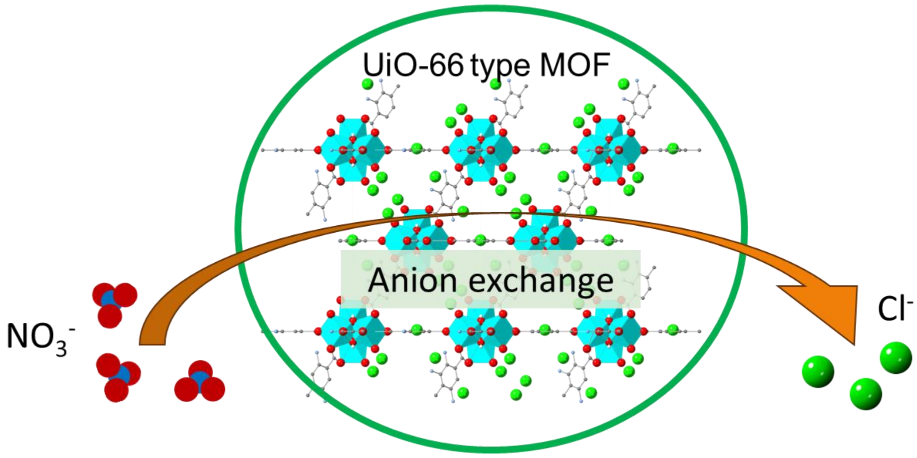

Figure. The nitrate removal by anion exchange in defective UiO-66.

References

[1] B. T. Nolan, K. J. Hitt, B. C. Ruddy, *Environ. Sci. Technol.* **2002**, 36, 2138-2145.

[2] Y. Yoshinaga, T. Akita, I. Mikami, T. Okuhara, *J. Catal.* **2002**, 207, 37-45.

[3] I. W. Aditya, X. Zheng, S. Noro, *Chem. Lett.* **2024**, 53, upae050.

UNVEILING HIGH PERFORMANCE MOFS FOR CH_4/H_2 SEPARATION THROUGH COMBINED MOLECULAR SIMULATION AND ML APPROACH

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Keywords: *Metal-Organic Framework, Molecular Simulation, Machine Learning, Adsorption, Gas Separation*

With the ever-growing number of synthesized and hypothetical metal-organic frameworks (MOFs), identifying the most selective adsorbents for CH_4/H_2 separation through experimental or computational methods has become increasingly complex. This work assesses the CH_4/H_2 separation capability of 126605 distinct types of MOFs by combining machine learning (ML) and molecular simulations. CH_4 and H_2 adsorption data for synthesized MOFs at various pressures were produced by grand canonical Monte Carlo (GCMC) simulations, which were then used to train ML models incorporating structural, chemical, and energetic features of MOFs. These ML models were subsequently transferred to hypothetical MOFs, allowing rapid and accurate screening of promising adsorbents for CH_4/H_2 separation. The top performing MOFs were determined by analyzing CH_4/H_2 selectivities and their key structural and chemical characteristics were examined. Synthesized (hypothetical) MOFs having narrow pores and pyridine-, histidine-, and imidazole-based (carboxylate-, benzoate-, and cubane-based) linkers demonstrated high selectivities up to 85 (115) at 1 bar and 298 K. Our findings highlight the potential of MOFs as superior alternatives to traditional adsorbent materials for CH_4/H_2 separation.

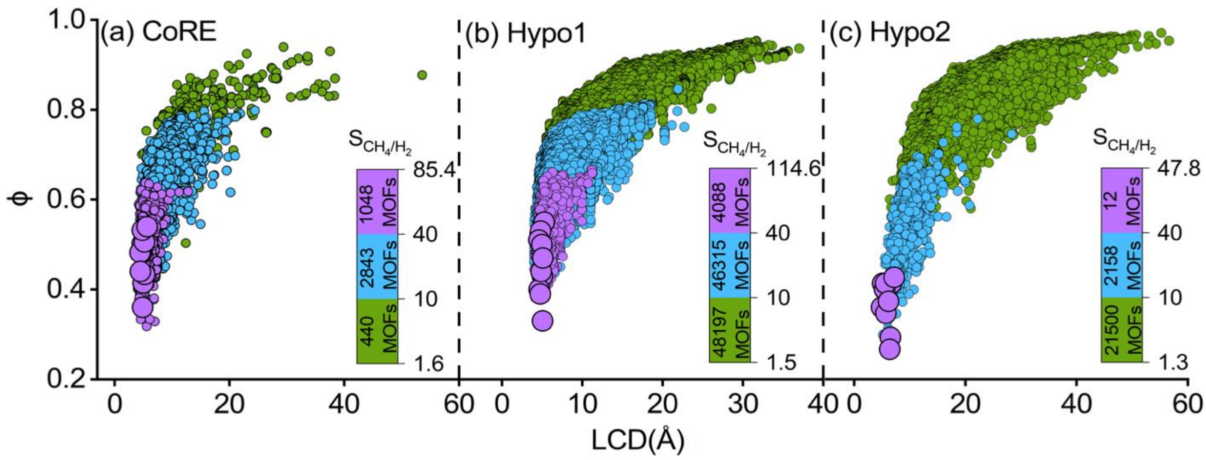

Figure A.1 Relation between porosities, pore sizes, and CH_4/H_2 selectivities computed at 1 bar for (a) 4331 CoRE MOF, (b) 98601 Hypo1, and (c) 23673 Hypo2 MOFs. The numbers in selectivity bars represent the number of MOFs having selectivities in the given range. Large purple spheres represent the top 10 MOFs having the highest selectivities in each database.

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Zn(II) COORDINATION POLYMER WITH HIGH GLASS-FORMING ABILITY FOR EFFICIENT GAS SEPARATION

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Keywords: *phase transition, glass-forming ability, gas separation*

Tremendous progress has been made in the development of solid crystalline coordination polymers (CPs) and metal-organic frameworks (MOFs). Recently, amorphous CPs/MOF solids, CP/MOF liquid and glasses have received attention as an emerging class of functional materials.[1] Upon phase transition to glass, great opportunities have been identified for fabrication of functional homogenous membranes facilitated by the grain-boundary-free nature of the glass.[2,3]

Melt-quenching is one common method to prepare CP/MOF glasses. However, only a limited number of cases have been demonstrated to date, as most CPs/MOFs undergo thermal decomposition upon heating, where decomposition temperatures (T_d) < melting temperatures (T_m). Our previous work has reported the successful synthesis of a three-dimensional glassy nonporous CP with relatively low T_m.[4]

In this study, we report a new Zn(II) CP (**1**) that readily undergoes phase transition upon heating. Structure analysis of **1** using single crystal X-ray diffraction analysis revealed that the Zn(II) ion is coordinated with four ligands, constructing a one-dimensional chain. Thermal analyses demonstrated that T_m of **1** is much lower than T_d. Correspondingly, **1** exhibits a high ratio of T_g/T_m (T_g: glass transition temperature), indicating a high glass-forming ability. Encouraged by this high glass-forming ability, we fabricated a membrane of glassy **1** for potential application in gas separation. The comprehensive findings will be introduced in the presentation.

References

[1] N. Ma and S. Horike, *Chem. Rev.* **2022**, 122, 4163-4203.

[2] Y. Wang, H. Jin, Q. Ma, K. Mo, H. Mao, A. Feldhoff, X. Cao, Y. Li, F. Pan, Z. Jiang, *Angew. Chem., Int Ed.* **2020**, 59, 4365-4369.

[3] J. Li, J. Wang, Q. Li, M. Zhang, J. Li, C. Sun, S. Yuan, X. Feng, B. Wang, *Angew. Chem., Int Ed.* **2021**, 60, 21304-21309.

[4] X. Zheng, M. Kato, Y. Uemura, D. Matsumura, I, Yagi, K. Takahashi, S. Noro, T. Nakamura, *Inorg. Chem.* **2023**, 62, 1257-1263.

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.

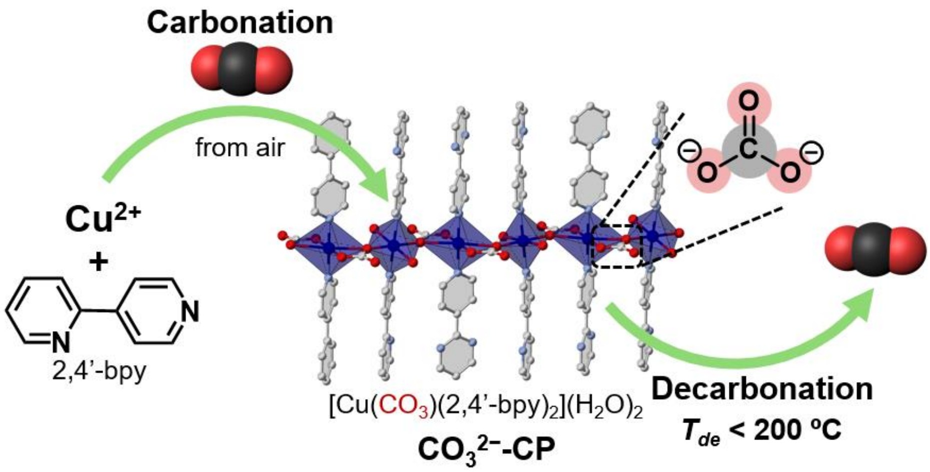

Figure 1. CO_2 capture through the carbonation and decarbonation of CO_3^{2-}-CP.

References

[1] E. S. Sanz-Pérez et al., *Chem. Rev.*, **2016**, 116, 11840-11876.

[2] K. Kadota and S. Horike, *Acc. Chem. Res.*, **2024**, 57, 3206-3216.

PHOTOINDUCED SINGLE-CRYSTAL-TO-SINGLE-CRYSTAL TRANSFORMATION IN Cd-INCLUDING WERNER COMPLEX

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Keywords: *Werner complex, [2+2] photodimerization, Single-crystal-to-single-crystal transformation*

Werner complexes with the composition $[M(A)_2(L)_4]\cdot xG$ (M = divalent metal cation, A = monovalent anion, L = pyridine derivative ligand, G=guest molecules) can adsorb a variety of guest molecules with structure changes, forming Werner clathrates. Our laboratory has recently focused on Werner complexes/clathrates with photoreactive ligands because a light stimulus may control their porous properties. For example, the cadmium-including Werner complex with photoreactive 4-styrylpyridine ligands exhibited the noporous to porous structural change after [2+2] photodimerization reaction, and the resulting porous amorphous polymer showed CO_2 gas adsorption.[1]

In this study, we report the Cd-including Werner complex **1** with another photoreactive ligand. This complex shows the single-crystal-to-single-crystal transformation from a mononuclear complex **1** to a two-dimensional coordination polymer **1′** by the [2+2] photodimerization reaction. In addition, **1** and **1′** exhibit different adsorption properties.

References

[1] Y.-Y. Zhang, X. Zheng, Y. Saito, T. Takeda, N. Hoshino, K, Takahashi, T, Nakamura, T. Akutagawa, S. Noro. *Angew. Chem. Int Ed*. **2024**, 63, e202407924.

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.

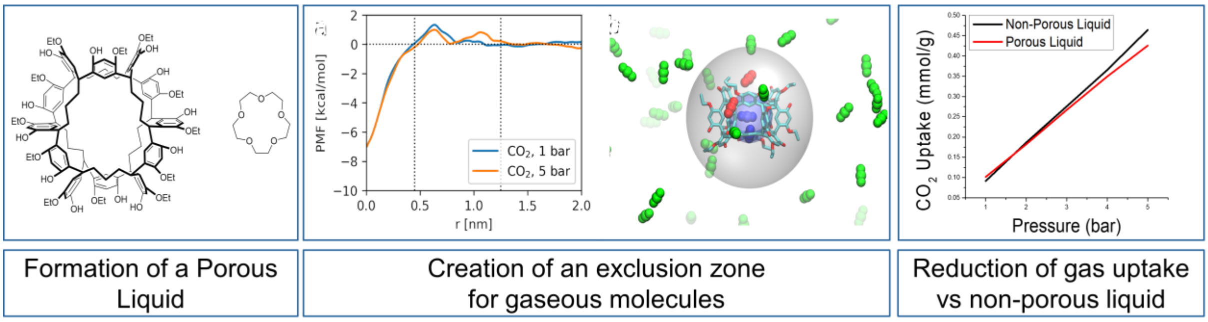

Figure 1 (left) Structures of Noria$_{OEt}$ and 15C5 which are used to form a T2PL. (centre) Graphical summary of MD simulations used to support the formation of a gas exclusion zone in the T2PL. (right) CO_2 uptake measurements of 15C5 and the T2PL showing the effect of the gas exclusion zone on the gas uptake properties of the T2PL.

[1] N. Giri, M. G. Del Pópolo, G. Melaugh, R. L. Greenaway, K. Rätzke, T. Koschine, L. Pison, M. F. C. Gomes, A. I. Cooper and S. L. James, *Nature*, 2015, **527**, 216–220.
[2] B. D. Egleston, A. Mroz, K. E. Jelfs and R. L. Greenaway, *Chemical Science*, 2022, **13**, 5042–5054.
[3] F. M. Alexander, S. F. Fonrouge, J. L. Borioni, M. G. Del Pópolo, P. N. Horton, S. J. Coles, B. P. Hutchings, D. E. Crawford and S. L. James, *Chem. Sci.*, 2021, **12**, 14230–14240.

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.

References

[1] Y. Sakamaki, M. Tsuji, Z. Heidrick, O. Watson, J. Durchman, C. Salmon, S. Burgin, M. Beyzavi. Journal of Chemical Education, **2020**, 97, 1109–1116.

[2] S. Bhattacharyya, S. Pang, M. Dutzer, R. Lively, K. Walton, D. Sholl, S. Nair. Journal of Physical Chemistry C, **2016**, 120, 27221–27229.

[3] A. Metawea and G. Walker. Journal of Industrial and Engineering Chemistry, **2025**.

[4] O. Yaghi and J. Yang. Porous aluminum pyrazoledicarboxylate frameworks. **2019**.

RARE EARTH METAL- ORGANIC FRAMEWORKS: STRUCTURAL DIVERSITY, STABILITY, AND LUMINESCENT PROPERTIES

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Keywords: *Metal Organic Frameworks (MOFs), Rare Earth metals (REM), Structural topology, f-block elements, and photoluminescence properties.*

Metal-organic frameworks (MOFs) are a class of crystalline materials composed of metal ions or clusters coordinated to organic ligands, forming extended networks.[1] The structural diversity of MOFs is vast, enabling the formation of highly porous materials with tunable pores and geometries. These materials can exhibit large surface areas and high crystallinity, characteristics that are often key to their unique properties.[2] Over 20,000 distinct MOF types have been documented and studied in recent decades.[3]

The most commonly studied MOFs have d-block metals nodes, which includes metals such as zinc(II), nickel(II) and copper(II), amongst others.[4] Of all of these, zirconium-based MOFs have been the subject of large amounts of interest due to their chemical and thermal stability. Now a growing amount of research is being conducted into the synthesis of MOFs with rare earth (RE) metal nodes, such as terbium(III), erbium(III), yttrium(III) and other f-block lanthanoids, due to their ability to exhibit +3 oxidation states and, in some cases, other oxidation states like +2 or +4, along with their flexible coordination numbers. These properties enable the formation of stable MOFs.[5].

Moreover, RE metals exhibit interesting properties due to their unique electronic structure, yielding high photostability because of well-defined luminescent emission due to 4f-4f electronic transitions. Upon excitation, REs characteristically emit photoluminescence in the UV-visible and near-infrared regions of the spectrum [6] i.e. Eu^{3+}, Tb^{3+}, Sm^{3+} and Tm^{3+} emit in the red, green, orange and blue region of the visible light, respectively. By changing the RE metal, we can effectively tune the fluorescent properties. As a result, there has been an increased interest in developing the RE-metal MOFs which can be used in different fields of life such as gas storage, separation, catalysis and sensors.[7] Furthermore, RE metals form a stronger bond with the organic ligands due to their higher charge density, making them more stable and less liable to decomposing under harsh conditions such as temperature and pressure.[8]

References

1. James, S.L.J.C.S.R., *Metal-organic frameworks.* 2003. **32**(5): p. 276-288.
2. Cai, G., et al., *Metal–organic framework-based hierarchically porous materials: synthesis and applications.* 2021. **121**(20): p. 12278-12326.
3. Hayat, A., et al., *Recent advance in MOFs and MOF-based composites: synthesis, properties, and applications.* 2024: p. 101542.
4. Bibi, S., *Synthesis and characterization of NI (II), CU (II) and ZN (II) coordination polymers and the applications in electrochemical studies and adsorption of DYES/Bibi Sherino*. 2018, University of Malaya.
5. Alnaqbi, M.A., et al., *Chemistry and applications of s-block metal–organic frameworks.* 2021. **9**(7): p. 3828-3854.
6. Nguyen, T.N., F.M. Ebrahim, and K.C.J.C.C.R. Stylianou, *Photoluminescent, upconversion luminescent and nonlinear optical metal-organic frameworks: From fundamental photophysics to potential applications.* 2018. **377**: p. 259-306.
7. Kang, F., et al., *Recent advances and prospects of persistent luminescent materials as inner secondary self-luminous light source for photocatalytic applications.* 2021. **403**: p. 126099.
8. Liu, K., et al., *Advances in reticular materials for sustainable rare earth element recovery.* 2025. **522**: p. 216199.

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]

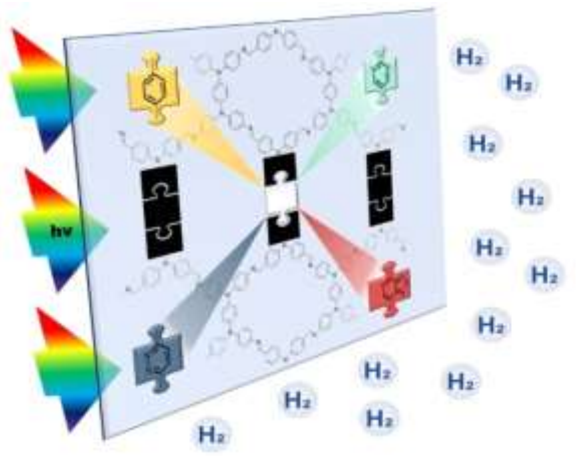

Figure 1: D-A-D COF series for PEC water splitting.[1]

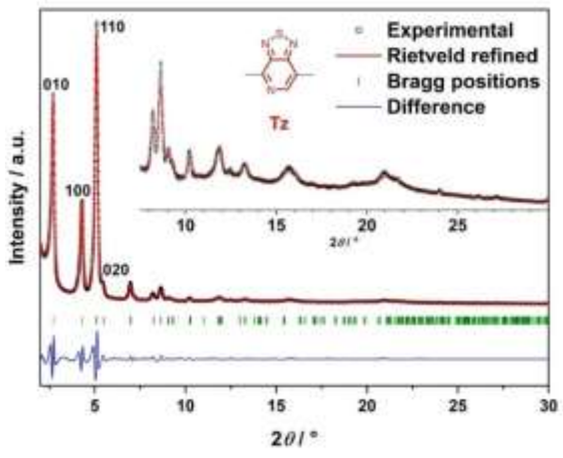

Figure 2: Simulated and experimental PXRD pattern of thiadiazolopyridine containing COF.[1]

References

[1] R. Guntermann, D. Helminger, L. Frey, P. M. Zehetmaier, C. Wangnick, A. Singh, T. Xue, D. D. Medina, T. Bein*, Angew. Chem. Int. Ed*. **2024**, 63, e202407166.

A SERIES OF CONDUCTING TETRATHIAFULVALENE-BASED 2D MOFS WITH LANTHANIDES IONS (Dy^{III}, Er^{III} & Yb^{III})

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Keywords: *Conductivity, Single-Molecule Magnet, Tetrathiafulvalene, Lanthanides*

Recently, particular attention has been paid to MOFs with high electrical conductivity, which have potential applications in electrocatalysis, energy storage, electrochemical sensing, molecular electronics and spintronics. Among them, tetrathiafulvalene (TTF) linkers have shown promising results in the development of the field due to their redox-active nature and the possibility to generate stable open-shell species, while keeping their framework intact. [1] The 2D Ln-TTF MOFs series, formulated as $[Ln_6(TTFTC)_5(H_2O)_{22}]\cdot x(H_2O)$ (Ln=Dy^{III}, Er^{III}, Yb^{III} and TTFTC=tetrathiafulvalene tetracarboxylate), have been obtained by layering a methanol solution of the corresponding Ln^{III} salts on top of an aqueous solution of the TTFTC linker, and recently by an optimised synthetic protocol in water. The structural data revealed a rare 2D topology with 1D open channels (~5Å diameter) filled by water molecules and stacked linker molecules running along the [111] direction, interconnected by Ln_6 clusters. The marterials have been characterized through a multi-technique approach involving: SCXRD, PXRD, Raman and DR Spectroscopy, quantum mechanical calculations, conductivity measurements and AC/DC magnetic susceptibility measurements. Remarkably, three different oxidation states of the linker (0, +0.5, +1) were confirmed experimentally and computationally. The different oxidation states and the strong π-π interaction among linkers allow the formation of good conduction pathway along the stacking direction. The conductivity of the MOFs as a function of temperature and pressure have been measured along single crystal [111], showing a semiconductor behaviour with room temperature conductivity of 1 mS/cm^{-1}, 10 mS/cm^{-1}, and 0.3 mS/cm^{-1} for Dy^{III}, Er^{III} and Yb^{III} MOFs, respectively. The obtained room temperature conductivity values are the highest among TTF-MOFs reported in literature up to now. Furthermore, AC magnetic susceptibility measurements revealed field-induced slow relaxation of the magnetization for Dy^{III} MOF accounting for two independent relaxation processes with energy barrier U_{eff}=9.5(3) K and U_{eff}= 1.7(5) K thanks to the strong magnetic anisotropy. [2] Finally, thanks to the novel optimised synthetic protocol, further studies on this class of MOFs, such as gas adsorption measurements, are in progress.

References

[1] H.Y. Wang, J. Su, and J.L. Zuo, *Acc. Chem. Res.* **2024**, 57, 1851-1869.

[2] F. Manna, et al., M. L. Mercuri* and N. Avarvari*, *Chem. Sci.* **2024**, 15(46), 19247-19263.

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.

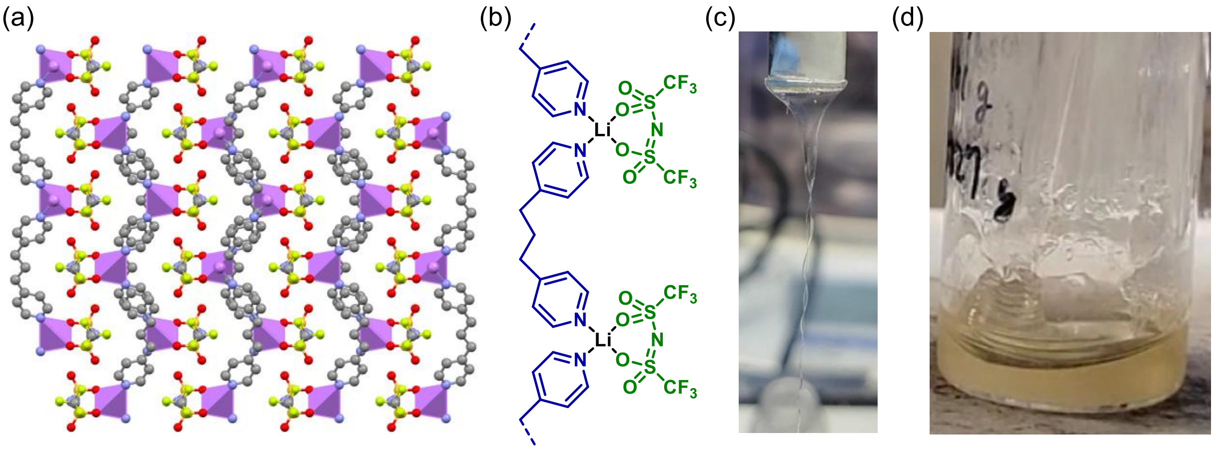

Fig. (a, b) Crystal structure of **1**. (c) Elongated supercooled liquid of **1**.
(d) Weissenberg effect in the supercooled liquid state of **1**.

References

[1] J. Endo *et al.*, *J. Am. Ceram. Soc.* **2015**, *98*, 2767-2771.

[2] S. Horike *et al.*, *Adv. Funct. Mater.* **2024**, *34*, 2307226.

[3] T. Nishiguchi, S. Horike *et al.*, *Chem. Sci.* **2025**, *16*, 621-626.

[4] K. Weissenberg, *Nature* **1947**, *159*, 310-311.

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.

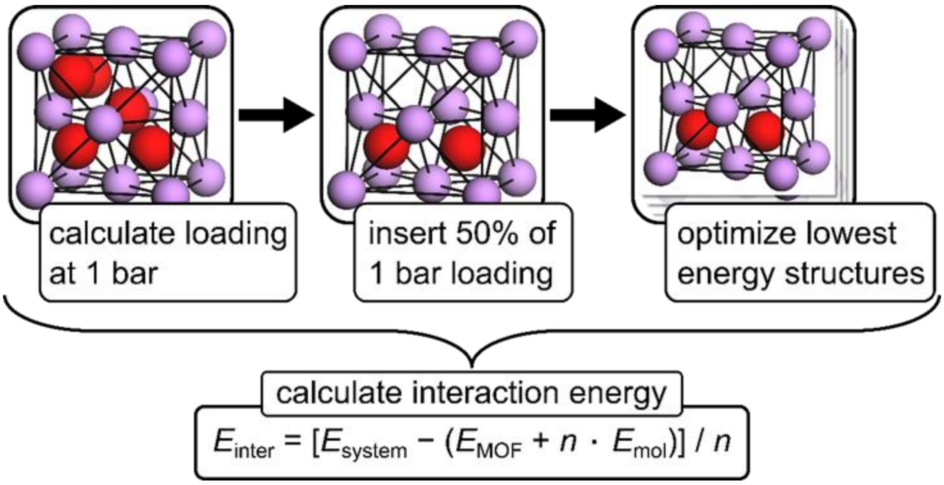

Fig. 1: Modeling workflow for multi-molecule adsorption in metal-organic frameworks.

References

[1] I. A. Buryakov, T. I. Buryakov, V. T. Matsaev, J. Anal. Chem. 2014, 69, 616–631.

[2] Z. Hu, B. J. Deibert, J. Li, Chem. Soc. Rev. 2014, 43, 5815–5840.

[3] T. Reinecke, J.-G. Walter, T. Kobelt, A. Ahrens, T. Scheper, S. Zimmermann, J. Sens. Sens. Syst. 2018, 7, 101–111.

ENVIROMENTAL APPLICATIONS OF METAL-ORGANIC FRAMEWORKS

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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]

Acknowledgments

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References

[1] B. Sierra-Serrano, A. García-García, T. Hidalgo, D. Ruiz-Camino, A. Rodríguez-Diéguez, G. Amariei, R. Rosal, P. Horcajada, S. Rojas. Copper Glufosinate-Based Metal−Organic Framework as a Novel Multifunctional Agrochemical. ACS Appl. Mater. Interfaces, **2022**, 14, 34955

[2] S. Rojas, A. Rodríguez-Diéguez, P. Horcajada. Metal–Organic Frameworks in Agriculture. ACS Appl. Mater. Interfaces, **2022**, 14, 16983

[3] MC. Contreras, P. Salcedo-Abraira, A. Zabala-Lekuona, A. Rodríguez-Diéguez, S. Rojas. Developing a Novel Agrochemical-Based MOF: A Multifunctional Platform with Herbicidal and Antibacterial Activities. ACS Appl. Mater. Interfaces, **2025**, 17, 4147–4154

INVESTIGATING THE GROWTH MECHANISMS INVOLVED IN A GREEN ALUMINUM FUMARATE SYNTHESIS

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Keywords: *Al-fumarate, growth mechanisms, in situ Raman, mass spectrometry*

Aluminum-based metal–organic frameworks (Al-MOFs) have attracted considerable attention due to their promising performance in key applications such as water adsorption and purification, or coating of heat exchangers. Their structural robustness towards moisture makes them suitable for large-scale use. We recently developed a green synthesis pathway for Al-MOFs based on aluminium alkoxides precursors such as aluminium isopropoxide[1]. Unlike previously reported aqueous-phase synthesis routes, which require basic conditions (e.g., NaOH addition[2]), the method presented here operates solely in water and does not require a filtration step (no saline co-products are formed). Al-fumarate is one of the candidates for this reaction pathway, and has been upscaled via spray-drying to a 100 kg scale.

As the knowledge about growth mechanisms and kinetics of this synthesis remains elusive, we decided to investigate those aspects via in situ and online monitoring methods. In situ Raman spectroscopy and ESI-mass spectrometry were used. Raman spectroscopy allowed us to identify spectral bands related to both reactants and products and follow their behaviour over the whole reaction time (Figure 1). It provided interesting information about reaction kinetics but proved limited to identify intermediate reaction species precisely. ESI-mass spectrometry was used as a complementary method to spot potential intermediate reaction species. To achieve that, a home-made set-up was built, allowing to acquire a spectrum every 5 seconds over the first reaction hours. Several mass peaks resulting from the MOF's reaction were identified, and tentatively attributed.

Surprisingly, both methods suggest very fast reaction kinetics, with the main steps happening within 15 minutes and a crystallisation completed by 4 hours. This study showed that Raman spectroscopy is a powerful yet simple tool to investigate reaction kinetics. As such, we are trying to apply it to a more complex polymorph Al-MOFs system – Al-BTC – to try and understand the phase selectivity.

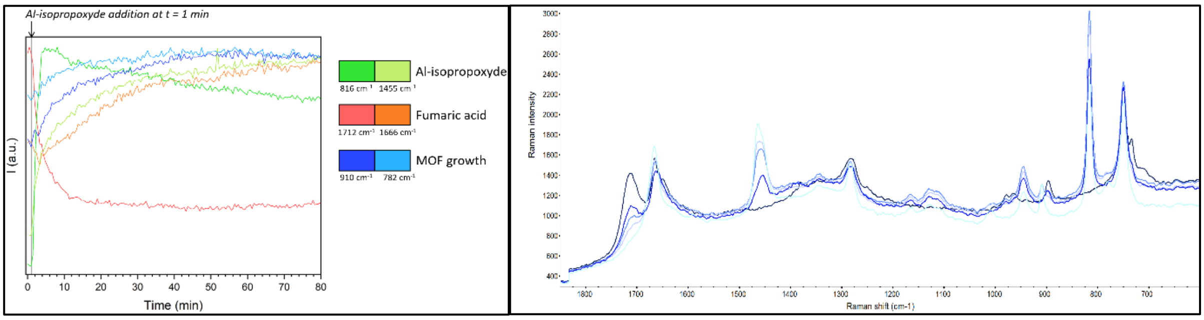

Figure.1: time series of relevant Raman bands for reactants and products (left) and evolution of Raman spectra aspect over time (right).

References

[1] M. Perbet, et al. *Ind. Eng. Chem. Res.* **2025**, 64 (12), 6541-6549.

[2] N. Tannert, et al. *Dalton Trans.* **2019**, 48 (9), 2967-2976.

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MACHINE LEARNING APPROACH FOR PREDICTION SECOND HARMONIC GENERATION IN METAL-ORGANIC FRAMEWORKS

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Keywords: *metal-organic frameworks, machine learning, second-harmonic generation, MOF,ML,SHG*

Modern photonic technologies based on nonlinear optics (NLO) as a cornerstone across diverse fields including laser technology, quantum information processing, optoelectronics, telecommunication and long-distance communication. Traditional NLO devices primarily rely on inorganic crystals such as lithium niobate and potassium titanyl phosphate, which present significant miniaturization challenges due to their phase-matching requirements and performance limitations at smaller scales[1].

Metal-organic frameworks (MOFs) have emerged as promising candidates for NLO applications due to their exceptional structural flexibility and chemical diversity. Their crystalline lattices, composed of metal ions and organic linkers, exhibit unique physicochemical properties that allow their application as sensors, catalysts, and for targeted drug delivery. While second-harmonic generation (SHG) efficiency has been experimentally investigated for select MOFs, the vast majority of these crystals remain unexplored for their nonlinear optical properties[2].

This study addresses a critical knowledge gap in the field of NLO materials by developing a comprehensive approach to predict SHG efficiency in MOFs. Our objective was to identify MOF structures with high SHG efficiency through machine learning techniques, thereby accelerating the discovery of novel materials for next-generation photonic applications while circumventing the constraints of traditional methods such as density functional perturbation theory (DFPT) or experimental measurements.

We established a comprehensive dataset of SHG values by integrating information from multiple scientific reviews, incorporating both experimental measurements of MOFs and computational data for various crystal classes obtained through DFPT simulations. Several graph neural network architectures were evaluated for transfer learning on this limited dataset. The optimal model was identified based on prediction accuracy and then applied to evaluate the SHG efficiency of a large collection of MOFs from the QMOF database[3].

Our machine learning approach successfully identified several MOF candidates with predicted high SHG efficiency values. The transfer learning technique demonstrated effective generalization despite the limited training data. The evaluation of structures from the QMOF database revealed several previously unexplored MOFs with exceptional predicted SHG performance, expanding the pool of potential materials for nanophotonic applications.

This research demonstrates the potential of machine learning techniques to accelerate the discovery and development of novel NLO materials. By enabling rapid screening of the vast chemical space of MOFs, our approach offers an alternative to computational and experimental methods. The identified MOF candidates provide new directions for potential applications in miniaturized photonic devices.

References

[1] S. K. Chandran, C. Elavarasi et al. Crystal Growth and Chirality - Technologies and Applications, IntechOpen, London, **2022**.

[2] C. Li, G. Qian, Y. Cui. *Inf Funct Mater*. **2024**, 1(2), 125-159.

[3] A. S. Rosen, S. M. Iyer et al. *Matter*, **2021**, 4, 5, 1578–1597.

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

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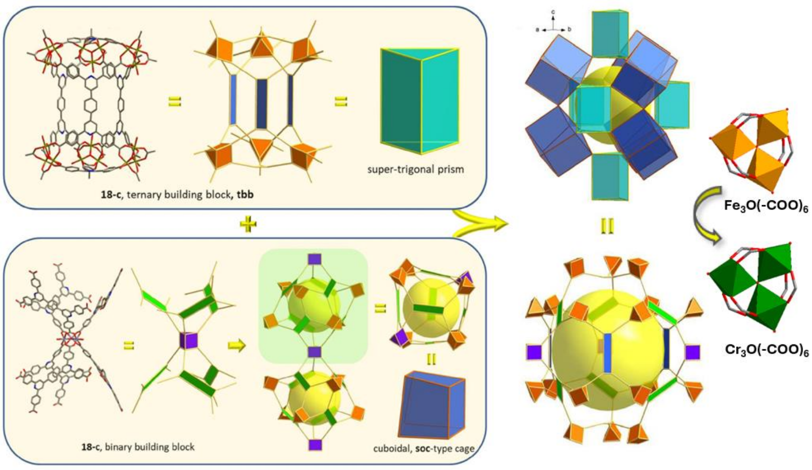
Keywords: *Metal-Organic Frameworks, Reticular Chemistry, Supermolecular Building Blocks, Gas Storage, Water Adsorption*

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.



[1] K. G. Froudas, P. N. Trikalitis, et al. *J. Am. Chem. Soc.* **2024**, 146(13), 8961–8970.
[2] K. G. Froudas, P. N. Trikalitis, et al. *work to be submitted*.

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.

References

[1] A. E. Thorarinsdottir, T. D. Harris, *Chem. Rev.,* **2020**, 120, 8716.

[2] C. J. Pickard, R. J. J. Needs, *Phys. Condens. Matter.,* **2011**, 23, 053201.

[3] J. P. Darby, M. Arhangelskis, A. D. Katsenis, J. M. Marrett, T. Friščić, A. J. Morris, *J. Chem. Mater.,* **2020**, 32, 5835.

[4] I. Batatia, et. al., *arXiv preprint, arXiv:2206.07697 [stat.ML],* **2023**

[5] I. Batatia, et. al., *arXiv preprint, arXiv:2401.00096 [physics.chem-ph],* **2024.**

PORPHYRIN METAL-ORGANIC FRAMEWORKS: ONE-POT SYNTHESIS

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Keywords: *porphyrin, MOF, one-pot synthesis*

Porphyrin metal-organic frameworks (pMOFs) are excellent candidates for arranging functional linkers in precise order ensuring accessibility of the porphyrin species. Due to the unique photophysical and electrochemical properties of aromatic porphyrin linkers and their metal complexes, pMOFs are promising materials for catalysis, sensing and biomedical applications[1,2]. However, the cost of the linker makes the final porous materials expensive compared to simpler linkers used to construct MOFs. The high cost of pMOFs remains a significant barrier to their large-scale application, for example as catalysts. To make pMOFs more affordable, we propose a one-pot synthesis method that combines two reactions with similar conditions (pH, temperature, solvent nature) of porphyrin and MOF synthesis in one process. The method requires inexpensive reactants, such as pyrrole and aryl aldehydes, significantly reduces purification costs, and makes pMOFs more sustainable and easier to scale up.

We have demonstrated that a novel one-pot method can be used to obtain MOFs with different porphyrins, including the most common tetra(4-carboxyphenyl)porphyrin TCPP and the less common tetra(3-carboxyphenyl)porphyrin TmCPP, and different metals in the inorganic building units of the MOF, including zirconium (IV). Using an optimised one-pot synthesis procedure, the highly crystalline and porous materials were obtained, as shown by PXRD and nitrogen absorption measurements (Figure 1). The BET surface area of the known pMOF PCN-224 based on TCPP and zirconium oxoclusters obtained by the one-pot method reaches 1400 m^2/g, which is slightly lower than the theoretical value but still very high. The method developed here is promising for a wider large-scale application of known pMOFs and is universal, opening the way to obtain new pMOFs with more complicated porphyrin linkers.

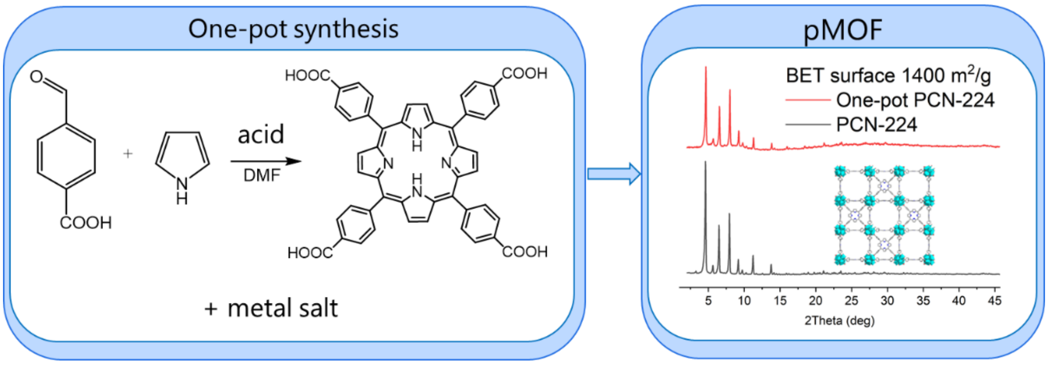

Figure 1. Schematic representation of the one-pot synthesis of pMOFs. Comparison of PXRD of materials obtained by one-pot and conventional methods.

The fine-tuning of the structure of the starting aldehydes, the metals present in the synthesis medium, the metal centres within the porphyrin units, paves the way for the establishment of a greener and more cost-effective route to pMOF production and the development of highly tunable systems containing different metal ions as porphyrin centres and structural units.

References

[1] X. Zhang, M. C. Wasson, et al. *Coordination Chemistry Reviews*. **2021**, 429, 213615

[2] Yu. G. Gorbunova, Yu. Yu. Enakieva, et al. *Russian Chemical Reviews*. **2022**, 91, RCR5038

IN SITU AND PDF NEUTRON DIFFRACTION FOR THE ADVANCED STRUCTURAL ANALYSIS OF MOF CATALYSTS FOR CARBON DIOXIDE VALORISATION

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Keywords: *multi-metal MOFs, neutron diffraction, catalysis, CO_2 reduction*

This project focuses on the structural analysis of metal-organic frameworks (MOFs) comprising multiple metal elements, and their calcination products using neutron diffraction techniques to unveil their unique structural features and role in catalysing CO_2 reduction through the reverse water-gas shift (RWGS) reaction. The RWGS reaction, which converts CO_2 and H_2 into CO and water requires efficient catalysts that enable high activity and selectivity towards CO.[1]

A series of lanthanide multi-metal MOFs has been investigated.[2],[3] They are made of cerium, partially replaced by lanthanum, neodymium or praseodymium at specific ratios. Neutron diffraction data has been collected for the multi-metal MOFs to investigate the position of the metal elements in the structures, by completing Rietveld refinements as well as with PDF analysis. Upon calcination of the MOFs, doped CeO_2 is obtained, which shows excellent activity and selectivity as a catalyst in the RWGS reaction.[4],[5] High-resolution neutron diffraction data was collected to accomplish complete crystallographic characterisation of the MOFs, and the calcined products before and after the catalytic reaction.

The oxides displayed a fluorite-type structure and crystallised in the *Fm*-3*m* space group with metal cations sharing equivalent crystallographic positions. The Rietveld refinements indicate that as the doping level increases, so does the number of oxygen vacancies —critical for RWGS reaction mechanism— and decreases the lattice dimensions. The undoped cerium sample shows virtually no defects, suggesting most vacancies arise from metal substitution. Additionally, an in-situ neutron diffraction experiment carried out under a reaction gas mixture investigated any structural changes resulting from the interaction of the gas molecules with the MOF-derived oxides. No phase transitions or significant structural changes were observed.

The study demonstrates the viability of using multi-metal MOFs as precursors for designing advanced catalysts with precisely controlled doping level and intrinsic oxygen vacancy defects. Neutron diffraction provided insights into the structural dynamics of MOF-derived oxides, establishing clear relationships between metal distributions and oxygen vacancies. This research highlights the potential to produce catalysts with precise compositions and enhanced performance, paving the way for sustainable CO_2 valorisation.

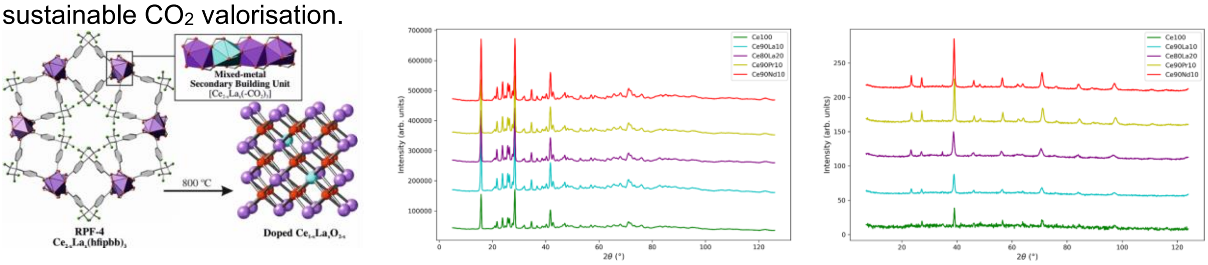

Figure 1: Mixed metal RPF-4 MOF structure and corresponding oxide (left). NPD patterns of samples as synthesised RPF-4 MOFs (centre) and calcinated products (right) measured at 2.52Å and 1.28Å respectively

References

[1] C. Ampelli et al., *Philos. Trans. R. Soc. A*, 2015, **373**, 1-35
[2] H. Furukawa et al., *Science*, 2013, **341**, 974-986
[3] F. Gándara et al., *Cryst. Growth Des.*, 2008, **8**, 378-380
[4] R. L. Vasile et al., *Chem. Mater.*, 2022, **34**, 7029–7041
[5] C. Castillo-Blas et al. *Nanoresearch,* 2021, **14,** 493-500

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.

References

[1] S. Suppi, K. Kasemets, A. Ivask, K. Künnis-Beres, M. Sihtmäe, I. Kurvet, et al. J Hazard Mater. **2015**;286.

BEYOND DRUG DELIVERY: COPPER-BASED METAL–ORGANIC FRAMEWORKS AS INTERVENTIONAL PLATFORMS FOR MICROBIOLOGICAL CONTROL

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Keywords: *synergistic antimicrobial effect, drug delivery, hydroxychloroquine carriers, antiviral properties, copper ions release*

The global rise in antimicrobial resistance and the emergence of novel viral pathogens have intensified the search for multifunctional therapeutic platforms. Copper-based metal–organic frameworks offer a promising dual-function approach, combining targeted drug delivery with intrinsic antimicrobial properties.[1] Their modular structure, nanometric dimensions, ability to deliver active pharmaceutical ingredients, and copper activity in irreversible structural damage of bacteria and viruses position them as ideal candidates for therapeutic development.

The study aimed to develop and evaluate Cu-MOFs as multifunctional carriers for the immunomodulatory drug hydroxychloroquine (HCQ) and sources of antimicrobial copper ions. After structural and morphological characterization by scanning electron microscopy, X-ray diffraction, Fourier-transform infrared spectroscopy, dynamic light scattering, and zeta potential measurements, the materials were investigated for drug loading and pH-dependent release behavior. Additionally, the antiviral efficacy of the systems was validated using SARS-CoV-2 pseudovirus infectivity assays in hACE2-expressing cells.

Two nanostructured MOFs—HKUST-1 and Cu-BDC—were synthesized solvothermally, yielding spherical (~85 nm) and rod-like particles (~200×50 nm), respectively. HKUST-1 exhibited high microporosity with a specific surface area of 979 m^2/g, whereas Cu-BDC was characterized by a significantly lower porosity (62 m^2/g), likely due to its layered topology and narrow pore structure. Both Cu-MOFs demonstrated affinity toward HCQ, with maximum loading capacities of 84 mg/g for HKUST-1 and 122 mg/g for Cu-BDC. At physiological temperature (37 °C) and across various pH levels (1.2, 6.8, and 7.2), the materials exhibited biphasic, semi-controlled drug release profiles. Compared to the rapid dissolution of pure HCQ within 30 minutes, 83.5% (HKUST-1) and 97.5% (Cu-BDC) of the drug were gradually liberated over 6 hours at pH 6.8. In parallel, the materials released in a sustained manner copper ions, supporting the contribution of copper to antimicrobial action. In antiviral assays, pure HCQ decreased infectivity by only 30%. Strikingly, when combined with carriers, the MOF/drug systems reduced viral infectivity by up to 79% (HKUST-1/HCQ) and 78% (Cu-BDC/HCQ). ELISA assays confirmed strong inhibition of spike protein–ACE2 binding, with the Cu-MOF/HCQ systems reducing interactions by nearly 50%. In addition to their antiviral performance, the materials' copper ion release profiles and low cytotoxicity in HEK293T-hACE2 cells (at concentrations ≤10 µg/mL) suggest their broader applicability as antimicrobial agents. Currently, studies are being pursued to further explore the antibacterial potential of these systems and clarify their mechanism of action.

References

[1] M. Hubab, M. A. Al-Ghouti, *Biotechnol. Reports* **2024**, 42, e00837.

GREEN SYNTHESIS OF MONOLITHIC ULTRAMICROPOROUS METAL-ORGANIC FRAMEWORKS FOR DIRECT AIR CAPTURE

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Keywords: *MOF, Direct-Air Capture, DAC, Monolith, Synthesis, Sol-Gel*

a) b) c) d)

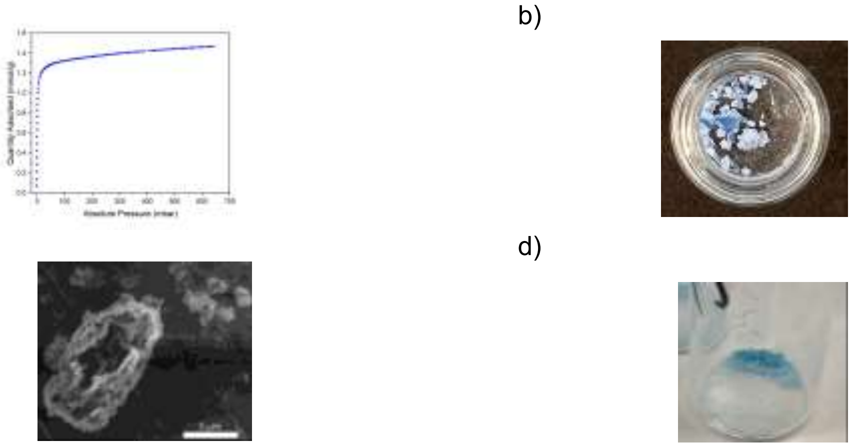

Figure 1 – a) CO2 Adsorption isotherm of Ultramicroporous MOF Monolith at 298 K b,d) As-synthesised MOF Monoliths c) SEM Image of Ultramicroporous MOF monolith showing packing of nanoscale crystallites.

Reduction of atmospheric concentrations of CO_2 by direct-air capture (DAC) is becoming an increasingly crucial topic of research in the fight against climate change.[1] Fluorinated ultramicroporous metal-organic frameworks (MOFs) with pore diameters below 4 Å are among materials with the strongest DAC performance, reaching uptakes of 1.3 mmol/ g at 400 ppm.[2] Exploiting physisorption interactions, CO_2 is adsorbed at low concentrations, while fluorination limits competitive adsorption from humidity. Typical synthesis of these MOFs proceeds via a solvothermal route to produce a powder.[2], [3] However, for the end-goal deployment of a DAC system, powders are challenging to handle in bulk, and suffer from poor volumetric performance due to the interstitial spaces between powder crystallite. Densification of powders to pellets via deployment of binders or mechanical compression can lead to the reduction of porosity and hence performance.[4] Here, we report two novel sol-gel synthetic routes, using only green solvents, to the densification of ultramicroporous MOFs to form self-shaping monolithic materials. These materials suffer only a minor reduction in gravimetric capacity but a boost to volumetric performance compared to the powder due to its significantly enhanced packing, seen in *fig 1c.* The strong volumetric performance and use of exclusively green solvents is promising for incorporation of these materials into a larger scale DAC system and is promising for the development of further DAC materials.

References

[1] S. Bose *et al.*, *Adv. Func. Mater.*, **2024** 34 (43), p. 2307478,
[2] [1] P. M. Bhatt *et al.*, *J. Am. Chem. Soc.*, **2016,** 138 (29), 9301–9307
[3] O. Shekhah *et al.*, *Nat Commun*, vol., **2014**, 5, 4228
[4] T. Tian, J. Velazquez-Garcia, T. D. Bennett, and D. Fairen-Jimenez, *J. Mater. Chem. A*, **2015,** 3 (6), 2999–3005

STRATEGIES TOWARDS TAILORING THE POROSITY OF METAL–ORGANIC FRAMEWORK (MOF) GLASSES

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Keywords: *Metal–organic frameworks, Porosity, Environmental remediation*

Metal–Organic Frameworks (MOFs) are a class of hybrid materials with continuous networks containing inorganic nodes/clusters which are linked by organic units. The framework structures can lead to the presence of cavities, that enable selective adsorption of guest molecules, classifying MOFs as porous materials.[1] Due to the wide variety of available building blocks, the structural and functional properties of MOFs can be finely tuned, offering significant potential for applications in environmental remediation. However, the low mechanical stability of crystalline MOFs presents challenges for processing techniques such as milling and sintering.[2] In addition to their crystalline forms, MOFs can also exist in amorphous glassy states. Notably, MOF glasses exhibit enhanced mechanical properties while retaining partial porosity, offering improved processability for practical applications.[1]

A family of MOFs, known as Zeolitic Imidazole frameworks (ZIFs) have long been a focus in literature due to their promising sorption and separation properties. ZIFs are frameworks with zeolite-type topology, consisting of tetrahedrally coordinated metal ions with imidazolate linkers.[3] A variety of ZIF glasses can be formed through melt-quenching, however, upon the formation of melt-quenched ZIF glasses, there is a significant decrease in porosity in contrast with their parent crystalline structure.[4] Hence, engineering and tailoring porosity are of interest in the development of MOF glasses. An avenue for tailoring the porosity of MOF glasses is by alternating the linkers, either by exchanging small quantities for different shapes and sizes or by creating missing linkers, thereby modifying the framework's properties and pore structure.[5] However, little investigation has been done regarding the formation of defects in a crystalline ZIF that subsequently undergoes glass formation, and how the pore structure is then affected. The study of defect-engineered pores through linker modifications in ZIF glasses is limited, however, due to the high glass-forming ability of ZIF-62, this method offers an interesting research avenue for tailoring the porosity of ZIF glasses.

By tuning the porosity of ZIFs through mixed linker incorporation, these materials could be tailored for specific applications, depending on the properties of the selected linkers and the resulting porous structure.[6] The crystalline material ZIF-62 can be made mechanochemically, with various ratios of substituted imidazolate linkers. Through thermal analysis methods, the thermal stability and glass-forming ability of these materials may be determined, and with gas sorption measurements the effect on porosity can be assessed. Mixed-linker strategies for tailoring the properties of MOF glasses offer a new avenue for the practical application of ZIF glasses, with the promise of precise control.

References

[1] J. McCarron, B. Turner, L. N. McHugh, *Advanced Engineering Materials*, 2402554.

[2] S. Li, S. Yu, S. M. Collins, D. N. Johnstone, C. W. Ashling, A. F. Sapnik, P. A. Chater, D. S. Keeble, L. N. McHugh, P. A. Midgley, D. A. Keen, T. D. Bennett, *Chemical Science* **2020**, *11*, 9910-9918.

[3] R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Science* **2008**, *319*, 939-943.

[4] T. D. Bennett, Y. Yue, P. Li, A. Qiao, H. Tao, N. G. Greaves, T. Richards, G. I. Lampronti, S. A. Redfern, F. Blanc, O. K. Farha, J. T. Hupp, A. K. Cheetham, D. A. Keen, *J Am Chem Soc* **2016**, *138*, 3484-3492.

[5] B. Bueken, N. Van Velthoven, A. Krajnc, S. Smolders, F. Taulelle, C. Mellot-Draznieks, G. Mali, T. D. Bennett, D. De Vos, *Chemistry of Materials* **2017**, *29*, 10478-10486.

[6] **Towards the Retention of Porosity in MOF Glasses via Mixed-Linker ZIFs**. B. Turner, A. Sispal, J. McCarron and L. N. McHugh*, 2025, in prep.

MOLECULAR LAYER DEPOSITION OF AlF-MOF FOR SELECTIVE CO_2 CAPTURE: A MOLECULAR LAYER DEPOSITION STUDY

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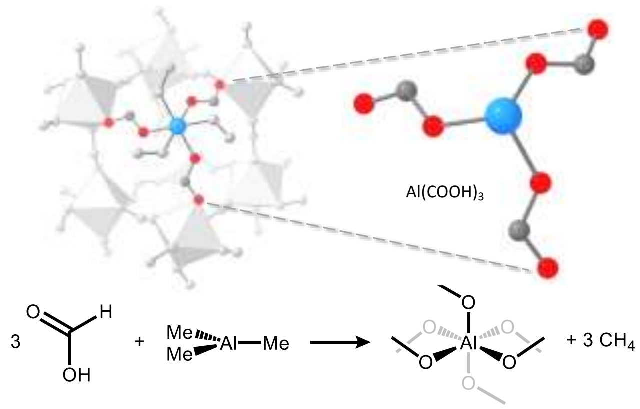
Keywords: *AlF-MOF, CO_2 capture, alucone, molecular layer deposition (MLD)*

Alucones are an exciting new class of hybrid inorganic-organic materials, made possible by molecular layer deposition (MLD), a precision-driven, layer-by-layer gas-phase method akin to atomic layer deposition (ALD). Using aluminum precursors like trimethylaluminum (TMA) and alcohol-functionalized organic ligands, alucones form porous, meso-ordered films with ultra-low dielectric constants, making them ideal for microelectronic spacers and masks. MLD's self-limiting nature ensures atomic-scale control over composition and structure.

In this work, we take MLD a step further, expanding beyond traditional alucones to deposit aluminum-containing metal-organic frameworks (MOFs) from the gas phase. With global demand for efficient CO_2 capture technologies, we undertook the deposition of MLD-deposited aluminum formate MOF (AlF-MOF), a material previously only accessible via solvothermal synthesis and known for its exceptional CO_2 selectivity.[1] Using a commercial ALD system (Picosun R200), we achieved gas-phase AlF-MOF deposition through an alternating TMA exposure sequence and formic acid on high-surface-area glass fiber.

AlF-MOF exhibits a high growth-per-cycle rate of 3.6Å, exceptional for ALD processes and comparable to other alucones. Mass spectrometry confirmed its polymeric nature, identifying aluminum triformate as the repeating structural motif. Spectroscopic techniques (FTIR and XPS) revealed the bridging interactions between formate ligands and aluminum centers, showing the characteristic node-and-bridge architecture of a MOF. Quartz crystal microbalance (QCM) analysis verified the precise, stepwise growth mechanism, while post-deposition exposure to formic acid vapour enabled crystallization, as confirmed by X-ray diffraction (XRD).

Most significantly, AlF-MOF demonstrated CO_2 capture capabilities when exposed to a CO_2/N_2 gas stream, confirming its selectivity for CO_2 and potential for industrial-scale implementation. Our findings pave the way for integrating MOFs into real-world environmental and industrial solutions, driving the next generation of sustainable materials forward. This presentation will demonstrate the intricate deposition mechanics, structural properties, and CO_2 adsorption performance of AlF-MOF and explore the landscape of MOF synthesis and carbon capture technology.



References

[1] H. A. Evans, D. Mullangi, Z. Deng, Y. Wang, S. B. Peh, F. Wei, J. Wang, C. M. Brown, D. Zhao, P. Canepa, A. K. Cheetham, Aluminum formate, $Al(HCOO)_3$: An earth-abundant, scalable, and highly selective material for CO_2 capture, Sci. Adv., **2022**, 8(44), eade1473.

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.

References

[1] H. Chen, J.B. Brubach, N.H. Tran, et al. *ACS Appl. Mater. Interfaces* **2023**, 16, 10, 12509–12520.

[2] L.L. Ling, W. Yang, P. Yan, M. Wang, H.L. Jiang, *Angew. Chem. Int. Ed.* **2022**, 61, 1–7.

[3] F. Li, J. Yang, X. Zhou, F. Han, Q. Huo, Q. Guan, W. Li, *Appl. Catal. B Environ*. **2024**, 355.

[4] Z. Fang, Z. Deng, X. Wan, Z. Li, X. Ma, S. Hussain, Z. Ye, et al. *Appl. Catal. B Environ*. **2021**, 296.

DEFEROXAMINE NANOCOMPOSITES FOR METAL BINDING

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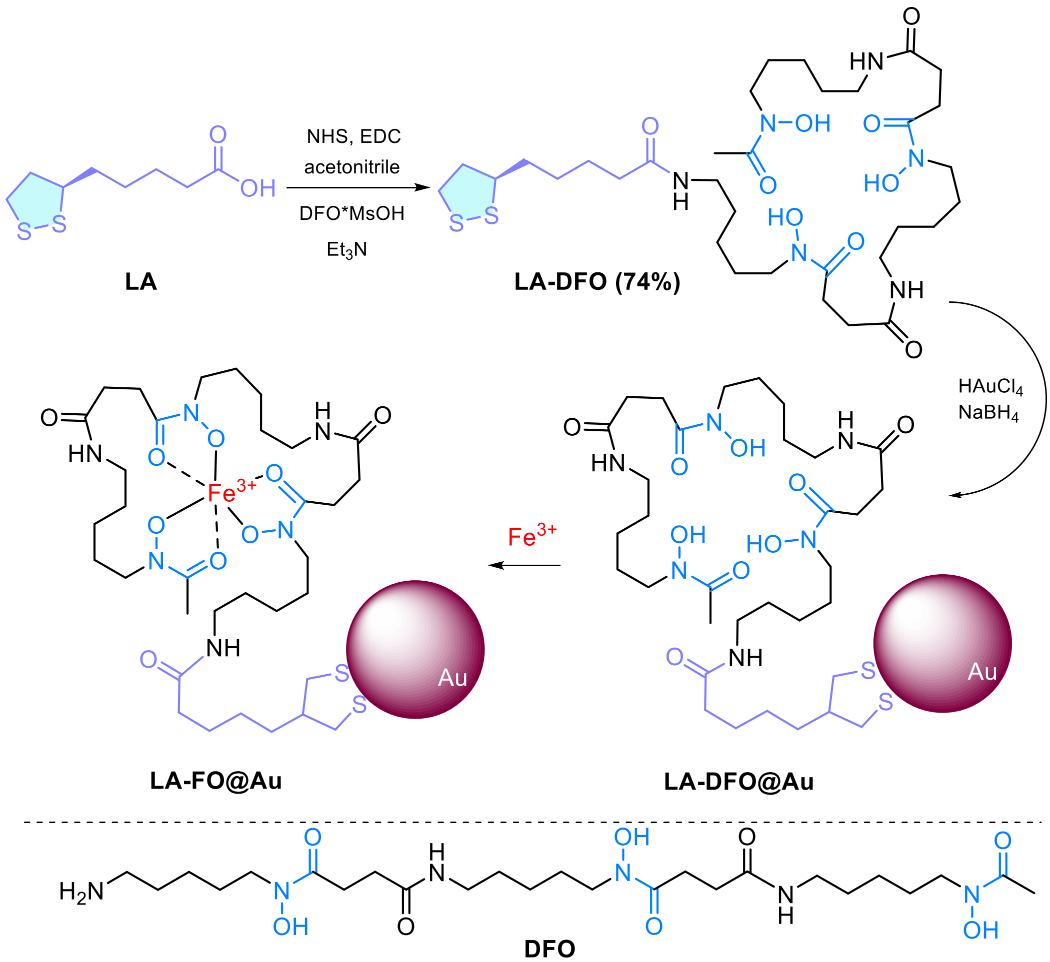
Keywords: *deferoxamine, lipoic acid, gold nanoparticles, adsorption, metals*

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.



References

[1] J.B. Porter, E.R. Huehns. *Baillieres Clin. Haematol*. **2009**, 2 (2), 459-474.

[2] Marzban, A., et al. *Can. J. Chem. Eng.* **2018**, 96, 107-112.

ELECTROCHROMISM IN A Cu-TRIAZOLE METAL-ORGANIC FRAMEWORK

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Keywords: electrochromism, metal-organic frameworks, spectroelectrochemistry, optoelectronic devices

Redox-active materials with electrochromic properties are considered a promising class of smart materials, holding great potential for the development of next-generation optoelectronic devices and sensors. Among these, metal-organic frameworks (MOFs) are gaining prominence due to their inherently high surface area and permanent nanoscale porosity, which facilitate efficient charge carrier transport to all active redox sites without causing lattice distortion.[1]

In this study, we investigate a metal-organic framework (MOF) composed of trinuclear copper and triazole (shown in Figure 1), employing a combination of optical spectroscopy and electrochemical techniques to identify the redox-active sites that enable electrochromic behavior in the material.

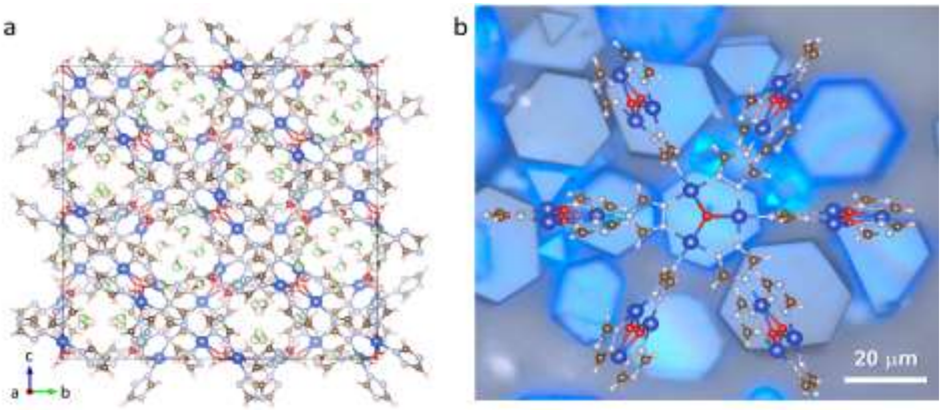

Figure 1: (a) Crystal structure of the Cu-triazole MOF, viewed along the [100] direction. (b) The trinuclear unit, with the six nearest neighbor units overlaid on a micrograph of Cu-triazole MOF microcrystals. [2]

References

[1] A. El Guerraf, et al. Adv. Electron. Mater. **2024,** 10, 2300854

[2] S. A. Siddiqui, A. Prado-Roller and H. Shiozawa, https://doi.org/10.26434/chemrxiv-2025-9tf68

ENGINEERING SYNERGISTIC BINDING SITES IN A ZIRCONIUM MOF FOR HIGHLY EFFICIENT CAPTURE 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.

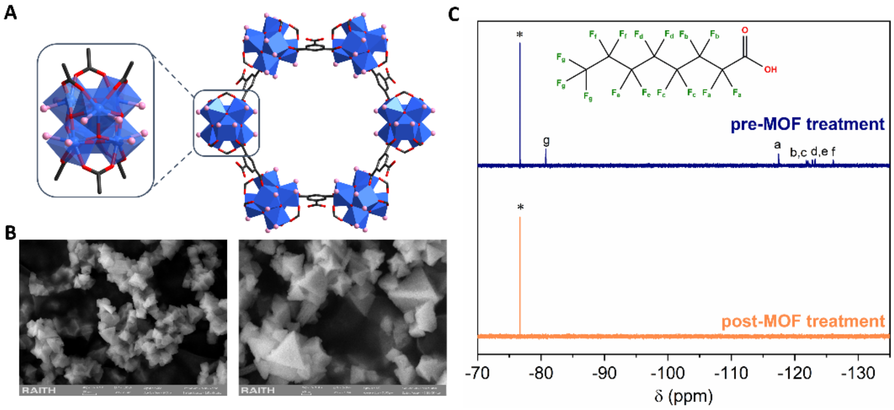

Figure 1. (A) The unsaturated cluster node and resulting hexagonal pores in MOF-808. (Zr: light blue, positions for potential metal insertion: pink). (B) SEM images of MOF-808 before (left) and after metalation (right). (C) ^{19}F-NMR spectra of an aqueous PFOA solution (C_0 = 100 ppm) before and after treatment with the modified MOF, revealing complete pollutant removal.

References

[1] S.Y. Wee, A.Z. Aris, *npj Clean Water* **2023**, 6, 57.
[2] E. Loukopoulos, S. Marugán-Benito, A. E. Platero-Prats et al. *Adv. Funct. Mater.* **2024**, 34 (51), 2409932.
[3] E. Loukopoulos, S. Marugán-Benito, A. E. Platero-Prats et al. **2025**, *submitted*.

STRUCTURAL REVELATION OF CYCLIC WATER TRIMERS IN A CUBOCTAHEDRAL CADMIUM-BASED MOF: SYNTHESIS, CHARACTERIZATION, AND HYDROPHILIC CONFINEMENT

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Keywords: *Metal-Organic Frameworks, Cyclic Water Trimer, and Crystallography*

Understanding water clusters, particularly cyclic trimers, is pivotal for unraveling hydrogen-bonding dynamics and condensation mechanisms. While cyclic $(H_2O)_3$ has been extensively studied in the gas phase and hydrophobic confinement, its structural elucidation within hydrophilic porous materials remains elusive.[1] Herein, we report the synthesis and characterization of a luminescent cuboctahedral cadmium-based metal-organic framework (MOF), $\mathbf{[\{Cd_{24}(HImtb)_{12}\}(H_2O)_4]_n}$, which encapsulates discrete cyclic water trimers on its triangular polyhedral faces (Figure 1). Single-crystal X-ray diffraction reveals a quasiplanar trimer stabilized by alternating O–H···O hydrogen bonds (2.8 Å O···O distance) with non-linear geometries, deviating from gas-phase configurations.[2] First-principles density functional theory (DFT) calculations confirm the trimer's global minimum energy structure within the MOF's metallosupramolecular cavities, highlighting host-guest interactions that enforce conformational constraints. Exposure of the MOF to ambient humidity induces bulk water adsorption, with in situ analysis revealing domain-specific water networks in the channels, underscoring its hydrophilic porosity. This work provides the first crystallographic evidence of cyclic water trimers in a MOF, bridging the gap between gas-phase clusters and condensed-phase hydration behavior. The findings advance the design of porous materials for water harvesting, molecular sensing, and studying confined aqueous systems.

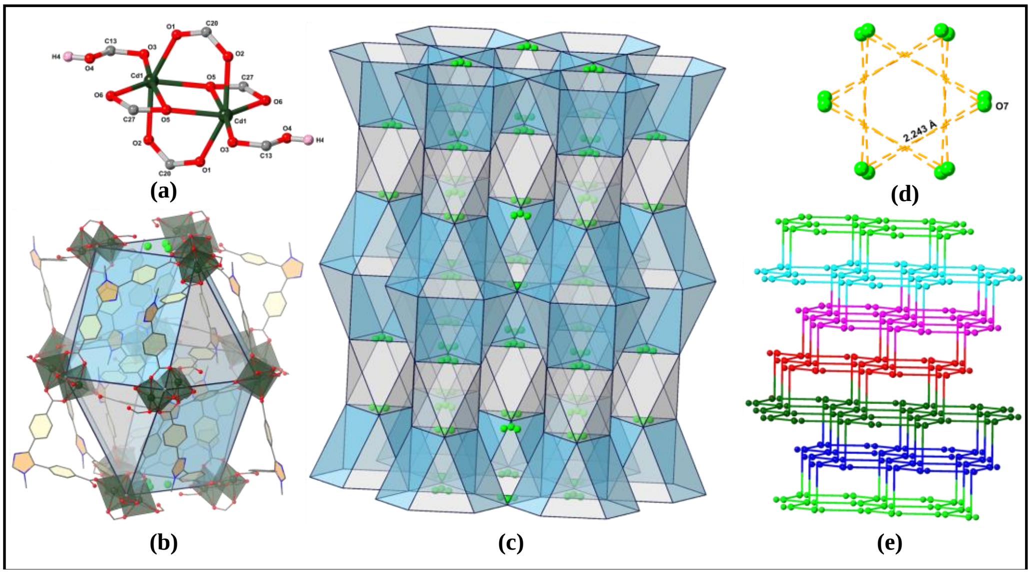

Figure-1: (a) SBU $[Cd_2(COO)_4(COOH)_2]$ (b) cuboctahedron shape of $\mathbf{[Cd_{24}(HImtb)_{12}]}$, (c) funnel-shaped representation of **Cd(HImtb)-MOF** with water trimer, (d) water trimers in the triangular faces of cuboctahedron and (e) six layered hexagonal sheet-like arrangement of water trimer.

References

[1] Keutsch, F. N.; Cruzan, J. D.; Saykally, R. J. *Chem. Rev.* **2003**, *103*, 2533–2577; Muñoz-Santiburcio, D.; Marx, D. *Chem. Sci.* **2017**, *8*, 3444–3452.

[2] Ramachandran, C. N.; Sathyamurthy, N. *Chem. Phys. Lett.* **2005**, *410*, 348–351; Slanina, Z.; Uhlík, F.; Nagase, S.; Akasaka, T.; Lu, X.; Adamowicz, L. *Chem. Phys. Lett.* **2018**, *695*, 245-248.

COPPER EMBEDDED Ti- METAL-ORGANIC FRAMEWORKS FOR PHOTOCATALYTIC H_2 PRODUCTION FROM FORMIC ACID

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Keywords: *metal-organic framework, hydrogen, heterogeneous photocatalysis, copper, formic acid*

Within the current environmental and energetic critical situation, finding more sustainable alternative energy resources has become a major challenge. In this regard, Ti-MOFs [4] are attracting more attention owing to their high promises as photocatalysts.[5]

Among the Ti-MOFs family, MIP-177(Ti)[3] is a phase-transformable titanium-carboxylate framework, exhibiting a dynamic structural adaptability and robust photoconductive properties. Its original form, MIP-177(Ti)-LT (MIP: Materials from Institute of Porous Materials of Paris; LT: Low Temperature), is composed of $Ti_{12}O_{15}$-clusters interconnected by tetracarboxylate linkers and decorated with formate ligands, while the thermal treatment induces the formate departure and, hence, the transformation of clusters to Ti oxide nanorods leading to the MIP-177(Ti)-HT (HT: High Temperature). These MOFs have been shown to enable efficient electron-hole pair generation and separation under light irradiation. This resulted in exceptional photoconductivity, surpassing conventional TiO_2 systems by minimizing charge recombination and maintaining performance through structural transitions, as well as very promising photocatalytic performances towards producing H_2 from water[6,7] and from formic acid (HCOOH, FA) aqueous solution.[1]

Building on these attributes, MIP-177(Ti) (LT anf HT forms) have been explored for photocatalytic hydrogen production from FA in vapor phase, a green hydrogen carrier with high volumetric capacity.[2] While pristine MIP-177(Ti) (HT & LT forms) predominantly follow the dehydration pathway (producing CO/H_2O) under UV light via Ti-oxo-units excitation, Cu-embedded MIP-177(Ti)s composites exhibit altered mechanisms. Indeed, post-metalation with Cu clusters (Ti/Cu > 10 at%) shifts MIP-177(Ti)s towards the dehydrogenation pathway (producing CO_2/H_2) under both UV and visible light. Interestingly, while the amounts of Cu seem tuning the reaction pathway, the presence of Cu is very likely promoting a charge transfer enabling the photocatalytic activity under visible light. In this communication, we will present more in details the MIP-177(Ti)s and their peculiar features together with a specific highlight on their photocatalytic activity for H_2 production from FA. Besides, the impact of Cu loading on the photophysical properties and catalytic mechanism will be also discussed.

References

[1] A. García-Baldoví, R. D. Angel et al. *Energy Environ. Sci.*, **2023**,*16*, 167-177.
[2] J. Eppinger, K-W. Huang, ACS Energy Lett., **2017**, *2*, 188-195.
[3] Wang, S., Kitao, T., Guillou, N. *et al. Nat Commun* **2018**, *9*, 1660.
[4] Hala Assi, Georges Mouchaham et al. *Chem. Soc. Rev.* **2017**, *46*, 3431-3452.
[5] Zahraa Abou Khalil, Raquel Del Angel et al. *J. Photochem. Photobio. C: Photochem. Rev.*, **2024**, *60–61*, 100680.
[6] B. Chen, A. Mansouri et al.. *Adv. Energy Mater.* **2025**, 2500211.
[7] A. Kuila, V. Diez-Cabanes et al. *Small* **2025**, *21*, 2407273.

SERS-ACTIVE HYBRID MATERIALS DERIVED FROM COVALENT ORGANIC POLYMERS AND GOLD NANOSTARS FOR SAXITOXIN DETECTION

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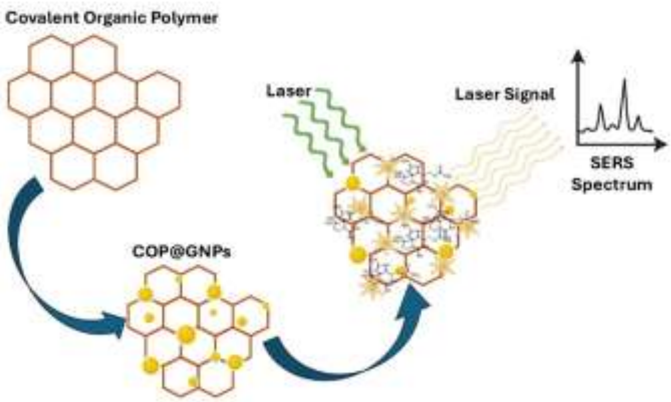
Keywords: *Covalent organic polymer*, *COP, Saxitoxin, SERS, Gold Nanoparticles*

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.



References

1 T. Wang, S. P. S. Fernandes, J. Araújo, X. Li, L. M. Salonen and B. Espiña, *J. Hazard. Mater.*, 2023, **452**, 131247.

2 L. R. Terry, S. Sanders, R. H. Potoff, J. W. Kruel, M. Jain and H. Guo, *Anal. Sci. Adv.*, 2022, **3**, 113–145.

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.

References

[1] Ali Saad, Subharanjan Biswas, Effrosyni Gkaniatsou, Clémence Sicard, Eddy Dumas, Nicolas Menguy, and Nathalie Steunou *Chem. Mater.,* **2021**, 33, 15, 5825–5849.

[2] José Navarro-Sánchez, Ana I. Argente-García, Yolanda Moliner-Martínez, Daniel Roca-Sanjuán, Dmytro Antypov, Pilar Campíns-Falcó, Matthew J. Rosseinsky, and Carlos Martí-Gastaldo *J. Am. Chem. Soc.***2017** *139* (12), 4294-4297

[3] Meili Ding, Robinson W. Flaig, Hai-Long Jiang and Omar M. Yaghi *Chem. Soc. Rev.* **2019**, 48, 2783-2828

INTESTINAL CROSSING OF METAL-ORGANIC FRAMEWORKS

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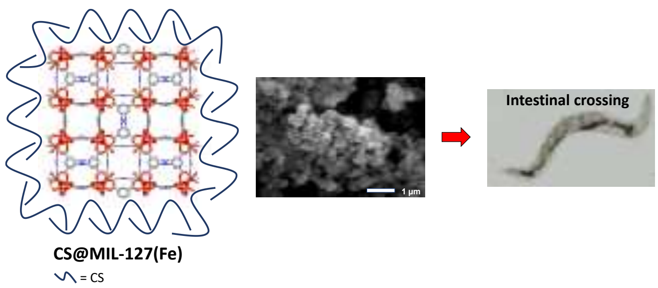
Keywords: *Metal-organic frameworks, intestinal crossing, drug delivery*

Drug delivery systems (DDSs) are one of the most promising tools for human healthcare owing to the temporary and local control of drug release. The design of new and intelligent treatments has resulted in the development of a new class of nontoxic carriers, known as metal−organic frameworks (MOFs). MOFs represent an interesting class of synthetic crystalline materials consisting of organic ligands bonded to metal ions in such a way as to generate a porous network accessible to host molecules. Particularly, biocompatible nanoscaled metal−organic frameworks (nanoMOFs) have been widely studied as DDSs, through different administration routes, with rare examples in the convenient and commonly used oral administration.

So far, the main objective of nanoMOFs as oral DDSs was to increase the bioavailability of the cargo, without considering the advantages of the MOF intestinal crossing. In this work, we propose to address for the first time the direct quantification and visualization of MOFs' intestinal bypass.[1] The microporous nanoMOF, MIL-127, exhibiting interesting properties as a nanocarrier (biocompatibility, large porosity, green and multigram synthesis, stability along the gastrointestinal tract) was selected and its outer surface was engineered with the biopolymer chitosan (CS@MIL-127) to improve the nanoMOF intestinal permeation. The biocompatibility and intestinal crossing of nanoMOFs is confirmed using Caenorhabditis elegans; these worms are able to ingest enormous amounts of nanoMOFs (>35 g per kg). Finally, an ex vivo intestinal model (rat) is used to further support the nanoMOFs' bypass across the intestinal barrier, demonstrating a fast crossing (only 2 h). This work on the intestinal crossing of intact nanoMOFs sheds light on the safe and efficient application of MOFs as oral DDSs.



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References

[1] S. Rojas, T. Hidalgo, Z. Luo. D. Ávila, A. Laromaine, P. Horcajada. ACS Nano 2022, 16, 5830-5838.

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.

[1] S. Dasgupta, E. Dumas, N. Steunou, C. Boissière, J. Rémy, I. Colson, A. Lattuati-Derieux et N. Timbart, *Techné*, **2023,** 56.

[2] K. Dedecker, R. Pillai, F. Nouar, J. Pires, N. Steunou, et al. *ACS Applied Materials & Interfaces*, **2018**, 10 (16), pp.13886 - 13894.

[3] S. Biswas, M. Haouas, C. Freitas, C. V. Soares, A. Al Mohtar, A. Saad, H. Zhao, G.Mouchaham, C.Livage, F. Carn, N. Menguy, G. Maurin, M. L. Pinto, and N. Steunou, *Chemistry of Materials* **2022,** 34 (21), 9760-9774

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.

References

[1] O. M. Yaghi, M. O'Keeffe, et al. *Nature* **2003**, 423, 705-714.
[2] S. Kitagawa, R. Kitaura, et al. *Angew. Chem. Int. Ed.* **2004**, 43, 2334-2375.
[3] D. L. Morse, J. W. Evenson *Int. J. Appl. Glass Sci.* **2016**, 7, 409-412.
[4] S. Horike, S. S. Nagarkar, et al. *Angew. Chem., Int. Ed.* **2020**, 59, 6652-6664.
[5] T. D. Bennett, S. Horike *Nat. Rev. Mater.* **2018**, 3, 431-440.
[6] N. Giri, S. L. James et al. *Chem. Eur. J.* **2007**, 13, 3020-3025.
[7] Z. Yang, S. Dai et al. *Chem. Sci.* **2024**,15, 17720-17738.

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.

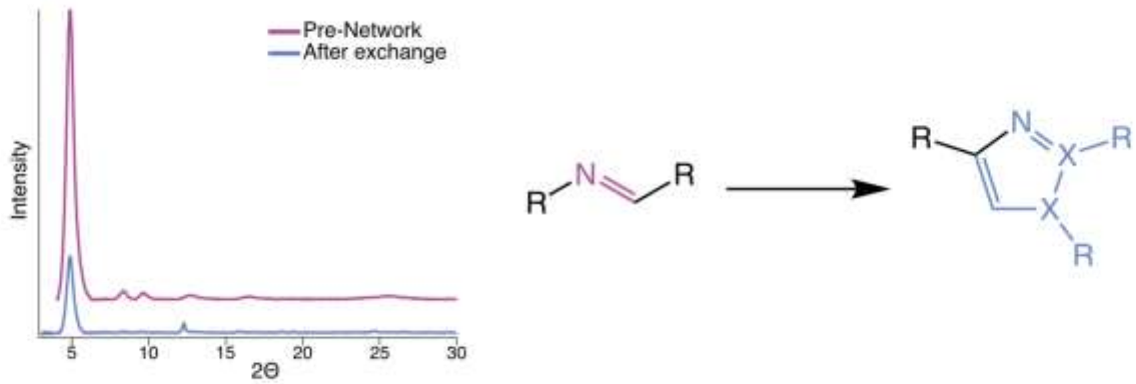

Figure: PXRD spectra of an imine linked pre-network as well as the thiazole linked product after exchange (left), and an imine linkage (purple) which we explore how to replace with heterocycles (blue).

References

1. Cao, L., Wu, H., Cao, Y., Fan, C., Zhao, R., He, X., Yang, P., Shi, B., You, X., & Jiang, Z. *Adv. Mater.* **2020**, 32 (52)

2. Mukherjee, D., Saha, A., Moni, S., Volkmer, D., and Das, M. C., *J. Am. Chem. Soc.* **2025**, 147 (7), 5515-5553

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.

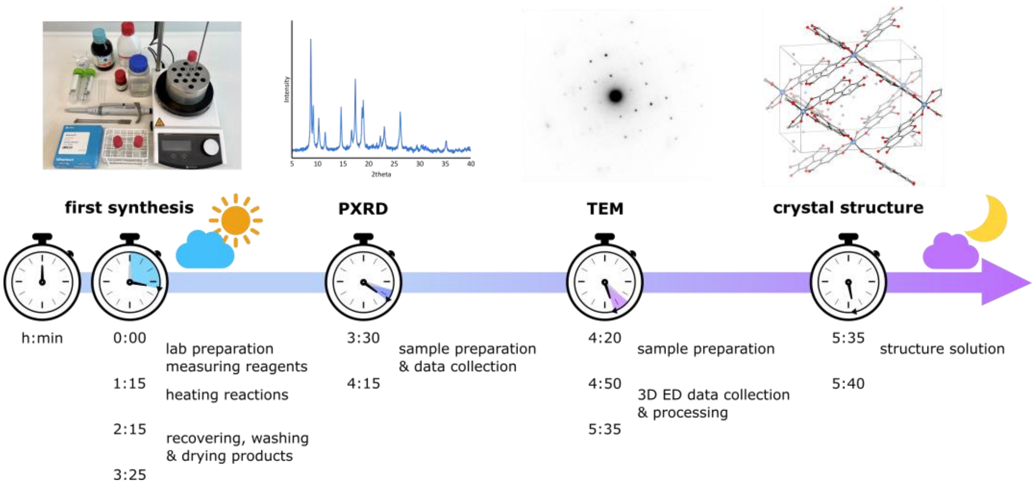

Figure. Schematic illustration of synthesis and structure solution of novel MOFs within in a single day.

References

[1] E. S. Grape, A. Lopez-Olvera, et al. *ChemRxiv* **2025**, doi:10.26434/chemrxiv-2024-n90rn-v2.

A COVALENT ORGANIC FRAMEWORK PLATFORM FOR COOPERATIVE PHOTOREDOX CATALYSIS

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Keywords: *Covalent Organic Framework, photoredox catalysis, dual catalysis*

Photoredox catalysis is an important development in organic synthesis, offering distinct reaction pathways under mild conditions. Most photocatalysts available to synthetic chemists are homogeneous metal-complexes or organic dyes, which raise issues of cost, recyclability, and waste production. Development of heterogeneous organic photocatalysts could address many of these issues but their application in organic synthesis is still in its infancy and underdeveloped. Dual catalysis between transition metal species and a photocatalyst can facilitate organic transformations that would otherwise require harsh conditions and stoichiometric reagents.[1]

Covalent organic frameworks (COFs) are crystalline, porous materials composed formed from organic building blocks. COFs exhibit tunable photochemical properties, and remarkable chemical and thermal stability, making them ideal heterogeneous catalysts that can tolerate a wide range of reaction conditions and substrates.[2] Indeed, they have seen application as photocatalysts in fields ranging from hydrogen production to photoredox organic transformations.[3] Furthermore, COFs can easily be functionalized with metals through chelation or physical adsorption, allowing them to act as hybrid materials for heterogeneous photoredox and transition metal dual catalysis.[4]

Here we present a COF photocatalyst platform for photoredox/transition metal dual catalysis for organic transformations. This photocatalyst provides access to common transition metal-mediated organic transformations in mild conditions with high yields while being recoverable and recyclable.

References

[1] Chan, A. Y.; Perry, I. B.; Bissonnette, N. B.; Buksh, B. F.; Edwards, G. A.; Frye, L. I.; Garry, O. L.; Lavagnino, M. N.; Li, B. X.; Liang, Y.; Mao, E.; Millet, A.; Oakley, J. V.; Reed, N. L.; Sakai, H. A.; Seath, C. P.; MacMillan, D. W. C. Metallaphotoredox: The Merger of Photoredox and Transition Metal Catalysis. *Chem. Rev.* **2022**, *122* (2), 1485–1542. https://doi.org/10.1021/acs.chemrev.1c00383.

[2] Chakraborty, A.; Roy, M.; Alam, A.; Adhikari, D.; Pachfule, P. Covalent Organic Frameworks as Heterogeneous Photocatalysts for Cross-Coupling Reactions. *Green Chem.* **2024**, *26* (18), 9619–9651. https://doi.org/10.1039/D4GC03467H.

[3] Yang, L.; Wang, J.; Zhao, K.; Fang, Z.; Qiao, H.; Zhai, L.; Mi, L. Photoactive Covalent Organic Frameworks for Catalyzing Organic Reactions. *ChemPlusChem* **2022**, *87* (11), e202200281. https://doi.org/10.1002/cplu.202200281.

[4] Fan, Y.; Kang, D. W.; Labalme, S.; Lin, W. A Spirobifluorene-Based Covalent Organic Framework for Dual Photoredox and Nickel Catalysis. *J. Am. Chem. Soc.* **2023**, *145* (46), 25074–25079. https://doi.org/10.1021/jacs.3c09729.

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.

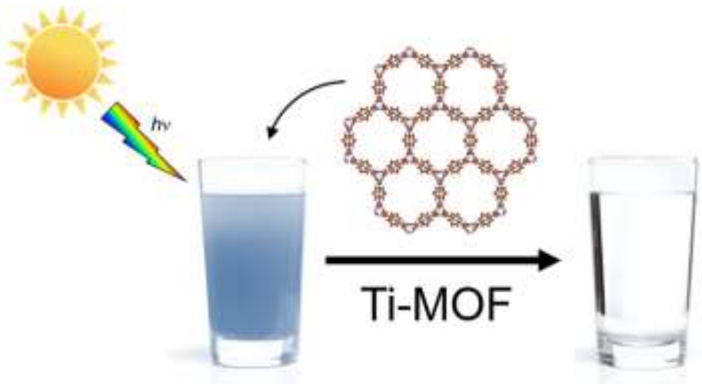

Figure 1 | The new layered, honeycomb-like titanium-based MOF shows efficient methylene blue adsorption and degradation under extended visible light irradiation (600 ± 40 nm).

References

[1] S. Assi, C. Serre, et al. *Chem. Soc. Rev.* **2017**, 46 (11), 3431–3452.

[2] B. Bueken, D. De Vos, et al. *Angew. Chem. Int. Ed.* **2015**, 54 (47), 13912–13917.

[3] H.L. Nguyen, O.M. Yaghi, et al. *JACS*. **2016**, 138 (13), 4330–4333.

[4] N.T.T. Nguyen, O.M. Yaghi, et al. *JACS*. **2015**, 137 (49), 15394–15397

ON THE INFLUENCE OF Cu-Ox VERSUS Cu-N_3 MOTIFS AND OXYGENATED GUEST MOLECULES IN Cu(I) CONTAINING UiO-67 MOFS FOR C-H ACTIVATION

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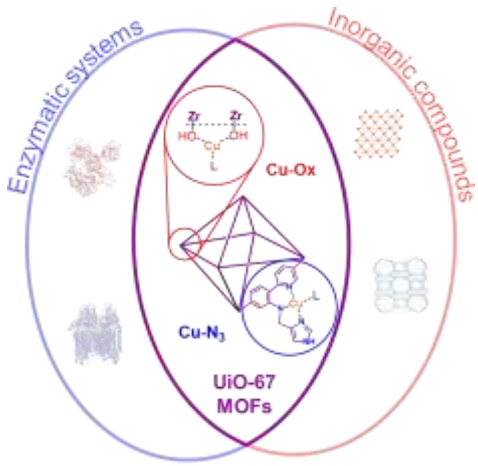
Keywords: *UiO-67 MOFs, Catalysis, heterogenisation, guest addition, Copper*



Enzymatic oxidants, more specifically, oxygenases are desirable models for the development of high-performance catalysts.[1] Several monooxygenases, such as the Lytic polysaccharide monooxygenases (LPMOs) and the particulate methane monooxygenase (pMMO), include copper as cofactor.[2,3] The active site on both those enzymes is composed of a copper center coordinated to histidine molecules.[2,3] In addition to the histidine residues (1st coordination sphere), these enzymes feature an additional oxygenated residue in their close vicinity, from tyrosine (LPMO) and asparagine (pMMO). These oxygenated groups have been shown to influence the kinetics of the catalytic oxidation cycle.[4,5] In addition, classic heterogeneous catalysts containing only metal-oxygen bonds such as metal oxides and zeolites have been immensely researched for C-H activation.[6] In order to compare and reproduce these enzymatic coordination environments against the inorganic ones, metal-organic frameworks (MOFs) functions as the ideal common matrix, as both said coordination moieties can be obtained.[7]

In this contribution, the heterogenization of an active copper site bearing histidine-like complex and an inorganic like site grafted on the Zr_6O_6 nodes were recreated into a UiO-67 MOF post-synthetically. The composition and defectivity of the materials synthesized were determined using TGA and liquid-phase ^{1}H-NMR on the frameworks. To the functionalized and pristine materials, copper incorporation using $Cu(MeCN)_4PF_6$ as a precursor was conducted under inert atmosphere to preserve the Cu(I) oxidation state. The Cu:Zr ratio was determined by MP-AES analysis of the MOFs.

To provide the oxygenated groups, present in the enzymatic residues, propionamide (C=O) was selected to be infused into the MOF. Propionamide was detected after impregnation into Cu-containing MOFs, but not in pristine MOF, suggesting its coordination to the copper ions. The oxidation state of the copper species, and the incorporation of the guest molecules within the MOF was investigated with XAS and NMR (liquid and solid state). The Cu(I) oxidation state was confirmed and the infusion and coordination of propionamide to Cu was verified.

Lastly, cyclohexene oxidation using *t*BuOOH as the oxidant allowed us to assess the catalytic activity of the copper-bearing MOFs. The cuprous ions grafted on the hexanuclear Zr nodes showed superior catalytic activity for cyclohexene oxidation compared to those coordinated to the enzyme-like motif of the bespoke linker, exhibiting a preference for the allylic oxidation of the substrate.

[1] X. Engelmann, I. Monte-Pérez and K. Ray, *Angew. Chem. Int. Ed.,* 2016, **55**, 7632–7649.
[2] R. J. Quinlan, M. D. Sweeney, L. Lo Leggio, *et al.*, *Proc. Natl. Acad. Sci.*, 2011, **108**, 15079–15084.
[3] R. L. Lieberman and A. C. Rosenzweig, *Nature*, 2005, **434**, 177–182.
[4] A. Paradisi, E. M. Johnston, M. Tovborg, *et al.*, *J. Am. Chem. Soc.*, 2019, **141**, 18585–18599.
[5] K. R. Hall, C. Joseph, I. Ayuso-Fernández, *et al.*, *J. Am. Chem. Soc.*, 2023, **145**, 18888–18903.
[6] N. F. Dummer, D. J. Willock, Q. He, *et al.*,*Chem. Rev.*, 2023, **123**, 9, 6359–6411.
[7] I. Gerz, E. S. Aunan, V. Finelli, *et al.*, *Dalton Trans.*, 2024,**53**, 8141-8153.

NONLINEAR OPTICAL MOF THIN FILM

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Keywords: metal-organic frameworks, thin films, nonlinear optics

Metal-organic frameworks (MOFs) are a class of crystalline porous organic-inorganic hybrid materials constructed by metal nodes and organic linkers with strong coordination bonding, which attract great attention in the applications of adsorption/separation1-3, catalysis, biology, optics, electronics and so on due to their structural and functionalities designability. In particular, MOFs with highly conjugated π-electron delocalized system show excellent performance in third-order nonlinear optics (NLO), exhibiting potential applications in optical limiting (OL), optical switching, and mode-locking. Moreover, MOF thin films have been used in various applications. In particular, the liquid-phase epitaxy (LPE) layer by layer method has been widely used for preparation of MOF thin films on substrate surfaces (also called surface-coordinated MOF thin films, SURMOFs) which showed controllable thickness, a homogeneous surface, compactness, controllable growth orientation and effective loading of functional guests into MOF pores. Such highquality MOF thin films offer an opportunity for tuning the third-order NLO performance and enhancing practical device applications, such as pulse compression, Q-switching, modelocking and optical limiting.

In our study, we reported a series of MOF thin films for studying the NLO by choosing the types of metal chelated ligands, constructing interpenetrated framework, breaking structural symmetry, regulating electric field stimulation and tuning the thickness of MOFs film as well as effectively optimized with external stimulations for expanding practical optical applications. Our finding not only offers new NLO material but also to provide new insight to understand nonlinear optical behavior, which is of great significance in optical applications.

References

[1] Z.-B. Jin, G. Zhou, Y. Han, Z. Huang, Z.-G. Gu*, J. Zhang, J. Am. Chem. Soc., 2024, 146, 36, 25016.
[2] X. Yang, N. Li, C. Li, Z. Jin, Z. Ma, Z.-G. Gu, J. Zhang, J. Am. Chem. Soc., 2024, 146, 23, 16213.
[3] H. Chen, Z.-G. Gu*, J. Zhang, J. Am. Chem. Soc. 2022, 144, 16, 7245.
[4] D.-J. Li, Q. Li, Z. Wang, Z.u Ma, Z.-G. Gu, J. Zhang J. Am. Chem. Soc. 2021, 143, 17162.
[5] Ma, Z. Li, Q., Wang, Z. Gu, Z.-G.; Zhang J. *Nat. Commun.*, 2022, 13, 6347.

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.

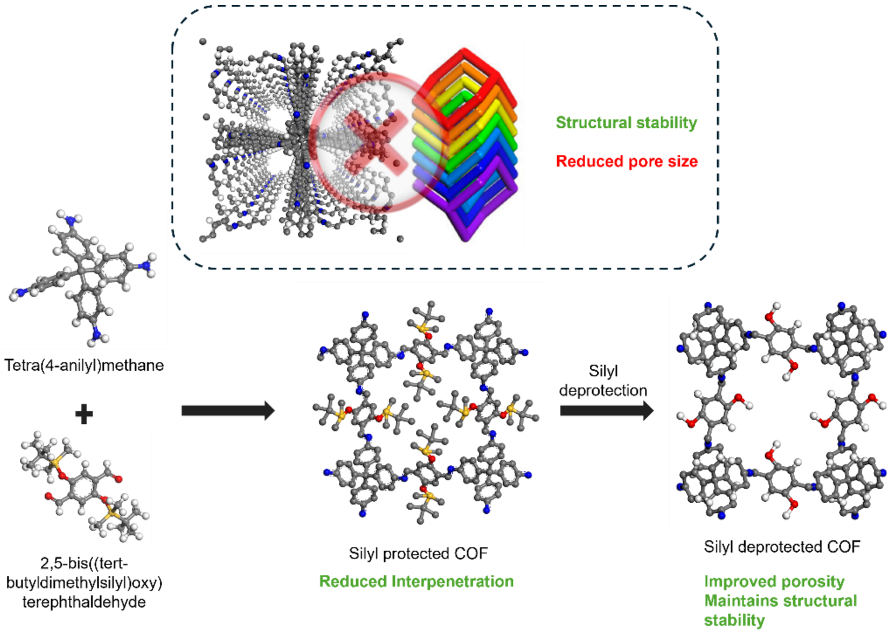

Figure 1: Schematic representation of a strategy to reduce interpenetration in COFs using bulky silyl-protected linkers. Incorporation of bulky groups limits interpenetration, and subsequent deprotection enhances porosity while maintaining structural integrity.

References

[1] Hani M. El-Kaderi, Joseph R Hunt, José L. Mendoza-Cortés et al. *Science* **316**, 268-272 (**2007**).

[2] Tianqiong Ma, Jian Li, Jing Niu et al. *J. Am. Chem. Soc.* **2018**, 140, 22, 6763–6766E.

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.

References

[1] W. Liang, et al. *Chem. Rev*. **2021**, 121(3), 1077-1129.

[2] M. Velásquez-Hernández, et al. *Coord. Chem. Rev.* **2021**, 429, 213651.

[3] W. Liang, et al. *J. Am. Chem. Soc.* **2019**, 141, 2348.

[4] P. Horcajada, et al. *Nat. Mater*. **2009**, 9(2), 172-178.

[5] S. Kitagawa, et al. *Angew. Chem., Int. Ed*. **2004**, 43(18), 2334-2375.

[6] H. Deng, et al. *Sci*. **2010**, 327(5967), 846-850.

[7] Y. Li, et al. *J. Am. Chem. Soc*. **2021**, 143, 15378.

[8] Y. Feng, et al. *Chin. J. Catal*. **2024**, 60, 386-398.

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]

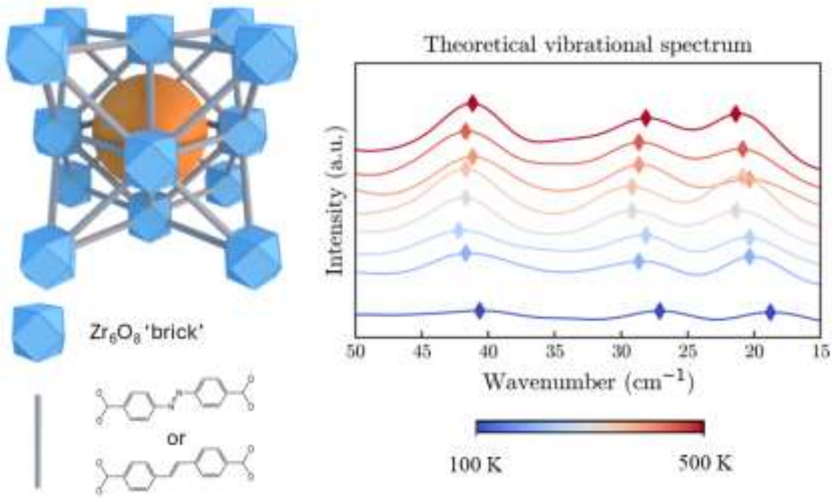

Figure 1: Left: topology of mixed-linker Zr-MOF system. Right: Vibrational spectra at different temperatures from molecular dynamics simulations, the diamond symbols indicate the local maxima of the spectra. From low to moderate temperatures, the peaks move to higher wavenumbers. From moderate to high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

References

[1] C. S. Coates et al. *Mater. Horiz.,* **2019**, 6, 211-218.

[2] A. D. Yeganeh et al., Mechanical Properties of Mixed-linker Zr-based Metal-organic Frameworks with Frustrated Backbones (**2025**) [unpublished manuscript]

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.

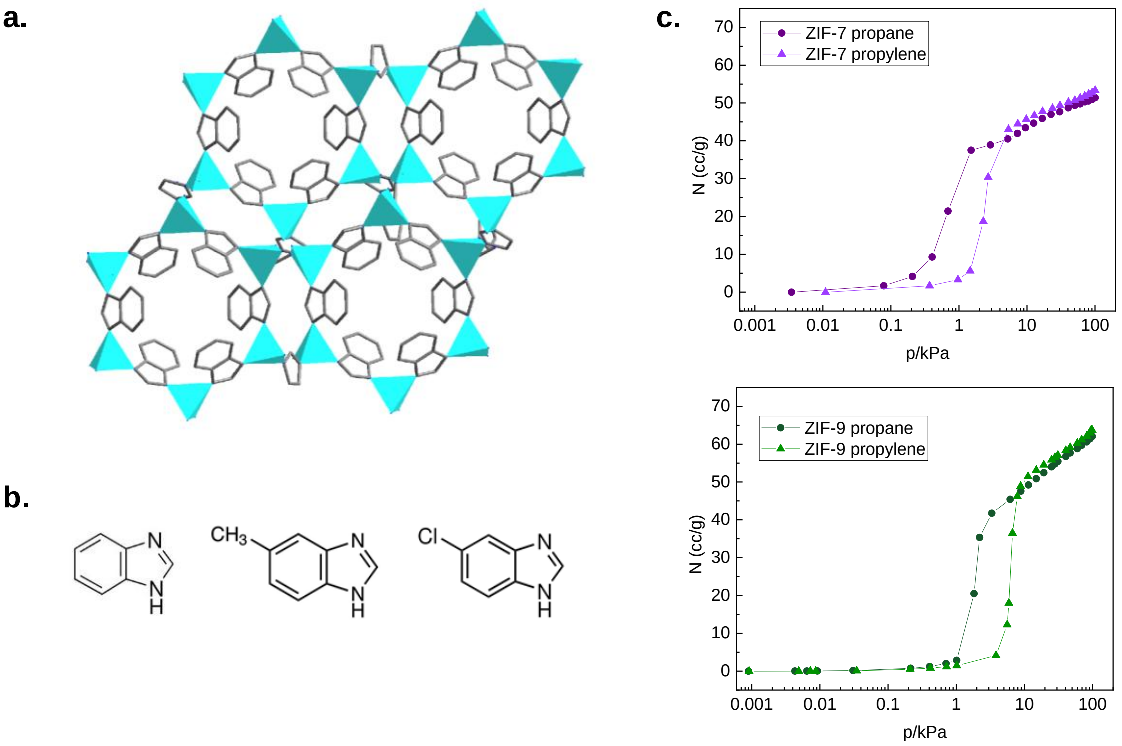

Figure 1. (a) ZIF-7 3D **sod** structure. (b) Benzimidazole linker and functionalized 5-methylbenzimidazole and 5-chlorobenzimidazole. (c) Propane and propylene adsorption isotherms for ZIF-7(Zn) and ZIF-9(Co).

References

[1] Kuah, W. C *et al. Industrial and Engineering Chemistry Research*, **2018**. 57(18), 6451–6463.
[2] Senkovska, I. *et al. Advanced Materials*, **2025,** 2414724.
[3] van den Bergh, J *et al*. *Chemistry – A European Journal,* **2011,** 17(32), 8832–8840.

CLUSTER-BASED LEARNING TO DESCRIBE DISORDERED METAL-ORGANIC FRAMEWORKS AT THE MESOSCALE

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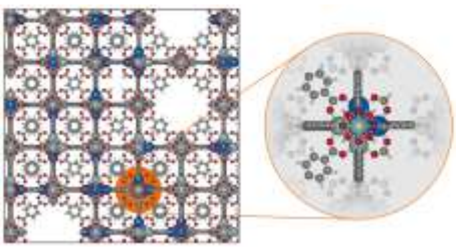
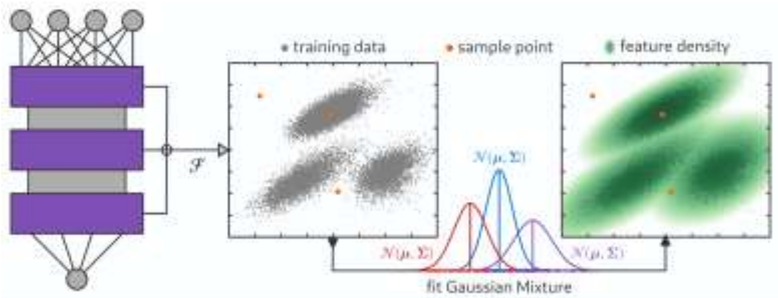
Keywords: *metal-organic frameworks, spatial disorder, machine learning potentials*

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.



References

[1] H. Furukawa, K.E. Cordova et al. *Science*. **2013**, 341, 1230444

[2] A. K. Cheetham, T. D. Bennet et al. *Dalton Trans*. **2016**, 45, 4113-4126

[3] P. Dobbelaere, S. Vandenhaute et al. *arxiv*. **2025**, arXiv:2504.03881 (Preprint)

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 ($T < 100$K) 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.

References

[1] M. Raimondo, L. Donà, B. Civalleri, "r^{2}SCAN-based composite methods for solid state calculations" in preparation

[2] J. W. Furness et al. J. Phys. Chem. Lett. 2020, 11(19), 8208–8215.

[3] J. Laun et al. J. Comp. Chem. 2021, 42(15), 1064–1072.

[4] S. Grimme et al. Chem. Rev. 2016, 116, 5105–5154.

[5] R. Sure et al. J. Comp. Chem. 2013, 34(19), 1672-1685.

[6] A. Erba et al. J. Chem. Theory Comput. 2023, 19, 6891−6932.

[7] A.S. Rosen et al. Matter 2021, 4, 1578-1597.

[8] I. Batatia et al. https://doi.org/10.48550/arXiv.2206.07697,https://doi.org/10.48550/arXiv.2401.00096

ATOMIC-LEVEL INSIGHTS INTO CO_2 ADSORPTION IN A DEFECTIVE AMINO-FUNCTIONALIZED MOF THROUGH *IN SITU* HR-PXRD

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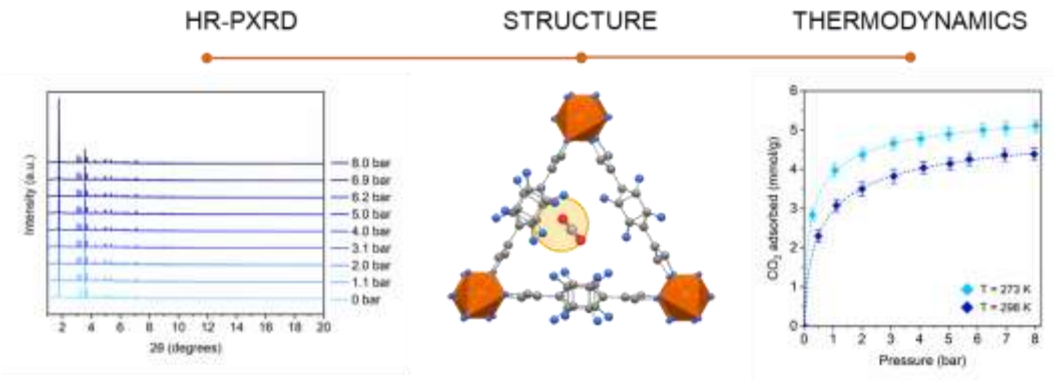
Keywords: *powder X-ray diffraction, CO_2 adsorption, in situ characterization.*

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.



References

[1] E. López-Maya, C. Montoro, et al. *Adv. Funct. Mater*. **2014**, 24, 6130-6135.

[2] R. Vismara, S. Terruzzi, et al. *Adv. Mater*. **2024**, 36, 2209907.

[3] Z. R. Herm, B. M. Wiers, et al. *Science* **2006**, 340, 960-964.

[4] A. Nuhnen and C. Janiak. *Dalton Trans*. **2020**, 49, 10295-10307.

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.

References

[1] J. R. Long, et al., Chem. Soc. Rev. **2009**, 38, 1213–1214.

[2] S. R. Batten, et al., Pure Appl. Chem. **2013**, 85, 1715–1724.

[3] S. Ma, et al., Chem. Commun. **2010**, 46, 44–53.

[4] H. Li, et al., Mater. Today **2018**, 21, 108–121.

[5] M. A. Nasalevich, et al., CrystEngComm **2014**, 16, 4919–4926.

[6] P. Kumar, et al., TrAC, Trends Anal. Chem. **2015**, 73, 39–53.

[7] V. Stavila, et al., Chem. Soc. Rev. **2014**, 43, 5994–6010.

[8] M. R. Ryder, et al., ChemPlusChem **2018**, 83, 308–316.

[9] P. Horcajada, et al., Nat. Mater. **2010**, 9, 172–178.

[10] P. Horcajada, et al., Chem., Int. Ed. **2006**, 118, 6120–6124.

[11] G. Férey, et al., Angew. Chem. **2004**, 116, 6456–6461.

[12] G. Férey, et al., Science **2005**, 309, 2040–2042.

[13] L. Donà, et al., J. Chem. Phys. **2019**, 151, 121101.

[14] S. Grimme, et al., J. Chem. Phys. **2010**, 132, 154104.

[15] H. Kruse, et al., J. Chem. Phys. **2012**, 136, 154101.

[16] A. Erba, et al., J. Chem. Theory Comput. **2023**, 19, 6891−6932.

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.

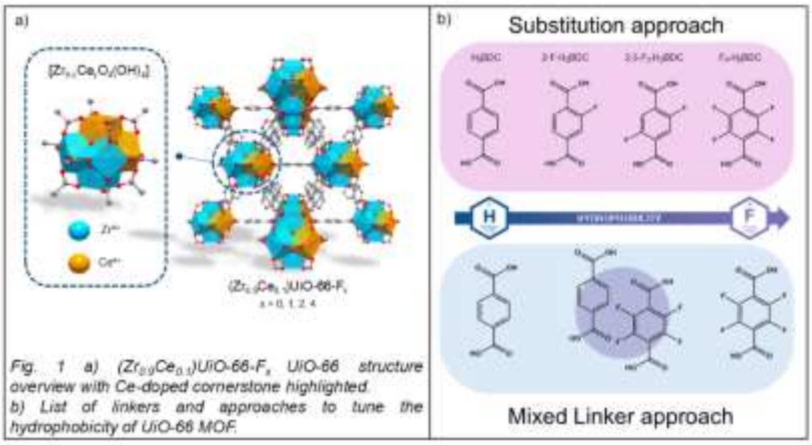

Fig. 1 a) $(Zr_{0.9}Ce_{0.1})$UiO-66-F_x UiO-66 structure overview with Ce-doped cornerstone highlighted. b) List of linkers and approaches to tune the hydrophobicity of UiO-66 MOF.

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.

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.

References

[1] K. A. Lomachenko, J. Jacobsen, A. L. Bugaev, et al., *J Am Chem Soc* **2018**, *140*, 17379–17383.
[2] L. Huo, L. Wang, J. Li, et al., *Journal of CO2 Utilization* **2023**, *68*, 102352.
[3] S. Rojas-Buzo, D. Salusso, A. Jouve, et al., *Applied Catalysis B: Environment and Energy* **2024**, *346*, 123723.
[4] K. Xuan, Y. Pu, F. Li, et al., *Journal of CO2 Utilization* **2018**, *27*, 272–282.
[5] S. Rojas-Buzo, D. Salusso, F. Bonino, M. C. Paganini, S. Bordiga, *Mater Today Chem* **2023**, *27*, 101337.

THEORETICAL INVESTIGATION OF MOF'S LINKER FUNCTIONALIZATION FOR ENHANCING DESALINATION

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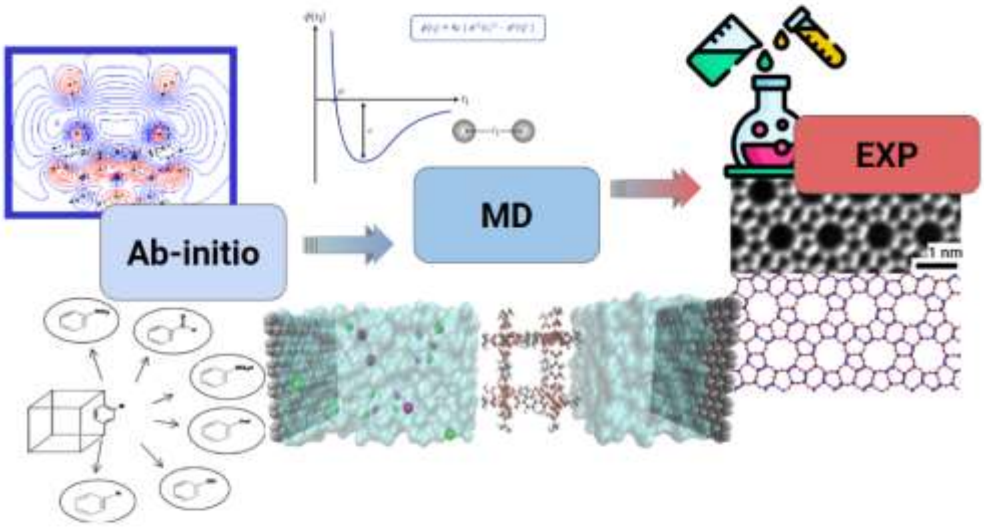
Keywords: *Metal–Organic Frameworks; Water; Salt; Desalination; Functionalization; Ab initio; Molecular Dynamics*



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.

References

[1] Giappa, R.M.; Papadopoulos, A.G.; Klontzas, E.; Tylianakis, E.; Froudakis, G.E. Linker Functionalization Strategy for Water Adsorption in Metal–Organic Frameworks. Molecules 2022, 27, 2614.

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.

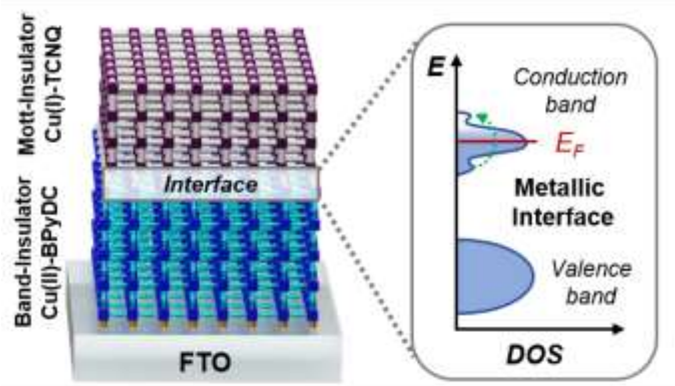

Figure 1: Schematic representation of heterostructure MOF thin film of Band-insulator (Cu(II)-BPyDC) and Mott-insulator (Cu(I)-TCNQ) indicating metallic-interface.

References

[1] P. Sindhu, K.S. Ananthram, A. Jain, K. Tarafder, N. Ballav, Charge-transfer interface of insulating metal-organic frameworks with metallic conduction. *Nat. Commun.* **2022**, 13, 7665.

[2] P. Sindhu, S. Saha, U. Bhoi, N. Ballav, Bistable Interface: Reversible Switching of Rectifying to Nonrectifying Current Across Heterostructured Thin Films of MOFs. *Adv. Funct. Mater.* **2024**, *34*, 2312515

[3] P. Sindhu, K.S. Ananthram, A. Jain, K. Tarafder, N. Ballav, Insulator-to-metal-like transition in thin films of a biological metal-organic framework. Nat. Commun. 2023, 14, 2857

[4] P. Sindhu, A. Prasoon, S. Rana, N. Ballav, Emergent Interface in Heterostructured Thin Films of Cu(II) and Cu(I) Coordination Polymers. J. Phys. Chem. Lett. 2020, 11, 15, 6242–6248

[5] P. Sindhu, N. Ballav, Thin Films of MOF-on-Guest@MOF: A Simple Strategy of Designing Electronic Heterostructures. Inorg. Chem. 2023, 62, 28, 10887–10891

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.

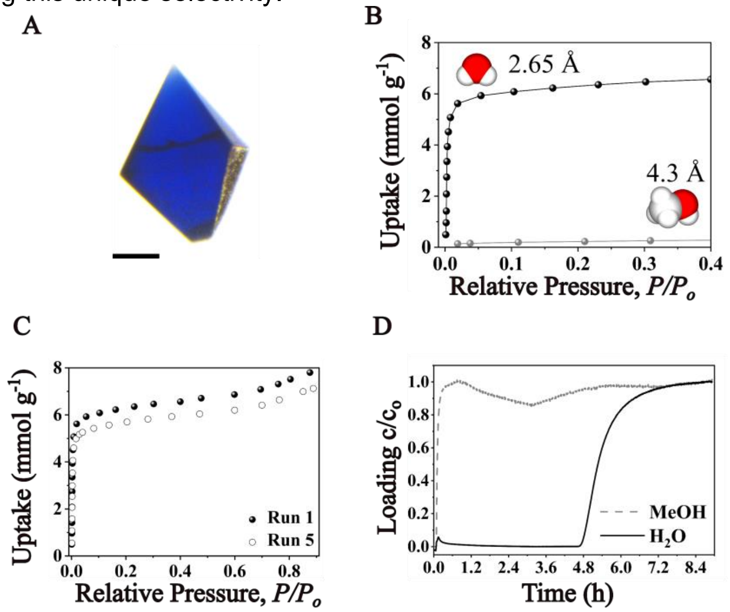

Figure 1 (A) Representative optical microscope image of the single-crystalline peptide-based coordination polymer (scale-bar 20 μm). (B) Single component vapor adsorption isotherms for Water (black) and Methanol (grey) vapors (inset: kinetic diameters for the respective molecules). (C) Water vapor adsorption 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.

[1]Pei-Qin Liao, Ning-Yu Huang, Wei-Xiong Zhang, Jie-Peng Zhang, Xiao-Ming Chen, Controlling guest conformation for efficient purification of butadiene. Science 356, 1193-1196 (2017)
[2]Michael Tsapatsis,Toward High-Throughput Zeolite Membranes. Science 334,767-768 (2011)
[3]Patent filed, Manuscript in preparation.

MACHINE LEARNING DERIVED ATOMIC CHARGES OF METAL- ORGANIC FRAMEWORKS FROM A WELL-CURATED SMALL DATASET

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Keywords: *Machine learning, atomic charges, dataset engineering*

The modular structure and chemical versatility of metal-organic frameworks cover a vast chemical space. High-throughput computational screening is then useful to explore all the chemical and physical properties of such materials but low-cost computational methods such as tailored force-fields are needed to speed up the calculations [1]. To this end, accurate atomic charges are crucial for correctly predicting long-range electrostatic interactions. These can either be derived from quantum-mechanical calculations or generated on the fly through simplified geometric schemes or, more recently, by Machine Learning (ML) predictive models. The latter requires suitable databases of structures and properties to be used to train the ML model. Several databases of MOFs and their properties are now available such as CoReMOF [2], QMOF [3] and ARC-MOF [4].

In this work, we present the results of predicting atomic charges from a reliable small dataset of MOFs as derived from the QMOF database. We trained several ML models by using XGBoost and RandomForest with atomic and environmental descriptors. The QMOF database, which contains more than 20000 cleaned-up experimental structures (< 300 atoms in the unit cell) for which DDEC charges are available, was analysed to understand how the size and composition (i.e. metal ion types) of the training dataset affect the prediction of the atomic charges. We built datasets with randomly extracted structures ranging from 500 to 3000 MOFs and compared them with a more balanced dataset of about 1500 MOFs with an equal composition in terms of different metal ions.

This strategy allowed us to achieve good results with a reduced number of MOFs compared to the largest dataset (i.e.165144 vs 2307962 charges of the entire QMOF database) with the RandomForest ML models giving better performance to XGBoost. We were also able to predict with higher accuracy the charges of the metallic species in the node which are less abundant compared to the other species present in the structure (e.g. H, C, O and N). Based on this result, Hirshfeld-I atomic charges were calculated using the low-cost hybrid HF/DFT sol-3c composite methods [5] on the reduced dataset by using the CRYSTAL [6] program, and a ML model was then trained. As a further validation test, the ML-based atomic charges were combined with UFF [7] to predict adsorption isotherms using the RASPA code [8].

References

[1] P. Xu, X. Ji, M. Li, e W. Lu, npj Comput. Mater. 9 (2023) 42

[2] Y. G. Chung, E. Haldoupis, B. J. Bucior, et al. (2020). CoRE MOF 2019 Dataset (1.1.3).

[3] J. Burner et al., Chem. Mater., 35 (2023) 900.

[4] A. S. Rosen et al., Matter 4 (2021) 1578–1597.

[5] L. Donà, J. G. Brandenburg, B. Civalleri, J. Chem. Phys., 156 (2022) 121101

[6] A. Erba, J.K. Desmarais, S. Casassa, B. Civalleri, L. Donà, et al. J. Chem. Theory Comput. (2023) 19, 6891−6932

[7] A. K. Rappe, et al., J. Am. Chem. Soc. 114 (1992) 10024–10035.

[8] D. Dubbledam, et al., Mol. Simul. 42 (2016) 80–101.

ENGINEERING PHOTOSWITCHING DYNAMICS IN 3D PHOTOCHROMIC METAL-ORGANIC FRAMEWORKS THROUGH METAL-ORGANIC POLYHEDRON DESIGN

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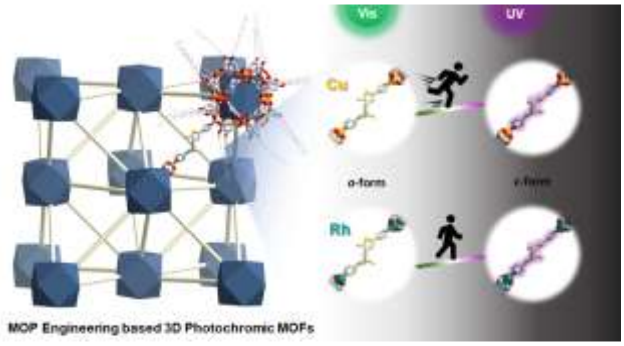
Keywords: *Photochromic MOFs, Metal-organic polyhedrons, Photoisomerization, Kinetics*

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.



References

[1] J. D. Evans, V. Bon, I. Senkovska, H.-C. Lee, S. Kaskel, *Nat. Commun*. **2020**, *11*, 2690.

[2] S. Horike, S. Shimomura, S. Kitagawa, *Nat. Chem*. **2009**, *1*, 695.

[3] E. Jin*, V. Bon, S. Das, A. D. D. Wonanke, M. Etter, M. A. Karlsen, A. De, N. Bönisch, T. Heine, S. Kaskel*, *J. Am. Chem. Soc*. **2025**, *147*, 8568–8577.

THE FORMATION AND PROPERTIES OF HYBRID GLASS MATERIALS

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Keywords: *hybrid glasses, metal–organic frameworks, hybrid organic–inorganic perovskites, amorphous materials.*

The discovery of a new family of hybrid glass materials, based upon metal organic frameworks (MOFs) and hybrid organic-inorganic perovskites (HOIPs), has opened a completely new avenue for investigation and innovation across the chemistry and materials fields.[1] This is due to the fact that, although amorphous in the long-range, these materials retain short-range order suggesting that properties of their crystalline forms may be carried over during the transformation between states.

Accessing these glassy states is most commonly achieved by means of melt-quenching the materials from their molten liquid states. Achieving a successful melt can sometimes be difficult due to the short temperature region between the molten state and the onset of decomposition. To avoid this issue, new synthesis and processing techniques must be employed. One possible route to accessing the glass states more easily is by the use of flux melting. This is the process by which one component of a multicomponent system melts at a temperature lower than the other components and in turn acts as a molten solvent allowing melting to occur for the other components at a temperature lower than they would in isolation.[2] Here we will discuss the applications of flux melting with respect to hybrid glass synthesis and explore the upper bounds at which the technique can be successfully utilized to facilitate the formation of amorphous materials at temperatures lower than normally observed. The mechanism by which this occurs will also be investigated using a range of techniques probing both thermal characteristics and structural features. Alongside this, the formation of advanced composite materials, created from careful selection of flux melting components, will be discussed as a route to the expansion of the ever-growing hybrid glass material family.[3]

Additionally, the altered properties of hybrid glass materials will be discussed in contrast to their crystalline counterparts, highlighting the possible benefits that can be harnessed by considering glassy and amorphous material states. Several reports have highlighted how material characteristics can be significantly altered between states. This presentation will highlight systems in which increased uptake behaviour in hybrid glass systems, compared to the crystalline precursor materials, is observed. Both gas and water uptake is enhanced by the transformation to the glassy state, behaviour contrasting to that typically observed in hybrid glasses where densification reduces uptake. The high levels of stability associated with these materials also positions them as promising candidates in applications where long-term resistance to external stimuli, such as moisture, is key to ensuring prolonged performances. As such, we suggest several possible energy-based applications which harness both the tunable band-gap of these materials alongside their high stability. These exciting observations have the possibility to greatly expand the scope of hybrid glass materials, particularly work on their applications relating to host-guest behaviours and emerging energy technologies.[4]

References

1 Jay McCarron; Bethan Turner; Lauren Nicole McHugh, *Adv. Eng. Mater.*
2 L. Longley, S. M. Collins, S. Li, G. J. Smales, I. Erucar, A. Qiao, J. Hou, C. M. Doherty, A. W. Thornton, A. J. Hill, X. Yu, N. J. Terrill, A. J. Smith, S. M. Cohen, P. A. Midgley, D. A. Keen, S. G. Telfer and T. D. Bennett, *Chemical Science*, 2019, **10**, 3592–3601.
3 J. McCarron, O. Dunlop, B. Turner, L. N. McHugh, Modified Melting Behaviour in a Metal-Organic Framework and Hybrid Organic-Inorganic Perovskite Composites, (In preparation).
4 J. McCarron, L. Hardy, O. Dunlop, I. Borne, B. Turner, S. D. Harding and L. McHugh, *ChemRxiv*, 2025, preprint, DOI: 10.26434/chemrxiv-2025-3rmtm-v2.

HCL-ASSISTED SYNTHESIS OF DEFECTIVE METAL-ORGANIC FRAMEWORK UiO-66(Zr) FOR GAS CAPTURE

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Keywords: *Metal organic framework, UiO-66, water effect, defects, CO_2 capture.*

In this study, we explored the synthesis of defective UiO-66 metal-organic frameworks (MOFs) using an alternative, more economical Zr-based precursor in place of the conventionally used ZrCl4 in CO2 capture. The resulting materials were designated as 1-U, 2-U, and 2-U-HCl (a modified version of 2-U). We employed various characterization techniques, including X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and CO2 solubility tests to analyze the synthesized MOFs. Notably, 1-U and the modified 2-U-HCl demonstrated comparable structural features. The average number of defects, quantified as linker loss per unit, was determined to be 3.65, 4.3, and 4.7 for 1-U, 2-U, and 2-U-HCl, respectively. CO2 adsorption experiments conducted at 1 bar and 20°C revealed uptake values of 1.62, 1.40, and 0.5 mmol/g for 1-U, 2-U-HCl, and 2-U, respectively. These findings provided direct evidence of the relationship between CO2 uptake capacity and the presence of defects in the MOF structure. While defects are generally associated with enhanced CO2 adsorption due to their role as active sites, we observed an interesting phenomenon with 2-U. Our results suggested that water molecules influenced CO2 diffusion in this sample, leading to a reduced overall adsorption capacity compared to traditional UiO-66. As part of our optimization strategy for 2-U-HCl, we investigated the effect of activation temperature. Our findings indicated that the most activated sample achieved superior performance compared to most UiO-66 materials reported in the literature, highlighting the potential of our synthetic and optimization approach[1]–[3].

This research underscores the significance of defects in large-scale applications while offering valuable insights into the effects of water molecules within MOFs.

References

[1] P. Niu, et al. Microporous and Mesoporous Materials. 2019, 281, 92–100.

[2] G. C. Shearer, et al. Chem. Mater. 2014, 26, 4068–4071.

[3] V. N. Le, T. K. Vo, K. S. Yoo, J. Kim. Sep. Purif. Technol. 2021, 274, 119079

ACCESSING CHARGE IN A SERIES OF REDOX-ACTIVE COVALENT ORGANIC FRAMEWORKS (COFS): HARNESSING STRUCTURE-PROPERTY CORRELATION TO BATTERY APPLICATION

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Keywords: *redox-active COFs, electropolymerization, structure-property correlation, charge-storage,* battery

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 battery when 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.

References

[1] T. Günther, K. Oka, S. Olsson, M. Ahlén, N. Tohnai, R. Emanuelsson. *J. Mater. Chem. A*, **2023**,11, 13923-13931.

METAL-ORGANIC FRAMEWORKS DRIVEN RANDOM LASING AND SOLID-STATE LIGHT EMISSION

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Keywords: *Guest@Host Metal Organic Framework, Random Lasing, Solid-State Photoluminescence*

Metal Organic Frameworks (MOFs) are an emerging class of hybrid porous nanomaterials. Their structure, composed by organic linkers connecting metaloxoclusters [1], hosts large cavities with high internal surface area. This makes the MOFs promising for several applications in the field of sensing and gas storage.

Luminescent MOFs are a class of MOFs which feature an intrinsic optical activity usually related to an excitation transfer from absorber center (e.g. the organic ligand) to the emitting centers (usually the metaloxo site) [2]. Moreover, the presence of large cavities allows to embed luminescent guests obtaining dual-emitting nano systems.

Here, we synthesized Zr-based MOF-808, that is known for its water stability and relatively large cavities ideal for trapping dyes such as Rhodamine B and Coumarin 343. We used optical spectroscopical techniques with different time resolutions to map the entire photocycle of the resulting dual-emitting hybrid system, and we found evidence of a nanosecond energy transfer from the photoexcited MOF to the embedded dye.

Finally, we capitalize on the information gained on the photocycle to use this hybrid system in random lasing applications. In fact, MOFs can be used as scatterers both in solution and in solid state which trigger an incoherent random lasing phenomenon [4] initiated by the fluorescence of the embedded dye. Through this mechanism, the composite is capable of producing narrow band lasing emission with a FWHM of 10 nm. These results pave the way for the use of MOFs in different, and yet unexplored photonic applications.

References

[1] *ACS Omega* 2022,7,44507
[2] Chem.Rev.,2022,122,10438
[3] Phys.Chem.Chem.Phys.,2024,26,22269
[4] Prog. In Quantum Electronics,2021,78,100343

[CU_2(TRZ-IA)$_2$] – AN ULTRAMICROPOROUS CU_2 PADDLE WHEEL TRIAZOLYL ISOPHTHALATE MOF: A COMPARATIVE STUDY OF ITS PROPERTIES IN DIHYDROGEN ADSORPTION AND ISOTOPOLOGUE SEPARATION

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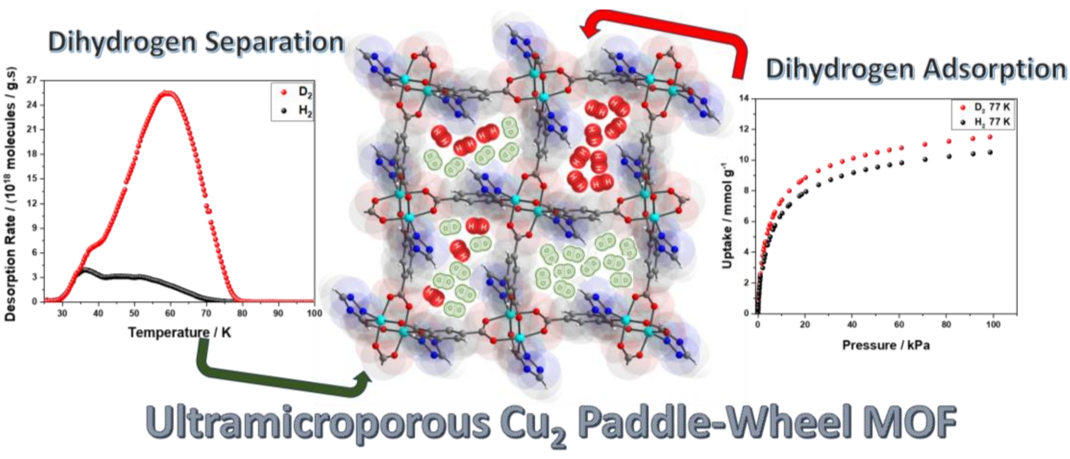
Keywords: *Ultra-microporous MOFs, Hydrogen Storage, Hydrogen Isotope Separation, Thermal Desorption Spectroscopy*

A Cu_2 paddle wheel-based Metal-Organic Framework, [Cu_2(trz-ia)$_2$] (trz-ia^{2-} = 5-(4H-1,2,4-triazol-4-yl) isophthalate), is investigated for hydrogen adsorption and hydrogen isotopologue separation. Its ultramicroporous structure with pore diameters ranging from 0.35 to 0.53 nm allows for strong interactions with dihydrogen molecules, resulting in steep H2 uptake and heat of adsorption Q_{st} = 9.7 kJ mol^{-1}. Notably, the hydrogen density inside the pores is 43.9 g L^{-1} at 77 K and 100 kPa. Thermal desorption spectroscopy (TDS) after exposure to a H_2/D_2 mixture indicates dihydrogen isotopologue separation with a selectivity of S = 6 at 30 K and a high uptake of D_2. These findings are compared to numerous other MOFs and related to their pore size.



References

Chetry, S.; Sarkar, P.; Lukman, M. F.; Bon, V.; Pöppl, A.; Hirscher, M.; Kaskel, S.; Krautscheid, H. *Inorg. Chem.*, **2025**, *64*(10), 5077–5085.

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.

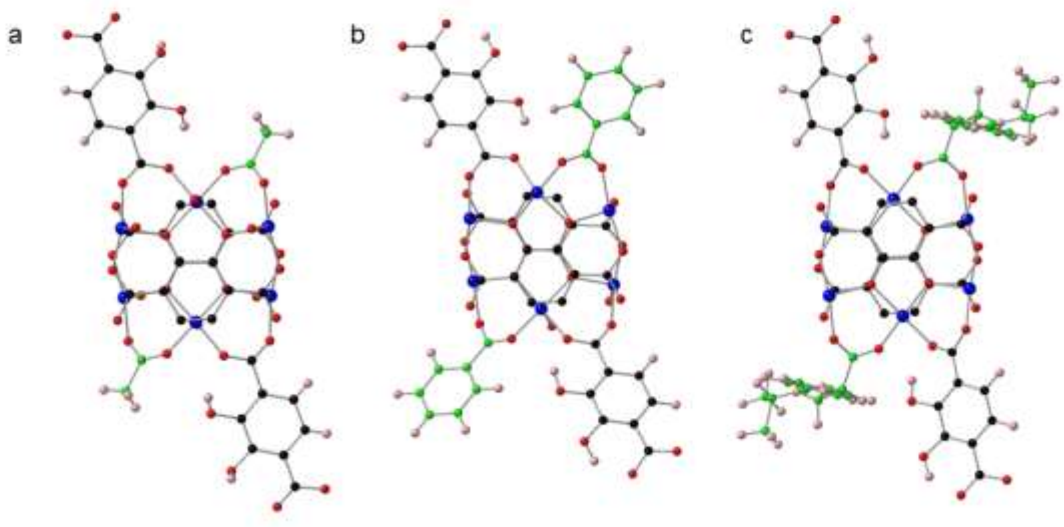

Figure 1: Ball and stick models of a new Cu MOF showing the structure of three different molecules (green): a) acetic acid, b) benzoic acid, c) isobutylphenylpropionic acid.

References

1. Hoshino, M., Khutia, A., Xing, H., Inokuma, Y. & Fujita, M. The crystalline sponge method updated. *IUCrJ* **3**, 139–151 (2016).

2. Huang, Z., Grape, E. S., Li, J., Inge, A. K. & Zou, X. 3D electron diffraction as an important technique for structure elucidation of metal-organic frameworks and covalent organic frameworks. *Coordination Chemistry Reviews* vol. 427 213583 (2021).

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.

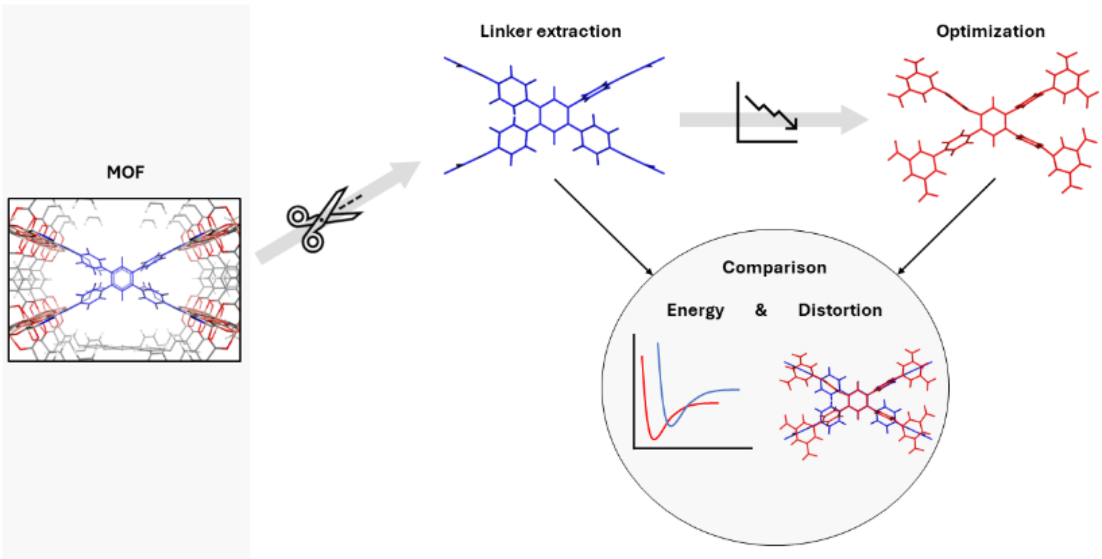

Figure 1: Workflow of synthesizability likelihood evaluation

References

[1] Rosen, A. S. QMOF Database **2023**.

[2] Chung, Y. G. et al. J. Chem. Eng. Data 64, 5985–5998 **2019**.

[3] Anderson, R. & Gómez-Gualdrón, D. A. CrystEngComm 21, 1653–1665 **2019**.

CONTROLLING THE SELF-ASSEMBLY AND MECHANICAL PROPERTIES OF ISOSTRUCTURAL DISULFIDE-BASED METAL–ORGANIC NANOTUBES

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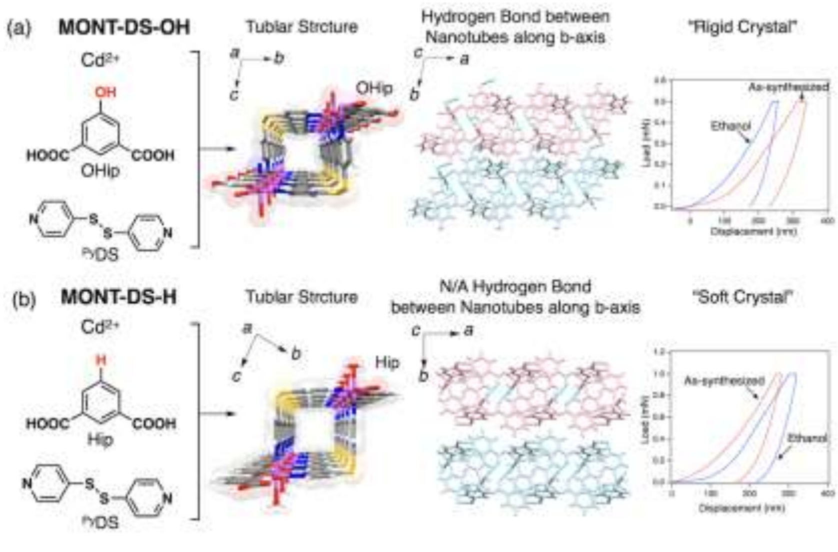
Keywords: *Mechanical force response, Metal-organic nanotubes, hydrogen Bond*

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.



References

1) K. Otsubo, H. Kitagawa et al., *Nat. Mater*. **2011**, *10*, 291–295.
2) J. Dou, M. Dincă et al., *Nat. Mater*. **2021**, *20*, 222–228.
3) H. Li O. M. Yaghi et al., *Nature* **1999**, *402*, 276–279.

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.

References

[1] Furukawa, Hiroyasu, et al. "The chemistry and applications of metal-organic frameworks." *Science* 341.6149 (2013): 1230444.
[2] Ongari, Daniele, Leopold Talirz, and Berend Smit. "Too many materials and too many applications: an experimental problem waiting for a computational solution." *ACS central science* 6.11 (2020): 1890-1900.
[3] Li, Dingyi, et al. "Enhancing photosynthetic CO2 fixation by assembling metal-organic frameworks on Chlorella pyrenoidosa." *Nature Communications* 14.1 (2023): 5337.
[4] Yang, Sihai, et al. "Selectivity and direct visualization of carbon dioxide and sulfur dioxide in a decorated porous host." *Nature chemistry* 4.11 (2012): 887-894.
[5] Thomas-Hillman, Ieuan, et al. "Developing a sustainable route to environmentally relevant metal–organic frameworks: ultra-rapid synthesis of MFM-300 (Al) using microwave heating." *Green Chemistry* 21.18 (2019): 5039-5045.

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.

References

[1] J. Mikosz, *Int. J. Environ. Sci. Technol.*, **2015**, 12, 827–836.

[2] S. Madhav, A. Ahamad, A. K. Singh, J. Kushawaha, J. S. Chauhan, S. Sharma and P. Singh, in *Sensors in Water Pollutants Monitoring: Role of Material*, ed. D. Pooja, P. Kumar, P. Singh and S. Patil, Springer Singapore, Singapore, **2020**, pp. 43–62.

[3] Y. Zhang, T. Zang, B. Yan and C. Wei, *Int. J. Environ. Res. Public Health*, **2020**, 17, 553

[4] C. Wang, W. Wang, S. Shao, W. Deng, C. Wang, X. Liu, H. Li, M. Wen, X. Zhang, G. Li and T. An, *Sci. Total Environ.*, **2024**, 917, 170407.

[5] S. L. Cruz, M. T. Rivera-García and J. J. Woodward, *J. Drug Alcohol Res.*, **2014**, 3, 1–8.

[6] M. Rooseboom, N. A. Kocabas, C. North, R. J. Radcliffe and L. Segal, *Regul. Toxicol. Pharmacol.*, **2023**, 141, 105387.

[7] Z. Mamaghanifar, A. Heydarinasab, A. Ghadi and E. Binaeian, *Water Conserv. Sci. Eng.*, **2020**, 5, 1–13.

[8] H. Anjum, K. Johari, N. Gnanasundaram, A. Appusamy and M. Thanabalan, *J. Mol. Liq.*, **2019**, 280, 238–251.

[9] S. L. James, *Chem. Soc. Rev.*, **2003**, 32, 276.

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.

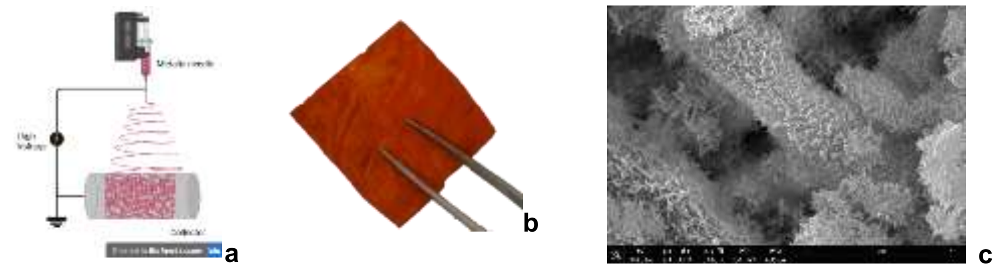

Figure 1 - Illustration of a) the electrospinning process; b) the produced membrane; c) the fiber morphology through SEM

References

[1] M. M. Khin, A. S. Nair, V. Jagadeesh Babu, R. Murugan, and S. Ramakrishna, "A review on nanomaterials for environmental remediation," Energy Environ Sci, **2012**, 5

[2] S. P. S. Fernandes, V. Romero, B. Espiña, and L. M. Salonen, "Tailoring Covalent Organic Frameworks To Capture Water Contaminants," Chemistry - A European Journal, **2019,** 25, pp. 6461–6473

[3] M. S. Lohse and T. Bein, "Covalent Organic Frameworks: Structures, Synthesis, and Applications," Adv Funct Mater, **2018**, 28,

[4] A. Mellah et al., "Adsorption of Pharmaceutical Pollutants from Water Using Covalent Organic Frameworks," Chemistry - A European Journal, **2018**, vol. 24, pp. 10601–10605

[5] S. P. S. Fernandes et al., "Study on the efficiency of a covalent organic framework as adsorbent for the screening of pharmaceuticals in estuary waters," Chemosphere, **2021**, vol. 278

SURFACE-CONFINED POLYMER ENGINEERING OF COVALENT ORGANIC FRAMEWORK MEMBRANES FOR ENHANCED REVERSE ELECTRODIALYSIS PERFORMANCE

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Keywords: *Reverse Electrodialysis, Covalent Organic Frameworks, Asymmetric Membrane, Surface tuning*

An intrinsic trade-off between ion conductivity and selectivity limits the performance of ion exchange membranes in reverse electrodialysis (RED) which converts the chemical potential difference between solutions of differing salinities into electricity. To address this constraint, asymmetric membranes—in which charge density, functionality, or channel dimensions vary across the membrane—are designed to enable preferential ion flux, thereby suppressing co-ion back diffusion and mitigating ion concentration polarization (ICP). Two-dimensional covalent organic frameworks (COFs) are particularly attractive because their highly aligned nanochannels and ultrathin profiles inherently support high permeability and can be precisely functionalized to introduce asymmetry. However, although existing COF-based strategies—stacking multiple layers, sequential COF-on-COF growth, or hybridizing with rigid supports—can boost selectivity, they also create interfacial mismatches and lengthen ion pathways that suppress permeability, preventing full structural benefits and capping net power gains.

We overcome these challenges with a simple polymer-based surface tuning of COFs that imparts charge asymmetry without extending channel length. The pristine COF membrane is first subjected to alkaline treatment to produce COF_A, whose hydrolyzed binding sites then enable anchoring of polyelectrolytes on one side of COFs, yielding asymmetric COF_L. The grafted polymer, approximately 3 nm in hydrodynamic diameter, carries a strong negative charge and is more hydrophilic than COF_A, thereby preserving the original channel architecture while promoting directional ion transport. Molecular dynamics simulations further confirm that this polymer functions as a dynamic ion reservoir, transiently capturing counterions and rapidly releasing them into the bulk solution, and these dynamics ultimately suppress ICP. As a result, under a 50-fold salinity gradient, COF_L achieves a power density approximately 15 times higher than that of the untreated COF (COF_Bare) and exhibits markedly increased permeability. By avoiding any added ion transport distance, this minimal surface tuning enhances selectivity without sacrificing permeability and offers a scalable pathway to high-performance osmotic energy harvesting membranes based on COFs and other two-dimensional materials.

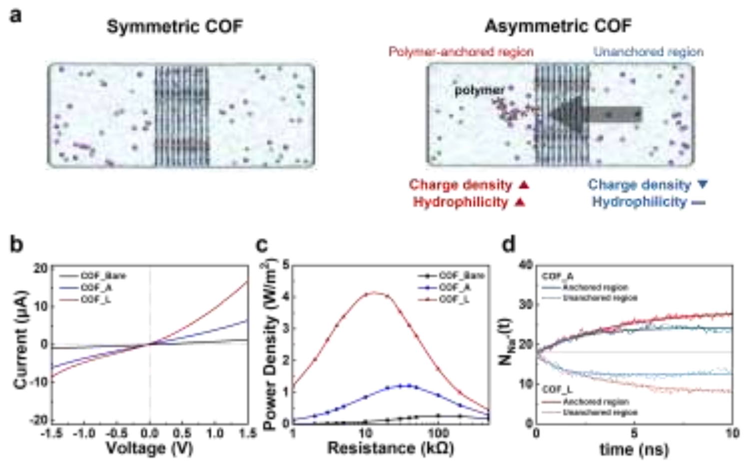

Figure 1. (a) Simulation snapshots of COF membranes before (Symmetric COF) and after modification (Asymmetric COF). (b) I–V curves and (c) output power density of COF membranes. (d) Molecular dynamics simulation results showing temporal evolution of Na^+ ion concentration during the application of a negative bias.

FORMULATING FLEXIBLE MOFS FOR GAS SEPARATION

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Keywords: *Flexible MOFs, Shaping, Molecular Sieving*

Metal-Organic Frameworks (MOFs) have emerged as a highly promising class of porous materials with a variety of potential applications, particularly in the field of separative adsorption. Indeed, MOFs exhibit suitable properties such as high surface area, molecule-sized pores, and can be easily tuned to adsorb specific molecules [1]. However, the synthesis of MOFs typically results in fine powder, which is a major drawback for industrial-scale applications due to its tendency to cause high pressure drop, clogging, and heat and mass transfer issues. In addition, the shaping of powder-based porous adsorbents facilitates their use in industrial processes, and generally improves their mechanical stability and abrasion resistance. However, a significant challenge remains: the shaped material must exhibit adsorption properties analogous to the original adsorbent powder. This requirement is even more challenging for flexible MOFs, which exhibit structure changes depending on the environmental conditions[2].

The goal of this work is to shape ZIF-8 flexible MOF in millimeter-sized extrudes while maintaining its flexibility. Different binder recipes were screened, using polymeric organic polyalcohol-based and cellulose-based binders. The shaped materials were compared based on the preservation of the textural properties and of their structural flexibility by nitrogen sorption (77 K), XRD and TGA. The addition of a binder is of interest in this case as his presence typically improves the mechanical properties of the shaped material. This aspect was investigated by compressibility tests. This work proposes binder recipes which allow the formulation of flexible MOFs, while retaining their breathing properties. The ultimate objective is to test these formulated materials for gas separation adsorption under mechanical stress.

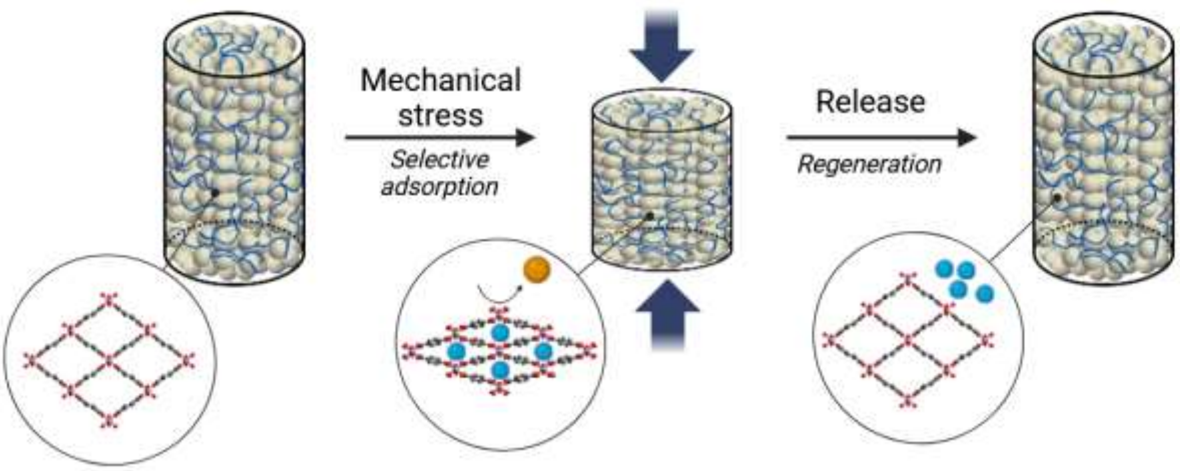

Figure 1 - Schematic representation of the concept: control of the breathing behavior of the flexible MIL-53 by applying a mechanical stress to induce a molecular-sieving type separation. In grey: MOF particles, in blue: binder.

References

[1] N. Singh, *et al. Sep. Purif. Technol.* **2024**, 341, 126820
[2] B. Yeskendir, *et al. Mater. Adv.* **2021**, 2 (22), 7139-7186
[3] N. Chanut, *et al. Nat. Commun.* **2020**, 11 (1), 1216

SYNERGISTIC DUAL FUNCTIONALIZATION OF IONIC COVALENT ORGANIC FRAMEWORKS MEMBRANES FOR ENHANCED PROTON CONDUCTION WITH 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 across various operating conditions is critically challenging for proton exchange membrane fuel cells.[1] Ionic covalent organic frameworks (iCOFs), possessing ordered ionic channels with abundant ion groups and high structural flexibility, have attracted considerable attention as proton exchange membranes. The proton conductivity of iCOFs primarily depends on their ion exchange capacity (IEC), which is inherently limited by the ionic groups provided by monomers. [2] Although post-synthetic modification (PSM) can enhance IEC by introducing additional ionic functionalities into established iCOFs, this approach is significantly hampered by steric hindrance and electrostatic interaction from pre-existing ionic groups [3]. Consequently, the systematic monomer engineering facilitating efficient PSM is crucial for developing post-modified iCOF-based membranes.

In this study, we introduce a dual-functionalization approach utilizing PSM on iCOF nanosheets to effectively surpass conventional IEC limitations and fabricate free-standing films. By systematically tuning the reactivity and solubility of monomers, we optimized solution processability of iCOFs nanosheets and PSM efficiency (Figure 1a). The synthesized β-ketoenamine-linked COF-$(SO_3H)_2$ intrinsically contains a high density of ionic groups, further augmented via targeted PSM to yield COF-$(SO_3H)_2$-PSM (Figure 1b). The controlled ionization state of sulfonic groups during monomer engineering regulates electrostatic repulsions, promoting in-plane anisotropic growth of nanosheets (Figure 1c). The excellent solution processability of nanosheets colloidal suspension enables efficient grafting of alkyl sulfonic groups onto enamine linkages and subsequent formation of mechanically robust, free-standing films (Figure 1d). The dual-functionalization with sulfonic groups from both intrinsic frameworks and additional PSM significantly boosts surface charge and IEC. Importantly, the incorporation of extended alkyl sulfonic chains through PSM significantly expands the hydrogen-bonding networks into internal ion channels. Additionally, these flexible alkyl chains dynamically reorganize to establish continuous proton conduction pathway, addressing spatial constraints of fixed and shorter ionic groups in the pristine iCOFs (Figure 1e). Consequently, these synergistic effects in both IEC and hydrogen-bonding networks elevate proton conductivity across diverse operating conditions. This work offers valuable guidelines for the rational design and fabrication of highly efficient iCOF-based ion exchange membranes for advanced energy applications.

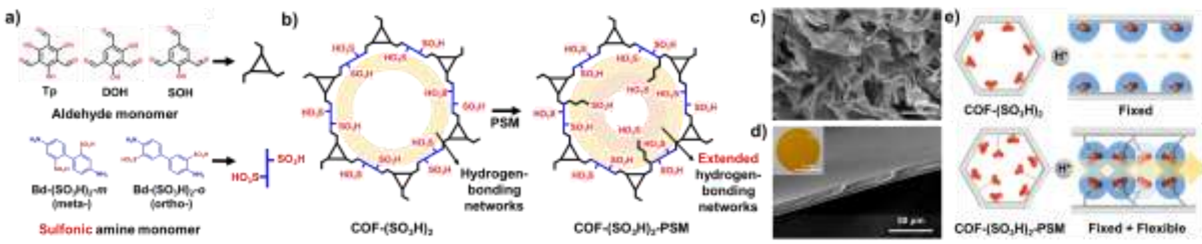

Figure 1. (a) Monomer engineering with various combinations, (b) he schematic illustration of COF-$(SO_3H)_2$-PSM,SEM images of COF-$(SO_3H)_2$-PSM (c) nanosheets and (d) free-standing films with its photo (inset), (e) The illustration of the ion channel structure of COF-$(SO_3H)_2$ and COF-$(SO_3H)_2$-PSM

References

[1] Jiao, K. et al. *Nature* **2021**, 595, 361-369
[2] Shi, B. et al. *Nat Commun* **2022**, 13, 6666.
[3] Sahoo, R. et al. *Adv. Energy Mater* **2021**, 11, 2102300.

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.

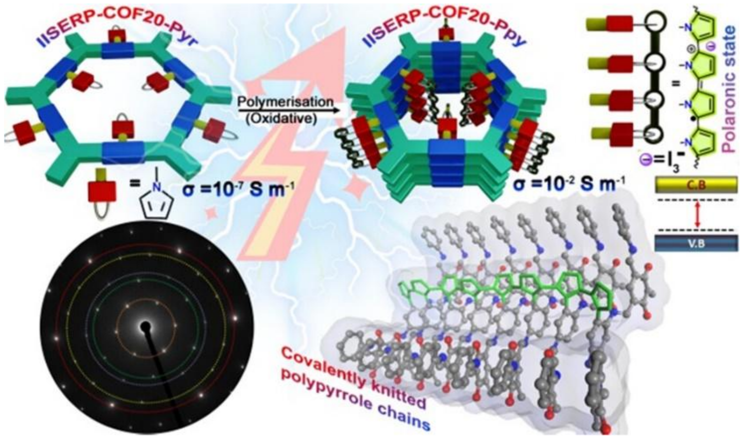

Fig. 1: Schematic representation of Transforming Non-Conducting 2D COFs into Conducting Quasi-3D Structures through Polypyrrole Interlayer Knitting

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.

References

[1] S. Duhović, M. Dincă, et al. *Chem. Mater*. **2015**, 27(16), 5487−5490.

[2] **C. Jain**, R. Kushwaha, D. Rase, et al. *J. Am. Chem. Soc*. **2024**, 146, 487-499.

POST-SYNTHETIC METALATION OF AL-PMOF FOR ENHANCED VISIBLE-LIGHT CO_2 PHOTOCONVERSION

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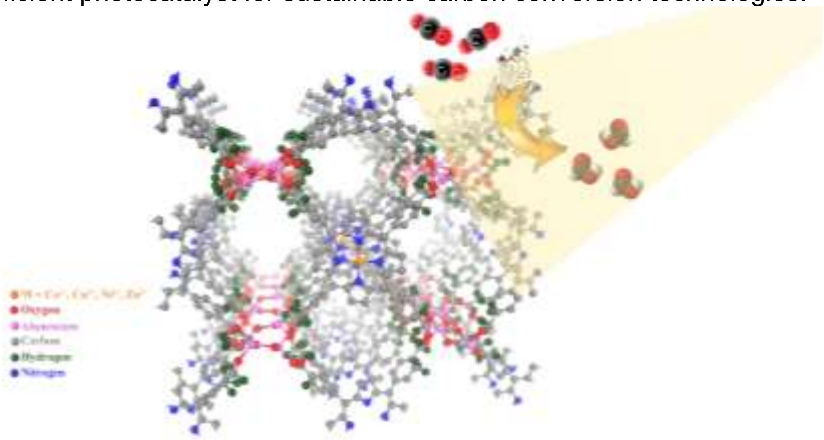
Keywords: *Porphyrin-based MOF, CO_2 Photoreduction, Post-synthetic modification, Visible-light photocatalysis, Aluminum-based MOF*

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.



This research was supported by the Polish National Science Center under the grant 2021/41/B/ST4/00849.

References

[1] Diercks CS, Liu Y, Cordova KE, Yaghi OM. The role of reticular chemistry in the design of CO2 reduction catalysts. Nature Materials. 2018;17(4):301-7.
[2] Shang S, Yang C, et al. CO2 capture from wet flue gas using transition metal inserted porphyrin-based metal-organic frameworks as efficient adsorbents. Separation and Purification Technology. 2022;301:122058.
[3] Wen H, Liu Y, et al. Heterogeneous catalysis in production and utilization of formic acid for renewable energy. Small. 2024;20(18):2305405.

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.

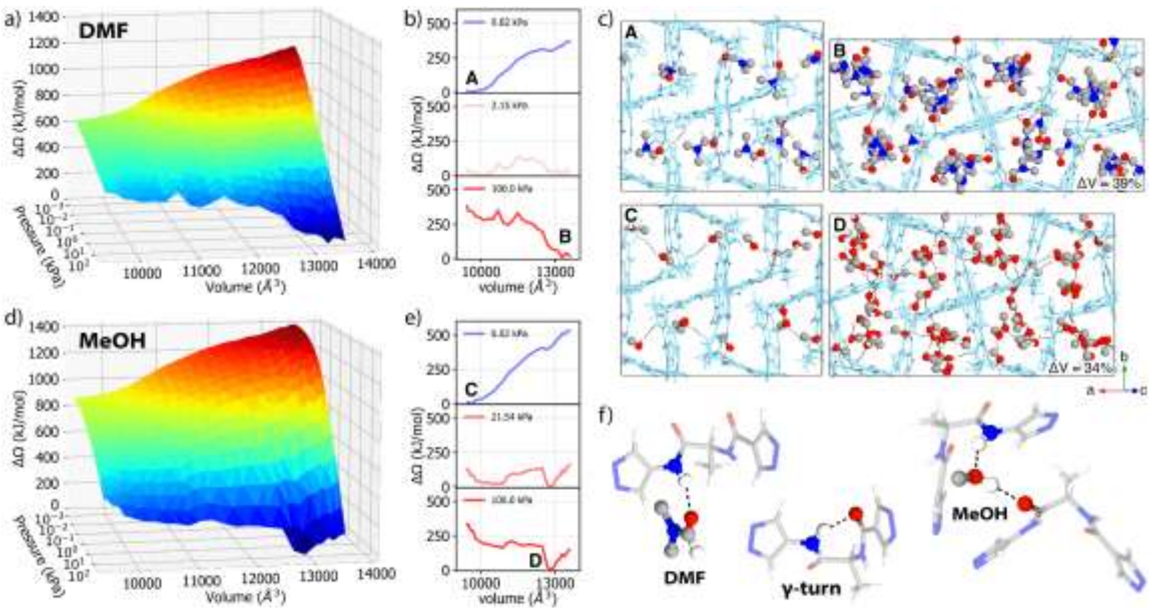

Figure 1. Osmotic surfaces for DMF **(a)** and MeOH **(d)** adsorption/intrusion at 300 K. Osmotic profiles for DMF **(b)** and MeOH **(e)** at selected pressures. **(c)** Representative configurations of the minimum structures indicated in the osmotic profiles, illustrating the closed and open phases 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).

References

[1] Carratalá, V., Misturini, A., Diouf, M. D. F., et al. *submitted in* **2025**.
[2] Rogge, S. M. J., Goeminne, R., Demuynck, R., et al. Adv. Theory Simul. 2019, 2, 1800177.
[3] Goeminne, R., Krause, S., Kaskel, S., et al. *J. Am. Chem. Soc.,* **2021**, 143, 4143-4147.

HARNESSING SYNERGISTIC EFFECT OF AL AND Zn IN NOVEL BIMETALLIC MOF FOR SUPERIOR ENVIRONMENTAL POLLUTANTS ADSORPTION

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Keywords: *Bimetallic MOFs, Synergistic Effects, Environmental Remediation, Reusable Materials, Dye Adsorption, Al/Zn MOFs.*

The integration of distinct metal centers in bimetallic metal-organic frameworks (BMOFs) offers unique synergistic advantages for adsorption [1]. This work presents the first investigation into a novel Al/Zn-BMOF, synthesized via a one-pot solvothermal method, harnessing the synergistic effects of Al(III) and Zn(II) for superior multi-pollutant removal [2]. The Al/Zn-BMOF demonstrated enhanced efficacy compared to its monometallic counterparts [3] in adsorbing anionic (Congo Red, CR), cationic (Methylene Blue, MB), and neutral (Neutral Red, NR) dyes from water. Exceptional maximum adsorption capacities were achieved: 202 mg/g (CR), 226 mg/g (MB), and 313 mg/g (NR) at 298 K, with rapid equilibrium (<30 min). Kinetics followed a pseudo-second-order model, and thermodynamics indicated a spontaneous, endothermic process. Adsorption mechanisms involve electrostatic forces, π-π stacking, and coordination bonds. This Al/Zn-BMOF shows remarkable selectivity, reusability (>5 cycles), and potential for treating diverse industrial effluents, highlighting the power of synergistic bimetallic design in advanced adsorbent materials.

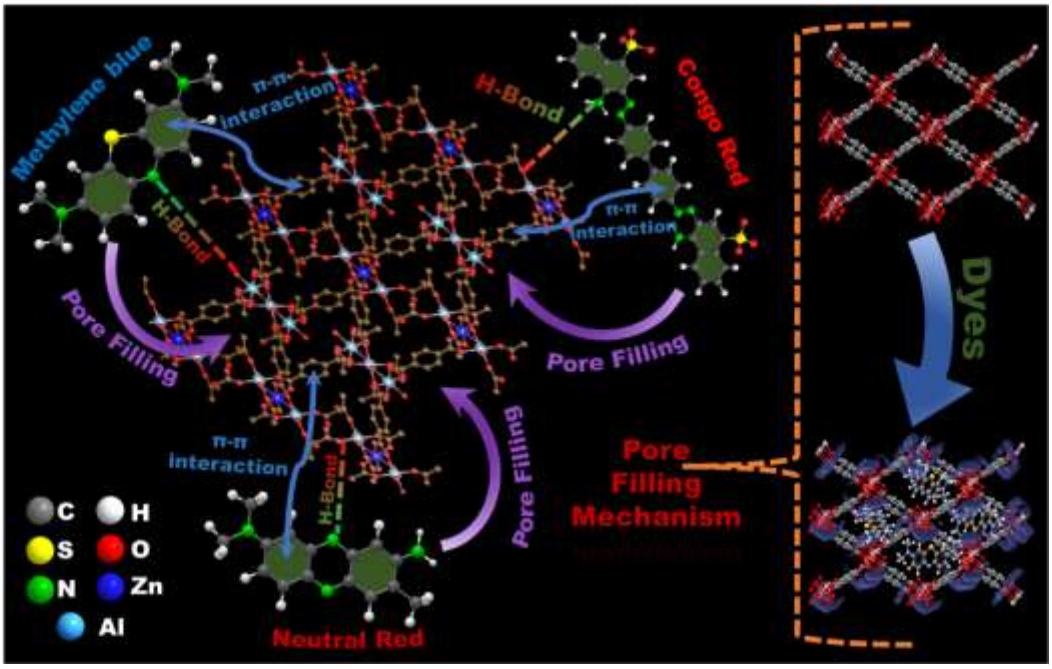

Figure 1. *The proposed schematic illustration of the adsorption mechanism of various organic dyes (Congo Red (CR), Methylene Blue (MB), and Neutral Red (NR)) on Al/Zn-BMOF.*

References

[1] W. Wang, M. Al Aiti, B.C. Ibarlucea, C. Huang, R. Dong, S. Huang, G. Cuniberti, Nanoscale Horizons, (2024).
[2] Abednatanzi, Sara, Parviz Gohari Derakhshandeh, Hannes Depauw, François-Xavier Coudert, Henk Vrielinck, Pascal Van Der Voort, and Karen Leus, Chemical Society Reviews 48, no. 9 (2019): 2535-2565.
[3] R. Essam, S.R. Abdel-Hafeez, M. EL-Rabiei, N. Burham, M. El-Shahat, A. Radwan, Applied Organometallic Chemistry, 39 (2025) e70135.

CATALYTIC NANOSHEETS: CATALYSING REACTIONS IN WATER

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Keywords: *Catalytic, Hydrolysis, Organophosphates, Metal-Organic Nanosheets, Continuous Flow*

Pollution from pesticides is a growing problem for both the population and environment due to their high toxicity and resistance to natural degradation. Catalysts which increase the rate of pesticide breakdown are therefore highly desirable, particularly those capable of operating under mild conditions. Metal-Organic Nanosheets (MONs) are two-dimensional supramolecular assemblies featuring metal nodes and organic linkers. Their high surface area, surface charge and tunability make them useful as catalysts as the substrate can interact with accessible active sites on the MON surface.[1] Zr-BTB (BTB = 1,3,5-tris(4-carboxyphenyl)benzene) are highly water stable examples.

Zr-BTB MONs were synthesized using a bottom-up method[2] and loaded heterogeneously onto an inert membrane. The MON-based membrane was then tested for its impact on the rate of hydrolysis of a pesticide mimic, 2-nitrophenyl dimethyl phosphate, in mild aqueous conditions via a simple flow setup. A feed containing the reagent was continuously pumped through the membrane and the formation of product was monitored by UV-vis spectroscopy until a steady state was reached.

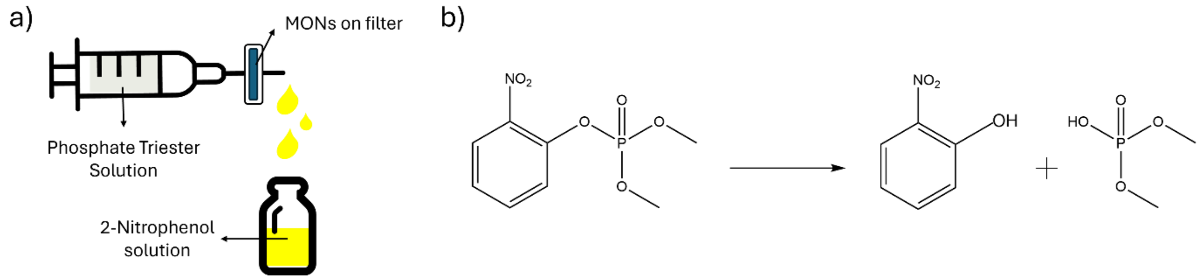

Figure 1: a) The flow setup for the MON-catalysed heterogeneous reaction, and b) hydrolysis of 2-nitrophenyl dimethyl phosphate into products 2-nitrophenol and dimethyl phosphate

A range of variables were altered to test their effect on the catalytic efficiency of the system: flow rate, MON loading, substrate concentration, and pH. Flow rate and MON loading had a significant effect; whereas substrate concentration and pH were found to be less important. Furthermore, four triesters featuring different leaving groups over a pKa range of 7.2-9.3 established a trend where increasing the pKa made the catalysis more challenging. The optimised system achieved 100% conversion at flow rates slower than 0.2 mL/min, using a MON loading of only 3 mg. Compared to previous reports using bulk metal-organic framework (MOF) catalysts, full conversion can be reached in both examples, but the MOF system required a much slower flow rate and higher loading of catalyst.[3] This comparison shows the enhanced catalytic activity and turnover when using Zr-BTB MON systems.

Overall, this work follows the development of a very promising system for the heterogeneous breakdown of high concentrations of toxic organophosphates under mild conditions and using very little catalyst. Currently, work is being undertaken to understand the specific mode of action of the catalysis, and optimisations carried out to maximise conversion at even faster flow rates.

[1] N. D. Savić, K. Declerck, R. R. R. Prasad, G. Kalandia, J. A. Foster and T. N. Parac-Vogt, Advanced Functional Materials, 2025, 35, 2570129
[2] Z. Tao, J. Wu, Y. Zhao, M. Xu, W. Tang, Q. Zhang, L. Gu, D. Liu and Z. Gu, Nature Communications, 2019, 10, 2911
[3] D. Nam, Y. Kim, M. Kim, J. Nam, S. Kim, E. Jin, C. Y. Lee and W. Choe, Inorganic Chemistry, 2021, 60, 10249-10256

ZINC-BASED HIGHLY POROUS MOF FOR HIGHLY SENSITIVE AND SELECTIVE 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*

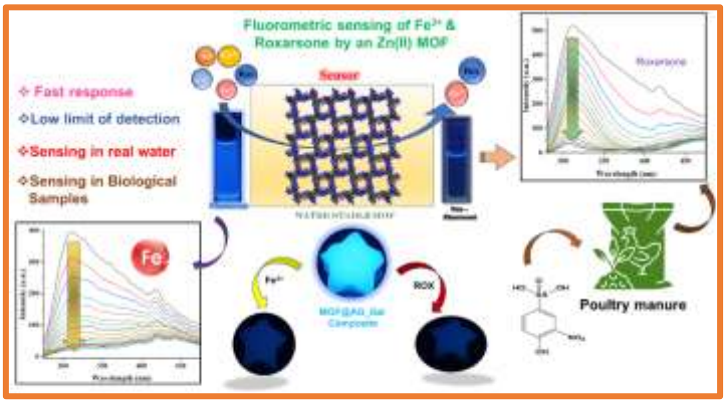

Figure 1. Graphical presentation of detection of Fe^{3+} ions and Roxarsone molecules.

Reference:

[1] S.C Pal, D. Mukherjee, M.C Das, Inorg. Chem. 2022, 61, 12396−12405.

[2] D. Cai, C.Q. Qiu, Z.H Zhu, T.F. Zheng, W.J. Wei, J.L Chen, S.J. Liu, H.R. Wen, Inorg. Chem. 2022, 61, 14770−14777.

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.

References

[1] M. R. R. Khan and S. W. Kang, “A high sensitivity and wide dynamic range fiber-optic sensor for low-concentration VOC gas detection,” *Sensors (Switzerland)*, vol. 14, no. 12, pp. 23321–23336, Dec. 2014, doi: 10.3390/s141223321.

[2] M. Treger, C. König, P. Behrens, and A. M. Schneider, “Fragment-based approach for the efficient calculation of the refractive index of metal-organic frameworks,” *Physical Chemistry Chemical Physics*, vol. 25, no. 28, pp. 19013–19023, Jun. 2023, doi: 10.1039/d3cp02356g.

[3] E. Talebian and M. Talebian, “A general review on the derivation of Clausius-Mossotti relation,” *Optik (Stuttg)*, vol. 124, no. 16, pp. 2324–2326, 2013, doi: 10.1016/j.ijleo.2012.06.090.

DYNAMICS AND CONFORMATIONAL ENERGETICS OF GUEST MOLECULES IN CRYSTALLINE SPONGES

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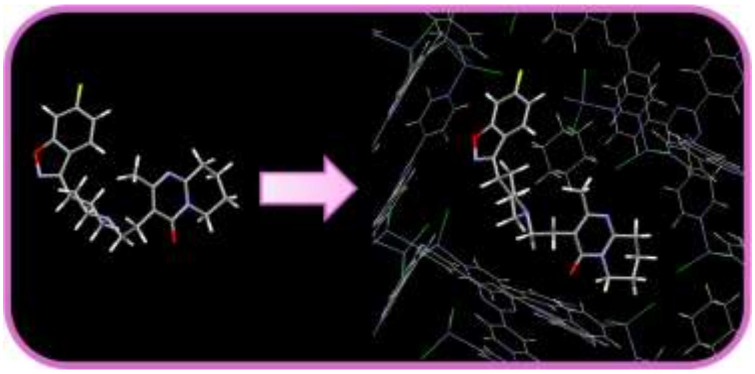
Keywords: *crystalline sponge, computational, modelling, energetics, dynamics*

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.



References

[1] E. M. Soper, S. J. Coles, G. M. Day, CrystEngComm, RSC Publishing, 2025, **27**, 1491-1502

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