

French MOF 2024

2024 French MOFs, COFs and Porous Polymers Conference

10 & 11 juin 2024 – Villeurbanne

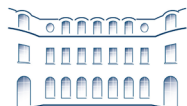
BOOK OF ABSTRACTS



SPONSORS



Université Claude Bernard



Fondation de la Maison de la Chimie



Société Chimique de France
Rhône-Alpes



TotalEnergies



micromeritics®



Rigaku



Surface Measurement Systems
World Leader in Sorption Science



Swagelok



PLENARY LECTURES

Metal-Organic Frameworks for the encapsulation of biological entities: potential as vaccine formulation

Clémence Sicard

Institut Lavoisier de Versailles, UVSQ, CNRS UMR 8180, Univ. Paris-Saclay, Versailles.

Institut Universitaire de France

E-mail: clemence.sicard@uvsq.fr

Bio-entities benefit from unparalleled activities of high interest in many applications such as environmental and medical field. However, these are fragile entities, easily degraded under non-native conditions. Encapsulation, i.e. inclusion within a host matrix, is particularly interesting for bio-entities stabilization and protection, and Metal-Organic Frameworks (MOFs) have arisen as a host matrix of choice, resulting in the design of novel functional materials.[1] However, the number of MOF/bio-entities couples is limited either due to size matching constraints or to a narrow window of compatible synthetic conditions.

In this presentation, we will present our efforts to expand synthetic routes and processing methods to explore new compositions and hierarchical structures of bio-entities-MOFs hybrids. We will describe the synthesis and characterization of MOFs-based living materials, using the mesoporous iron polycarboxylate MIL-100(Fe).[2] We will also present our latest finding on the design of bio-entities@Al-MOF.[3] We will show that the bio-entities@Al-MOF act as a potent vaccine formulation as it demonstrated *in-vivo* a stronger adjuvant effect than the benchmark Al-adjuvant, was fully resorbable, disappearing from the injection site, was not exhibiting any toxicity, and was stable for two years.

References:

- 1- (a) E. Gkaniatsou *et al.*, *Mater. Horiz.* **2017**, 55; (b) R. J. Drout *et al.*, *Chem. Rev.* **2019**, 150, (c) X. Wang *et al.*, *ACS Cent. Sci.*, **2020**, 9; (d) S. Huang *et al.*, *Angew. Chem. Int. Ed* **2020**, 8786; (e) W. Liang *et al.*, *Chem. Rev.* **2021**, 1077.
- 2- A. Permyakova *et al.*, *ACS Materials Letters*, **2023**, 79.
- 3- I. Christodoulou, E. Gkaniatsou *et al.*, *ChemRxiv* **2023**.

Redox-active Covalent Organic Frameworks as promising organic electrodes for metal-ion batteries

Manuel Souto,^{a,b}

^a CIQUS, Centro Singular de Investigación Química Biológica e Materiais Moleculares, Departamento de Química Física, Universidade de Santiago de Compostela, 15782, Santiago de Compostela, Spain

^b Department of Chemistry, CICECO-Aveiro Institute of Materials, University of Aveiro, Aveiro, 3810-393, Portugal

Keywords: electroactive porous frameworks, redox-active COFs, organic batteries.

A breakthrough in chemistry and materials science has been the development of Lithium-Ion Batteries (LIBs), which show great potential for storing energy from renewable sources and as the power source for electric cars.¹ However, commercially available LIBs are based on transition metal oxide cathodes, presenting significant development bottlenecks in terms of efficiency and raw materials availability. Organic materials have received much attention as alternative electrodes because of their high theoretical capacity, resources availability, and sustainability.^{2,3} In particular, Covalent Organic Frameworks (COFs), crystalline porous polymers based on organic building blocks linked by strong covalent bonds, have emerged in the past few years as promising organic electrode materials due to their insolubility in electrolyte, porosity, and outstanding chemical and structural versatility.⁴⁻⁵ However, there are still some challenges that need to be addressed, such as the processing of these materials as well as their relatively low electrical conductivity.⁶ In the talk, I will present an approach to improve the electrochemical performance of an anthraquinone-based COF (**DAAQ-TFP-COF**) cathode material in metal anode (Li, Mg) based batteries through proper selection of the electrolyte and binder.⁷ Our findings demonstrate that the appropriate choice of electrolyte and binder is crucial to maximize the performance of COF-based materials in different post-lithium-ion metal anode batteries. Finally, the synthesis and electrical properties of a series of redox-active tetrathiafulvalene (TTF)-based COFs that were explored as organic p-type cathode materials for lithium batteries will be presented.⁸

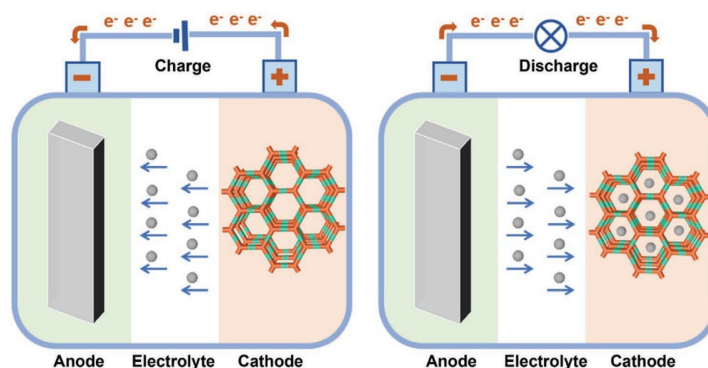


Figure 1. Schematic representation of the electrochemical working process in COF-metal batteries.

Acknowledgements

This work has received funding from the European Research Council (ERC) under the European Union's Horizon Europe Framework Programme (ERC-2021-Starting Grant, grant agreement no. 101039748-ELECTROCOFS). This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, Grants UIDB/50011/2020 and UIDP/50011/2020, financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. We thank FCT for funding the project PTDC/QUI-ELT/2593/2021.

References

- [1] J. B. Goodenough, *Nat. Electron.* **2018**, *1*, 204.
- [2] M. Armand, J.-M. Tarascon, *Nature* **2008**, *451*, 652–657
- [3] Z. Song, H. Zhou, *Energy Environ. Sci.* **2013**, *6*, 2280–2301.
- [4] R. Dantas, C. Ribeiro, M. Souto. *Chem. Commun.* **2024**, *60*, 138-149.
- [5] M. Souto, K. Strutyński, M. Melle-Franco and J. Rocha, *Chem. Eur. J.*, **2020**, *26*, 10912.
- [6] M. Souto, D. F. Perepichka. *J. Mater. Chem. C* **2021**, *9*, 10668–10676.
- [7] O. Luzanin, R. Dantas, R. Dominko, J. Bitenc, M. Souto. *J. Mater. Chem. A* **2023**, *11*, 21553.
- [8] G. Valente *et al.*, **2024**, *submitted*.

ORAL POSTER

Big-data and Metal-Organic Frameworks: Science Beyond Understanding

Berend Smit

*Laboratory of molecular simulation, Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland
e-mail: Berend.Smit@epfl.ch*

Metal-organic frameworks (MOFs) present a vast chemical landscape with potential for diverse applications such as gas separation, storage, sensing, and catalysis. The allure of MOFs lies in their customizable structures, enabling the synthesis of seemingly boundless variations tailored for specific functionalities. The holy grain of MOF synthesis is to design an optimal MOF for a given application. There are some fundamental reasons why we still need to reach this goal.

The infinitude of possible MOF structures renders traditional experimental and computational screening methods insufficient. The optimal material for a given application must be discerned from this boundless design space, which often encompasses multi-objective scenarios, defying a singular ranking system for material evaluation. Furthermore, the synthesis of a theoretically optimal MOF cannot be guaranteed in practice. This lecture delves into how data science methodologies can bridge the gap between theoretical MOF design and practical application.¹ We explore the instrumental role of data science in providing insights into complex chemical questions beyond the reach of conventional theories, such as determining the oxidation state of metals within MOFs,² ascertaining the color of the frameworks,³ or the heat capacity of a MOF.⁴

Moreover, we will demonstrate the application of data-driven approaches in identifying key characteristics of high-performance materials, specifically for carbon capture processes. We aim to navigate the MOF design space more effectively and efficiently by integrating data science techniques with chemical intuition. This approach heralds a new era where data science complements traditional research methods and becomes a cornerstone in the quest for ideal MOF synthesis, leading to accelerated discovery and innovation in Chemistry and Chemical Engineering.⁵

References

- ¹ K. M. Jablonka, D. Ongari, S. M. Moosavi, and B. Smit, *Big-Data Science in Porous Materials: Materials Genomics and Machine Learning* Chem. Rev. **120** (16), 8066 (2020) <http://dx.doi.org/10.1021/acs.chemrev.0c00004>
- ² K. M. Jablonka, D. Ongari, S. M. Moosavi, and B. Smit, *Using collective knowledge to assign oxidation states of metal cations in metal-organic frameworks* Nat. Chem. **13**, 771 (2021) <http://dx.doi.org/10.1038/s41557-021-00717-y>
- ³ K. M. Jablonka, B. Smit, S. M. Moosavi, M. Asgari, C. Ireland, and L. Patiny, *A data-driven perspective on the colours of metal-organic frameworks* Chem Sci **12**, 3587 (2021) <http://dx.doi.org/10.1039/D0SC05337F>
- ⁴ S. M. Moosavi, B. Á. Novotny, D. Ongari, E. Moubarak, M. Asgari, Ö. Kadioglu, C. Charalambous, A. Ortega-Guerrero, A. H. Farmahini, L. Sarkisov, S. Garcia, F. Noé, and B. Smit, *A data-science approach to predict the heat capacity of nanoporous materials* Nat Mater **21**, 1419 (2022) <http://dx.doi.org/10.1038/s41563-022-01374-3>
- ⁵ C. Charalambous, E. Moubarak, J. Schilling, E. Sanchez Fernandez, J.-Y. Wang, L. Herraiz, F. Mcilwaine, K. M. Jablonka, S. M. Moosavi, J. Van Herck, G. Mouchaham, C. Serre, A. Bardow, B. Smit, and S. Garcia, *Shedding Light on the Stakeholders' Perspectives for Carbon Capture*. ChemRxiv (2023) <http://dx.doi.org/10.26434/chemrxiv-2023-sn90q>

**ORAL
COMMUNICATIONS**

Towards the Selective Detection of Carbon Monoxide using Cobalt Corrole-based Porous Materials

Laurie André^a, Margerie Loze^a, Stéphane Brandès^a, Virginie Blondeau-Patissier^b, Meddy Vanotti^b, Sacha Poisson^b, Nicolas Desbois^a, Claude P. Gros^a

^aUniversité de Bourgogne, ICMUB (UMR CNRS 6302), 9 Av. Alain Savary, 21078 Dijon, France

^bInstitut FEMTO-ST (UMR CNRS 6174), 26 chemin de l'Épitaphe, 25030 Besançon, France

e-mail: laurie.andre@u-bourgogne.fr

Carbon monoxide (CO) is a well-known odourless and colourless gas which toxicity can be lethal. Indeed, the use of devices for CO detection is imperative for the prevention of intoxication, leading to a wide range of symptoms (e.g. nausea, coma, ...) and potentially causing death, in both domestic and industrial environments. Corroles are molecules derivatives of the porphyrin that present new properties when metalated.^[1] In particular, cobalt corroles have demonstrated a highly selective behaviour for the chemisorption of CO(g) on the cobalt site. However, the pi-stacking of the corroles deposited directly on a sensor proved to hinder the accessibility to about half of the cobalt sites. Dispersing cobalt corroles within a stable and porous structure could improve the accessibility to the active sites and enhance the CO adsorption overall capacity.^[2,3] The development of new materials based on the integration of cobalt corroles in porous structures such as POP (Porous Organic Polymer), COFs (Covalent Organic Frameworks), and MOFs (Metal Organic Frameworks) will be presented. Furthermore, another approach consisting of the grafting of corroles inside an already existing, very stable, Zr-MOF PCN-222 possessing natural vacancies on its metal cluster is also being studied at the moment and will be introduced. The materials were analysed using XRD, SEM images, 1H NMR, BET analysis, and CO sorption measurements.

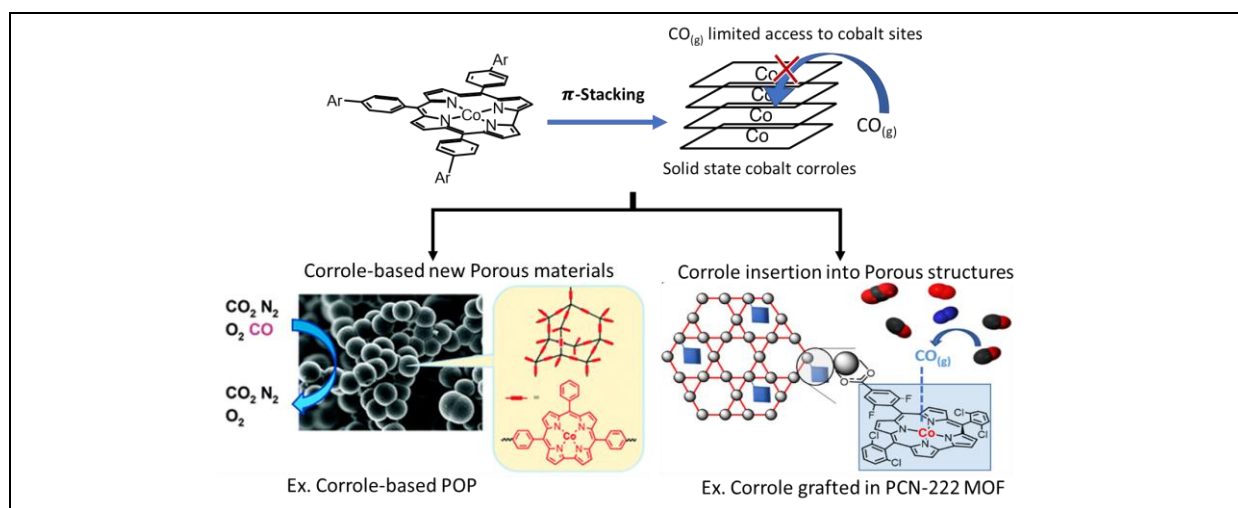


Fig. 1: Synthesis of corrole-based porous materials, or the insertion of corroles inside pre-existent porous materials could help alleviate the issue of $\text{CO}_{(g)}$ access to the corroles cobalt sites.

Acknowledgements: Work supported by the CNRS (UMR UB-CNRS 6302, the “Université de Bourgogne”, and the “Conseil Régional de Bourgogne” (ICE PhD thesis). The French Research Agency (ANR) is acknowledged for financial support (ANR-22-CE42-0016-02).

References

- [1] Di Natale C., Gros C.P., Paolesse R., *Chem. Soc. Rev.*, **2022**, 51, 1277-1335. doi: 10.1039/d1cs00662b.
- [2] Yang J., André L., Desbois N., Gros C.P., Brandès S., *Mater. Today Chem.*, **2023**, 28, March 2023, 101357. doi: 10.1016/j.mtchem.2022.101357.
- [3] Brandès S., Quesneau V., Fonquernie O., Desbois N., Blondeau-Patissier V. and Gros C.P., *Dalton Trans.* **2019**, 48, 11651-11662. doi: 10.1039/c9dt01599j.

Screening of scintillating MOFs as performant radioactive gas sensors.

Guillaume H.V. Bertrand¹, Sharvane Mauree¹, Vincent Villemot¹, Pauline Vergnory,
Matthieu Hamel¹, Benoît Sabot¹

¹Université Paris Saclay, CEA, List, F-91120 PALAISEAU, FRANCE

Corresponding Author Email: Guillaume.bertrand@cea.fr

Radioactive gases are the hardest type of contamination to contain, evaluate and quantify. The common isotopes ⁸⁵Kr, ³H and ²²²Rn are beta and alpha emitters, with emissions weakly penetrating and consequently strongly sensitive to self-shielding. This makes traditional planar detectors unsuitable. Specialized solutions exist but each of them with drawbacks as delay measurements, sensitivity, bulkiness.... As opposed to this state of art, we developed a family of porous scintillators in order to have a large contact area between the gases and the scintillating medium. Hybrid organic-inorganic scaffold such as Metal Organic Frameworks (MOF) are ideal porous candidates for this application. They are the material with the highest surface areas, up to 6000 m²g⁻¹, and highly flexible chemical design that allow the incorporation of fluorescent and scintillating properties.

We present here a comprehensive summary of our scintillating MOFs design as well as a study of their response towards ⁸⁵Kr, ²²²Rn and ³H. This achievement was made possible through a unique in the world radioactive gas test bench couple to a triple-to-double coincidence ratio set up (TDCR). The highlights of our findings includes fast response time (<5min), reproducible and linear calibration curves for ⁸⁵Kr and measurement of ²²²Rn half-life. We also demonstrate that MOF can act as a radioactive gas sponges that concentrate ⁸⁵Kr in its pores, hence giving us access to a higher local concentration of radioactive species [1].

The overall system is also transportable and could be already more practical than commercially available radioactive gas detection methods.

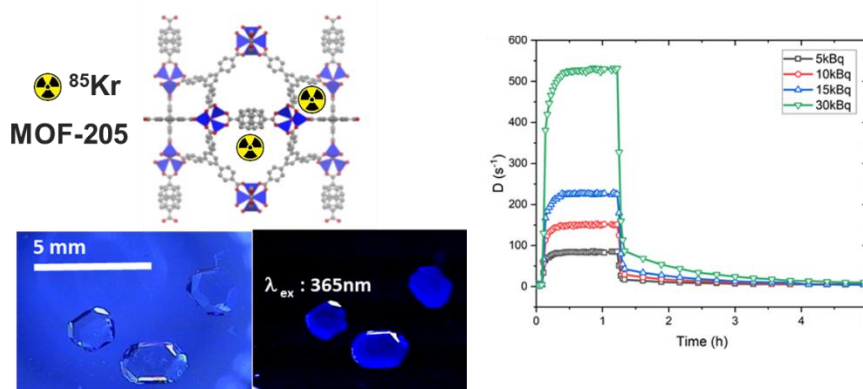


Figure 1: MOF-205 structures, crystals, and scintillation response toward a radioactive atmosphere

Acknowledgments

This project has received funding from the European Union's Horizon 2020 research and innovation program under the name SPARTE, grant agreement no. 899293.

Référence

- [1] S. Mauree, V. Villemot, M. Hamel, B. Sabot, S. Pierre, C. Dujardin, F. Belloni, A. Comotti, S. Bracco, J. Perego, G. H. V Bertrand, S. Mauree, V. Villemot, M. Hamel, S. Pierre, F. Belloni, G. H. V Bertrand, B. Sabot, A. Comotti, S. Bracco, J. Perego, **2023**, DOI 10.1002/adfm.202302877.

A tunable MOF platform for chiral chromatographic separations

Soraya Bouras^{a,b}, Jérôme Vial^b, Didier Thiebaut^b, Christian Serre^a, Antoine Tissot^a

^a*Institut des Matériaux Poreux de Paris, Ecole Normale Supérieure, ESPCI Paris, PSL University, CNRS, Paris, France.*

^b*Laboratoire Sciences Analytiques, Bioanalytiques et Miniaturisation (LSABM), CBI ESPCI Paris, PSL University, CNRS, Paris, France*

e-mail: soraya.bouras@ens.psl.eu

Current stationary phases used in chiral High-Performance Liquid Chromatography (HPLC) or Supercritical Fluid Chromatography (SFC) mainly rely on the use of functionalized cellulose or amylose. They allow efficient separation of many chiral mixtures but their cost remains excessively high regardless of the column.

MOFs are a class of porous hybrid crystalline solids promising for many applications related to gas separation/storage, catalysis, environment and health among others, thanks to their high porosity combined with a wide range of possible functionalization^[1].

The use of MOFs as stationary phases has been investigated within the past decade but the same issues remain: low column efficiency and excessive column backpressure have been reported as a result of the irregular shape, sub-micrometer and wide size distribution of the MOFs particles^{[2],[3]}.

Therefore, this project aims to design for the first time a tunable platform of cheap and efficient pure MOF chiral stationary phases for chromatography through the preparation of mesoporous MOFs, bearing specific affordable chiral groups, shaped through spray-drying as mechanically stable micrometric particles.

The MOF selected for this study, MIP-206, is a zirconium oxoclusters based mesoporous solid built with substituted feedstock derived isophthalic acids (IPA) whose large 1D pores (2.6 nm) offer an ideal platform for chromatographic separation. Along with their high chemical stability, MIP-206s can be modified with functional groups either through ligand modification or by grafting onto Zr(IV) sites in the pores^[4].

MIP-206 has first been functionalized through post-synthesis modification (PSM) with a chiral group, camphorsulfonic acid (CSA). MIP-206/CSA was then shaped by spray-drying into ‘doughnuts’ like particles and packed into a HPLC column under 200 bars. As first result, the obtained column demonstrated a separation of carvone enantiomers with a promising selectivity of more than 1.2.

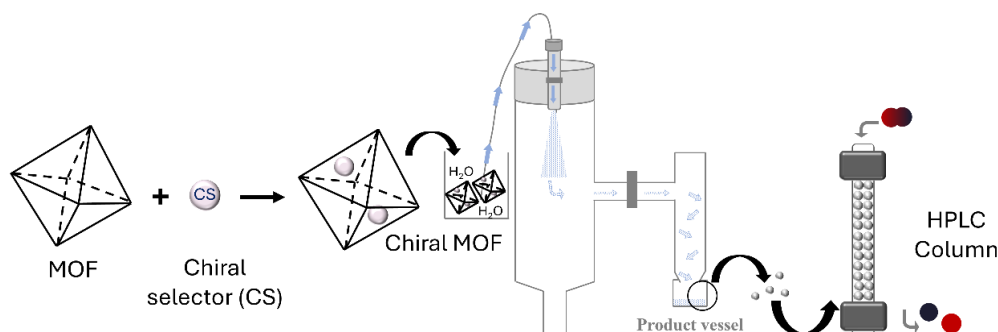


Fig. 1: Strategy of the project.

References

- [1]. Telfer, S. & Xu, Q. Special issue for The 6th International Conference on Metal-Organic Frameworks & Open Framework Compounds (MOF2018). *Coordination Chemistry Reviews* **398**, 112982 (2019).
- [2]. Padmanaban, M. *et al.* Application of a chiral metal–organic framework in enantioselective separation. *Chem. Commun.* **47**, 12089 (2011).
- [3]. Jiang, H. *et al.* Highly Stable Zr(IV)-Based Metal–Organic Frameworks for Chiral Separation in Reversed-Phase Liquid Chromatography. *J. Am. Chem. Soc.* **143**, 390–398 (2021).
- [4]. Wang, S. *et al.* A Mesoporous Zirconium-Isophthalate Multifunctional Platform. *Matter* **4**, 182–194 (2021).

Exploring the Potential of Novel BioMOF@PAN Mixed Matrix Membranes for Efficient Removal of Heavy Metal Ions from Water

Paula Escamilla,^a Rita Percoco,^b Teresa F. Mastropietro,^b Marcello Monteleone,^c Mariagiulia Longo,^c Johannes C. Jansen,^c Rosangela Elliani,^b Antonio Tagarelli,^b Emilio Pardo^{a*} and Donatella Armentano^{b*}

^a Instituto de Ciencia Molecular (ICMol), Universidad de Valencia, 46980 Paterna, Valencia, Spain

^b Dipartimento di Chimica e Tecnologie Chimiche, Via P. Bucci 14/C, Università della Calabria, Rende 87036, Cosenza, Italy

^c Institute on Membrane Technology, CNR-ITM, Via P. Bucci 17/C, 87036 Rende (CS), Italy

e-mail: paula.escamilla@uv.es

One of the most serious environmental problems faced by our modern society is the contamination of aquatic ecosystems. Among the wide variety of contaminants arising from human activities, heavy metals represent one of the most important environmental concerns.^[1] Membrane-based separation technology can play a key role in water remediation.^[2] In this study, two novel biological metal-organic frameworks (BioMOFs), embedded in polyacrylonitrile membranes, were designed, and synthesized to efficiently adsorb heavy metal ions from oligomineral water. The performances of these BioMOF@PAN membranes were investigated in a dynamic regime for the simultaneous removal of Pb²⁺, Cd²⁺, and Hg²⁺ heavy metals from aqueous environments in the presence of common interfering ions. The new composite adsorbing materials are capable of reducing the concentration of heavy metal pollutants at a higher rate with respect to the neat polymeric membrane. The enhanced performances of the mixed matrix membranes are attributed to the presence of multiple recognition sites which densely decorate the BioMOF channels : i) the thioether groups, derived from the *S*-methyl-*L*-cysteine and (*S*)-methionine amino acid residues, able to recognize and capture Pb²⁺ and Hg²⁺ ions, and ii) the oxygen atoms of the oxamate moieties, which preferentially interact with Cd²⁺ ions, as revealed by single crystal X-ray diffraction. The flexibility of the pores environments, allow these sites to work synergically for the simultaneous capture of different metal ions. The stability of the membranes for a potential regeneration process, a key-factor for the effective feasibility of the process in real life applications, was also evaluated.

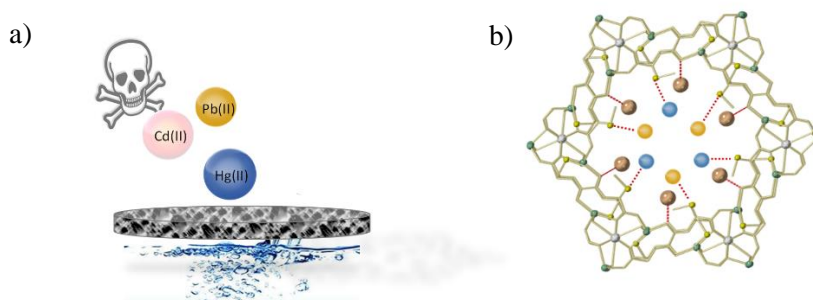


Fig. 1: a) Schematic representation of the filtration process by bioMOF@PAN membrane. b) Detail of the interaction between heavy metal ions and functional groups decorating MOFs channels.

References

[1] Sousa, J.C.G., Ribeiro, A.R., Barbosa, M.O., Pereira, M.F.R., Silva, A.M.T., 2018. A review on environmental monitoring of water organic pollutants identified by EU guidelines. *J. Hazard. Mater.* 344, 146–162.

[2] Baker, R. W. *Membrane Technology and Applications* (John Wiley & Sons, 2012).

Investigating the structure and adsorption properties of MOFs based on machine learning potential

Dong Fan^a, Shanping Liu^a, Romain Dupuis^{a,b}, Supriyo Naskar^a, Aydin Ozcan^c, Pengbo Lyu^d, Salma Benzaria^e, Mickaele Bonneau^e, Prashant Bhatt^e, Mohamed Eddaoudi^{e,*}, Guillaume Maurin^{a,*}

^a ICGM, Univ. Montpellier, CNRS, ENSCM, Montpellier, 34095, France.

^b LMGC, Univ. Montpellier, CNRS, Montpellier, France

^c TUBİTAK Marmara Research Center, Materials Technologies, Gebze, Kocaeli, 41470, Turkey

^d Hunan Provincial Key Laboratory of Thin Film Materials and Devices, School of Material Sciences and Engineering, Xiangtan University, Xiangtan, 411105, China

^e Division of Physical Science and Engineering, Advanced Membrane and Porous Materials Center, King Abdullah, University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia

e-mail: mohamed.eddaoudi@kaust.edu.sa (M.E.); guillaume.maurin1@umontpellier.fr (G.M.)

Recently, the incorporation of machine learning potential (MLP) approaches into materials science has revolutionised the way properties of more complex materials such as MOFs can be predicted. We first investigated the mechanical and thermodynamic properties of two typical MOF architectures, three-dimensional (3D) CALF-20 and two-dimensional (2D) NiF₂(pyz)₂, by using the MLP-bead molecular dynamics (MLP-MD) simulation approach. For the CALF-20 structure, our simulations showed that it exhibits negative area compression and negative thermal expansion simultaneously, making the material attractive for mechanical/thermal sensing applications in addition to CO₂ capture. Interestingly, we also demonstrated an unconventional *strain-softening* behaviour of CALF-20 both at 0 K and at room temperature under uniaxial tensile stress, eventually leading to the formation of a metastable structure. Using the 2D NiF₂(pyz)₂ MOF as a case study, we discovered a counterintuitive negative in-plane stretchability phenomenon in the structure, where the surface area decreases with the applied tensile strain, making this 2D MOF ideal for flexible wearable electronics and ultrathin sensor applications. We have also demonstrated the unique ability of MLP to accurately predict the finite-temperature properties of MOFs on a large scale, exemplified by MLP-MD simulations with a dimension of 28.2 × 28.2 nm², which is relevant to the experimentally achievable length scale for the fabrication of MOF films. Besides exploring the structural properties of MOFs, we also developed a computational workflow to probe the gas adsorption performance based on MLP. By adopting Al-soc-MOF-1d as the material of interest, the MLP of H₂@Al-soc-MOF-1d was developed. Based on well-trained MLP, a grand canonical Monte Carlo (GCMC) simulation method was developed and performed to predict the H₂ adsorption isotherm of Al-soc-MOF-1d at 77 K, which was further confirmed by the adsorption data we collected on this sample. The results of these investigations will accelerate the development of new MOF materials with improved gas adsorption performance, thereby addressing critical challenges in energy storage and environmental sustainability.

References

- [1] D. Fan, S. Naskar, G. Maurin. Unconventional mechanical and thermal behaviours of MOF CALF-20. *Nat. Commun.* 2024, **15**, 3251.
- [2] D. Fan, A. Ozcan, P. Lyu, G. Maurin, Unravelling abnormal in-plane stretchability of two-dimensional metal-organic frameworks by machine learning potential molecular dynamics. *Nanoscale* 2024, **16**, 3438-3447
- [3] S. Liu, R. Dupuis, D. Fan, S. Benzaria, M. Bonneau, P. Bhatt, M Eddaoudi, G. Maurin, Machine learning potential for modelling H₂ adsorption/diffusion in MOFs with open metal sites. *Chem. Sci.* 2024, **15**, 5294-5302

ORAL POSTER

Investigation of Structure-Property Relationship in MOFs for Efficient Benzene Adsorption

Kevin Dedecker, Martin Drobek and Anne Julbe

Institut Européen des Membranes (IEM); CNRS, ENSCM, Univ Montpellier; Place Eugène Bataillon; 34095 Montpellier; France

e-mail: kevin.dedecker@umontpellier.fr

Volatile organic compounds (VOCs), particularly benzene, pose significant threats to air quality, human health, and the environment. To address this concern, effective capture methods are essential. Metal-Organic Frameworks (MOFs) have emerged as promising materials due to their high surface area and tuneable adsorption properties [1].

This presentation aims to explore the reticular chemistry of MOFs by integrating experimental data and theoretical modelling. Specifically, the impact of metal ions and ligand aromaticity on benzene affinity within isostructural/isorecticular MOFs will be investigated in details. A thorough understanding of these fundamental aspects allows proposing relevant strategies for the design of MOF-based adsorbents for benzene capture, thereby contributing to improving air quality and human health. Two examples will be reported and discussed, highlighting respectively the impact of palladium as a metal node and the role of highly conjugated ligands (e.g. pyrene-like) for the efficient capture and detection of benzene.

Despite the well-known affinity of palladium for rich π systems, research on Pd(II)-based MOFs for VOC capture remains limited. We have compared the adsorption properties of isostructural $[\text{Pd}(2\text{-pymo})_2]_n$ and $[\text{Cu}(2\text{-pymo})_2]_n$, focusing on their selectivity for linear, cyclic, and aromatic VOCs [2]. We have demonstrated that $[\text{Pd}(2\text{-pymo})_2]_n$ exhibits a higher affinity for aromatic compounds than for saturated hydrocarbons, unlike $[\text{Cu}(2\text{-pymo})_2]_n$. Additionally, $[\text{Pd}(2\text{-pymo})_2]_n$ exhibits preferential adsorption of benzene over toluene due to steric hindrance effects.

Another computational study was carried out on a series of isorecticular IRMOFs (-1, -10, -14 and -16) to assess the effect of ligand aromaticity on the adsorption affinity for benzene and its non-aromatic analogue, cyclohexane [3]. We observed that while K_H values decrease with elongation of the ligand (IRMOF-10, -16), insertion of a pyrene core (IRMOF-14) significantly increases the adsorption efficiency for both cyclohexane and benzene by ~290% and 54%, respectively.

Acknowledgement

Authors acknowledge the ANR (SensMOFAir project #ANR-20-CE04-0012) for funding this research.

References

- [1] Dedecker, K. *et al.*, chapter 5 - Metal-organic frameworks for the capture of volatile organic compounds and toxic chemicals, *Metal-Organic Frameworks (MOFs) for Environmental Applications*; Ed. Sujit K. Ghosh, Elsevier, 2019; pp 141–178.
- [2] Dedecker, K. *et al.*, A Palladium-Based MOF for the Preferential Sorption of Benzene. *ACS Appl. Mater. Interfaces* 2023, 15 (5), 6831–6838.
- [3] Dedecker, K. *et al.*, Effect of Ligand Aromaticity on Cyclohexane and Benzene Sorption in IRMOFs: A Computational Study. *J. Phys. Chem. B* 2023, 127 (51), 11091–11099.

Metal-Organic Frameworks: Evaluating cytotoxicity assays and their antiviral activity against coronaviruses

Orfeas-Evangelos Plastiras,^{a,b} Peggy Bouquet,^c Jeremy Dhainaut,^a Jean-Philippe Dacquin,^a Anne Goffard^b and Christophe Volkringer^a

^a UMR CNRS 8181, Unité de Catalyse et Chimie du Solide, Centrale Lille, CNRS, Université de Lille, 59000 Lille, France.

^b U1019 – UMR 9017 – CIIL - Center for Infection and Immunity of Lille, Institut Pasteur de Lille, Université de Lille, CNRS, INSERM, CHU de Lille, 59000 Lille, France.

^c Clinical Microbiology Unit, Institut Pasteur de Lille, Lille F-59000, France.

e-mail: orfeas.plastiras@centralelille.fr

Severe acute respiratory syndrome coronavirus-2 (SARS-CoV-2) is responsible for the corona virus disease of 2019, or else COVID-19, which originated from Wuhan of China in December of 2019.¹ Up to this day, this disease that was declared a pandemic by WHO on March 11 of 2020 is accountable for 6.8 million deaths and 758 million cases worldwide as of March 6th 2023.²

In this work, five metal-organic frameworks synthesized with different metals (Zr, Cu, Fe, Ti) were used to evaluate different cytotoxicity methods in three cell lines, named MTS, Neutral Red and LDH as cytotoxicity methods and Huh7 TMRSS2, VeroE6 and Vero81.6 as cell lines. Different levels of concentrations were tested and the Neutral Red method was found to be the most precise and accurate, while MTS and LDH gave similar results, but with high standard deviations. 1 mg/mL was the highest concentration that was not toxic for every MOF in every cell line except the one with copper, whose maximum safest value was 0.1 mg/mL. Furthermore, their efficiency against CoV-type viruses (HCoV-229E and SARS-CoV-2) was examined with different tests, that were able to determine both the viral titer and the infectivity of the virus. The Cu and Ti MOFs showed a significant drop of the viral titer of HCoV-229E, while for SARS-CoV-2 the aforementioned MOFs and the Fe MOF exhibited an important decrease.³

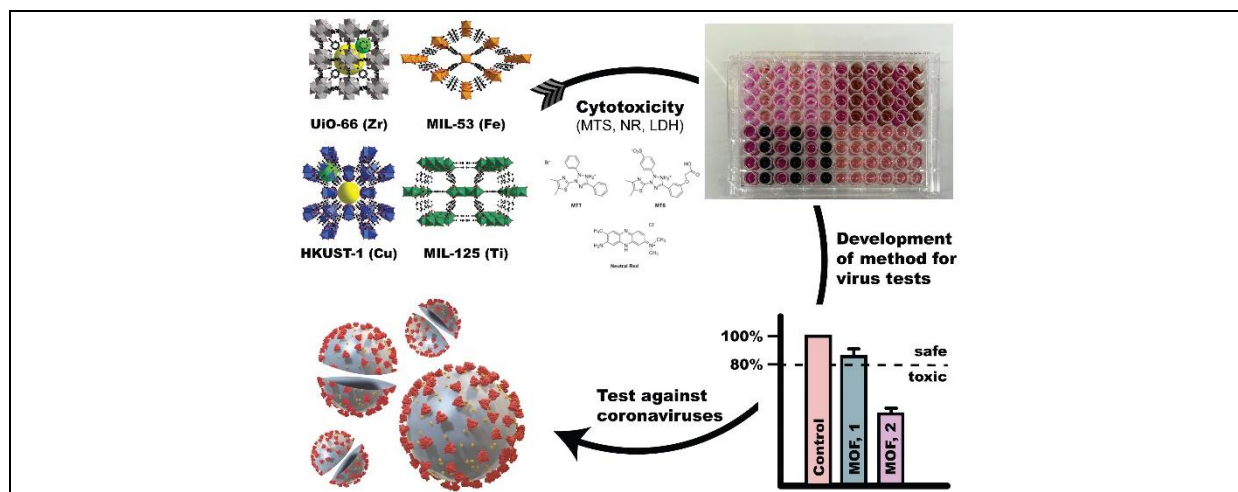


Fig. 1: Representative graphical scheme of the protocol used for the inactivation of coronaviruses.

References

- [1] Zheng, J., *Int. J. Biol. Sci.*, **2020**, 16 (10), 1678-1685.
- [2] <https://www.who.int/emergencies/diseases/novel-coronavirus-2019> (Accessed on March 6th 2023)
- [3] Plastiras, O.-E. et al., *Microporous Mesoporous Mater.*, **2024**, 367, 112975.

ORAL ☒

POSTER ☒

WHOLE CELL THERAPEUTIC AND PROPHYLACTIC VACCINES AGAINST UTI USING METAL ORGANIC FRAMEWORK

**Ikeda Trashi^a, Yalini Wijesundara^b, Jashkran Gadhvi^c, Fabian Castro^d, Samuel Cornelius^e,
Ujjaini Basu^f, Nicole De Nisco^g, Jeremiah Gassensmith^h**

^{a,b,c,d,e,f,g,h} *University of Texas at Dallas, Richardson, Texas, United States, 75080*

e-mail: ikeda.trashi@utdallas.edu

Gassensmith@utdallas.edu

----- ONE PAGE ONLY -----

Main text describing the main results

Conclusions

Urinary tract infection (UTI) stands as the prevailing bacterial infection in adults globally, predominantly attributed to uropathogenic *Escherichia coli* (UPEC) in approximately 80% of uncomplicated cases.¹ Notably, recurrent UTIs affect 25-50% of patients within a year, emphasizing the imperative need for innovative, non-antibiotic-based therapies to empower the immune system in combating bacterial challenges, thereby reducing reliance on antibiotics.² Current challenges in vaccine strategies against recurrent UTIs lie in their potential failure to target the requisite immunological mechanisms for inducing enduring memory. It is predicted that up to 10 million deaths will be attributed to drug-resistance by 2050 and surpass cancer deaths.³ The need for a vaccine that clears the infections but also makes it easier to transport and reach everyone is very necessary. We are studying a novel method to create whole-cell UPEC vaccines, using Zeolitic Imidazolate Frameworks (ZIFs). ZIFs are a subclass of solid-state crystalline porous metal-coordination polymers (PCPs). ZIF-8, a PCP composed of a repeated framework of zinc ions interlinking 2-methylimidazole (HMIM) molecules, self-assembles on protein surfaces through interactions between Zn²⁺ and peptide backbones.⁴ The resulting ZIF-8 shell has exceptional thermodynamic stability against high temperatures but dissolves completely in the presence of biological phosphates and chelators such as EDTA. These characteristics make ZIF-8 an ideal material for reversible immobilization, meaning that material can be encapsulated but also easily released from the framework.⁵⁻⁷ We have demonstrated that ZIF encapsulations completely inactivated the UTI bacteria within 30 minutes and kept the bacteria fimbria intact, which allows the immune system to generate an immune response. We found out that our vaccine can slowly supply the body with antigens to create a memory immune response and clear out the bacteria in the bladder after infection. We are currently investigating the "prime and pull" vaccination strategy, proven effective in viral and bacterial infections, entails an initial subcutaneous or intramuscular "priming" vaccination to activate CD4⁺ and CD8⁺ T effector cells, followed by a critical second step involving the instillation or deposition of an antigen depot to induce Tissue-resident memory T cells (TRMs) in targeted tissues.⁸⁻¹⁰ This innovative approach aims to harness the potential of TRM cells for sustained protection during periods of heightened circulating effector cells.

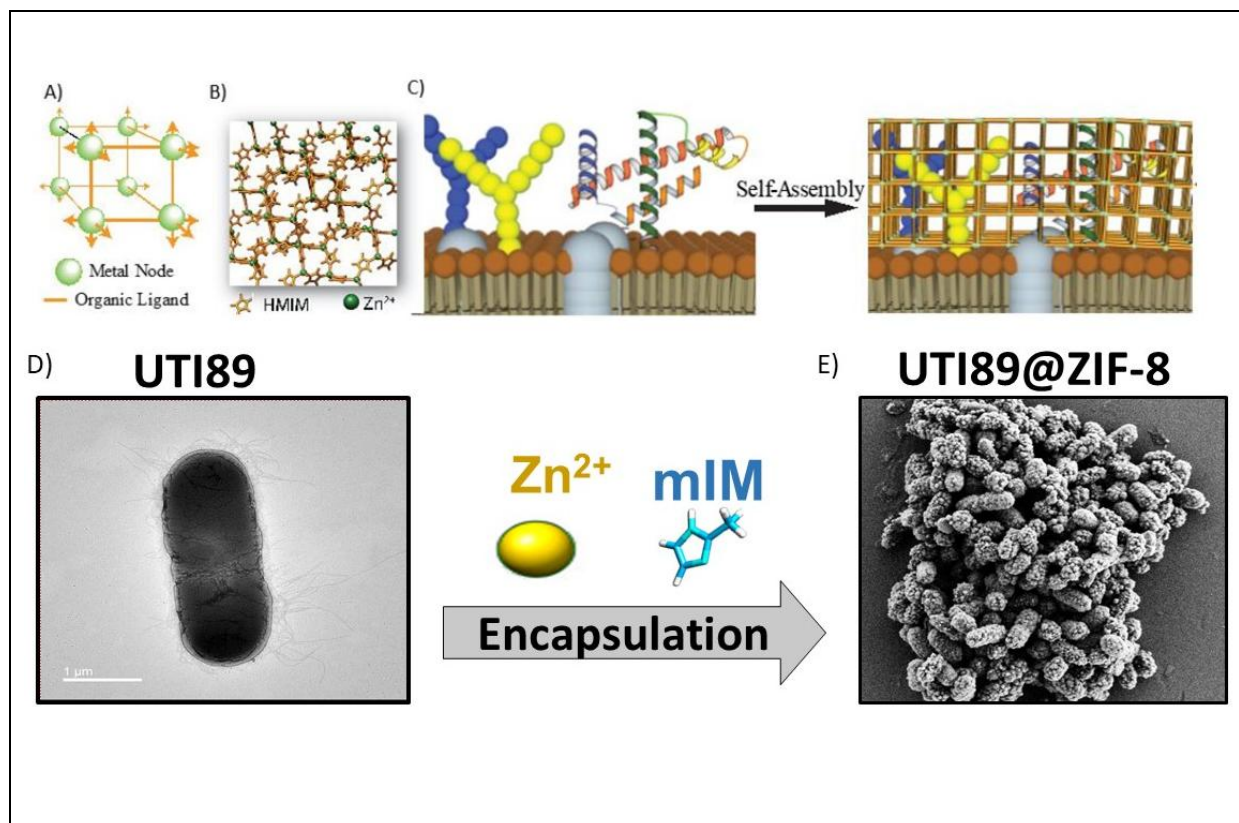


Fig. 1: A) Construction of a ZIF polymer. (B) Crystal structure of ZIF-8 showing cage and pores in an extended lattice. (C) Schematic of the biomimetic mineralization process and (D) UTI89 bacteria before encapsulation and the result of discretely encapsulated bacteria.

References

1. A. J. Westermann, L. Barquist and J. Vogel, *PLoS pathogens*, 2017, **13**, e1006033.
2. G. G. Zhanel, T. L. Hisanaga, N. M. Laing, M. R. DeCorby, K. A. Nichol, L. P. Palatnick, J. Johnson, A. Noreddin, G. K. Harding and L. E. Nicolle, *International journal of antimicrobial agents*, 2005, **26**, 380-388.
3. M. Ahmad and A. U. Khan, *Journal of global antimicrobial resistance*, 2019, **19**, 313-316.
4. V. P. O'Brien, T. J. Hannan, H. V. Nielsen and S. J. Hultgren, *Urinary Tract Infections: Molecular Pathogenesis and Clinical Management*, 2017, 589-646.
5. M. A. Luzuriaga, F. C. Herbert, O. R. Brohlin, J. Gadhvi, T. Howlett, A. Shahriarkevisshahi, Y. H. Wijesundara, S. Venkitapathi, K. Veera and R. Ehrman, *ACS nano*, 2021, **15**, 17426-17438.
6. M. Mellata, N. M. Mitchell, F. Schödel, R. Curtiss 3rd and G. B. Pier, *Vaccine*, 2016, **34**, 656-662.
7. O. Clermont, S. Bonacorsi and E. Bingen, *Applied and environmental microbiology*, 2000, **66**, 4555-4558.
8. F. C. Knight and J. T. Wilson, *Advanced therapeutics*, 2021, **4**, 2000230.
9. N. Çuburu, R. Kim, G. C. Guittard, C. D. Thompson, P. M. Day, D. E. Hamm, Y.-Y. S. Pang, B. S. Graham, D. R. Lowy and J. T. Schiller, *The Journal of Immunology*, 2019, **202**, 1250-1264.
10. S. Haddadi, M. Vaseghi-Shanjani, Y. Yao, S. Afkhami, M. R. D'Agostino, A. Zganiacz, M. Jeyanathan and Z. Xing, *Frontiers in immunology*, 2019, **10**, 2075.

ORAL ☒

POSTER □

Discovery and Photocycle Assessment of an Acridinium-Based Mesoporous Covalent Organic Framework Photocatalyst

Ipsita Nath,* Jeet Chakraborty, Kuber Singh Rawat, Yanwei Ji, Pieter Geiregat, Veronique Van Speybroeck, Pascal Van Der Voort*

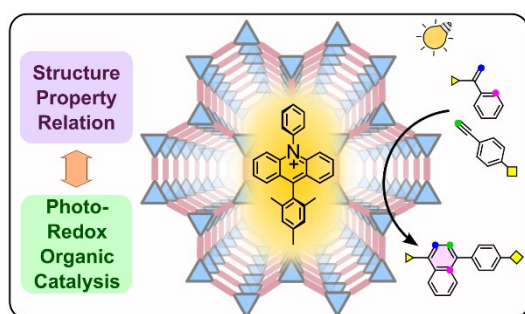
Universiteit Gent, Gent, Belgium, 9000

e-mail: inath.nath@ugent.be; pascal.vandervoort@ugent.be

Covalent Organic Frameworks (COFs) are a growing class of lightweight extended organic networks featuring programmable chemical design, permanent nano-porosity, high surface area, and long-range molecular ordering.^[1] Handpicking photo-responsive redox-active organic moieties as monomers for COFs endows a heterogeneous platform for the merger of traditional photocatalysis with high surface area, ordered channels, and pores of COF, which further initiates a nano-confinement effect. The pores with densely decorated photocatalytic units serve as nano-reactors by integrating efficient mass flow and interfacial charge transfer, *ergo* augmenting catalytic activity.^[1]

The extended conjugation instigates a semiconducting nature in COFs that appends an added attribute to the spatiotemporal charge dynamics in the materials. A detailed analysis of the formation, delocalization, and decay of the excited-state species, *e.g.*, excitons, excimers, trap- and free-charges, etc. in these materials and their impact on the interfacial charge transfers can help us understand the holistic photocycle and the photocatalysis process from a fundamental perspective across both length- and timescale.^[2] The current lack of such comprehensive understanding, and limited valence and conduction band (VB-CB) potentials of COFs often constrain their catalytic applicability only to a limited range of reactions.

Acridiniums (ACR) are a class of homogeneous expensive metal-free photocatalysts widely used for various organic transformations.^[3] Merging ACRs and COFs with detailed photocycle assessment could change the state-of-the-art photocatalysis horizon by addressing the shortcomings of both homogeneous and heterogeneous photocatalysts while offering a holistic understanding of the excited-state processes.



Based on this premise, we herein report a novel post-synthetic modification (PSM) strategy to synthesize acridinium-based COF (ACR-COF) for a wide-range photocatalytic activity (Fig. 1). A triflic acid-catalyzed PSM of a pristine triphenylamine (TPA)-based COF (TPA-COF) with mesityl chloride afforded the first-of-its-kind ACR-COF. We thoroughly studied the structural constraints to obtain the material. ACR-COF was custom-designed to contain *ca.* 5 nm pores, ensuring efficient

Fig. 1: Acridinium-based COF for oxidative mass flow during catalysis, even for large substrates. The [4+2] annulation.

The detailed photophysics and optoelectronics of the material were assessed using ultrafast absorption spectroscopy with parallel theoretical support from DFT calculations. These analyses underpinned the high mobility of the excitons across COF planes and the existence of long-lived excimers and trap charges. This stability of these excited-state species resulted in efficient interfacial charge transfer, and eventual oxidative Diels-Alder annulation of styrenes and alkynes to corresponding fused naphthalenes under a green and sustainable condition. A mechanism backed with experimental, spectroscopic, and theoretical support was proposed.

References

[1] *Science* **2017**, 355, eaal1585; *Science* **2005**, 310, 1166; *Chem. Soc. Rev.* **2020**, 49, 8469.

[2] *Adv. Mater.* **2024**, 2314056.

[3] *Chem. Soc. Rev.*, **2021**, 50, 766; *Chem. Rev.*, **2016**, 116, 10075.

Heterogenized Molecular Photocatalysis for CO₂ to Formic Acid Conversion Using Visible Light

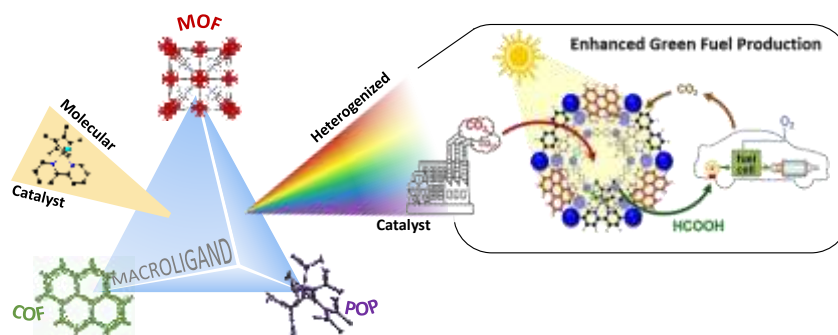
R. Kumari Riddhi, J. Canivet E. A. Quadrelli

Université Claude Bernard Lyon 1, CNRS, IRCELYON - UMR 5256, 2 Avenue Albert Einstein, 69626 Villeurbanne Cedex, France

e-mail: riddhi.kumari@ircelyon.univ-lyon1.fr

The incorporation of a homogeneous catalyst onto a molecularly defined porous solid support can help overcome various limitations associated with traditional homogeneous catalysts, including issues related to recyclability, stability, selectivity, and ease of product purification. On the other hand, visible-light photoredox catalysis has emerged as a powerful and sustainable alternative to harsh thermal conditions for chemical bond activation and forming reactions.¹ Merging the heterogenization of molecular catalysts with visible light photoredox catalysis can be crucial for bridging the gap between molecular and heterogeneous catalysis^{2,3} and at the same time can offer enhanced long-term productivity, eliminate the need for external photosensitizers, and promote more sustainable catalytic process.

Herein, we discuss photoactive porous materials containing bipyridine moieties as macroligands⁴ for the immobilization of a rhodium-based molecular catalyst for visible-light-driven CO₂ reduction.⁵ The immobilization of rhodium catalyst allows the visible light-mediated CO₂ photoreduction of a cumulative productivity of up to 8.3 grams of formic acid per gram of catalyst. The porous organic polymers enable these catalysts to achieve the same intrinsic productivity as the parent molecular complexes, without electronic or steric detrimental effects such as diffusion limitations, while also offering advantageous recycling capabilities. Therefore, the synthetic versatility of porous organic polymers, envisioned as porous macroligands, presents promising prospects for developing novel heterogeneous catalysts for more sustainable molecular catalytic processes.



References

- [1] Maximilian. D. Palkowitz, *Acc. Chem. Res.* **2023**, 56, 2851–2865.
- [2] F. M. Wisser, J. Canivet, *ACS Appl. Energy Mater.* **2023**, 6, 9027–9043.
- [3] F. M. Wisser, P. Berruyer, L. Cardenas, Y. Mohr, E. A. Quadrelli, A. Lesage, D. Farrusseng, J. Canivet, *ACS Catal.* **2018**, 8, 1653–1661.
- [4] F. M. Wisser, Y. Mohr, E. A. Quadrelli, J. Canivet, *Chem. Cat. Chem.* **2020**, 12 (5), 1270–1275.
- [5] R. Newar, A. C. Ghosh, R. Kumari Riddhi, R. Rajapaksha, P. Samanta, F. M. Wisser, J. Canivet *Adv. Energy Sustainability Res.* **2023**, 2300209.

IMPROVEMENT OF PHOTOCATALYTIC CO₂ REDUCTION ACTIVITY VIA THE ENCAPSULATION OF POLYOXOMETALATES IN MOF-545

K. Talbi^{a,b}, A. L. Robinson^{a,b}, Y. Benseghir^{a,b}, H. Chen^b, A. Solé-Daura^c, M. Gomez-Mingot^b, M. Fontecave^b, P. Mialane^a, C. Mellot-Draznieks^{a,b}, A. Dolbecq^a

^a Université Paris-Saclay, UVSQ, CNRS UMR 8180, Institut Lavoisier Versailles, 45 av. des Etats-Unis, 78000, Versailles, France

^b LCPB, CNRS UMR 8229, Collège de France, Sorbonne Université, PSL Research University, 11 Pl. Marcelin Berthelot, 75231 Paris Cedex 05

^c Institute of Chemical Research of Catalonia, The Barcelona Institute of Science and Technology (ICIQ-BIST), Tarragona 43007, Spain

e-mail: amanda.robinson@college-de-france.fr; anne.dolbecq@uvsq.fr

Photocatalytic transformation of CO₂ into added-value carbon-based compounds (e.g., CO, HCO₂H, CH₄ ...) is a promising approach to valorizing excess CO₂ in the atmosphere. Our group has previously focused on modifying UiO-67 and MOF-545 to enhance their photoreduction of CO₂ to formate (HCO₂⁻).¹⁻³ Taking advantage of the high porosity of MOFs, we have notably shown that the polyoxometalate (POM) [PW₁₂O₄₀]³⁻ (PW₁₂) can be encapsulated in Cp*Rh@UiO-67 to make a (PW₁₂,Cp*Rh)@UiO-67 composite material. Due to the capacity of PW₁₂ to act as an electron reservoir, the composite material is twice as active for formate production as compared to its parent material.² In this oral presentation, we further demonstrate the utility of this strategy by encapsulating either the [SiW₁₂O₄₀]⁴⁻ (SiW₁₂) or the [W₁₀O₃₄]⁴⁻ (W₁₀) POMs within MOF-545. Both of the POM@MOF-545 composites were much more active than the parent MOF-545 for the production of formate (Fig. 1). DFT calculations are ongoing to elucidate information about the catalytic mechanism that governs these photochemical reactions, including the position of the POMs in MOF-545.

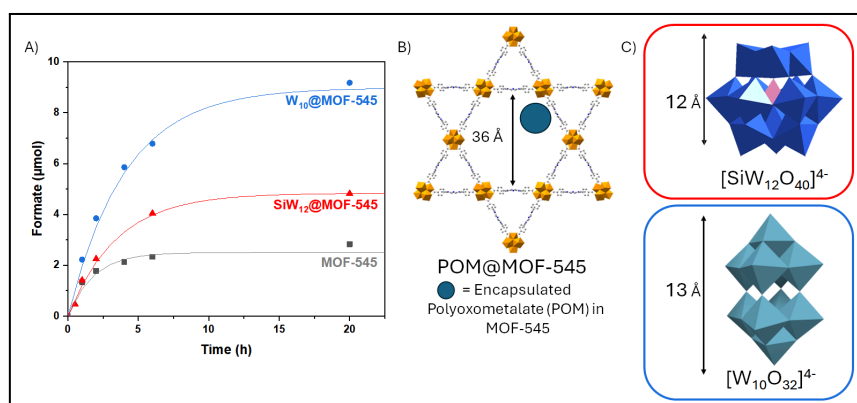


Fig. 1: (A) Formate production (in µmol) for MOF-545 and the POM@MOF-545 materials over time (2 mg in 2 mL acetonitrile/triethanolamine 20:1, irr. 400-1100 nm, 100 mW/cm²). (B) Representation of the POM@MOF-545 materials. (C) Structures of the encapsulated POMs used in this study.

References

- [1] M. B. Chambers et al., *ChemSusChem*, **2015**, *8*, 603-608.
- [2] Y. Benseghir et al. *J. Am. Chem. Soc.*, **2020**, *142*, 9428-9438.
- [3] Y. Benseghir et al., *J. Mater. Chem. A.*, **2022**, *10*, 18103-18115.

Metal-Organic Framework for Hydrogen Production through Light-driven Water Splitting

Edouard Vöggtli^a, Anthony Beauvois^b, Georges Mouchaham^a, Laurent Barthe^b, Antoine Tissot^a, Sergio Navalón^c, Hermenegildo García^c, Valérie Briois^b, Christian Serre^a

^a Institut des Matériaux Poreux de Paris, Ecole Normale Supérieure, ESPCI Paris, CNRS, PSL University, Paris, 75005 France.

^b Synchrotron SOLEIL, Centre National de la Recherche Scientifique, L'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette Cedex, France.

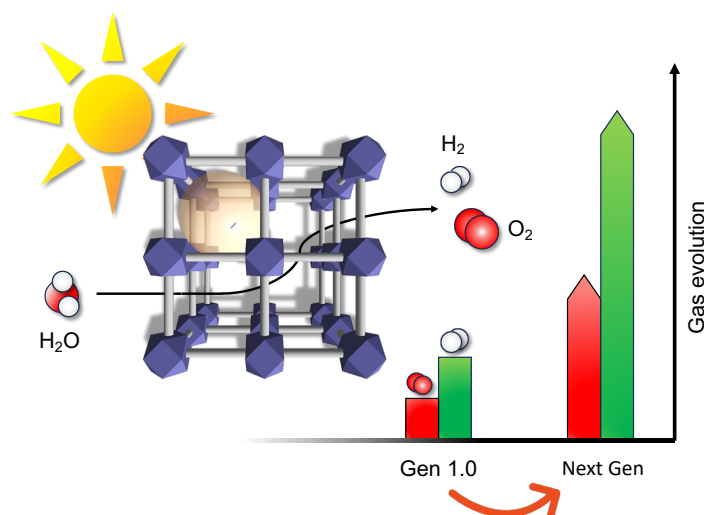
^c Universitat Politècnica de València = Universidad Politécnica de Valencia = Polytechnic University of Valencia (UPV), Camino de Vera, s/n 46022 Valencia, Spain.

email: edouard.voggtli@espci.fr

Non-sustainable fossil fuel dependent processes still account for most of the worldwide hydrogen production.^[1] Among alternatives, photocatalyzed water dissociation into H₂ and O₂ is particularly appealing owing to its intrinsic sustainable nature.^[2] However, hitherto reported catalysts for light-driven water splitting still do not meet the techno-economical requirements for industrial implementation as they suffer from either a lack of solar-to-hydrogen conversion (STH) efficiency and/or stability under operation, require complex synthesis processes and are in most cases inactive under visible light irradiation.^[3,4]

Over the last couple of years, metal-organic frameworks (MOF) have drawn increasing interest as candidate catalysts but most reported studies deal with either of the half reactions, i.e., the hydrogen and oxygen evolution reactions (HER and OER, respectively), thus requiring the use of sacrificial agents.^[4] Inspired by nature, a MOF was selected that is made of a multicopper-containing metalloligand reminiscent of the active site of certain reductive enzymes and found to be an efficient catalyst for the photo-induced water splitting reaction. This noble metal-free material is stable in water for several months, while no decrease in activity is observed over four successive reaction cycles. The underlying reaction mechanism was investigated using time-resolved X-ray absorption spectroscopy (XAS) under *operando* conditions, with the results hinting at the metalloligand for being the active site. If confirmed, this could pave the way for the development of new generations of related catalysts of improved performance.

In this communication, I will present our ongoing work directed at improving the catalysts' performances along with a specific highlight on the development of an experimental set-up, in particular its photocatalytic reactor, to carry out the *operando* XAS studies.



References

- [1] P. J. Megía et al. *Energy Fuels*, 2021, 35, 20, 16403–16415; [2] V. Balzani et al. *Science*, 1975, 189, 852–856; [3] M. Z. Rahman et al. *Chem. Soc. Rev.* 2020, 1887; [4] S. Navalón et al. *Chem. Rev.* 2023, 123, 1, 445–490.

Development of copper MOF-based composites with enhanced chemical stability and high CO₂ uptake

Y. KHADIRI^{a,b}, C. Volkringer^a, A. Anouar^b, S. Royer^a, A. El Kadib^a, T. Loiseau^a, J. Dhainaut^a

^a Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 UCCS – Unité de Catalyse et Chimie du Solide, F-59000 Lille, France

^b Euromed Research Center, Engineering Division, Euro-Med University of Fes (UEMF), Route de Meknes, Rond-point de Bensouda, 30070 Fès, Morocco.

e-mail: yassine.khadiri@univ-lille.fr

Metal Organic Frameworks (MOFs), are a class of hybrid materials formed by inorganic clusters that are connected to each other by organic linkers, forming organized and open crystalline networks. They are known for their high specific surface areas, permanent nanocrystalline porous structure. These materials have invaded several fields of chemistry thanks to their high porosity and structural flexibility. However, their use in industrial fields remains limited due to their difficult processing and their low chemical and thermal stability. The combination of MOFs with polysaccharides such as chitosan is one of the strategies adapted to overcome these limitations and to obtain composites for different shaping like monoliths, films, or microspheres [1]. On the other hand, the combination of MOFs with second partner like graphene oxide (GO) was one of the solutions suggested to attenuate the effect of humidity on MOFs stability [2].

Numerous studies have shown that when using chitosan biopolymer as a platform to grow and process MOFs in in form of beads or monolith form, it is widely acknowledged that incorporating a supercritical CO₂ drying step is crucial to prevent the collapse of the porous structure [3]. However, this drying method also has some disadvantages: high cost and long processing time. In our studies, to address the stability and shaping challenges of MOFs and circumvent the drawbacks of supercritical drying, we selected HKUST-1 (Cu-BTC), a well-studied MOF known for its instability in water. We integrated it with graphene oxide within a chitosan matrix under mild conditions to form self-standing beads., followed by a simple atmospheric drying step to prepare water stable porous xerogels with high crystallinity and a specific surface area exceeding 800 m²g⁻¹. The as-prepared CS@HKUST-1 and CS-GO@HKUST-1 beads (Figure on the side) were used for CO₂ uptake where they showed promising performances (2.60 mmol/g at 298K).

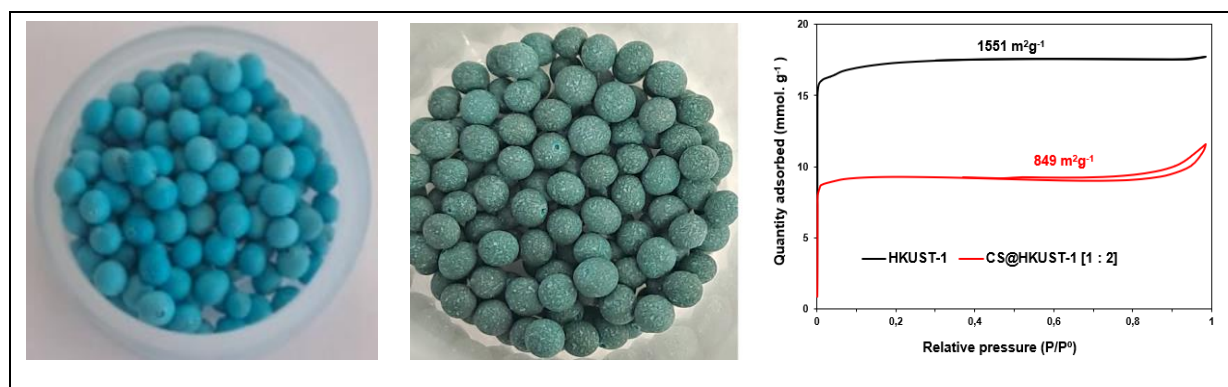


Fig. 1: As-prepared CS@HKUST-1 beads (left) and CS-GO@HKUST-1 beads (middle), and N₂ sorption isotherms of as-prepared CS@HKUST-1 and HKUST-1 powder (right).

References

- [1] El Hankari, S, *et al.*. Progress in Materials Science, 106 (2019): 100579.
- [2] Miao, Q, *et al.* A review." Journal of Water Process Engineering, 50 (2022): 103348.
- [3] El Kadib, A. The Chemical Record, 20 (2020), 753-772.

Investigating polymeric membranes for CCS under industrial conditions

S. McIntyre¹, Lisa Sun¹, A. Foster², P. Budd², D. R. Williams³, P. Iacomi^{1*}

¹Surface Measurement Systems, London, UK, ²The University of Manchester, Manchester, UK,

³Imperial College London, London, UK

*piacomi@surfacemeasurementsystems.com

Keywords: Carbon Capture, Polymers of Intrinsic Microporosity, Humidity, Gas selectivity

An attractive type of membrane material for CCS applications are polymers with intrinsic microporosity (PIMs) – forming flexible and easy-to-manufacture single-component membranes with high gas permeabilities and selectivity for CO₂ over N₂ and O₂ – primary components of flue gas. In this work, a novel membrane analyzer was developed to observe the multi-component permeation of flue gas constituents through membranes of PIM-1 and its more hydrophilic carboxylate functionalized version, cPIM-1, to reveal the impact of contaminants and industrial process conditions on the membrane separation efficiency.

Humidity was first introduced to the membranes for 3 hours, followed by 10% CO₂ in N₂ whilst maintaining the selected humidity. The permeation curves were measured using CO₂ and humidity probes at the inlet and outlet, with nitrogen measured using a TCD.

The carboxylated PIM-1, cPIM-1, was studied under the same conditions as PIM-1. The carboxylation is known to make the cPIM-1 membrane more hydrophilic and thus the effect of increasing relative humidity was found to be more pronounced, with a 40% decrease in CO₂ permeation observed in cPIM-1 compared to the 20% decrease observed for PIM-1. The CO₂/N₂ selectivity of cPIM-1 was found to decrease by 20% over the same humidity range. Separate water permeation studies found that the behavior of the cPIM-1 membrane when exposed to water was opposite to that behavior of PIM-1 owing to the hydrophilicity of cPIM-1, with the water permeation and diffusion constant increasing with relative humidity.

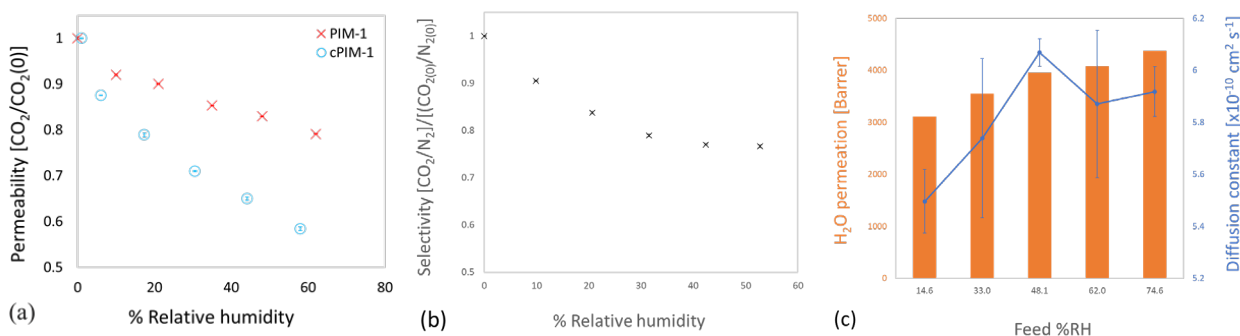


Figure 1: (a) The impact of humidity on PIM-1 and cPIM-1 CO₂. (b) cPIM-1 CO₂/N₂ gas selectivity change due to humidity (c) The impact of humidity on water permeation through cPIM-1

Further studies were undertaken using Dynamic Vapor Sorption (DVS) to confirm the membrane uptake behavior, most importantly that of water in the Langmuir voids [1,2] of the polymers and the subsequent impact of this water build-up on CO₂ uptake.

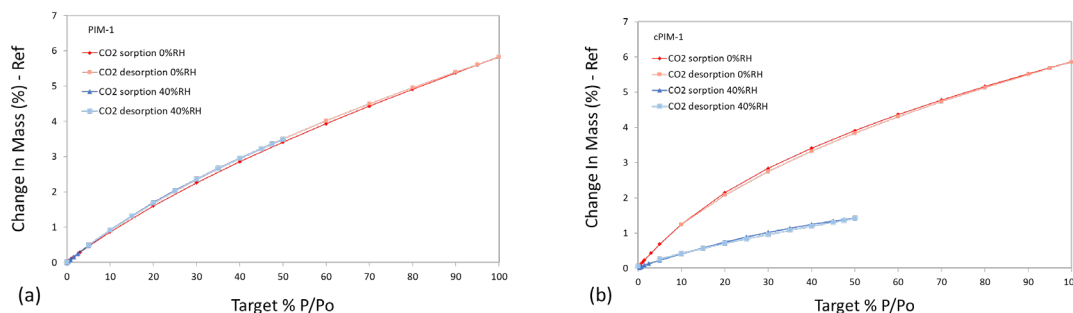


Figure 2: DVS experiments charting the change in CO₂ uptake with changing humidity in (a) PIM-1 (b) cPIM-1

References

1. E. Lasseguette, M.-C. Ferrari, S. Brandani, *Energy Procedia*, **2014**, 63, 194-201.
2. P. Li, T. S. Chung, D. R. Paul, *Journal of Membrane Science*, **2014**, 450, 380-388.

MOFs Learning : a data-based platform to accelerate functional MOF discovery

Arthur Hardiagon^a, Aysu Yurdusen Ozturka^b, Georges Mouchaham^b, Christian Serre^b, Jérémy Audevard^c, Mickael Carboni^c, François-Xavier Coudert^a

^aChimie ParisTech, CNRS, Institut de Recherche de Chimie Paris, PSL University, Paris, France

^bInstitut des Matériaux Poreux de Paris, Ecole Normale Supérieure, ESPCI Paris, CNRS, PSL University, Paris, France

^cInstitut de Chimie Séparative de Marcoule, CEA, Bagnols-sur-Cèze, France

Metal-organic frameworks (MOFs) are highly porous crystalline solids researched for applications in gas storage, separations, catalysis, sensing, and biomedicine. Their synthesis and the vast array of building blocks (metal precursors and organic linkers) allow for structural tuning to specific needs. The systematic cataloging in the Cambridge Structure Database (CSD) and other databases facilitates property characterization using molecular simulations, covering adsorption, thermal, mechanical, and electronic properties. However, synthesized materials often exhibit more complexity than monophasic crystal structures resolved by X-ray diffraction, and synthesis conditions are challenging to extract from literature due to the lack of metadata and standardized data formats.

The "MOFs Learning" project, part of the national French PEPR DIADEM, sets best practices for managing and digitizing data in materials research. Collaborating with synthesis (IMAP), molecular modeling (IRCP), and materials (CEA) testing laboratories, the project utilizes a broad range of measurements (volumetric and gravimetric adsorption, TGA calorimetry, XRD, FTIR, column adsorption, simulations, ...) to characterize materials. This work presents our management strategy and the tools developed to create a library of functional porous materials. We replicate materials like MIL-53, MIL-160 or CAU-20 ensuring accurate identification and property comparison with existing databases (NIST, synthesis mining). We emphasize the importance of providing detailed metadata and clear material identifiers in our daily research. Additionally, we discuss tools currently under development that aim to enhance the interoperability of MOF databases. These tools also aim to expand the application of existing Natural and Large Language Models for parsing more complex synthesis workflows and characterization conditions. The final project architecture will be presented as a database of standardized Sample Identity Cards (SID) integrating synthesis, characterization and simulation data and will eventually be available hosted on a web platform.

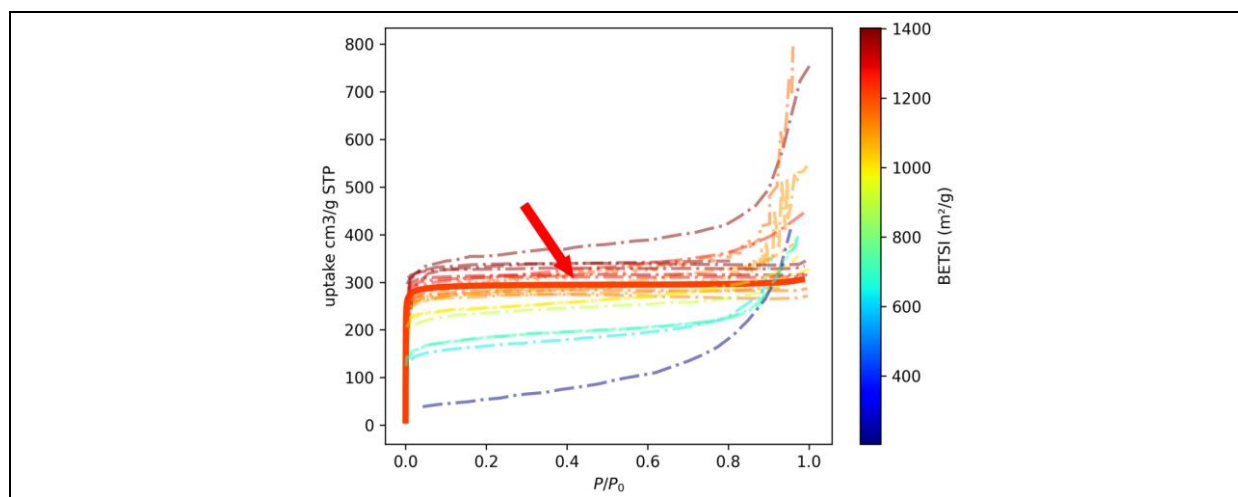


Fig. 1: N_2 adsorption isotherm in MIL-53, as measured by collaborators from IMAP/Paris (red arrow) and comparison with literature data from NIST/ARPA database (depicted as dashed lines). The color scale represents the BET surface area using a FAIR approach (BETSI code).

References

- [1] Hardiagon, A.; Coudert, F.-X. ChemRxiv, submitted March 13, 2024.
- [2] Jablonka, K. M.; Ongari, D., et al. Nat. Chem. 2021, 13 (8), 771–777.
- [3] Bobbitt, N. S.; Snurr, R. Q., et al. J. Chem. Eng. Data 2023, 68 (2), 483–498.

Microscopic Mechanism of Thermally Induced Ordered-Disordered Phase Transitions in Zeolitic Imidazolate Frameworks Revealed via Molecular Dynamics and Machine Learning Techniques

Emilio Mendez^a, Rocio Semino^a

^a Sorbonne Université, CNRS, Physico-chimie des Electrolytes et Nanosystèmes Interfaciaux, PHENIX, F-75005 Paris, France.

E-mail: rocio.semino@sorbonne-universite.fr

Amorphous MOFs are materials that can retain some of the porosity of their crystalline counterparts while improving the mechanical robustness and malleability. In this presentation, I will highlight our recent study[1] of the molecular mechanism of ordered-disordered phase transitions undergone by two zeolitic imidazolate frameworks composed by Zn^{2+} and imidazolate: a porous (ZIF-4) and a dense, non-porous (ZIF-zni) polymorph, via a combination of data science and computer simulation approaches. Molecular dynamics simulations were carried out at the atomistic level through the nb-ZIF-FF force field[2] that incorporates ligand-metal reactivity. In order to automatically follow the process of amorphization/melting in space and time, we computed local symmetry functions over a database of structures of four phases: ZIF-4, ZIF-zni, glass and liquid. This data was used as input to train a neural network that predicts the probabilities of belonging to each of the phases at the local Zn^{2+} level with 90% accuracy.

Conclusions: We find that the amorphization of ZIF-4 and the melting of ZIF-zni involve connectivity changes in the first neighbour ligands around the Zn^{2+} cations. In addition, the former is a non-isotropic process and we trace back the origins of this behaviour to density and lability of coordination bonds.

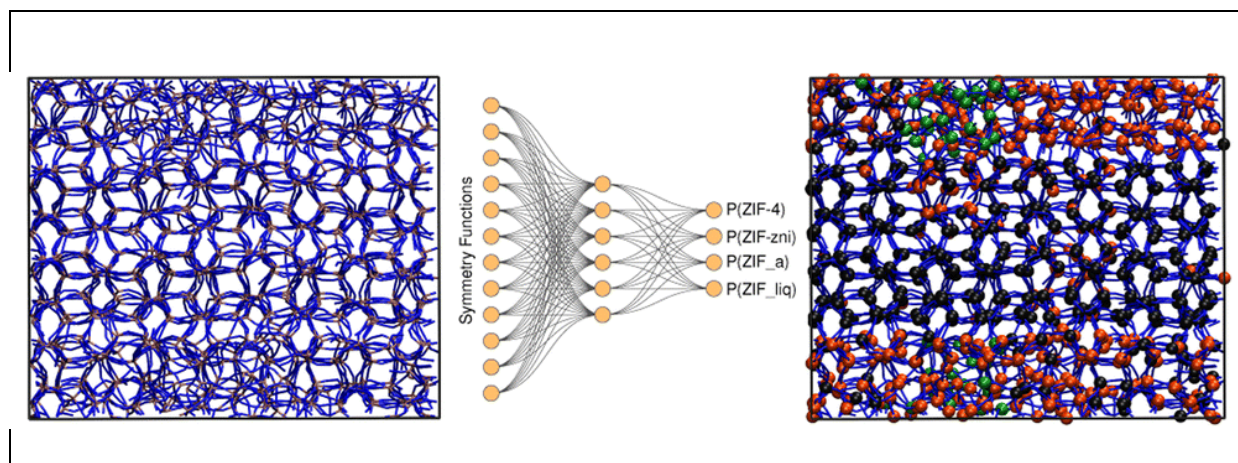


Fig. 1: Schematics of our neural network trained over atom-centred symmetry functions of ZIF-4, ZIF_a, ZIF-zni and ZIF_liq microstates that allows the classification of Zn^{2+} -centred environments. Left and right hand illustrations: before and after the classification (colour code: ZIF-4- (black), ZIF_liq- (orange) and ZIF_a-like environments (green)).

References

- [1] E. Mendez and R. Semino; J. Mater. Chem. A, 12, 4572-4582 (2024)
- [2] S. R. G. Balestra and R. Semino; J. Chem. Phys, 157, 184502 (2022)

ORAL ☒

POSTER ☐

EXPLORING THE OPPORTUNITIES IN STRAIN ENGINEERING: FROM INTRODUCING FLEXIBILITY IN RIGID MOFS TO CLASSIFYING ELUSIVE AMORPHOUS STATES

Sven M.J. Rogge^a

^a Center for Molecular Modeling, Ghent University, Technologiepark-Zwijnaarde 46, 9052 Ghent, Belgium
e-mail: Sven.Rogge@UGent.be

We recently introduced strain engineering as a new *in silico* design tool to fundamentally alter a nanostructured material's polymorphism and macroscopic functionality by introducing well-defined strain fields in the material [1,2]. Strain engineering is built on the observation that polymorphism-inducing external triggers – stress, adsorption, temperature – and internal disorder both deform a material, resulting in time-dependent strain fields that propagate through the material and may interact with one another. As a result, by introducing well-chosen disorder, the material can be designed to exhibit targeted flexibility under well-defined external triggers.

In this contribution, we will highlight two recent case studies of strain engineering on metal-organic frameworks (MOFs). We first focus on the rigid UiO-66 MOF. By creating well-defined linker vacancies, we show that this rigid MOF becomes locally flexible [1]. Besides forming an intermediate between completely rigid and completely flexible MOFs, the so-created reversible crumple zones in this strain-engineered material also focus the strain, thereby preserving the integrity and adsorption capacity of the remainder of the material. This size-independent observation can be further amplified by combining orthogonal crumple zones [1], which may find applications in shock absorbers or sensors. Furthermore, these strain-engineered materials hint toward a mechanical analogy of Braess's paradox [1]. The counterintuitive flexibility observed for this rigid MOF is akin to the stimuli-induced phase coexistence induced earlier in the soft porous crystals CoBDP, DMOF-1(Zn), and MIL-53(Al)-F [1,3]. They are easier to synthesise than the strain-engineered UiO-66 materials above and illustrate our strain-engineering approach's general applicability. We demonstrate that increasing the temperature or adsorbing guests leads to a dynamic redistribution of the strain in the material disfavoured phase coexistence [1]. In addition, we reveal the existence of buffer layers at the interface of the two coexisting phases [1]. This can be exploited to design strain-engineered materials in which well-defined zones of the material are stabilised in one phase while others remain in a different phase.

In a second case study, we focus on the rich polymorphism of zeolitic imidazolate frameworks (ZIFs), especially ZIF-4 [4]. Compared to polymorphism in crystalline materials, phase transitions to amorphous states are ill-understood, mainly because of a lack of tools to properly characterise the structure of these states lacking long-range order. As a result, structure-function relationships, which are abundant in crystalline materials, remain scarce in amorphous materials. Therefore, in this second case study, we explore how combining strain engineering with a nuclear magnetic resonance (NMR) protocol characterises the different states encountered in amorphous states. As a result, we can map the different local states in amorphised ZIF-4, which can, in turn, be correlated with the macroscopic function exhibited by these materials, opening up the opportunity to create structure-function relationships for amorphous materials.

References

- [1] S.M.J. Rogge, S. Borgmans, V. Van Speybroeck. *Matter* **2023**, 6, 1435-1462.
- [2] J.L. Teunissen, T. Braeckvelt, I. Skvortsova, J. Guo, B. Pradhan, E. Debroye, M.B.J. Roeffaers, J. Hofkens, S. Van Aert, S. Bals, S.M.J. Rogge, V. Van Speybroeck. *J. Phys. Chem. C* **2023**, 127, 23400-23411
- [3] S.M.J. Rogge, M. Waroquier, V. Van Speybroeck. *Nat. Commun.* **2019**, 10, 4842.
- [4] R.N. Widmer, G.I. Lampronti, S. Chibani, C.W. Wilson, S. Anzellini, S. Farsang, A.K. Kleppe, N.P.M. Casati, S.G. MacLeod, S.A.T. Redfern, F.-X. Coudert, T.D. Bennett. *J. Am. Chem. Soc.* **2019**, 141, 9330-9337.

ORAL POSTER

OPTIMIZING THE SYNTHESIS OF STABLE, REPRODUCIBLE AND UP-SCALABLE MIXED-LINKERS Ce-UiO-67 METAL-ORGANIC FRAMEWORKS

Valeria Finelli^{a,b}, Giuseppe Mastronardi^a, Natale Gabriele Porcaro^a, Matteo Signorile^a, Francesca Bonino^a, Petra Ágota Szilágyi^c and Silvia Bordiga^a

^a Department of Chemistry, NIS and INSTM Reference Centre, University of Turin, Via P. Giuria 7 I-10125 and Via G. Quarello 15/A I-10135, Turin, Italy

^b University School for Advanced Studies IUSS Pavia, Palazzo del Broletto, Piazza della Vittoria 15 I-27000, Pavia, Italy

^c Centre for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, Sem Sælands vei 26, N-0315 Oslo, Norway
silvia.bordiga@unito.it

Metal-organic frameworks (MOFs) are extremely versatile materials not the least because their structure and properties can be finely engineered by introducing mixed-metal nodes and various ligands decorated with different functional groups, making them suitable for several applications.

Among all the metal candidates for building-up the nodes of MOFs, rare earth metals, especially cerium - their most earth-abundant representative, have recently gained scientific interest. The possibility of realizing MOFs with Ce nodes has several advantages: among all, the cost-effectiveness and redox activity of its metal source. Focussing on the Ce-UiO-66 and Ce-UiO-67 MOFs [1],[2], their syntheses are carried out with extremely rapid reaction times (15 min) and at mild temperatures (100 °C). Such synthetic strategy opens the possibility for an easy scale-up of the procedure, that is not often the case for MOFs.

In this context, our contribution aims at synthesising mixed-linkers Ce-UiO-67 frameworks replacing the archetypal 4,4'-biphenyl dicarboxylic acid (H₂BPDC) linker with 5% nominal 2,2'-bipyridine-5,5'-dicarboxylic acid (H₂BPyDC), aiming at a post-synthetic functionalization for isolated metal species insertion. This approach offers much promise for catalytic applications on account of a synergistic redox activity that can take place for the Ce-metal redox pair [3].

After the synthesis optimization, we managed to reproduce and up-scale our procedure for obtaining crystalline, and chemically and thermally stable MOFs. We have thoroughly analysed the mixed-linker MOFs by basic characterization techniques, including PXRD, TGA, ¹H-NMR, N₂ physisorption, and spectroscopical insights, e.g., FT-IR, Raman, and UV-Vis spectroscopy.

References

- [1] Lammert et al., Chem. Commun., 2015, 51, 12578
- [2] Lammert et al., Cryst. Growth. Des., 2017, 17, 1125–1131
- [3] Rojas-Buzo et al., Mater. Today Chem., 2023, 27, 101337

Urea-based solvents for Metal-Organic Framework synthesis

Michaël Teixeira^a, Renata A. Maia^a, Benoît Louis^b, Stéphane A. Baudron^a

^a UMR 7140, University of Strasbourg-CNRS, 4 rue Blaise Pascal, 67000 Strasbourg, France

^b UMR 7515, University of Strasbourg-CNRS, 25 rue Becquerel, 67087 Strasbourg, France

e-mail: michael.teixeira@etu.unistra.fr

Urea-based solvents represent an emerging class of alternative media for the preparation of Metal-Organic Frameworks (MOFs). For example, ionothermal synthesis using Deep Eutectic Solvents (DESs) of the choline chloride/urea derivative type has demonstrated its ability to yield porous materials with a noticeable impact on crystal morphology, textural properties and chirality [1-2]. Alternatively, the urothermal method consisting in using molten urea-based species as solvents has also shown great promises [3]. In this context, we are investigating the potential of these two synthetic methods for the elaboration of MOFs with a particular focus on alkaline earth MOFs as these are less toxic and often exhibit important CO₂ sorption capabilities [4].

Following our work on the impact of DESs on the synthesis of Mg-MOF-74 [5], the synthesis of novel alkaline earth MOFs in ethylene urea-based systems was studied [6]. Depending on the cation, the ligand and the nature of the solvent used, various new architectures could be obtained. Interestingly, many of these structures are based on the same pillar, in which ethylene urea is bridging metallic cations. Taking advantage of this recurring secondary building unit, we attempted to engineer new porous materials. These results, as well as more recent advances, will be presented in this contribution.

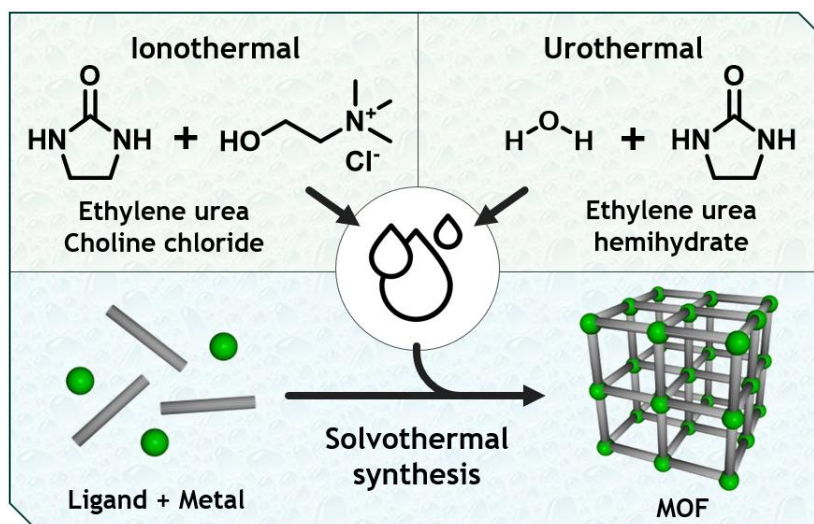


Fig. 1: Ionothermal and urothermal syntheses for the preparation of MOFs

References

- [1] E. L. Smith, A. P. Abbott, K. S. Ryder, *Chem. Rev.*, **2014**, *114*, 11060.
- [2] R. A. Maia, A. Fluck, C. Maxim, B. Louis, S. A. Baudron, *Green Chem.*, **2023**, *25*, 9103.
- [3] J. Zhang, J. T. Bu, S. Chen, T. Wu, S. Zheng, Y. Chen, R. A. Nieto, P. Feng, X. Bu, *Angew. Chem.*, **2010**, *49*, 8876.
- [4] Y. Zang, L.-K. Li, S.-Q. Zang, *Coord. Chem. Rev.*, **2021**, *440*, 213955.
- [5] M. Teixeira, R. A. Maia, S. Shanmugam, B. Louis, S. A. Baudron, *Micropor. Mesopor. Mat.*, **2022**, *343*, 112148.
- [6] M. Teixeira, R. A. Maia, L. Karmazin, B. Louis, S. A. Baudron, *CrystEngComm*, **2022**, *24*, 601.

ORAL POSTER

MOF SCALE-UP SYNTHESIS BY SPRAY-DRYING

Estelle DALOD^a

^a *Axel'One - Rond-point de l'échangeur - Les Levées - 69360 SOLAIZE*

e-mail: estelle.dalod@axel-one.com

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

The platform offers access to 35 M€ shared tools from fundamental research to pre-industrial stage (from TRL 3 to 7) in the field of advanced materials and polymers, smart processes, on-line analysis, digital solutions and industrial catalysis. Its activities support industrial companies from the chemical, textile & composite, recycling, water treatment and energy sectors, among others.

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

Following an introduction of Axel'One activities, the presentation will be focused on spray-drying principle and its relevance in MOFs production scale-up. The European project PRODIA and its success story on HKUST-1 spray-drying production will be presented.

Microwave assisted synthesis of Covalent Organic Frameworks for application in supercapacitor

Lavillunière, H., Pham-Truong, T.N., Vancaeyzeele, C., Aubert, P.-H.^a,

^a *CY Cergy Paris Université, Laboratoire LPPI, 5 mail Gay Lussac, F-95000 Cergy, France, e-mail: pierre-henri.aubert@cyu.fr*

Covalent organic frameworks (COFs) are crystalline porous materials formed by covalent bonds, having a large specific surface (i.e. 500 – 7000 m².g⁻¹), a low density and a structure forming variable and adjustable pore sizes (from 1.5 to 10 nm).¹ COFs are known today for their use in gas storage, in catalysis or optoelectronic,² but their characteristics also make them potentially interesting candidates as ultraporous electrode materials for the energy storage in EDLC type supercapacitors (electrochemical double layer capacitor). In this context, we worked on a COF belonging to the family of boronic ester, the COF-5,³ synthesized from hexahydroxytriphenylene (HHTP) and 1,4-(diboric acid)benzene (BDDBA) (Figure 1 Left). The most common route for synthesizing this material is solvothermal method, which turned out to be long and has many limitations. Within this context, more efficient synthetic pathway is required for improving the quality of obtained COF-5. Among them, microwave assisted method, which is widely known to provide increased reaction kinetics, fast/homogeneous heating and clean products, could be considered as powerful alternative.⁴ Then, this study focuses on the optimization of the microwave assisted synthesis of the COF-5, resulting to an unprecedented specific surface area of 2600 m².g⁻¹ for the as-prepared COF-5 (vs. 1700 m².g⁻¹ for COF-5sv).⁵ The better organization of the 2D layers of COFs, and the increase in the homogeneity of the structure were evidenced by a wide range of characterization techniques, including SAXS, FTIR and EDX analysis. Accordingly to the increase of C/O ratio, the increase of the ratio of basal plane/edge plane combined with larger basal plane of hexagonal structure at q-1 of 0.25 Å⁻¹ indicate crucial role of microwave irradiation in the formation of highly organized structure of covalent organic frameworks. To go further, electrochemical performances of both COFs were studied by carrying out CVs in aqueous medium with LiClO₄ (1M). Two times higher performances have been measured for optimized material (Figure 1 right), but the conductivity had to be improved by combining the material to carbon nanotubes or polyaniline before to be dropcasted onto the electrode. Huge increase of specific capacitance of few hundreds of F.g⁻¹ were recorded and results will be presented at both electrode and coin cell level.

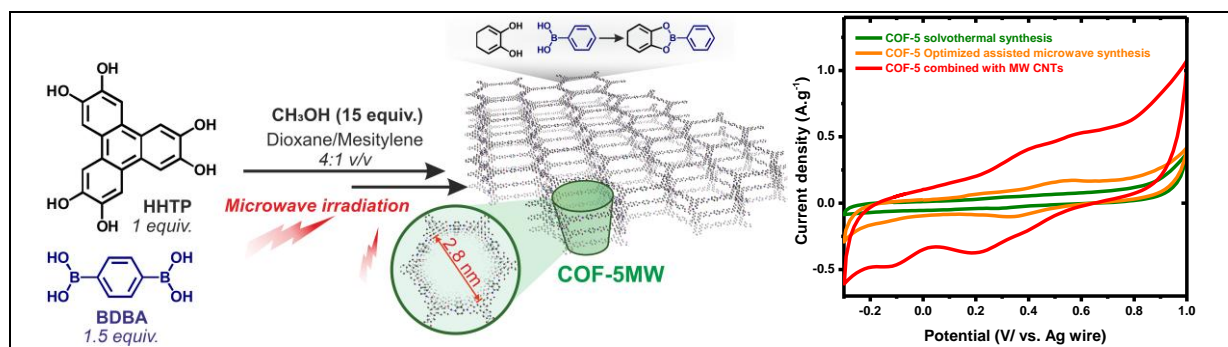


Fig. 1: (left) Scheme of the microwave assisted synthesis of COF-5; (right) Cyclic voltammetry of the COF-5mw, COF-5sv and the COF-5mw (with MWCNTs) at 2 mV.s⁻¹ in LiClO₄ (1M)/H₂O .

References

- (1) Li, J.; Jing, X.; Li, Q.; Li, S.; Gao, X.; Feng, X.; Wang, B. Bulk COFs and COF Nanosheets for Electrochemical Energy Storage and Conversion. *Chem. Soc. Rev.* **2020**, *49* (11), 3565–3604. <https://doi.org/10.1039/d0cs00017e>.
- (2) Geng, K.; Arumugam, V.; Xu, H.; Gao, Y.; Jiang, D. Covalent Organic Frameworks: Polymer Chemistry and Functional Design. *Prog. Polym. Sci.* **2020**, *108*, 101288. <https://doi.org/10.1016/j.progpolymsci.2020.101288>.
- (3) Smith, B. J.; Dichtel, W. R. Mechanistic Studies of Two-Dimensional Covalent Organic Frameworks Rapidly Polymerized from Initially Homogenous Conditions. *J. Am. Chem. Soc.* **2014**, *136* (24), 8783–8789. <https://doi.org/10.1021/ja503786g>.
- (4) Campbell, N. L.; Clowes, R.; Ritchie, L. K.; Cooper, A. I. Rapid Microwave Synthesis and Purification of Porous Covalent Organic Frameworks. *Chem. Commun.* **2008**, No. 36, 4342–4344. <https://doi.org/10.1039/b805656k>.
- (5) Lavillunière, H.; Pham-Truong, T. N.; Nguyen, T. K. L.; Vancaeyzeele, C.; Aubert, P.-H. Controlled Microwave-Assisted Synthesis of Covalent Organic Frameworks Opens the Way towards More Suitable Porous Supercapacitors Electrodes. *ACS Appl. Energy Mater.* **2023**.

Layered iron-thiolate MOFs: structure, thermal behavior, stability and redox properties

Nusik Gedikoglu,^a Pablo Salcedo-Abraira,^a Long H. B. Nguyen,^b Nathalie Guillou,^c Nicolas Dupré,^a Nicolas Stephant,^a Nicolas Gautier,^a Christophe Payen,^a Philippe Poizot,^a Nicolas Louvain,^b Lorenzo Stievano,^b Thomas Devic^a

^a Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, F-44000 Nantes.

^b ICGM, Univ. Montpellier, CNRS, ENSCM, Montpellier.

^c Institut Lavoisier de Versailles, UMR CNRS 8180, Université de Versailles St-Quentin en Yvelines, Université Paris Saclay, 78035 Versailles..

e-mail: thomas.devic@cnrs-immn.fr

Metal Organic Frameworks built up from metal-sulfur (M-S) bonds have shown great promises in the last decade thanks to their impressive electronic properties arising from the more covalent nature of the M-S bond when compared to M-O. Pure S-based ligands such as 1,2-dithiolene lead to materials with outstanding electronic properties (metallic, and even superconducting behaviours have been reported), but generally poorly crystallized. Alternatively, mixed O, S-based ligands, such as carboxylate-thiolate, are of interest to achieve both improved electronic properties and a decent crystallinity for in-depth structural characterizations. We aim at expanding the scope of available S-based MOFs to high oxidation state cations M^{n+} ($n \geq 3$). The systematic exploration of the reactivity of the mixed thiolate-carboxylate ligand 2,5-disulphydrylbenzene-1,4-dicarboxylic acid (H_4 DSBDC) with Fe(III) salts lead to the identification of a new family of layered Fe thiolate MOFs. The structure of these materials consists of the same hybrid layers made of chains of edge-sharing FeS_4O_2 octahedra connected by fully deprotonated DSBDC⁴⁻, alternating with either organic (dimethylammonium, $H_2N(CH_3)_2^+$) or inorganic (Na^+ , K^+ , $Fe^{3+/2+}$) cations (Fig.1, left). The Fe-S connection leads to a strong absorption in the visible range, while the +III oxidation state of intralayer Fe, evidenced by Mössbauer spectroscopy, ensures a fairly good stability towards oxygen and water, higher than that typically observed with +II cations. Eventually, we will discuss how the nature of the interlayer layer cation A impacts of the redox activity, with behaviours ranging from a reversible electrochemical insertion of alkaline cation (Fig. 1, right)^[1] to an irreversible activity involving both interlayer iron oxidation and exsolution.^[2]

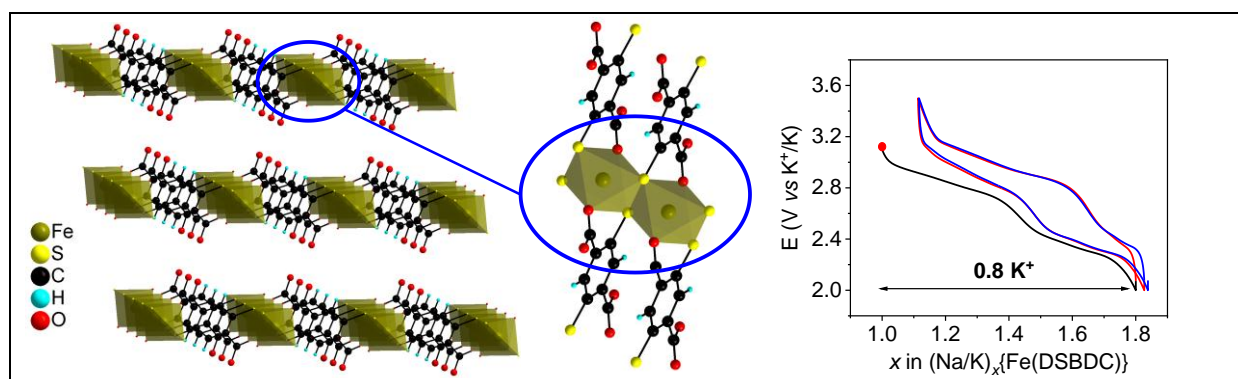


Fig. 1. Left: crystal structure of $A\{Fe(DSBDC)\}$ (interlayer A cations not shown); right: electrochemical behavior of $Na\{Fe(DSBDC)\}$ vs K .

References

[1] N. Gedikoglu, P. Salcedo-Abraira, L. H. B. Nguyen, N. Guillou, N. Dupré, C. Payen, N. Louvain, L. Stievano, P. Poizot, T. Devic, *J. Mater. Chem. A* **2023**, *11*, 23909-23921

[1] P. Salcedo-Abraira, N. Gedikoglu, L. H. B. Nguyen, N. Guillou, N. Stephant, N. Gautier, C. Payen, N. Louvain, L. Stievano, T. Devic, *in preparation*.

On the road to electrical-conductivity: Redox-active Metal Organic Frameworks based on metal bis(dithiolene) ligands

Y. Cheret,^a N. Zigon,^a T. Devic,^b and N. Avarvari,^a

^a University of Angers, MOLTECH-Anjou Laboratory CNRS-UMR 6200, 2 bd. Lavoisier, 49045 ANGERS, France.

^b Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, F-44000 Nantes, France

e-mail: cheret.yohan@univ-angers.fr

The preparation of electroactive ligands bearing an extended π -core to build self-assembled structures such as Metal-Organic Frameworks (MOFs, also known as porous coordination polymers: crystalline porous materials made of metal ions/clusters and organic linkers,^[1] is a very active field for the last decade. Unfortunately, most of these networks are not conductive because of their huge HOMO-LUMO gap and/or weak orbital overlap between the ligand and the inorganic part.^[2] Well-known electroactive building blocks such as tetrathiafulvalene-tetrathiabenzate (TTFTB) have been largely explored.^[3] This ligand was associated with Zn(II) to produce a MOF that displays 5 Å diameter cylindrical pores, an overall 39% pore volume, and a conductivity of 1.34×10^{-7} S/cm. An analogous MOF was prepared using the Ni(II)-bis(dithiolene)-tetrabenzoate (Ni(II)-BDTTB) as a linker; this MOF shown interesting properties as a glucose sensor but its conductivity has not been yet studied. Metal-bis(dithiolene) complexes show good conducting properties, e.g. metal-bis(maleonitriledithiolate) (M(mnt)₂) respectively showing a conductivity of 40 S/cm and 9 S/cm for the Ni(II) and Au(III) dithiophene-TTF salt.^[4] Ni(1,3-dithiole-2-thione-4,5-dithiolate)₂ shows a superconducting behavior at 5 K as its tetramethylammonium salt.^[5] Using such linkers within MOF structures should therefore provide porous materials with good conducting properties. These salts are known to yield neutral open-shell conductors, in particular with Au(III), which is of the outmost interest for the synthesis of conductive porous materials as no inner counter-ion is required such as for TTF.

This project is focused on the use of Ni(II) and Au(III)-bis(dithiolene) complexes as metalla-ligands bearing carboxylates or pyridines coordination unit to prepare closed-shell or open-shell neutral networks exhibiting good electrical conductivity. (**Fig. 1**)

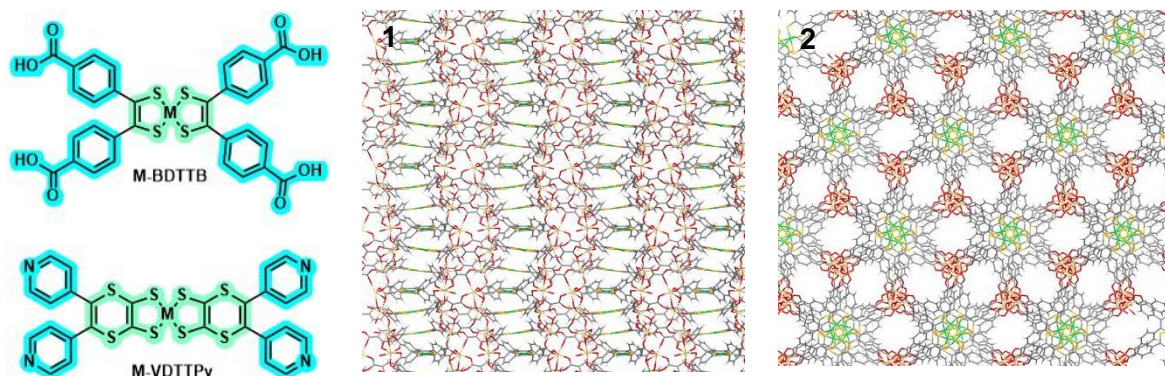


Fig. 1: Ligands structures (left) and X-Ray structure for Ni(II)-BDTTB-Cd(II) MOF (right) : (1) a axis view (2) c axis view.

References

- [1] L. S. Xie, G. Skorupskii, M. Dincă, *Chem. Rev.* **2020**, 120 (16), 8536.
- [2] A. Walsh, K. T. Butler, C. H. Hendon, *MRS Bull.* **2016**, 41 (11), 870.
- [3] S. S. Park, E. R. Hontz, L. Sun, *et al.*, *J. Am. Chem. Soc.* **2015**, 137 (5), 1774.
- [4] E. Ribera, C. Rovira, J. Veciana, *et al.*, *Chem. Eur. J.* **1999**, 5 (7), 2025.
- [5] A. Kobayashi, H. Kim, Y. Sasaki, *et al.*, *Chem. Lett.* **1987**, 16 (9), 1819.

ZIF-8, a hard to desorb BTEX adsorbent

Thibaud Aumond^a, Corentin Collomb^a, Cécile Daniel^a, David Farrusseng^a

^aIRCELYON, CNRS, 2 Avenue Albert Einstein 69626 Villeurbanne Cedex

e-mail: thibaud.aumond@ircelyon.univ-lyon1.fr

Benzene, Toluene, Ethylbenzene, and Xylenes, known as BTEX airborne volatile organic compounds (VOCs), are a class of toxic pollutants responsible for indoor and outdoor pollution that cause health issues [1]. Adsorption in microporous solids, particularly activated carbons and hydrophobic zeolites, is used to capture VOCs in dynamic systems whether in fixed bed columns or as coatings on rotor concentrators. While the adsorption capacity is a key criterion as it determines the usage time, the desorption of VOCs from the filter to the environment is a major problem. Indeed, a temperature rise of a few degrees could lead to fast desorption of accumulated VOCs over a long period leading to much higher VOCs concentrations in the ambient atmosphere.

We anticipated that MOFs with flexibility triggered by guest-host interactions could enhance adsorption strength and hence reduce and/or slow down the release of VOCs upon temperature increase. We chose two hydrophobic MOFs, ZIF-7 and ZIF-8, which exhibit two different types of structural flexibility upon adsorption: “breathing” associated with a phase-to-phase transition for ZIF-7, and gate-opening phenomenon associated with the rotation of the imidazole linkers for ZIF-8 [2-3]. Dynamic adsorption experiments of toluene (1000 ppm) at 20 °C under humid conditions (RH 70%) were conducted over these two MOFs as well as an active carbon as reference. As expected, the adsorption capacities of the two hydrophobic MOFs are not affected by the relative humidity while a small decrease is observed for AC. Nevertheless, huge differences must be highlighted concerning the desorption under dry flow (figure 1). Indeed, while AC desorbs half of the adsorbed toluene at 40 °C (55 %), ZIF-7 desorbs almost the entirety of the VOC and only 7 % of the adsorbed toluene remains encapsulated. On the contrary, ZIF-8 allows to maintain 86 % of the toluene even when the temperature reaches 50 °C. An increase to 150 °C permits the total regeneration of the adsorbent.

While no significant differences have been observed in the adsorption profiles between the two MOFs, the two different types of structural flexibility underlying the adsorption mechanism have been shown to impact the desorption of the VOC into the atmosphere, ZIF-8 resulting in a hard to desorb toluene adsorbent.

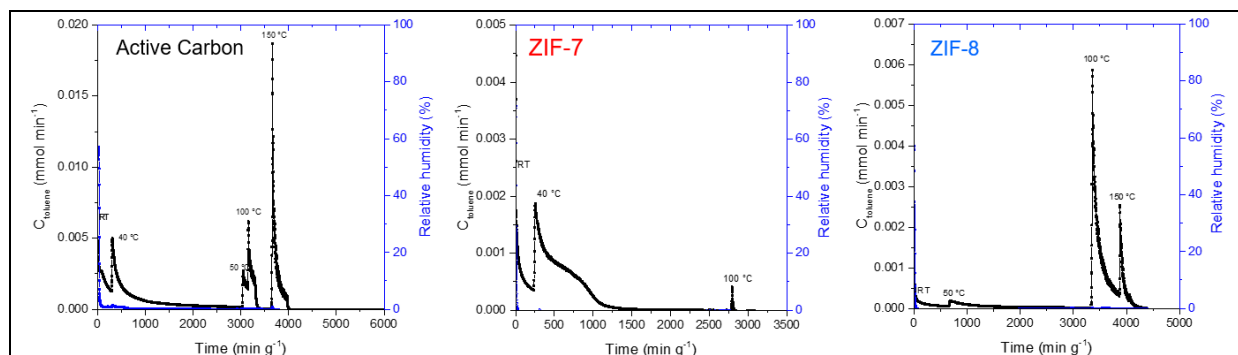


Figure 1. Desorption profile of toluene encapsulated in AC (left), ZIF-7 (middle), and ZIF-8 (right).

References

- [1] B. Siu *et al.*, *Coordination Chemistry Reviews*, **2023**, 485, 215119
- [2] S. Aguado *et al.*, *New J. Chem.*, **2011**, 35, 546-550
- [3] D. I. Kolokolov *et al.*, *J. Phys. Chem. C*, **2015**, 119, 27512-27520

POSTERS

FTIR-TRACED TRANSFORMATIONS OF ZIRCONIUM SITES WITHIN DEFECTIVE PORES OF UiO-66 DURING POST-SYNTHETIC MODIFICATIONS

Vera V. Butova, Videlina R. Zdravkova, Konstantin I. Hadjiivanov

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

e-mail: v.butova@svr.igic.bas.bg

UiO-66, a notable member of the MOF family, was initially reported in 2008 [1]. It comprises $Zr_6O_4(OH)_4$ clusters linked by 12 terephthalate linkers. This high connectivity renders this MOF exceptionally tolerant to defects [2, 3]. In the coordination modulation approach, a monocarboxylic acid acts as a modulator and competes with linkers for Zr^{4+} coordination. In some cases, Zr^{4+} ions within the MOF crystal retain modulators in their coordination sphere instead of linkers, forming defects [3, 4].

In the present study, we synthesized UiO-66 using benzoic acid as a modulator. Although the obtained material contained Zr sites within defect pores, they were inaccessible to the CO probe molecule. As a subsequent step, we modified the UiO-66 powder by substituting benzoate ions within defect pores with formate ions. This modification revealed Zr ions within defect pores after activation, rendering them accessible to CO. Finally, Zr sites within defect pores were functionalized with ammonium sulfate. It is noteworthy that the post-synthetic substitution of benzoate ions with formate ions enabled us to quadruple the sulfur content in our samples. All transformations were monitored via FTIR spectroscopy, and active sites were analyzed using probe molecules.

Based on comprehensive analysis, we conclude that after the synthesis of UiO-66 in the presence of benzoic acid, zirconium ions in defect pores are coordinated with benzoate ions, blocking them for interaction with probe molecules. These benzoate ions cannot be removed by evacuating up to 548 K. However, they can be substituted with another anion. In the current protocol, we have substituted benzoate residuals with formate ions. The latter can be eliminated by evacuation at 523 K, thus providing access to Zr^{4+} in defect pores. These ions can be utilized for further modification. We successfully introduced sulfate groups into the UiO-66 structure using Zr active sites in defect pores.

This research was supported by the Bulgarian Science Fund, the grant number КП-06-ДВ-1.

References

- [1] J.H. Cavka *et al.*, *J. Am. Chem. Soc.*, 130 (2008) 13850-13851. DOI: 10.1021/ja8057953
- [2] G.C. Shearer *et al.*, *Chem. Mater.*, 28 (2016) 7190-7193. DOI: 10.1021/acs.chemmater.6b02749
- [3] C. Atzori *et al.*, *J. Phys. Chem. C*, 121 (2017) 9312-9324. DOI: 10.1021/acs.jpcc.7b00483
- [4] V.V. Butova *et al.*, *Nanomaterials*, 13 (2023) 1675. DOI: 10.3390/nano13101675

ORAL □

POSTER ✕

Imine-based Covalent Organic Frameworks (COFs) used for Electrochemical Energy Storage

Nicolas Arrault, Xavier Sallenave, Thuan Nguyen Pham Truong, Cedric Vancaeyzele, Pierre-Henri Aubert

*Laboratoire de Physicochimie des Polymères et des Interfaces - Cergy-Paris University
nicolas.arrault@cyu.fr*

In the current context of global energy transition, the development of ever more efficient materials for electrochemical energy storage is essential to ensure the sustainability of energy systems. Covalent Organic Frameworks (COFs) are emerging in this context as promising candidates in this field due to their unique and adjustable properties. We are interested in the development of different COFs, 2D or 3D (Fig 1b), allowing to obtain a material with a high specific capacitance usable as electrochemical storage material.

This work explores the advantages of imine-based COFs as electrode materials for a wide range of applications, from supercapacitors to batteries. COFs, with their well-defined crystalline structure and high specific surface area, allow us to consider electrodes with improved performance by facilitating ion adsorption and diffusion [1]. Additionally, the versatility of 2D and 3D structures allows for tuning properties to meet specific electrochemical application requirements. Imine bonds offer advantages such as $\pi - \pi$ bond conjugation, enhancing electronic conductivity and enabling faradaic storage contribution, alongside excellent chemical and thermal stability (Fig 1a-b) [2]. These properties are studied by a wide range of structural (FT-IR, BET, XRD), morphological (MEB), thermal (TGA) and electrochemical (CV, EIS) characterization techniques.

However, several challenges must be addressed to fully harness the potential of COFs in electrochemical energy storage [3]. Enhancing the electron conductivity, optimizing specific capacitance, controlling pore size distribution and specific surface area are critical aspects that require further research and development efforts.

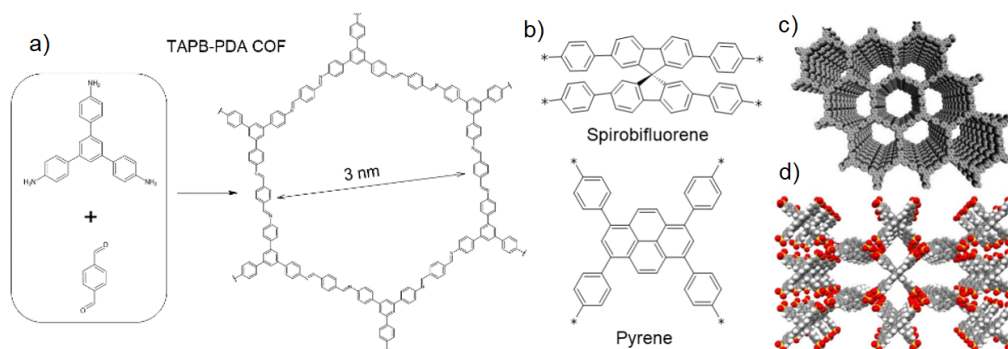


Figure 1: a) Synthesis of **TAPB-TPA** COF ; b) Based units of interest for electrochemistry ; c) Representation of **TAPB-TPA** 2D COF [4] and d) **spiroBPS-TPMA** 3D COF [5].

References

- ¹H. R. Abuzeid, A. F. M. EL-Mahdy, and S.-W. Kuo, "Covalent organic frameworks: Design principles, synthetic strategies, and diverse applications", *Giant* **6**, 100054 (2021).
- ²C. Qian, L. Feng, W. L. Teo, J. Liu, W. Zhou, D. Wang, and Y. Zhao, "Imine and imine-derived linkages in two-dimensional covalent organic frameworks", *en, Nature Reviews Chemistry* **6**, 881–898 (2022).
- ³M. Chafiq, A. Chaouiki, and Y. G. Ko, "Advances in COFs for energy storage devices: Harnessing the potential of covalent organic framework materials", *Energy Storage Materials* **63**, 103014 (2023).
- ⁴W. Ji, L. S. Hamachi, A. Natraj, N. C. Flanders, R. L. Li, L. X. Chen, and W. R. Dichtel, "Solvothermal depolymerization and recrystallization of imine-linked two-dimensional covalent organic frameworks", *en, Chemical Science* **12**, Publisher: The Royal Society of Chemistry, 16014–16022 (2021).
- ⁵K. Okubo, K. Oka, K. Tsuchiya, A. Tomimoto, and N. Tohnai, "Spirobifluorene-Based Porous Organic Salts: Their Porous Network Diversification and Construction of Chiral Helical Luminescent Structures", *en, Angewandte Chemie International Edition* **63**, e202400475 (2024).

ORAL ☒

POSTER ☐

METAL-ORGANIC FRAMEWORK-BASED CATALYSTS FOR CO₂-TO-METHANOL PROCESS

Anna Liutkova, Fabio André Peixoto Esteves, Marco Ranocchiari

Energy System Integration, Energy and Environment Research Division, Paul Scherrer Institute, Forschungsstrasse 111, 5232 Villigen PSI, Switzerland. E-mail: anna.liutkova@psi.ch

The presented study is crucial for resolving the important issue of CO₂ capture and hydrogenation: the development of a highly selective catalyst toward valuable methanol. We aim to establish the structure-activity relationships of the metal-organic catalysts modified with the metal nanoparticles in CO₂-to-methanol reaction.

We synthesized the Mg-IRMOF-74-II (MOF) catalyst following the procedure[1] (Fig. 1a) and prepared Cu-Zn nanoparticles via the chemical reduction method (Cu:Zn 1:1 mol, NPs)[2] to install them in the MOF using incipient wetness impregnation (Fig. 1b). We were able to observe the characteristic features of the Mg-IRMOF-74-II linkers[1] (Fig. 1a,e) by ¹H liquid state NMR and ATR-IR spectroscopies. We observe that the MOF possesses high crystallinity and stability in the range of temperatures relevant for the methanol synthesis (Fig. 1c) by in situ XRD and TGA-MS in H₂-containing atmosphere. We tested the MOF-NPs catalyst (CuO:ZnO:MOF 1:1:12 mol) in a batch system[4] at 52 bar and low CO₂:H₂ ratio and compared it with the existing industrial analog, CZA (CuO:ZnO:Al₂O₃:MgO 8:3:1:0.3 mol). The MOF-NPs catalyst performed better at lower temperatures (Fig. 1d). Reduction of the Cu already took place at 150 °C after the catalytic test (Fig. 1e). ATR-IR of the used catalyst demonstrated the appearance of the new bands in 2800 – 3000 cm⁻¹ region over the used MOF-NPs catalyst, which can be assigned to the adsorbed methoxy groups and methanol[3]. This underlines the role of the MOF as efficient environment for the synthesis of methanol in the presence of Cu-Zn nanoparticles.

In conclusion, the synthesized MOF-NPs materials are active in the CO₂-to-methanol process. These results significantly contribute to the catalysis and MOF chemistry community, providing new fundamental insights into a promising but poorly understood catalytic system.

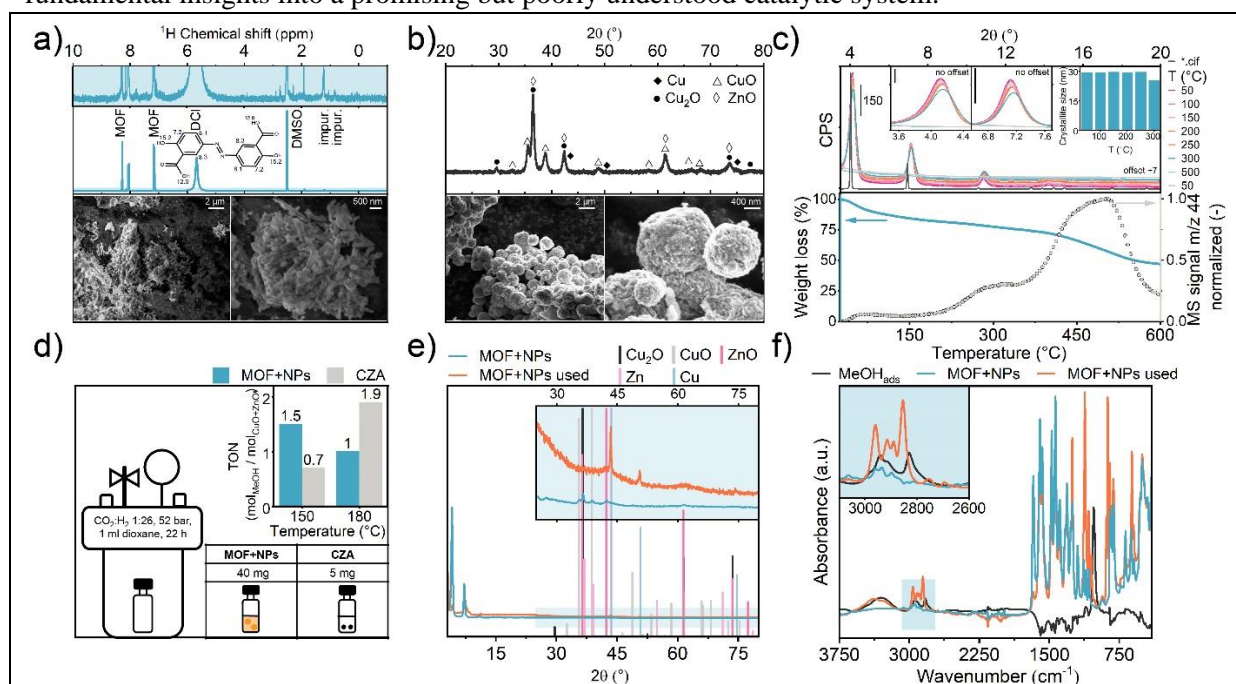


Fig. 1: Physical and chemical properties of the MOF-NPs system. a) ¹H NMR of the Mg-IRMOF-74-II (MOF, top) and its SEM images (bottom); b) XRD of the Cu-Zn nanoparticles (NPs, top) and their SEM images (bottom); c) in situ XRD (top) and TGA-MS (bottom) of the MOF in a H₂-containing atmosphere. MOF particle size were calculated using Scherrer equation (insert). MS signal m/z 44 corresponds to CO₂. Conditions: XRD in situ 40 mL/min N₂ + 1.5 mL/min H₂, 50 – 500 °C, 1 bar; TGA-MS 19 mL/min He + 1 mL/min H₂, 50 – 600 °C, 1 bar. d) Catalytic tests of the MOF+NPs and industrial CZA catalyst. The TON are calculated per mol of CuO+ZnO. Conditions: 150 and 180 °C, 52 bar, CO₂:H₂ 1:26, 420 mL autoclave, 40 mg of the MOF-NPs or 5 mg of the CZA in 1 mL dioxane, 22 h test; e,f) XRD and ATR-IR of the MOF+NPs catalyst before and after the reaction at 150 °C, the reference spectra of methanol adsorbed on the MOF is provided. The diffractograms and the spectra were taken at RT, in air atmosphere.

References

- [1] Z. Zhu *et al.*, “Cooperative Carbon Dioxide Capture in Diamine-Appended Magnesium–Olsalazine Frameworks,” *J. Am. Chem. Soc.*, vol. 145, no. 31, pp. 17151–17163, Aug. 2023, doi: 10.1021/jacs.3c03870.
- [2] J. Xiong, Y. Wang, Q. Xue, and X. Wu, “Synthesis of highly stable dispersions of nanosized copper particles using L-ascorbic acid,” *Green Chem.*, vol. 13, no. 4, pp. 900–904, 2011.
- [3] A. Liutkova *et al.*, “Ca Cations Impact the Local Environment inside HZSM-5 Pores during the Methanol-to-Hydrocarbons Reaction,” *ACS Catal.*, vol. 13, no. 6, pp. 3471–3484, Feb. 2023, doi: 10.1021/acscatal.3c00059.
- [4] A. K. Fellenberg *et al.*, “Covalent organic frameworks for design of ruthenium catalysts with high single-atom site density for CO₂ hydrogenation into formic acid,” *Cell Reports Phys. Sci.*, 2024.

Enantiopure natural deep eutectic solvents for MOF chiral induction

Renata A. Maia,^a Audrey Fluck,^a Catalin Maxim,^b Benoît Louis,^c Stéphane A. Baudron^a

^a UMR 7140, University of Strasbourg-CNRS, 4 rue Blaise Pascal, 67000 Strasbourg, France

^b Faculty of Chemistry, University of Bucharest, 4-12 Regina Elisabeta Boulevard, 030018, sector 3, Bucharest, Romania

^c UMR 7515, ICPEES, University of Strasbourg-CNRS, 25 rue Becquerel, 67087 Strasbourg, France
e-mail: sbaudron@unistra.fr

Deep Eutectic Solvents (DESs) represent an emerging class of solvents featuring some characteristics of their ionic liquid cousins - low vapor pressure, relatively wide liquid range, non-flammability and the ability to dissolve polar species - along with unique specificities, such as their limited toxicity and an improved biocompatibility.[1] Their use as media for the preparation of Metal-Organic Frameworks (MOFs) has been recently explored, showing that not only DESs represent green and less toxic alternatives to solvents commonly used in the synthesis of these porous crystalline materials, but also that they may play different roles in the MOF construction.[2] For example, the use of DES can impact the properties of the porous materials such as crystal morphology, textural properties[3] and water sensitivity.[4]

In this contribution, our recent efforts aiming at the chiral induction of the MIL-103 MOF [5] using the enantiopure natural DES proline:thymol (1:7) and menthol-thymol (1:1) will be presented (Fig. 1).[6] The preparation and characterization of the porous materials prepared in these DES will be described as well their enantioenrichment, as demonstrated by circular dichroism.

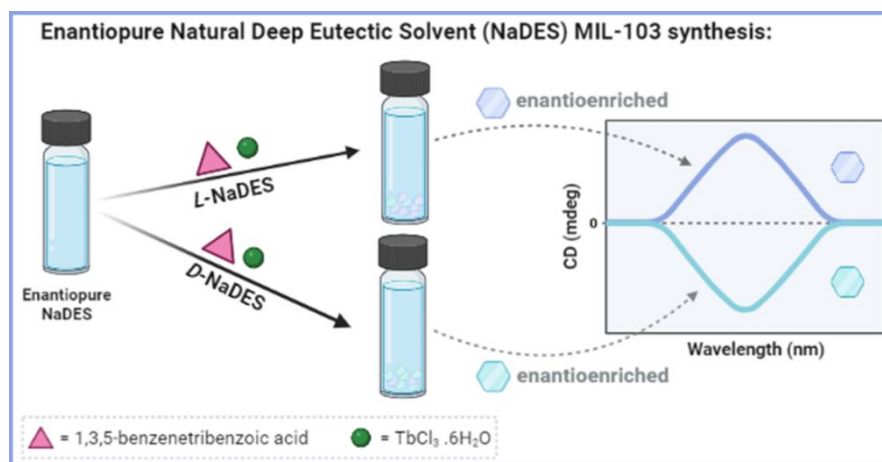


Fig. 1: Strategy for the chiral induction of the MIL-103 MOF via the use of enantiopure natural DES

References

- [1] B. B. Hansen, St. Spittle, B. Chen, D. Poe, Y. Zhang, J. M. Klein, A. Horton, L. Adhikari, T. Zelovich, B. W. Doherty, B. Gurkan, E. J. Maginn, A. Ragauskas, M. Dadmun, T. A. Zawodzinski, G. A. Baker, M. E. Tuckerman, R. F. Savinell, J. R. Sangoro, *Chem. Rev.*, **2021**, *121*, 1232.
- [2] a) E. R. Cooper, C. D. Andrews, P. S. Wheatley, P. B. Webb, P. Wormald, R. E. Morris, *Nature*, **2014**, *430*, 1012. b) R. A. Maia, B. Louis, S. A. Baudron, *CrystEngComm.*, **2021**, *23*, 5016.
- [3] a) R. A. Maia, B. Louis, S. A. Baudron, *Dalton Trans.*, **2021**, *50*, 4145. b) M. Teixeira, R. A. Maia, S. Shanmugam, B. Louis, S. A. Baudron, *Micropor. Mesopor. Mat.*, **2022**, *343*, 112148.
- [4] M. Teixeira, R. A. Maia, L. Karmazin, *CrystEngComm*, **2022**, *24*, 601.
- [5] T. Devic, C. Serre, N. Audebrand, J. Marrot, G. Férey, *J. Am. Chem. Soc.*, **2005**, *127*, 12788.
- [6] R. A. Maia, A. Fluck, C. Maxim, B. Louis, S. A. Baudron, *Green Chem.*, **2023**, *25*, 9103.

XTALAB SYNERGY-ED: A VERSATILE TOOL FOR THE SMALLEST OF CRYSTALS

Christian Schürmann,^a Robert Bückner,^a Fraser White,^a Mathias Meyer,^b Michał Jasnowski,^b Akihito Yamano,^c Sho Ito,^c Eiji Okunishi,^d Yoshitaka Aoyama,^d Joseph Ferrara^e

^aRigaku Europe SE, Neu-Isenburg, Germany

^bRigaku Polska Sp. Z o. o., Wrocław, Poland

^cRigaku Corporation, Tokyo, Japan

^dJEOL Ltd., Tokyo, Japan

^eRigaku Americas, The Woodlands TX, USA

e-mail: Christian.Schuermann@rigaku.com

The Rigaku XtaLAB Synergy-ED is a fully integrated electron diffractometer with a seamless workflow from data collection to 3D structure determination.[1] The XtaLAB Synergy-ED is the result of Rigaku's collaboration with JEOL, synergistically combining each partner's core technologies: Rigaku's hybrid-pixel electron detector (HyPix-ED) and CrysAlisPro software, and JEOL's long-standing excellence in electron beam generation and control.

Using 3D electron diffraction (3DED), a.k.a. microED, single crystals of all classes below one-micron in size can be studied. The XtaLAB Synergy-ED offers a wide range of experiments, including low temperature, which confers benefits such as: reduced beam damage; improved resolution; reduced disorder; and in the case of electron diffraction, stabilization of samples in vacuo. As electron diffraction requires samples to be studied under high vacuum, cryo-transfer - freezing of samples prior to introduction to vacuum - is essential for sensitive compounds, e.g. proteins or MOFs, see figure 1. Combining cryo-transfer with variable detector distance further allows the study of solvated crystals, including proteins, in the XtaLAB Synergy-ED.

Herein, we report MOF and small molecule samples benefiting from strong interactions with electrons for structure elucidation.

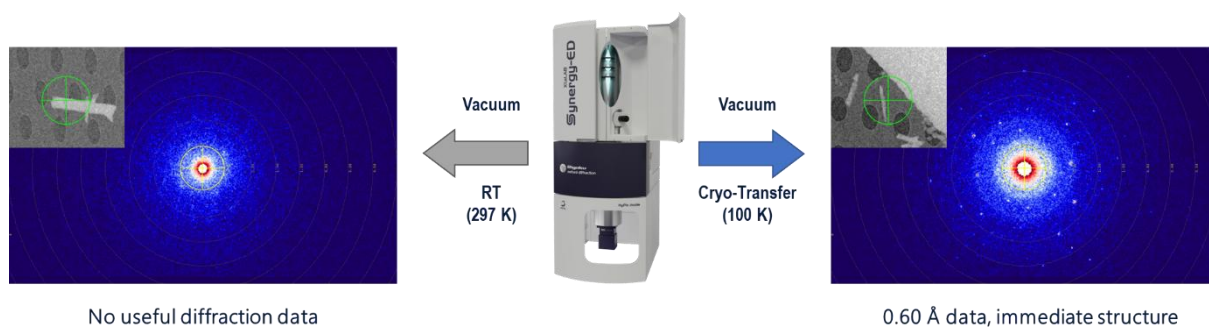


Fig. 1: A MOF example illustrating cryo-transfer is important. (left) porous structure measured at ambient conditions and (right) using a cryo-transfer process. Cryo-transfer conditions prevent lattice collapse.

References

[1] S. Ito, F. J. White, E. Okunishi, Y. Aoyama, A. Yamano, H. Sato, J. D. Ferrara, M. Jasnowski, M. Meyer, *CrystEngComm*. **2021**, 23, 8622-8630.

Sustainable Synthesis of adaptable MOFs Using PET Waste for Efficient Phosphate Removal

Elmehdi Moumen, Khaireddin Boukayouht, Samir El Hankari

*Chemical and Biochemical Sciences, Green Process Engineering, Mohammed VI Polytechnic University (UM6P), Lot 660 - Hay Moulay Rachid, Ben Guerir 43150, Morocco
e-mail: elmehdi.moumen@um6p.ma*

The exploration of metal-organic frameworks (MOFs) in the adsorption of phosphate is a growing research area. However, the manufacturing and processability of MOFs for practical applications are often hindered by their cost and their powder form[1,2]. This study pioneers the use of water-soluble organic ligands, specifically disodium terephthalate (DST) sourced from waste plastic, in the design and assembly of different MOFs such as Fe-MOF, Zr-MOF and Al-MOF in an aqueous medium. Fe-MOF demonstrated a superior phosphate adsorption capacity ($72.16 \text{ mg}\cdot\text{g}^{-1}$) which led to its selection for processing into PET composite chips, thereby enhancing recovery and recycling processes. The effect of some parameters such as contact time, the initial concentration, pH, and temperature were investigated. This innovative approach showcases the potential of sustainable MOF materials in addressing phosphate removal challenges while promoting environmental awareness.

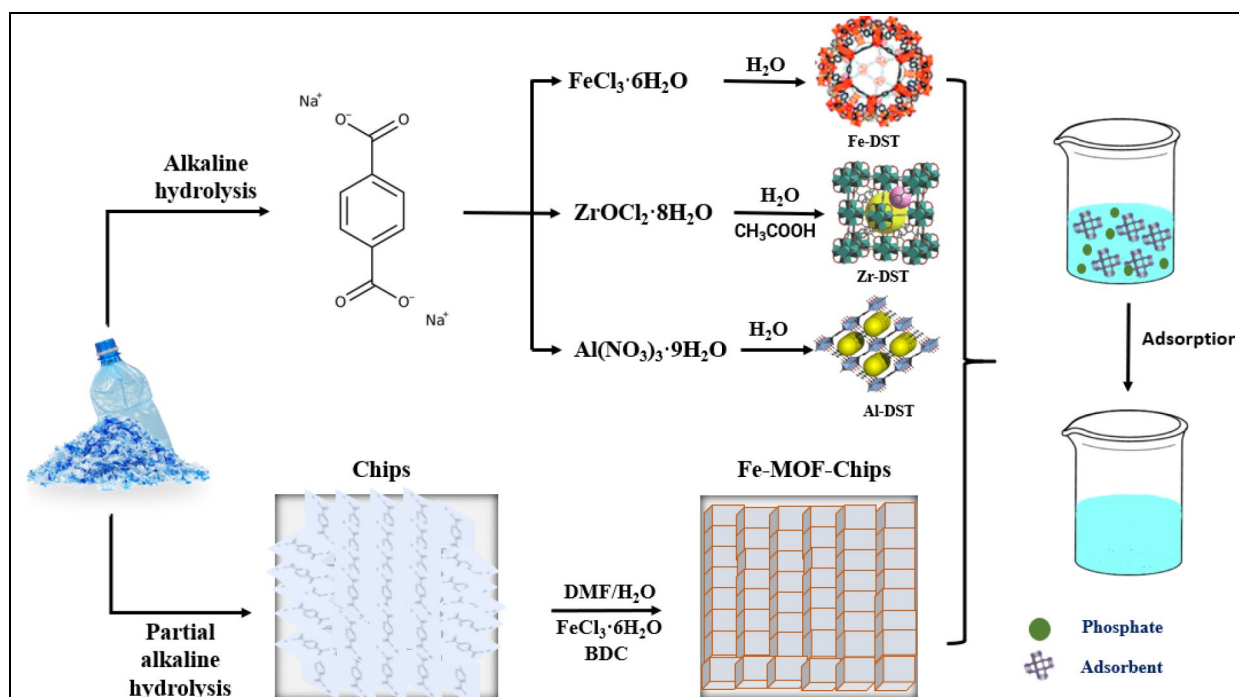


Fig. 1: Schematic illustration of PET hydrolysis and synthesis of various MOFs and Fe-MOFs-Chips and their application in phosphate adsorption.

References

- [1] E. Moumen, L. Bazzi, S. El Hankari, Metal-organic frameworks and their composites for the adsorption and sensing of phosphate, *Coord. Chem. Rev.* 455 (2022) 214376. <https://doi.org/10.1016/j.ccr.2021.214376>.
- [2] E. Moumen, L. Bazzi, S. El Hankari, Aluminum-fumarate based MOF: A promising environmentally friendly adsorbent for the removal of phosphate, *Process Saf. Environ. Prot.* 160 (2022) 502–512. <https://doi.org/10.1016/j.psep.2022.02.034>.

Porphyritic Metal-Organic Frameworks: design and synthesis of stable porous materials for applications in photocatalysis

Fangbing Liu^a, Catherine Marichy^a, Catherine Journet^a, Alexandra Fateeva^a

^a Université Claude Bernard Lyon 1, CNRS, LMI UMR 5615, Villeurbanne, F-69100
6 rue Victor Grignard, 69100 Villeurbanne, France
e-mail: alexandra.fateeva@univ-lyon1.fr

In recent years, porphyrin-based and porphyrin-containing metal organic frameworks (noted PMOFs) have particularly attracted attention for their photoactivity. Photoactive MOFs are interesting materials for emerging applications such as overall water splitting (OWS) and water decontamination.^{1,2}

Based on the hard and soft acids and bases (HSAB) theory, the combination of high valent and low polarizable metal ions with hard ligands such as carboxylates and polyphenolate porphyrins lead to stable frameworks. It is established that the strong interaction between Zr(IV) and carboxylate make the resultant MOFs chemically stable. In addition, as reported work^{3,4}, with fluoruous ligand, a series of functional properties could be expected to fluoruous MOFs, such as enhanced hydrophobicity and higher stability to oxidation and light. Bearing these in mind, we firstly elaborated a polyfluorous porphyrin 5,10,15,20-tetrakis-(4-carboxy-2,5,6-tetrafluorophenyl)porphyrin (F₁₆TCPP) and then constructed a polyfluorinated MOF-525⁵ analog by combining Zr precursor and F₁₆TCPP through adjusting the reaction conditions. On the other hand, Ti⁴⁺ ion has a high Z/r value, which also could form a strong electrostatic interaction with the hard ligand, further resulting in an ultrastable framework. In our work, we used a high pKa ligand, the catechol porphyrin (CatP: 5,10,15,20-tetrakis(3,4-dihydroxyphenyl)porphyrin)) to achieve a new Ti-porphyrin MOF. The Schematic Diagram of two novel porphyritic MOFs synthesis was shown in Fig. 1.

In conclusion, we have constructed two novel MOFs and carried out the relevant structural, spectroscopic and textural properties characterization. The association with our collaborators towards photocatalytic applications is undergoing, including overall water splitting, photothermal CO₂ reduction and contaminants degradation in water. In addition, porphyritic MOFs are an ideal platform for pre/post-synthetic metalation to impart specific properties or catalytic activity.

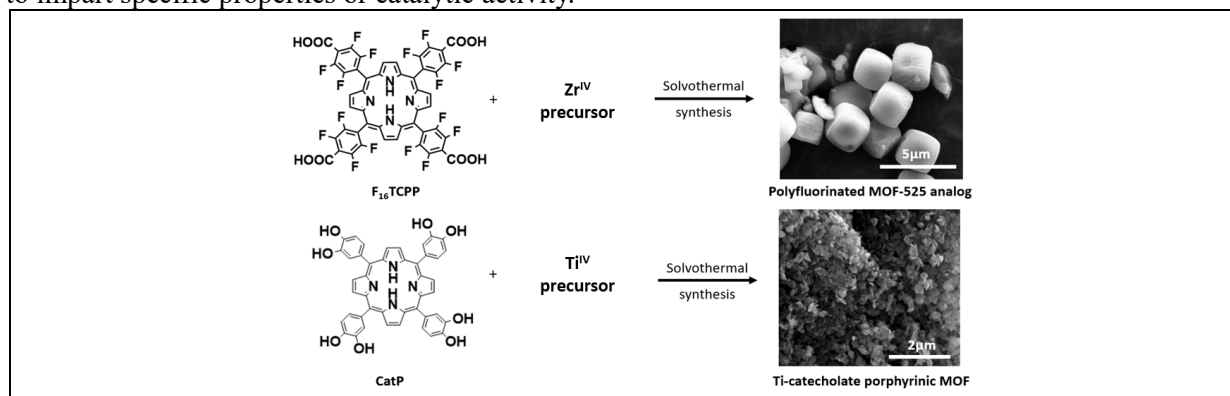


Fig. 1: Schematic Diagram of two novel Porphyritic MOFs synthesis.

References

- Deng, Q. *et al.* Porphyrin MOF Dots–Based, Function-Adaptive Nanoplatform for Enhanced Penetration and Photodynamic Eradication of Bacterial Biofilms. *Adv. Funct. Mater.* **29**, 1903018 (2019).
- Gikonyo, B. *et al.* Mixed-metal Zr/Ti MIL-173 porphyritic metal–organic frameworks as efficient photocatalysts towards solar-driven overall water splitting. *J. Mater. Chem. A* **10**, 24938–24950 (2022).
- Nyffeler, P. T., Durón, S. G., Burkart, M. D., Vincent, S. P. & Wong, C.-H. Selectfluor: Mechanistic Insight and Applications. *Angewandte Chemie International Edition* **44**, 192–212 (2005).
- Yang, C. *et al.* Fluorous Metal–Organic Frameworks with Superior Adsorption and Hydrophobic Properties toward Oil Spill Cleanup and Hydrocarbon Storage. *J. Am. Chem. Soc.* **133**, 18094–18097 (2011).
- Morris, W. *et al.* Synthesis, Structure, and Metalation of Two New Highly Porous Zirconium Metal–Organic Frameworks. *Inorg. Chem.* **51**, 6443–6445 (2012).

PROTON CONDUCTIVE MOF-BASED MIXED MATRIX MEMBRANES FOR PEMFC

Getachew T. Gebreslassie^a, Vanessa Pimenta^a, Christian Serre^a

^a *Institute of Porous Materials (IMAP), ENS, ESPCI, Paris, France*
e-mail: christian.serre@espci.fr ; vanessa.pereira-pimenta@espci.fr

Proton Exchange Membrane Fuel Cells (PEMFCs) are a promising clean energy technology that converts chemical energy from hydrogen directly into electricity, nonetheless their advancement relies on surpassing limitations of the current standard membrane material. The current workhorse PEMFC, Nafion, has several limitations. These limitations include high cost, potential gas crossover, environmental concerns regarding its production, a poorly understood proton conduction mechanism, and a strong dependence on humidity and temperature for optimal performance¹. Metal-Organic Frameworks (MOFs) appear as promising alternatives, due to their designable structures, high surface area, and excellent proton conductivity². However, their inherent mechanical instability necessitates incorporation into a polymer matrix to create Mixed-Matrix Membranes (MMMs). MMMs combine MOF benefits with the mechanical stability, flexibility, and gas permeation properties of polymers³, making them exciting candidates for next-generation PEMs.

Water-stable, highly proton-conductive MOF nanoparticles were first synthesized using green and scalable methods⁴. These nanoparticles were then incorporated into biodegradable polymers like polyvinyl alcohol, chitosan, and carboxymethylcellulose. A systematic approach investigated how MOF loading, MOF-to-polymer interaction, and polymer type affect the MMMs' performance. The membrane microstructure was characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), porosimetry, and their proton conductivity probed by electrochemical impedance spectroscopy (EIS).

By tuning several parameters such as filler ratio, casting thickness, and polymer concentration, stable and defect-free composite membranes were successfully prepared. These sustainable MMMs exhibited improved proton conductivity compared to the bare polymers. This emphasizes the synergistic effects of the MOF and polymer potentially due to a favorable interfacial morphology that facilitated proton transport. Overall, these findings demonstrate the promising potential of MMMs based on proton-conducting MOFs and biodegradable polymers as next-generation PEMs for fuel cell applications. The enhanced performance of these MMMs suggests they could address the limitations of conventional PEMs and pave the way for more sustainable and efficient fuel cells.

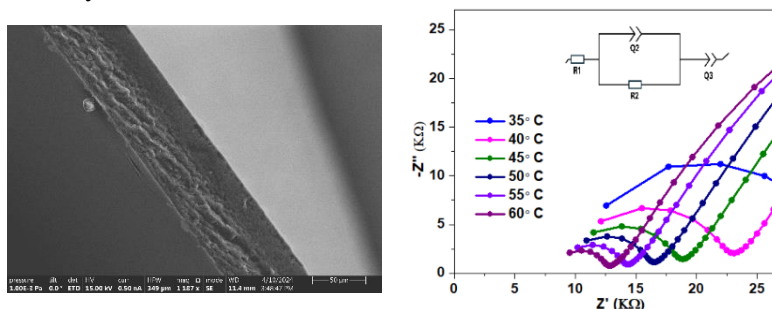


Fig. 1: Nyquist plot of Membrane

References

- [1] Mauritz, K.A.; Moore R.B. *Chem. Rev* 2004, 104, 4535-4586.
- [2] Shimizu, G. et al. *Chem. Rev* 2014, 43, 5913-5932.
- [3] Escorihuela, J. et al. *Adv. Mater. Interfaces* 2019, 6, 1801146.
- [4] Serre, C. et al. *Nature. Comm* 2018, 9, 4937.

Effect of the dimensionality in $[M(m\text{-SPhCO}_2\text{R})]_n$ (M= Cu, Ag; R= H, Me) Coordination Polymers on the photophysical properties

Alexis Giraudon,^{1,3} Oleksandra Veselska,¹ Nathalie Guillou,² Florent Perret,³ Aude Demessence¹

¹ Université Claude Bernard Lyon 1, Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), UMR 5256 CNRS, Villeurbanne, France

² Université Paris-Saclay, UVSQ, CNRS, Institut Lavoisier de Versailles (ILV), UMR 8180, Versailles, France

³ Université Claude Bernard Lyon 1, Institut de Chimie et Biochimie Moléculaires et Supramoléculaires (ICBMS), UMR 5246 CNRS, Villeurbanne, France

e-mail: alexis.giraudon@ircelyon.univ-lyon1.fr

The development of new luminescent materials constitutes an active field of research as their application can be very diversified.^{[1][2]} Among them, we find a lot of luminescent solids made of Critical Raw Materials (CRM), like heavy rare earth. Because the sustainability of these elements is a problem, the use of d^{10} coinage metals, such as Cu and Ag, to design new materials can be a solution, as these metals exhibit good emission efficiency and various luminescent properties.^{[1][3]} Coordination polymers (CPs), have been reported as a good alternative, and more specifically thiolate-based ligand CPs, due to their ability to form stable compounds thanks to the strong interaction between the sulfur and the d^{10} coinage metal.^[3]

In this context, four CPs ($[\text{Cu}(m\text{-SPhCO}_2\text{H})]_n$ (**1**), ($[\text{Ag}(m\text{-SPhCO}_2\text{H})]_n$ (**2**), $[\text{Cu}(m\text{-SPhCO}_2\text{Me})]_n$ (**3**) and, $[\text{Ag}(m\text{-SPhCO}_2\text{Me})]_n$ (**4**) have been prepared to understand the effect of the carboxylic acid and the methyl ester in the *meta* position of the thiolate ligands on the dimensionality of the materials and their physical properties. (**Fig. 1**) The four compounds were obtained in solvothermal conditions and the structures were determined by single crystal and powder x-ray diffraction. While (**1**) and (**2**) are 2D lamellar materials and non-luminescent at room temperature, (**3**) and (**4**) have a 1D structure and exhibit intense photoemission. (**Fig. 1**)

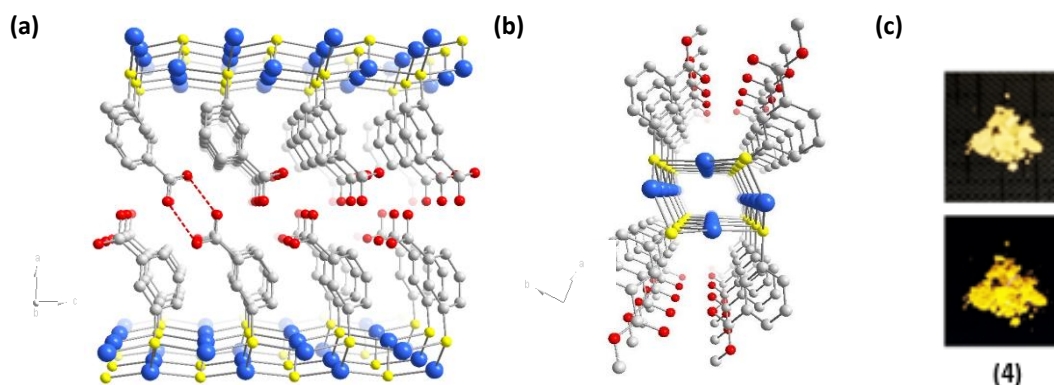


Fig.1 (a) Projection of the 2D lamellar structure of (**2**) and (b) projection of the 1D structure of (**4**). Blue : Ag, yellow : S, grey : C, Hydrogen are omitted for clarity. Hydrogen bonds are represented with red dashed lines. (c) Photograph of (**4**) at RT under ambient light (top) and under UV light (bottom).

References

- [1] O. Veselska, D. Podbevšek, G. Ledoux, A. Fateeva, A. Demessence, *Chem. Commun.*, **2017**, 53, 12225.
 [2] J-Q. Liu, Z-D. Luo, Y. Pan, A. Kumar Singh, M. Trivedi, A. Kumar, *Coord. Chem. Rev.*, **2020**, 406, 213145.
 [3] S. Hawila, A. Abdallah, J-L. Rukemampunzi, A. Fateeva, G. Ledoux, R. Debord, S. Pailhès, N. Guillou, F. Massuyeau, R. Gautier, A. Mesbah, A. Demessence, *Chem. Commun.*, **2022**, 58, 8081.

Reducible Fe-MOFs for the environmental abatement of NO_x

Isaac Dansette^a, Farid Nouar^{a*}, Marco Daturi^{b*}, Christian Serre^{a*}

^a Institute of Porous Materials (IMAP), ENS, ESPCI, CNRS, PSL university, Paris, France

^b Normandie Univ., ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie, Caen, France

e-mail: christian.serre@espci.fr; farid.nouar@espci.fr; daturi@ensicaen.fr

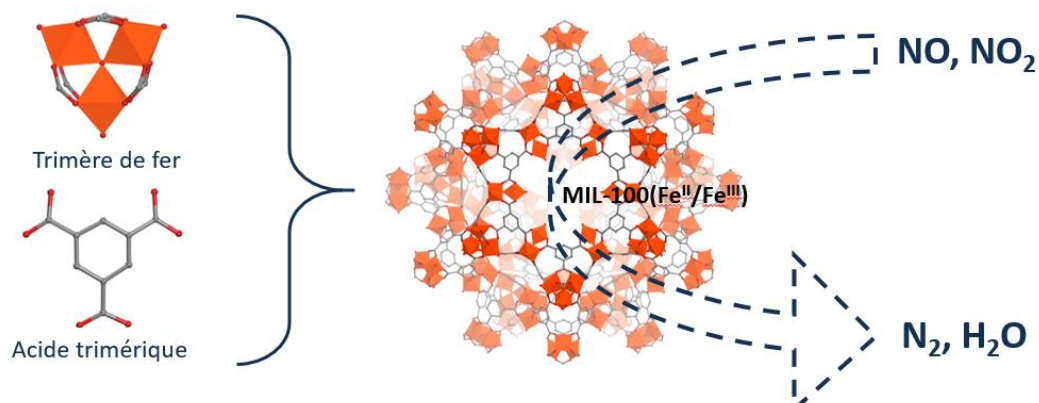
Keywords: NO_x, Air Quality, MOFs, Catalysis

Air pollution is an important issue, particularly in urban areas, and is linked to combustion processes. The emission of nitrogen oxides (NO_x) constitutes a critical environmental problem, and it can affect severely human health. The main two components are nitrogen monoxide (NO) and nitrogen dioxide (NO₂) and come from different human sources. The first source of emission comes from the motor vehicles, especially diesel engines, due to high-temperature combustion. Burning fossil fuels in power plants to generate electricity also releases significant amounts of NO_x as well as industrial processes, such as nitric acid production and fertilizer manufacturing. It can cause smog and respiratory problems such as asthma and increase the risk of cardiovascular and respiratory diseases¹. The World Health Organisation has updated its recommendations on exposure to nitrogen oxides for 2021: Annual average concentration of nitrogen dioxide (NO₂): 10 µg/m³ compared with 40 µg/m³ according to the 2005 guideline.

The current catalytic degradation technique is SCR (selective catalytic reduction) which requires both high temperature conditions (300-400°C), a catalyst who plays an important role (V₂O₅-WO₃/TiO₂) as well as sacrificial agent (ammonia or urea) to transform the NO_x into harmless gases (nitrogen and water). This leads to an efficiency of over 90% under the right operating conditions². Metals-Organic-Frameworks (MOFs) are crystalline porous materials that can be a good alternative to the current SCR catalyst. In particular, the mesoporous iron trimers based MOF denoted MIL-100(Fe) (MIL stands for Materials from Institut Lavoisier), once carefully thermally reduced into a mixed valence Fe(III/II) material, has demonstrated at room temperature, in the presence of oxygen and humidity, without the need of a sacrificial agent, an unprecedented conversion of NO_x into N₂ and O₂³.

References

- [1] M. Corso, M. Blanchard and V. Wagner, *Impact à court terme du dioxyde d'azote (NO₂) sur la mortalité dans 18 agglomérations françaises, 2010-2014*, Santé publique France, 2019.
- [2] Busca G. et al. *Applied Catalysis B: Environmental*, **1998**, 18, 1-36
- [3] (a) A. Vimont, P. H. Cortes, Y. K. Hwang, G. Férey, M. Daturi, J.-S. Chang, C. Serre and J. W. Yoon, EP2435183B1, 2009; (b) M. Daturi et al, 10.26434/chemrxiv-2023-qgr9n-v2



CORROLES-BASED METAL-ORGANIC FRAMEWORK FOR THE DETECTION OF SMALL VOLATILE MOLECULES

Ken Rapady, Nicolas Desbois, Stéphane Brandès, Claude P. Gros, Laurie André

Université de Bourgogne, ICMUB (UMR CNRS 6302), 9 Av. A. Savary, 21000 Dijon, France

ken.rapady@u-bourgogne.fr

Keywords: Metal-Organic Frameworks, Corrole, Porphyrin, Volatile Organic Compounds, Toxic Gases

In the atmosphere many Volatile Organic Compound (VOCs) such as CO₂, CO and NH₃ are present, and some of which can cause serious illnesses. Air quality must be a priority and it is important to develop methods to detect and monitor these small molecules. In this regard, corrole metalated with cobalt can be a good candidate for gas detection. In fact, the cobalt centre can selectively detect carbon monoxide (CO) at low pressure, but the CO sorption is hindered by π - π stacking interactions, when the corroles are deposited as a layer.^[1,2] Therefore, building a porous material based on cobalt corroles could minimize the corrole π - π interactions in the solid state and optimize their CO sorption capacity. Metal-Organic Frameworks (MOFs) are known for their high surface area, their crystallinity, their customizability, and their application in gases sorption and capture. Herein, inspired from the literature,^[3] we develop a protocole to synthesize a corrole-based MOF with cobalt corrole complexes unit. The latter are used as linkers of the MOF structure. Then we need activate the material and remove the protective ligand from the cobalt site and prepare the material for CO sorption. The prepared material was characterized by XRD, ¹H NMR, BET, TGA and SEM.

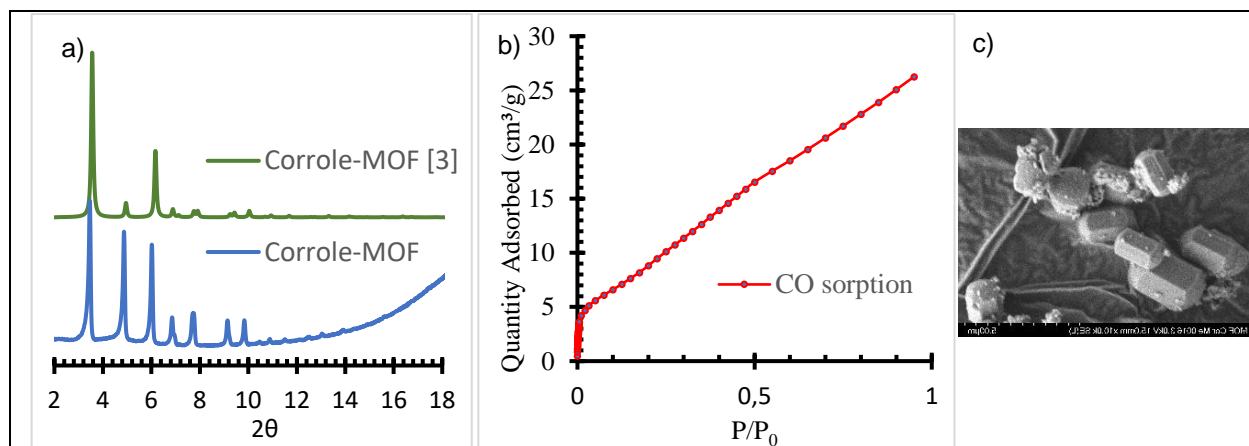


Fig. 1: a) XRD of corrole-MOF (green =reference from the literature, blue = synthesized MOF) b) CO sorption of corrole-MOF c) SEM of corrole-MOF.

Acknowledgments: This work was supported by the CNRS (UMR UB-CNRS 6302), the “Université de Bourgogne (UB)”. The French Research Agency (ANR) is acknowledged for its financial support (ANR-22-CE42-0016-02) and the French Ministry of Research for the funding of the PhD thesis.

References

- [1] M. Vanotti, S. Poisson, V. Soumanna, V. Quesneau, S. Brandès, N. Desbois, J. Yang, L. André, C. P. Gros, V. Blondeau-Patissier, *Sens. Actuator B-Chem.* **2021**, 332, 129507
- [2] C. Di Natale, C. P. Gros, R. Paolesse, *Chem. Soc. Rev.* **2022**, 51, 1277.
- [3] Y. Zhao, S. Qi, Z. Niu, Y. Peng, C. Shan, G. Verma, L. Wojtas, Z. Zhang, B. Zhang, Y. Feng, Y-S. Chen, S. Ma, *J. Am. Chem. Soc.* **2019**, 141, 36, 14443–14450

ORAL POSTER

Grafted Metalloporphyrins in Porphyrin-Based Metal-Organic Frameworks for CO Detection

Margerie Loze,^{a*} Nicolas Desbois,^a Stéphane Brandès,^a Claude P. Gros,^a Virginie Blondeau-Patissier^b and Laurie André^a

^a Université de Bourgogne, ICMUB (UMR CNRS 6302), 9 Av. A. Savary, 21000 Dijon, France

^b Institut FEMTO-ST (UMR CNRS 6174), 26 chemin de l'Épitaphe, 25030 Besançon, France
e-mail: Margerie.Loze@u-bourgogne.fr

Keywords: Metal-Organic Frameworks, Cobalt porphyrins, grafting, CO adsorption

Summary: Carbon monoxide (CO) is an odorless and colorless gas that cannot be detected by humans without the use of a specific sensor. CO is responsible of severe intoxications that can lead to death. It is imperative to develop new technologies that can detect this imperceptible and deadly gas at low concentrations (ppm-ppb levels) before it reaches harmful levels.^[1] In this work, our approach is to synergistically combine the high selectivity of cobalt porphyrins for CO and the high porosity of Metal-Organic Frameworks (MOFs) in order to avoid porphyrin π -stacking and to improve the access of CO to cobalt complexes. Indeed, porphyrins are tetrapyrrolic macrocycles of the porphyrinoid family that, when metalated with cobalt, are capable of CO coordination (sorption) with high selectivity for CO over common interferents such as nitrogen and dioxygen.^[2] Here we consider MOFs as suitable porous materials to host the metalloporphyrins due to their well-known high porosity and superior tunability. In particular, it is possible to take advantage of the natural vacancies present in a porphyrin-based MOF such as the PCN-222 (Fig. 1a) which can then be used to graft cobalt porphyrins on the MOF cluster. In this way, the active molecule for detection is strongly anchored by coordination to the zirconium oxide cluster and hangs inside the MOF pores, allowing free access to the cobalt metal center (Fig. 1a). In this study, the synthesis of the designed cobalt porphyrins grafted on porphyrin-based MOFs have been analyzed and compared with respect to their crystallinity, morphology, and specific surface area thanks to XRD, SEM images, ¹H NMR, BET analysis and adsorption gas selectivity of CO, N₂, O₂ and CO₂ (Fig. 1b)

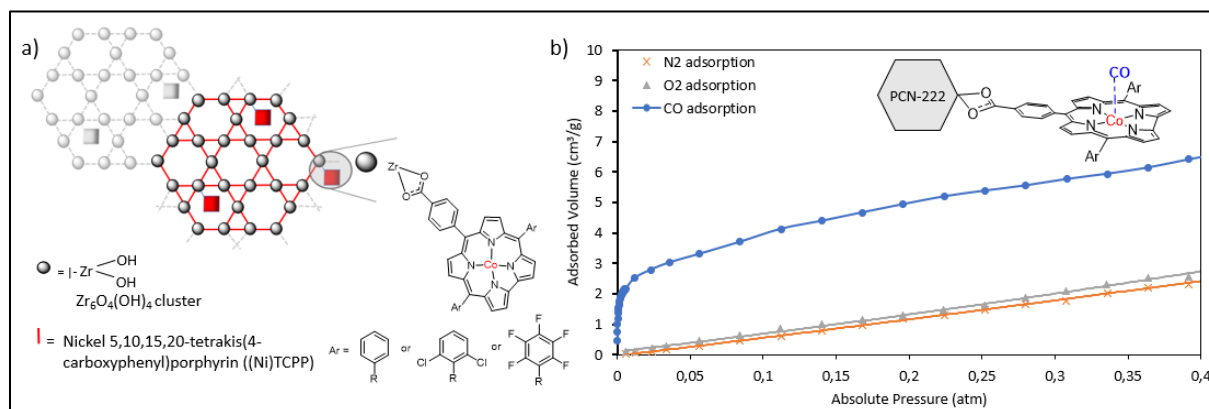


Fig. 1: a) Structure of a cobalt porphyrin grafted on PCN-222; b) N₂, O₂ and CO adsorption of the grafting material.

Acknowledgements: This work was supported by the CNRS (UMR UB-CNRS 6302, the “Université de Bourgogne Franche-Comté (UBFC)”, and the “Conseil Régional de Bourgogne” (ICE PhD thesis). The French Research Agency (ANR) is acknowledged for financial support (ANR-22-CE42-0016-02).

References

- [1] L. André, N. Desbois, C. P. Gros, et S. Brandès, « Porous materials applied to biomarker sensing in exhaled breath for monitoring and detecting non-invasive pathologies », *Dalton Trans.*, vol. 49, n° 43, p. 15161-15170, 2020, doi: 10.1039/D0DT02511A.
- [2] S. Brandès, V. Quesneau, O. Fonquernie, N. Desbois, V. Blondeau-Patissier, et C. P. Gros, « Porous organic polymers based on cobalt porphyrins for carbon monoxide binding », *Dalton Trans.*, vol. 48, n° 31, p. 11651-11662, 2019, doi: 10.1039/C9DT01599J.

Etude de composés de type MOF (Metal Organic Frameworks) pour la séparation isotopique H/D/T

M. Georgelin^{a,b}, I. Bezverkhyy^c, G. Mouchaham^a, S. Thiébaud^b, C. Serre^a

^a *Institut des Matériaux Poreux de Paris, Ecole Normale Supérieure, ESPCI Paris, PSL Université, Paris, France*

^b *CEA, DAM, Valduc, Is sur Tille, France*

^c *Laboratoire Interdisciplinaire Carnot de Bourgogne, Université de Bourgogne Franche-Comté, Dijon, France*

Afin de trouver une alternative aux zéolites, qui sont actuellement employées pour la séparation des différents isotopes de l'hydrogène, les Metal-Organic Frameworks (MOFs) peuvent être considérés comme des candidats prometteurs. En effet, ils montrent une grande versatilité dans leurs domaines d'applications, grâce à leurs structures diverses, ainsi qu'à leurs différentes propriétés physicochimiques modulables à dessein.

Parmi les différents mécanismes de séparation, deux sont typiquement connus pour la séparation isotopique d'hydrogène ($H_2/D_2/T_2$). Le premier connu comme « Kinetic Quantum Sieving » (KQS) repose sur une séparation cinétique induite [1] par un confinement dans de petits pores ayant des diamètres très proches de ceux du H_2 et de ses isotopes. Le second, le « Chemical Affinity Quantum Sieving » (CAQS) [2], permet la séparation isotopique grâce à des affinités chimiques différentes entre l'adsorbant et l'adsorbat, notamment sur des sites d'adsorption forts comme les sites métalliques accessibles (OMS). Ainsi dans le cadre de ce projet en collaboration entre l'IMAP et le CEA Valduc, nous nous reposons notamment sur ces deux mécanismes de séparation afin de guider nos choix pour trouver des MOFs performants, combinant à la fois de très bonnes sélectivité et capacité d'adsorption.

En parallèle de ce travail de recherche sur la séparation, les MOFs sélectionnés subiront des tests de stabilité aux rayonnements afin d'évaluer leur résistance aux rayonnements bêta du tritium présent en faible quantité dans le mélange de gaz à traiter. Ces tests auront donc pour objectif de reproduire un environnement représentatif des conditions réelles, un critère essentiel pour cette application.

Ce poster sera l'occasion de présenter le sujet de cette thèse, les différents aspects de la séparation isotopique d'hydrogène mais également de comparer les données de certains des matériaux actuellement utilisés dont certains MOFs décrits dans la littérature. Il fera l'objet de comparaisons, tant sur des tests de résistance aux rayonnements, que sur les tests de séparation et de sorption effectués précédemment.

Références :

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

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

ORAL POSTER

Etude des propriétés physiques et chimiques d'un bioplastique renforcé à la fibre de coco et/ou au métakaolin

MEITE Namory^{1*}, KOUAKOU Lébé Prisca Marie - Sandrine¹, KOUAMÉ Niamien Alfred¹, SANOU Ali², SANDE Loua Sidibe³, GOURÉ Doubi Bi Irié Hervé⁴, KONAN Koffi Léon¹

¹Université Félix Houphouët-Boigny (UFHB), UFR SSMT, Laboratoire de Constitution et Réaction de la Matière (LCRM), 22 BP 582 Abidjan 22, Côte d'Ivoire

²Institut National Polytechnique Félix Houphouët-Boigny (INP-HB), Laboratoire des Procédés Industriels de Synthèses, de l'Environnement et des Energies Nouvelles (LAPISEN), BP 1313 Yamoussoukro, Côte d'Ivoire

³Laboratoire des Sciences et Technologies de l'Environnement, UFR Environnement, Université Jean Lorougnon Guédé, BP 150 Daloa, Côte d'Ivoire

⁴Laboratoire de Sciences Biologiques, Université Péléforo Gon Coulibaly de Korhogo, BP 1328 Korhogo, Côte d'Ivoire

*Corresponding author : namorymeite2986@gmail.com

Abstract

L'utilisation croissante des matières plastiques issues de la pétrochimie a une incidence sur l'environnement car la grande majorité de ces déchets plastiques n'est pas biodégradable [1]. Par ailleurs, l'incinération de ces déchets est très polluante. En effet, ils libèrent des quantités importantes de dioxyde de carbone et d'autres gaz toxiques nocifs pour l'environnement et la santé humaine [2]. Il est donc nécessaire de développer des biopolymères biodégradables comme alternative aux polymères synthétiques. Dans ce contexte, compte tenu des propriétés de l'amidon [3], des matériaux argileux [4] et des fibres de coco [5], ce travail a pour but d'élaborer des films bioplastiques à base d'amidon de manioc avec une ou deux charges naturelles (fibre de coco et métakaolin). Différentes analyses ont été effectuées sur les biocomposites telles que: l'analyse chimique par EDS (Energy-Dispersive X-ray Spectroscopy), la microscopie électronique à balayage (MEB) et la résistance thermique. Les résultats obtenus montrent que le métakaolin se disperse relativement mieux que les fibres de coco dans les bioplastiques. Les bioplastiques sont tous constitués de silice (SiO₂); ce qui est un atout pour la diffusion de chaleur. A 150 °C, tous les films plastiques sont partiellement carbonisés à l'exception du film plastique BPK_T (Bioplastique renforcé avec le métakaolin). Cela suggère que l'argile constitue une barrière à la diffusion de la chaleur. L'incorporation des charges naturelles accélère la biodégradation des bioplastiques.

Keywords: bioplastiques, métakaolin, biodégradabilité, résistance thermique.

References:

- [1] Méité N., Konan K.L., Tognonvi M.T., Doubi B.I.H.G., Gomina M., et al. (2021). Carbohydrate Polymers, 254, pp.117322.
- [2] Belyamani, I. (2012). University of Jean Monnet, St Etienne, France. Retrieved from <https://tel.archives-ouvertes.fr/tel-00702749>
- [3] Tyagi V. & Bhattacharya B. (2019). MOJ Food Process Technol., 7(4), 128–130.
- [4] Islam H.B.M.Z., Susan M.A.B.H. & Imran A.B. (2020). ACS Omega, 5(28), 17543-17552.
- [5] Food and Agriculture Organization, (2022), Fibres du futur. (fibrecoco-fao.org)

MOFs FOR VOCs CAPTURE AND DETECTION USING A SYNERGETIC EXPERIMENTAL AND COMPUTATIONAL APPROACH

Pedro Brântuas^a, Paul Iacomi^{a,b}, Ezgi Gulcay-Ozcan^a, Guillaume Maurin^a, Sabine Devautour-Vinot^a

^a ICGM, Univ. Montpellier, CNRS, ENSCM, Montpellier, France

^b Surface Measurement Systems, London HA0 4PE, U.K

e-mail: pedro.freire-brantuas@umontpellier.fr

The World Health Organization (WHO) has recognized volatile organic compounds (VOCs) as one of the major sources of indoor air pollution. Their ubiquitous presence is due to being released from building and finishing materials (paints, varnishes, wallpapers, floor covering, solvents, adhesives), burning processes and cleaning products.^[1, 2]

Their emissions, even at low concentration levels in indoor air, are a danger to both human health and sensitive machinery. Therefore, the detection and reduction of airborne pollutants traces (ppb to ppm) is an ongoing challenge to preserve clean and safe environments for living and working places.

In this context, porous solids like MOFs (Metal-Organic Frameworks) appear as promising materials due to both their tailorable chemical and physical properties as well as highly porous structures, acting as sorption media for direct air capture of pollutants,^[2] or as components in electronic devices designed for monitoring concentration of contaminants.^[3] Nevertheless, given the large number of synthesizable structures, the choice of a material to target a specific contaminant is more often than not a question of serendipity.^[4,5]

To overcome this limitation, a hand-in-hand synergetic computational/experimental approach is herein devised for screening and identifying the best MOFs for the adsorption of specific VOCs pollutants (Fig. 1). This method combines high-throughput molecular simulations to identify key promising materials, followed by advanced adsorption experiments at very low pollutant concentrations as well as sensing tests. We further detail several classes of MOF materials which were identified through this approach that are applicable to the capture and/or the detection of various species of VOCs pollutants.

References

- [1] V. Van Tran, D. Park, Y.-C. Lee, Int. J. Environ. Res. Public Health, 2020, 17, 2927
- [2] C. Lai, Z. Wang, L. Qin, Y. Fu, B. Li, M. Zhang, S. Liu, L. Li, H. Yi, X. Liu, X. Zhou, N. An, Z. An, X. Shi, C. Feng, Coordination Chemistry Reviews, 2021, 427, 213565.
- [3] M. D. Allendorf, R. Dong, X. Feng, S. Kaskel, D. Matoga, V. Stavila, Chem. Rev., 2020, 120, 8581–8640.
- [4] P. Z. Moghadam, A. Li, X.-W. Liu, R. Bueno-Perez, S.-D. Wang, S. B. Wiggin, P. A. Wood, D. Fairen-Jimenez, Chem. Sci., 2020, 11, 8373–8387.
- [5] S. Curtarolo, G. L. W. Hart, M. B. Nardelli, N. Mingo, S. Sanvito, O. Levy, Nature Mater, 2013, 12, 191–201.

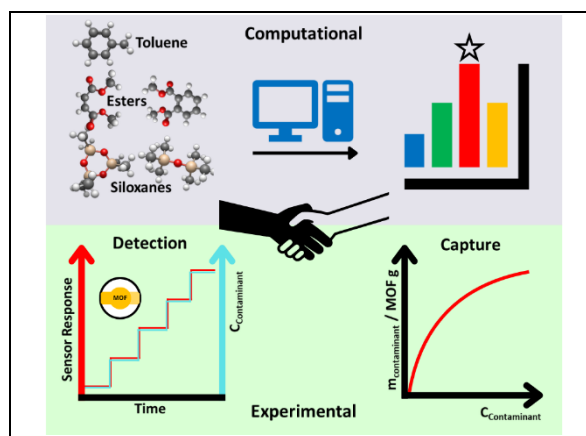


Fig. 1: Combined computational/experimental approach for VOCs capture and detection.

Towards large-scale production of aluminium fumarate

M. Perbet^a, E.A. Quadrelli^a, D. Farrusseng^a

^a IRCELYON, CNRS, 2 Avenue Albert Einstein 69626 Villeurbanne Cedex

e-mail: miriam.perbet@ircelyon.univ-lyon1.fr

Metal Organic Frameworks (MOFs), in particular aluminium-based MOFs are promising candidates for several applications like water harvesting [1], thermal heat management [2] or enhanced gas storage and separation. Unfortunately, significant obstacles associated with the synthesis of these materials, such as the use of toxic solvents, harmful reagents, demanding pressure and temperature conditions, pose challenges for scaling up their production. As a result, their production at large industrial scale and at competitive cost point are prevented.

Our work aims to develop industrial scale synthesis solutions. We developed a green, water-based, non-toxic synthesis pathway for the MOF aluminium fumarate [3]. This material is made out of Al-OH-Al chains, linked together by fumarate. This structure contains one dimensional lozenge-shaped pores of approximately $5.7 \times 6.0 \text{ \AA}^2$ free surface [3]. Our study on aluminium fumarate extends from the lab-scale synthesis to a pilot-scale production of several tens kg of MOF using a spray-drying technique. This allows to advantageously get the MOF directly shaped as small spheres, typically of diameters between 50 and 200 μm , as represented in Figure 1. Unlike bulk powder, this shape helps mitigate issues such as caking, clogging or inhalation of particles during powder handling.

As a perspective, the successful spray-drying of aluminium fumarate is promising to explore its use in other areas like fluidization – to minimize pressure drop during adsorption/catalysis application –, or for expanding our synthesis approach to other aluminium-based MOFs, such as MIL-160(Al) or trimesic acid-based MOFs (Al-BTC).

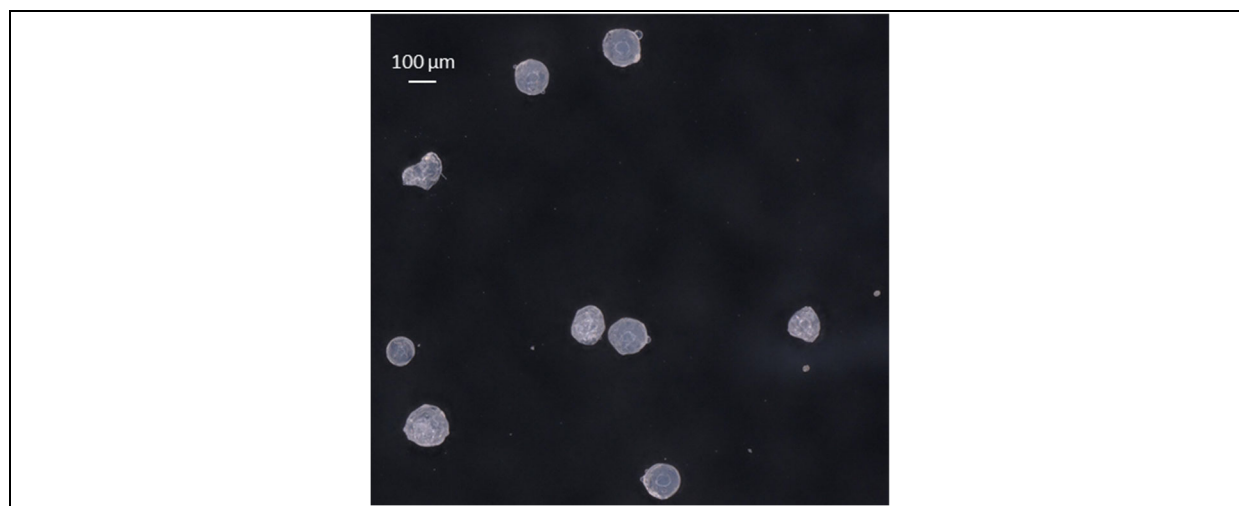


Fig. 1: MEB picture of pilot-scale spray-dried Al-fumarate MOF.

This project has received funding from the European Union's Horizon Europe research and innovation program AMBHER under grant agreement No 101058565.

References

- [1] M. Solovyeva, I. Krivosheeva, et al, *Energies* **2021**, *14*, 2586. DOI: 10.3390/en14123586
- [2] H. Kummer, F. Jeremias, et al, *Ind. Eng. Chem. Res.* **2017**, *56*, 8393-8398. DOI: 10.1021/acs.iecr.7b00106
- [3] E. Alvarez, N. Guillou, et al, *Angew. Chem. Ind. Ed.* **2015**, *54*, 3664-3668. DOI: 10.1002/anie.201410459

Building photocatalytic active biomaterials from Polyoxometalates and proteins

Alisa Ranscht^a, Nada Savić^a, Noha Ebrahim^a, Tatjana N. Parac-Vogt^{*a}

^a Department of Chemistry, KU Leuven
Celestijnenlaan 200F
3001 Leuven
Belgium
e-mail: tatjana.vogt@kuleuven.be

Sophisticated protein environments in enzymes have the ability to govern chemical transformations towards high selectivity.^[1] Boosting their activity and stability under conditions relevant for fine chemical synthesis is however an ongoing challenge.^[2] Introducing artificial catalytically active metal centers into protein environments is one way to address this. Polyoxometalates (*POMs*) are well defined anionic metal-oxo cluster molecules. Besides being highly active as photo-oxidation catalysts, their versatility in application and interaction with other chemical species can be further tuned through a modification with organic groups, generating hybrid *POMs* (*H-POMs*).^[3]

This opens up the design of hybrid biomaterials providing interesting opportunities for developing artificial enzymatic reactions while at the same time the stability of molecular *POM* catalysts can be increased through incorporation of the active center within porous materials.^[4]

Recently, our group published a novel hybrid biomaterial built from a ditopic *H-POM* crosslinked by a quatrotopic streptavidin protein through strong intermolecular interactions between the biotin functional groups as part of the *H-POM* and the protein's specific binding sites, paving the way towards the development of heterogenous artificial enzymes.^[5]

Furthermore, preliminary results in the homogeneous phase targeting the oxidative C-C bond cleavage of 1,2-diphenyl-1,2-ethanediol and using iron(III) substituted Wells-Dawson $K_7[Fe(P_2W_{17}O_{61})(H_2O)]$ *POM* (*Fe-POM*) showed a 30% increased yield (70%) in presence of Human Serum Albumin (*HSA*) protein compared to *Fe-POM* catalyst alone, showcasing the importance of the protein environment on the catalytic efficiency of the *POM* catalyst. The reaction was performed in aqueous media and using visible light ($\lambda = 456$ nm) as sole energy source.

Our aim is to build a photoactive hybrid material from photoactive *H-POMs* through a well-controlled assembly with a protein, resulting in a new class of photoactive heterogenous artificial enzymes.

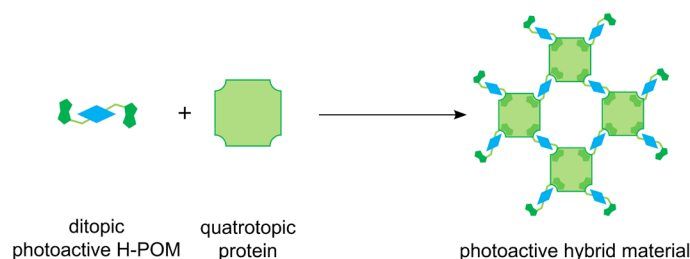


Figure 1: Strategy adapted from Salazar Marcano (2024) et al.^[5] for the controlled assembly of *H-POM* and protein to form a photoactive material.

References

- [1] Lu, Y.; Yeung, N.; Sieracki, N.; Marshall, N. M. Design of Functional Metalloproteins. *Nature* 2009, 460, 855–862.
- [2] Renata, H.; Wang, Z. J.; Arnold, F. H. Expanding the Enzyme Universe: Accessing Non-Natural Reactions by Mechanism-Guided Directed Evolution. *Angewandte Chemie International Edition* 2015, 54 (11), 3351–3367.
- [3] Anyushin, A. V., Kondinski, A., & Parac-Vogt, T. N. Hybrid polyoxometalates as post-functionalization platforms: from fundamentals to emerging applications. *Chemical Society Reviews*, 2020, 49(2), 382–432.
- [4] Ranscht, A., Rigodanza, F., Gobato, T., Crea, I., Quadrelli, E. A., Canivet, J., & Bonchio, M. Combined Covalent and Supramolecular Polymerization To Reinforce Perylenebisimide Photosynthetic “Quantasomes”. 2024, *Chemistry—A European Journal*, e202303784.
- [5] Salazar Marcano, D.E.; Lentink, S.; Chen, J.J.; Anyushin, A. V.; Moussawi, M. A.; Bustos, J.; Van Meerbeek, B.; Nyman, M.; and Parac-Vogt, T. N. Supramolecular Self-Assembly of Proteins Promoted by Hybrid Polyoxometalates. *Small*, 2024, 2312009

Atomistic Modelling of the Crystal Growth of ZIF-8

Sahar Andarzi Gargari^a, Emilio Méndez^a, Rocio Semino^a

^a Sorbonne Université, CNRS, Physico-chimie des Electrolytes et Nanosystèmes Interfaciaux, PHENIX, F-75005 Paris, France.

E-mail: rocio.semino@sorbonne-universite.fr

Metal-organic frameworks (MOFs) have fascinating properties and excellent performance in many applications requiring guest sieving and/or confinement. However, synthesising new MOFs still relies heavily on trial-and-error searches, which makes the synthesis of new MOFs with targeted topology or composition extremely time- and resource-consuming. In this context, understanding the physico-chemistry underlying the self-assembly of MOFs is essential for driving the synthesis of new structures. While several experimental studies have addressed the crystal growth of MOFs by various *ex situ* and *in situ* analytical techniques, the required resolution to fully understand the first stages of this complex process cannot yet be experimentally achieved. From the modelling standpoint, only a handful of studies have been devoted so far to the simulation of the pre-nucleation process of MOFs in solution, and despite their promise, many questions remain unsolved. In this work we summarize our current work devoted to studying the growth of a ZIF-8 nucleus in methanol as synthesis solvent. ZIF-8 is an archetypical MOF, of formula $\text{Zn}(\text{2-methyl-imidazole})_2$, featuring a high thermal and chemical stability. We perform our simulations relying on a non-bonded force field nb-ZIF-FF developed previously in our group,[1] that allows for metal-ligand bond breaking and formation. We employ enhanced sampling techniques and the constant chemical potential ensemble within a molecular dynamics scheme to model rare events that are necessarily involved in the crystal growth process.

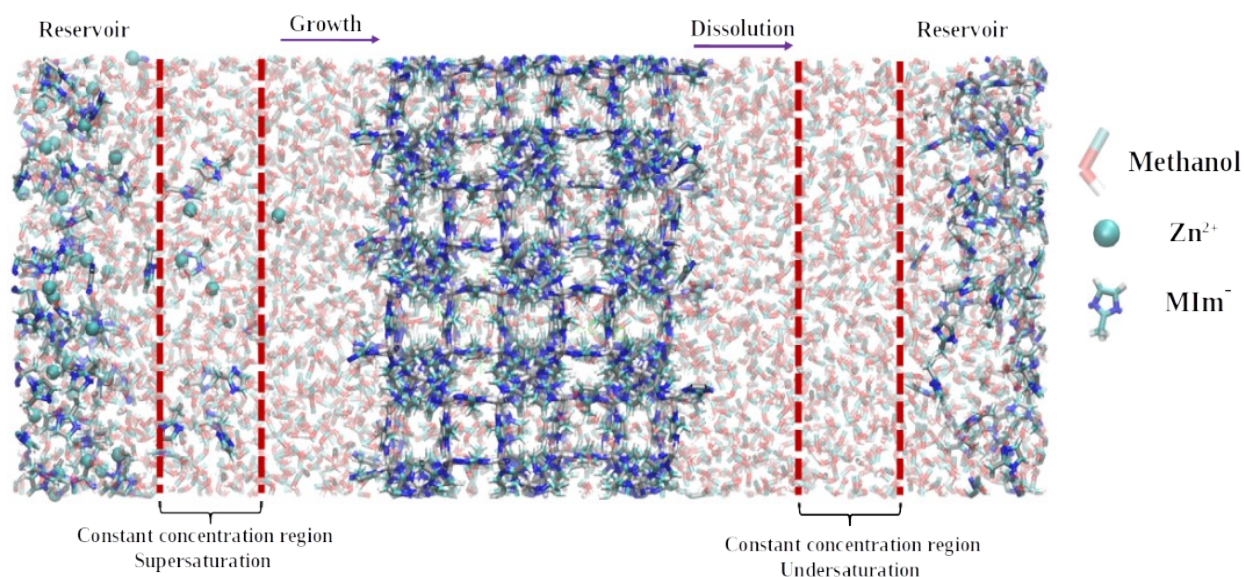


Fig. 1: Simulation snapshot of the setup to study growth of a ZIF-8 surface slab under constant chemical potential conditions.

References

- [1] S. R. G. Balestra and R. Semino; J. Chem. Phys, 157, 184502 (2022)

Development of MOF A520-based composites as moisture scavengers in pharmaceutical packaging

Marie Froehly^{a,b}, Gérald Chaplais^b, Habiba Nouali^b, Vincent Roucoules^b, Frédéric Payet^a, Jean Daou^a

^a APTAR CSP Technologies, Niederbronn-les-Bains, France

^b Institut de Science des Matériaux de Mulhouse (IS2M), Université de Haute Alsace (UHA), Université de Strasbourg (UniStra), CNRS, IS2M UMR 7361, Mulhouse, France

e-mail: marie.froehly@uha.fr

Molecular contamination is a major concern for pharmaceutical industry as it can affect the quality and the performance of a drug. Depending on storage conditions, atmospheric moisture can accelerate the degradation process of the product. To increase the shelf life of these moisture-sensitive compounds, APTAR CSP Technologies has developed so-called “3-Phase” formulations (made up of a main polymer + a secondary polymer + an adsorbent). The current adsorbent is LTA zeolite (4A), which displays the property of adsorbing moisture [1]. These formulations are used to produce pharmaceutical packaging by extrusion/injection. However, their effectiveness against moisture is limited by the adsorption capacity of zeolite 4A (254 mg_{water}/g_{zeolite 4A}). This study aims to identify an alternative adsorbent to zeolite 4A in the formulation with a higher sorption capacity such as a hydrophilic Metal-Organic Framework (MOF). Among the hydrophilic MOFs reported in the literature, MOF A520 appears to be an excellent candidate (thermal stability, production cost, adsorption capacity of 452 mg_{water}/g_{MOF A520}) [2]. This material was incorporated at various loading rates (30 to 55 wt.%) into 3-Phase formulations as the adsorbate, and corresponding composites were shaped as granulates, films and injected parts (Figure 1 a). Water adsorption measurements performed in a climatic chamber at 22 °C and 80 % relative humidity have shown that MOF A520/polymer composites exhibit significantly higher water capacities than those of zeolite 4A/polymer composites (Figure 1 b). However, MOF-based composites only achieve a water adsorption performance of around 80 % compared with powder (100 % for zeolite-based composites). This result can be explained by a potential interaction between the secondary polymer and the MOF, with partial blocking of the pores. Optimisation of polymer formulations will therefore be further explored to achieve 100 % performance with MOF-based composites.

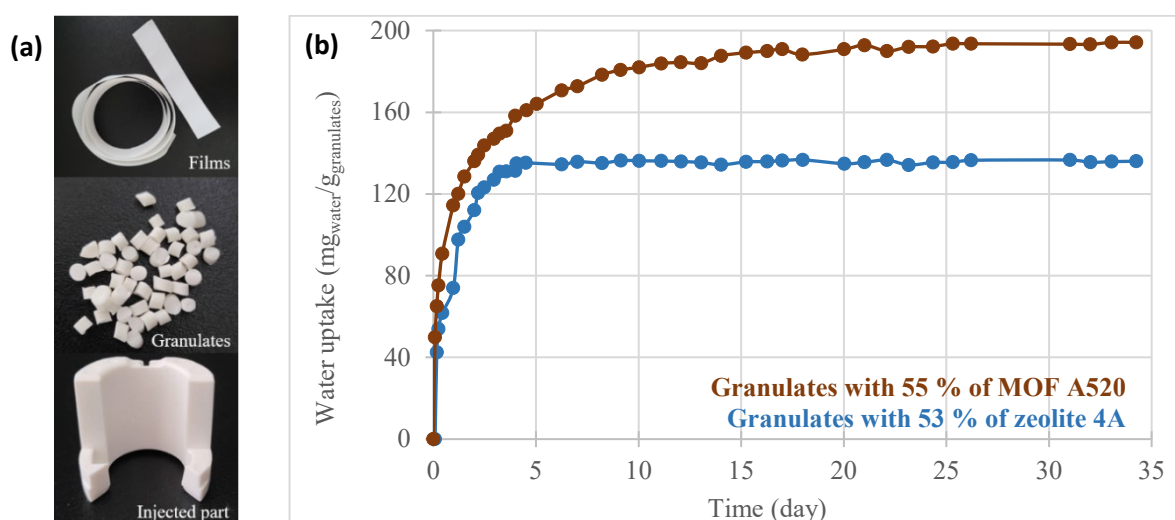


Fig. 1: (a) Photographs of various shaped MOF A520/polymer composites. (b) Water adsorption kinetics of MOF A520 and zeolite 4A granulates at 22 °C and 80 %RH.

References

- [1]. Tahraoui, Z.; Nouali, H.; Marichal, C.; Forler, P.; Klein, J.; Daou, T. J., *Molecules*. 26, 4815, 2021
- [2]. Kayal S.; Chakraborty, A.; Teo, H. W. B., *Mater. Lett.* 221, 165-167, 2018

Antibacterial MOF composite films for food packaging

Laura Premet,^{a,b} Gérald Chaplais,^a Emmanuel Oheix,^a Laurent Pieuchot,^a Jean Daou^b

^a Institut de Science des Matériaux de Mulhouse (IS2M), Université de Haute Alsace (UHA), Université de Strasbourg (UniStra), CNRS, IS2M UMR 7361, F-68100 Mulhouse, France

^bAPTAR-CSP Technologies, 67110 Niederbronn-les-Bains

e-mail : laura.premet@uha.fr

Bacterial contamination is a major issue in food and pharmaceutical industries. Indeed, contaminated product can endanger the health of the users. Metal-Organic Frameworks (MOFs) appear to be excellent antibacterial materials thanks to their chemical compositions and/or their abilities to encapsulate substances acting as bactericidal agents [1]. The MOFs ZIF-8 and ZIF-dia(Zn) are polymorphs formed of divalent zinc ions tetracoordinated by imidazolate-type ligands [2-3], and are used in this study for their antibactericidal properties. However, these materials must be shaped in order to be used in packaging. Several formulations of polymer/MOF composite films were extruded and then tested against *Escherichia Coli* (*E. Coli*) by different methods. The results indicate antibacterial activity by contact, from 32 wt.% of MOF in the composite film (Figure 1).

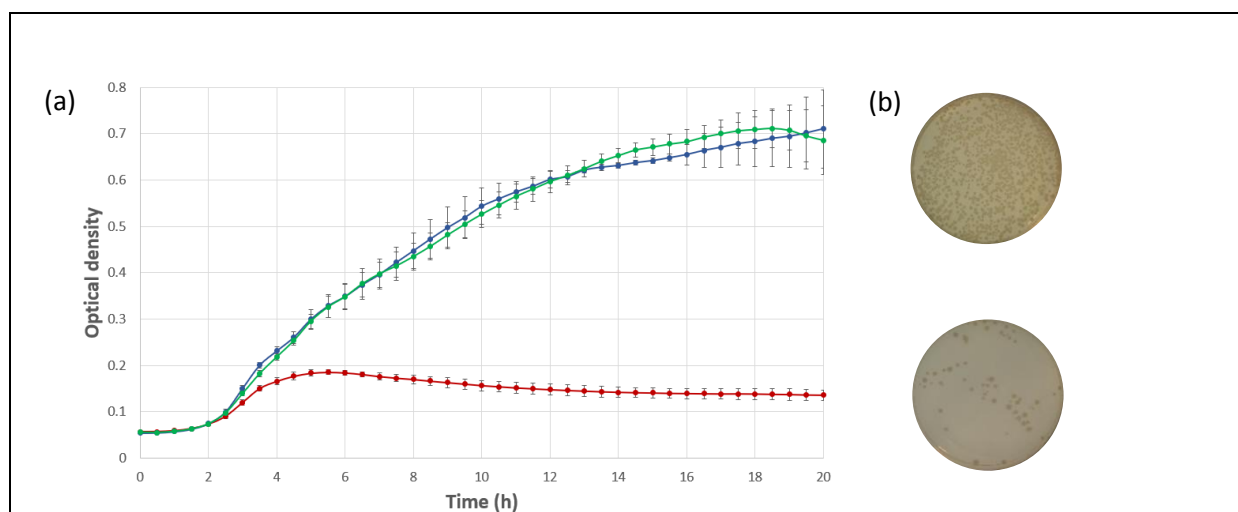


Figure 1: (a) Evolution of the optical density of a bacteria solution of *E. Coli* at 10^6 CFU/mL, in contact with (-) blank film; (-) film with 10 % ZIF-8/ZIF-dia(Zn); (-) film with 32 % ZIF-8/ZIF-dia(Zn);

(b) Representation of the antibacterial activity without (up) and with the 32 % ZIF-8/ZIF-dia(Zn) film (down)

References

- [1] Karimi Alavijeh, R.; Beheshti, S.; Akhbari, K.; Morsali, A., *Polyhedron* **2018**, *156*, 257-278.
- [2] Fairen-Jimenez, D.; Moggach, S. A.; Wharmby, M. T.; Wright, P. A.; Parsons, S.; Duren, T., *J. Am. Chem. Soc.* **2011**, *133* (23), 8900-8902.
- [3] Shi, Q.; Chen, Z.; Song, Z.; Li, J.; Dong, J., *Angew. Chem. Int. Ed.* **2011**, *50* (3), 672-675.

ORAL POSTER

Efficient Nickel and Cobalt Recovery by Metal–Organic Framework based Mixed Matrix Membranes (MMM-MOFs)

Waseem Iqbal,^a Amira Nour,^a Javier Navarro-Alapont,^b Jesús Ferrando-Soria,^b Pietro Magarò,^c Rosangela Elliani,^a Antonio Tagarelli,^a Carmine Maletta,^c Teresa F. Mastropietro,^{*a} Emilio Pardo,^{*b} Donatella Armentano^{*a}

^a *Dipartimento di Chimica e Tecnologie Chimiche (CTC), Università della Calabria, Rende 87036, Italy*

^b *Instituto de Ciencia Molecular (ICMol), Universidad de Valencia, 46980 Valencia, Spain*

^c *Dipartimento di Ingegneria Meccanica, Energetica e Gestionale, Università della Calabria, Rende 87036, Cosenza, Italy*

e-mail: teresafina.mastropietro@unical.it, Emilio.pardo@uv.es, donatella.armentano@unical.it

The electric vehicle rechargeable battery market has seen a substantial boost due to the green energy transition. This surge has sparked a high demand for raw materials such as cobalt and nickel, both vital constituents in lithium-ion batteries (LIBs). However, the current mining protocols and the concentrated localization of these ores have transformed cobalt and nickel into mineral puzzles. Shortages in their supply threaten to hinder the progress of the renewable energy transition. In this study, our aim is to advance sustainable recycling practices for valuable metals found in lithium-ion batteries (LIBs) and wastewater. We investigate the efficiency of four mixed matrix membranes (MMMs) incorporating different organic frameworks, **MIL-53(Al)**, **MIL-53(Fe)**, **MIL-101(Fe)** and $\{Ca^{II}Cu^{II}_6[(S,S)\text{-serimox}]3(OH)_2(H_2O)\}.39H_2O$ (**SrCu₆Ser**) embedded in polyether sulfone (PES). Our focus is on recovering cobalt (II) and nickel (II) metal cation from mixed cobalt-nickel aqueous solutions containing common interfering ions. While the neat PES membrane slightly contributes to the adsorption of metal ions, showing reduced removal efficiency values of 10.2% and 9.5% for Ni (II) and Co (II), respectively, the inclusion of MOFs in the polymeric matrix substantially improves the adsorption performances. The four MOF@PES MMMs efficiently remove these metals from water, with the **MIL-53(Al)@PES** being the one that presents higher removal efficiencies, with a removal efficiency up to 95% of Ni and Co. Remarkably, the MOF@PES MMMs containing **SrCu₆Ser** exhibit outstanding selectivity towards cobalt(II) cations in front of nickel(II) ones, with removal efficiency of 63.7 % for Co(II) and of 15.1 % for Ni(II). Overall, the remarkable efficiencies, versatility, high environmental robustness, and cost-effective synthesis, shown by this family of MOF@PES MMMs situate them among the best adsorbents for the extraction of this kind of contaminant.

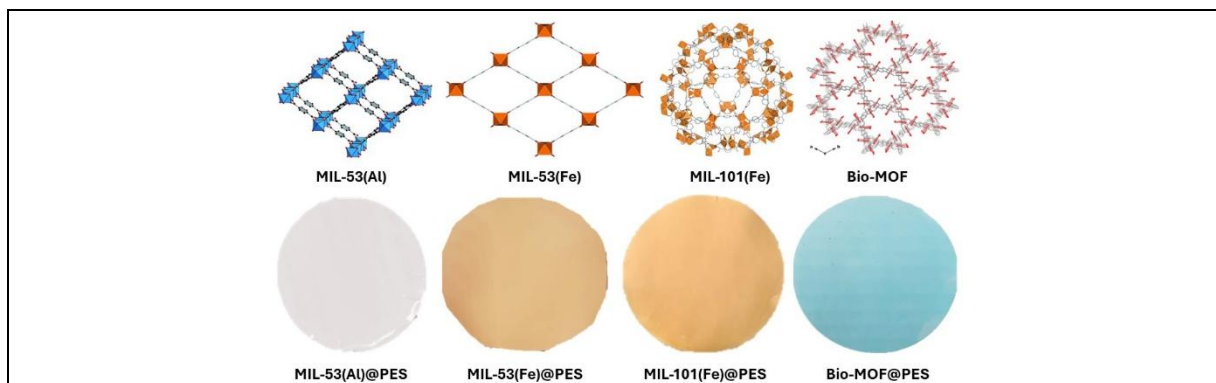


Figure 1. The top row views of the three-dimensional structures of different MOFs. The bottom row shows photographs of MOF mixed matrix membranes.

References

- [1] Huo, J.; Yu, G.; Wang, J. J. *Hazard. Mater.* 2021, 411, 125117.

A p-type Semi-Conducting Copper(I)-1,3-Benzenedithiolate 2D Coordination Polymer with High Seebeck Coefficient

C. Andrade^a, S. Hawila^a, A. Abdallah^a, J-L. Rukemampunzi^a, A. Mesbah^a, N. Guillou^b, F. Perret^c, S. Wuttke^d, T. Niehaus^e, R. Debord^e, O. Boisron^e, S. Pailhès^e and A. Demessence^{a,d}

^aIRCELYON, UMR5256 Université Lyon 1-CNRS, Université de Lyon 69626 Villeurbanne, France

^bILV, UMR8180 UVSQ-CNRS, Université Paris-Saclay, 78035 Versailles, France

^cICBMS, UMR5246 Université Lyon 1-INSA Lyon-CPE Lyon-CNRS, 69622 Villeurbanne, France

^dBCMaterials, Université du Pays basque (UPV/EHU), Bilbao, Spain

^eILM, UMR5306 Université Lyon 1-CNRS, Université de Lyon 69622 Villeurbanne, France

e-mail: chloe.andrade@ircelyon.univ-lyon1.fr

During the past two decades, coordination polymers (CPs) have emerged as a highly versatile platform for wide-ranging potential applications from gas storage to separations, heterogeneous catalysis, and biomedicine, among others. These are crystalline extended networks consisting of metal ions and multidentate ligands, where metal ions act as nodes between the bridging ligands. Metal Organic Thiolates (MOT) CPs have appeared as stable and highly electrical conducting materials, with a record of $1580 \text{ S}\cdot\text{cm}^{-1}$ for the 2D copper-benzenehexathiolate CP ^[1]. Thus, conducting CPs could provide vast potential technological impacts especially because their structural complexity, which provides additional possibilities and a route for disentangling the electronic transport and the heat transport as needed for optimizing the heat conversion into electricity by the thermoelectric effects. In this poster, we will present the synthesis, the structural characterization and the transport measurements (conductivity and Seebeck) of a new p-type semi-conducting CP, the copper(I)-1,3-benzenedithiolate, made of thiolate-based ligand and Cu(+I) which is stable up to 200 °C under air. While this CP has a 2D structure, our structural and theoretical studies reveal that the electronic conduction is mostly dominated by the electronic states from CuS chains embedded in the organic matrix. The 1D character of the electronic bands lead to high Seebeck values with an anomalous temperature dependence ^[2].

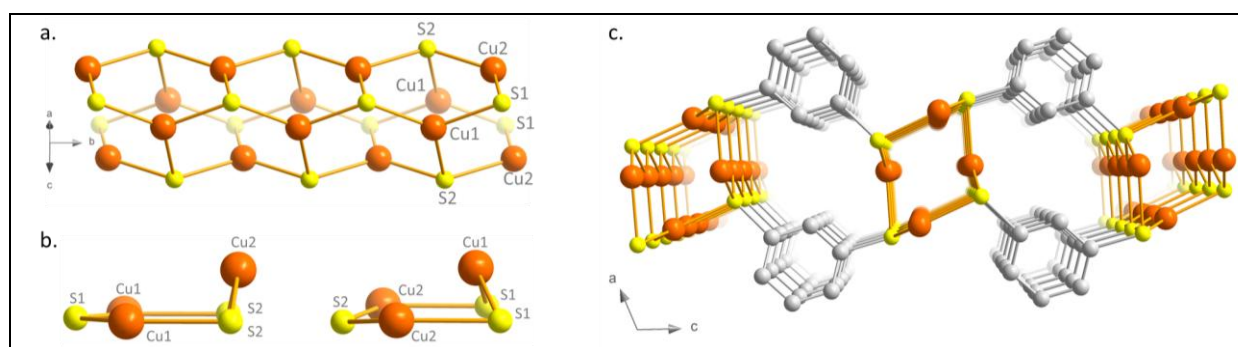


Fig. 1: Structure of $[\text{Cu}_2(1,3\text{-BDT})]_n$: a. the Cu-S chain along the b axis; b. the two deformed Cu_3S_3 hexagons and c. the central projection along the b axis. Orange, yellow and gray spheres correspond to copper, sulfur and carbon atoms. Hydrogen atoms were omitted for clarity.

References

- [1] X. Huang, H. Yao, Y. Cui, W. Hao, J. Zhu, W. Xu, D. Zhu, *ACS Appl. Mater. Interfaces* **2017**, 9, 40752-40759.
- [2] C. Andrade, S. Hawila, A. Abdallah, J-L. Rukemampunzi, A. Mesbah, N. Guillou, F. Perret, S. Wuttke, T. Niehaus, R. Debord, O. Boisron, S. Pailhès and A. Demessence, *J. Mater. Chem. C*, **2023**, <https://doi.org/10.1039/D3TC02379F>

This work was supported by the French National Agency (MOTIC ANR-21-CE08-0045).

Monolithic assembly of Metal-Organic Frameworks (MOFs) using Pickering emulsion

Fabrice Lorignon^a, Alban Gossard^b, Sabrina Medjouel^a, Michaël Carboni^a, Daniel Meyer^a

^aICSM, CEA, Univ Montpellier, CNRS, ENSCM, Marcoule, P 17171, Bagnols-sur-Cèze Cedex, France

^bCEA, DES, ISEC, DMRC, Univ Montpellier, Marcoule, P 17171, Bagnols-sur-Cèze Cedex, France
e-mail: sabrine.medjouel2@cea.fr

MOFs are hybrid materials with interesting properties, such as thermal stability and high specific surface area, for catalysis, compound separation or gas purification. However, the result of the synthesis is a crystalline powder, and the shaping of MOFs into porous materials is necessary for a wider application outside the batch process. Templating with MOF-stabilized Pickering emulsions is a technique used in the literature to incorporate particles into hierarchically porous (monolithic) materials [1]. In the literature, the final properties of the monoliths are highlighted, while the microstructures of the emulsions are rarely described in detail. Our study consists in characterizing the microstructural and rheological properties of Pickering emulsions stabilized solely by MOFs particles [2]. The continuous phase of the emulsion is then polymerized to form porous monoliths (polyHIPEs) whose macropores are a replica of the droplets. Hydrodynamic measurements of pressure drop show good fluid flow through the pores of polyHIPEs [3]. The final step was to optimize the shaping process. It has been demonstrated that it is possible to increase the accessible surface area of MOFs in the polyHIPE while maintaining interconnected macroporosity. Indeed, to avoid the pore blocking induced by the embedment of the MOF particles; our strategy was to modify their hydrophilic/hydrophobic balance with a controlled adsorption of hydrophobic molecules on MOF particles [4]. This will induce a displacement of the MOF position at the paraffin–water interface in the emulsion and then make the particles less embedded into the polymer wall. This leads to the formation of hierarchically structured monoliths integrating MOF particles with higher accessibility, maintaining their original properties and allowing their application in fixed-bed processes.

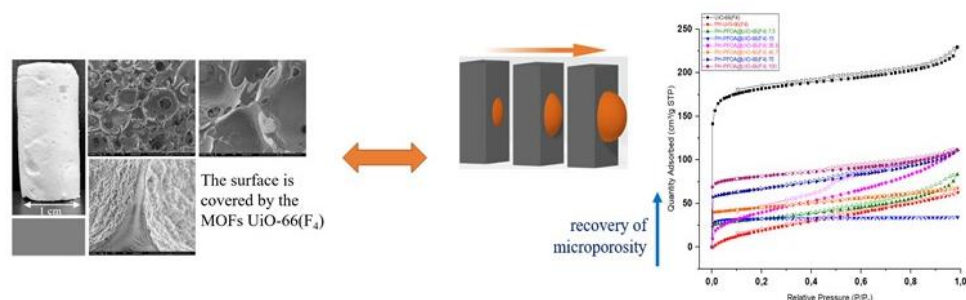


Fig. 1: Improving the surface properties of monoliths by modifying the hydrophobicity of MOF particles stabilising a Pickering emulsion.

References

- [1] F.Lorignon, A.Gossard, M. Carboni, Chem. Eng. J., 393, 124765 (2020)
- [2] F.Lorignon, A.Gossard, M. Carboni, D.Meyer, J. Colloid Interface Sci., 586, 305 (2021)
- [3] F.Lorignon, A.Gossard, M. Carboni, D.Meyer, Mater. lett., 296, 129931 (2021)
- [4] F. Lorignon, A. Gossard, S. Medjouel, M. Carboni, D. Meyer, ACS Appl. Mater. Interfaces, 15, 25, 30707 (2023)

Influence of humidity on the sorption of CO₂ in prototypical MOFs materials: insight and challenges

Lisa Mingzhe Sun^{1,*}, Sean McIntyre¹, Majid Naderi¹, Daryl Williams^{1,2} Paul Iacomi¹

¹ Surface Measurement Systems Ltd., London, UK, piacomi@surfacemeasurementsystems.com,

²Department of Chemical Engineering, Imperial College London, UK

MOFs materials are one of the most promising candidates for the implementation of carbon capture (CC), both for direct air capture (DAC) solutions and point sources. Bringing a promising material from the lab to industry requires a realistic screening of its performance in process relevant conditions. The main goal from a materials standpoint is identifying and screening sorbents with the necessary affinity at the relevant CO₂ concentration (from 400 ppm up to 100%), long term usability, and thermal properties. One of the most pertinent challenges relies in the presence of humidity in the process stream, leading to several possible effects on a material's CO₂ capture potential. Water molecules compete with CO₂ for sorption sites in MOFs and can even destroy the structures.

Therefore, assessing the influence of moisture on the CO₂, and the amount taken up of each from a multicomponent mixture, is of crucial importance. In this work we explore several methods of accomplishing this difficult task – gravimetry and breakthrough analysis – and then walk through several examples on prototypical MOFs materials.

Enhanced Bioelectrocatalysis and H₂O₂ Sensing via Dual-Encapsulation in Zeolitic Imidazolate Frameworks

M. Joharian^a, A. J. Gross^{*a}

^a *Department of Molecular Chemistry, Univ. Grenoble Alpes, CNRS, 38000 Grenoble, France*
e-mail: andrew.gross@univ-grenoble-alpes.fr

The encapsulation of enzymes in metal organic frameworks (MOFs) gives rise to new opportunities to improve the stability and/or activity of fragile and complex enzymes. In this study, we focus on the niche application that combines MOFs with oxidoreductase enzymes for enzyme-confined biosensing at carbon nanotube electrodes via H₂O₂ reduction. We have explored the synthesis of new redox-active ZIF-8 derivatives with encapsulated enzyme and/or redox mediators. The MOFs and their composites have been characterized by a wide range of techniques including XRD, ATR-FTIR, UV-vis, Raman, BET and SEM. UV-visible spectroscopy protocols were developed to estimate mediator and enzyme loadings as well as specific enzyme activity, shedding light on encapsulation efficiency and enzyme reactivity under confinement. Electrochemical characterization and biosensing experiments demonstrate how the global MOF structure significantly affects both stability and activity of the peroxidase at carbon nanotube electrodes for sensing, especially under harsh conditions.

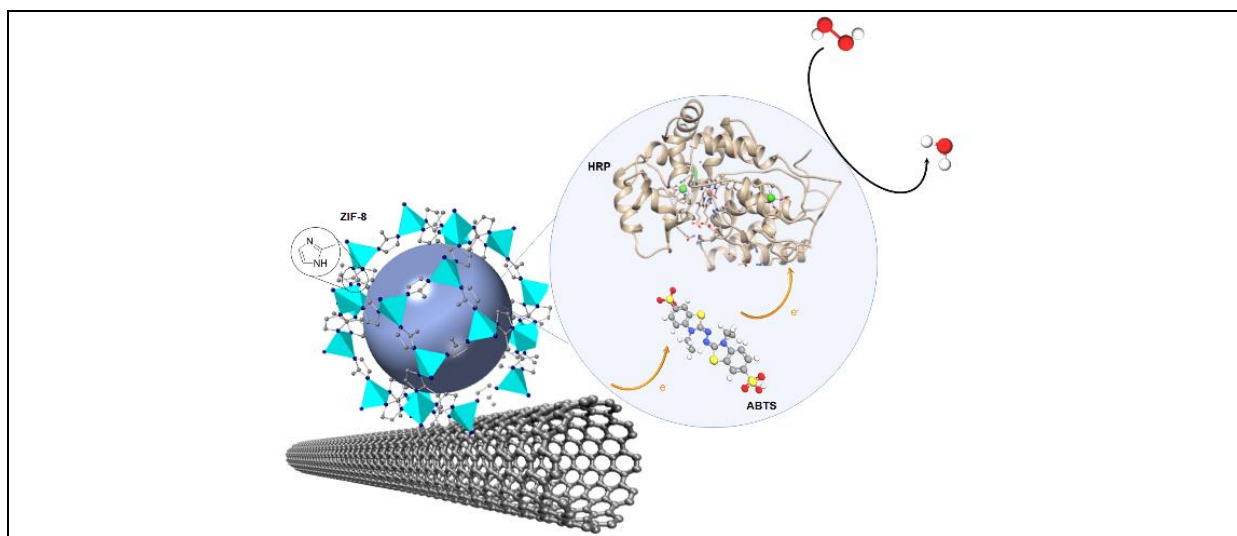


Fig. 1: Dual enzyme/mediator confinement via ZIF-8 at multiwalled carbon nanotubes for electrochemical biosensing at 0.1 V vs. Ag/AgCl at neutral pH

References

- [1] B. Auer, S. Telfer, A. J. Gross, *Electroanalyses*, **2023**, 35 (1), 2200145.
- [2] L. Ma, F. Jiang, et al ; *Adv. Mater.* **2020**, 32, 2003065.

Innovative Therapeutic Approach for Organophosphate Poisoning Using Zirconium-Based Metal-Organic Frameworks to Enhance Enzyme Delivery

Orikedata Trashi^a, Ikeda Trashia^a, Fanrui Sha^b, Yalini H. Wijesundara^a, Omar Farha^b, Jeremiah J. Gassensmith^a

^a*University of Texas at Dallas, United States*

^b*Northwestern University, United States*

Organophosphate (OP) compounds, prevalent in pesticides, nerve agents, and industrial applications, pose substantial health risks to individuals worldwide.¹ Effective treatment strategies for OP poisoning are imperative to address both acute and chronic manifestations of toxicity. While current therapies, primarily based on atropine and pralidoxime (2-PAM), mitigate acute symptoms, they often inadequately manage long-term neurotoxic effects.^{2,3} This study proposes an innovative therapeutic paradigm integrating recent advancements in enzyme formulations (OPAA) and metal-organic framework (MOF) materials, focusing specifically on zirconium-based MOFs (Zr-MOFs), to enhance treatment outcomes for OP poisoning.⁴

Zr-MOFs, exemplified by NU-1003, exhibit favorable characteristics for enzyme encapsulation, including high biocompatibility and porous structures conducive to enhanced enzymatic activity. These unique properties enable the creation of tailored environments for enzyme stabilization and improved catalytic efficiency. Preliminary investigations demonstrate that Zr-MOF-encapsulated enzymes exhibit prolonged release profiles and enhanced activity against OP compounds compared to free enzyme formulations. These findings underscore the potential of Zr-MOFs to serve as effective carriers for OP-scavenging enzymes, thereby extending the therapeutic window and enhancing treatment efficacy.

The proposed therapeutic strategy aims to revolutionize OP poisoning management by addressing both acute and chronic aspects of toxicity. Key objectives include optimizing the encapsulation of OP-scavenging enzymes within Zr-MOFs to enhance stability and catalytic efficiency,⁵ evaluating the pharmacokinetics and biodistribution of Zr-MOF-encapsulated enzymes *in vivo* and assessing the therapeutic efficacy of the developed formulations in animal models of OP poisoning. Additionally, the study seeks to elucidate the mechanisms underlying the enhanced efficacy of Zr-MOF-encapsulated enzymes in scavenging OPs and mitigating neurotoxic effects. Through comprehensive preclinical evaluations, including toxicity assessments and efficacy studies, the aim is to establish the safety and efficacy of the developed formulations for potential clinical translation.

In conclusion, this study represents a significant advancement towards the development of next-generation treatments for OP poisoning. By leveraging innovative approaches and focusing on enhancing treatment efficacy, we aim to improve patient outcomes and reduce the global burden of this health concern. The integration of Zr-MOFs into therapeutic strategies for OP poisoning holds promise for addressing the evolving needs of patients worldwide and advancing public health initiatives aimed at mitigating the risks associated with OP exposure.

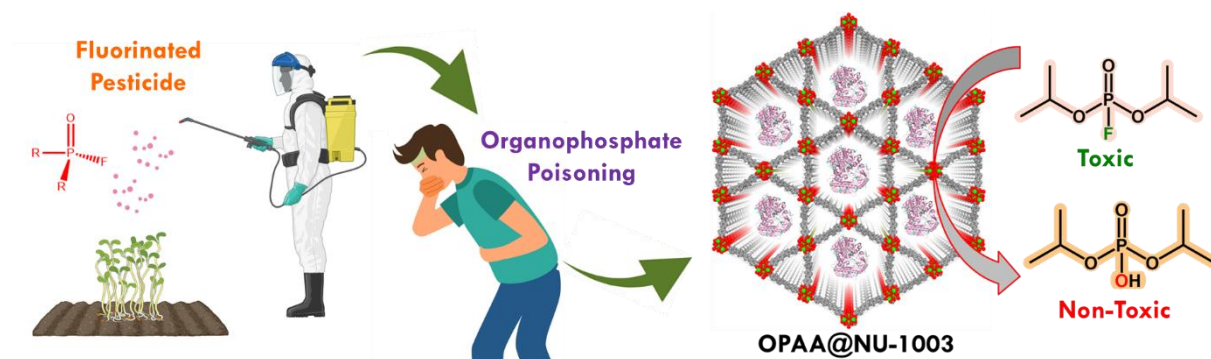


Fig 1. Illustration of organophosphate poisoning from consumption of crops treated with pesticides and the possible treatment by OPAA@NU-1003 formulation which is able to convert toxic fluorinated molecules into non toxic molecule.

References

- [1] SX Naughton, AV Terry Jr, *Toxicology*. **408**,101-112, 2018
- [2] R Kuruba, X Wu, DS Reddy. *Biochim. Biophys. Acta Mol. Basis Dis.* **1864(9)**, 2845-2858, 2018
- [3] DD Johnson, WC Wilcox. *Eur. J. Pharmacol.***34(1)**,127-32, 1975
- [4] P Li, SY Moon, MA Guelta, L Lin, DA Gómez-Gualdrón, RQ Snurr, SP Harvey, JT Hupp, OK Farha. *ACS nano.* **10(10)**, 9174-82, 2016
- [5] X Wu, H Yue, Y Zhang, et.al, J Ge. *Nat. Commun.* **10(1)** 5165, 2019

ELECTROCHEMICAL PROPERTIES OF BODIPY BASED COF MATERIALS

B. Çoşut¹, B. Topaloğlu Aksoy¹, A. Seifi¹, E. Tanrıverdi Eçik², K. Atacan³

¹ Gebze Technical University, Department of Chemistry, Kocaeli, 41400 TURKEY

² Atatürk University, Department of Chemistry, Erzurum, 25240 TURKEY

³ Sakarya University of Applied Sciences, Department of Engineering Basic Sciences, Sakarya, 54000 TURKEY

Covalent organic frameworks (COFs), recognized as cutting-edge smart materials of the new era, have attracted considerable attention since Yaghi et al. introduced them in 2005 [1]. These materials are a type of crystalline porous organic polymer noted for their permanent porosity and highly ordered structures. The adjustable pore size and structure of COFs, along with their persistent porosity, large surface area, thermal stability, and low density, enhance their functionality and expand their application potential. Boron complexes of dipyrromethene compounds are known as 'bordiopyromethene' or simply BODIPY compounds. They are widely used because of their high molar absorption, high fluorescence quantum yields, and long singlet excited state lifetimes [2].

To investigate the electrochemical behaviour of COF structures, thin films of the prepared structures were coated on FTO substrates using the electrophoretic deposition method for use as the working electrode. The electrochemical properties will be examined using Linear Sweep Voltammetry (LSV), Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), Mott-Schottky (M-S) measurements, and Tafel slopes. The obtained measurements will be compared and interpreted in relation to the hydrogen production potential of the COF structures. The main aim of this study is to create porous covalent organic frameworks, where the pore size and conjugation can be adjusted using BODIPY-based photosensitizers, which are renowned for their highly efficient photonic applications and investigate their electrochemical properties.

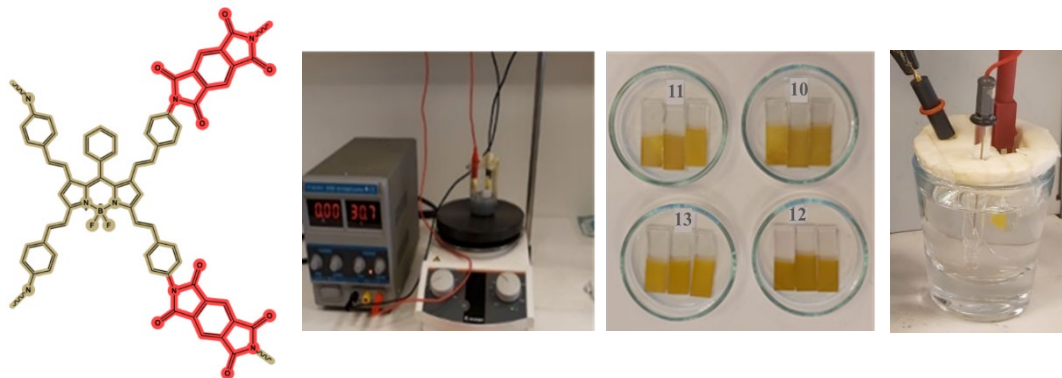


Figure 1: The prepared films of BODIPY based COF material

References:

- [1] A. P. Cote, A.I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger, O. M. Yaghi, *Science* **2005**, 310, 1166–1170.
- [2] A. Treibs, F.H. Kreuzer, *Justus Liebigs Annalen der Chemie* **1968**, 718, 208-223.

We would like to thank TÜBİTAK for their support to the project numbered 122Z471.