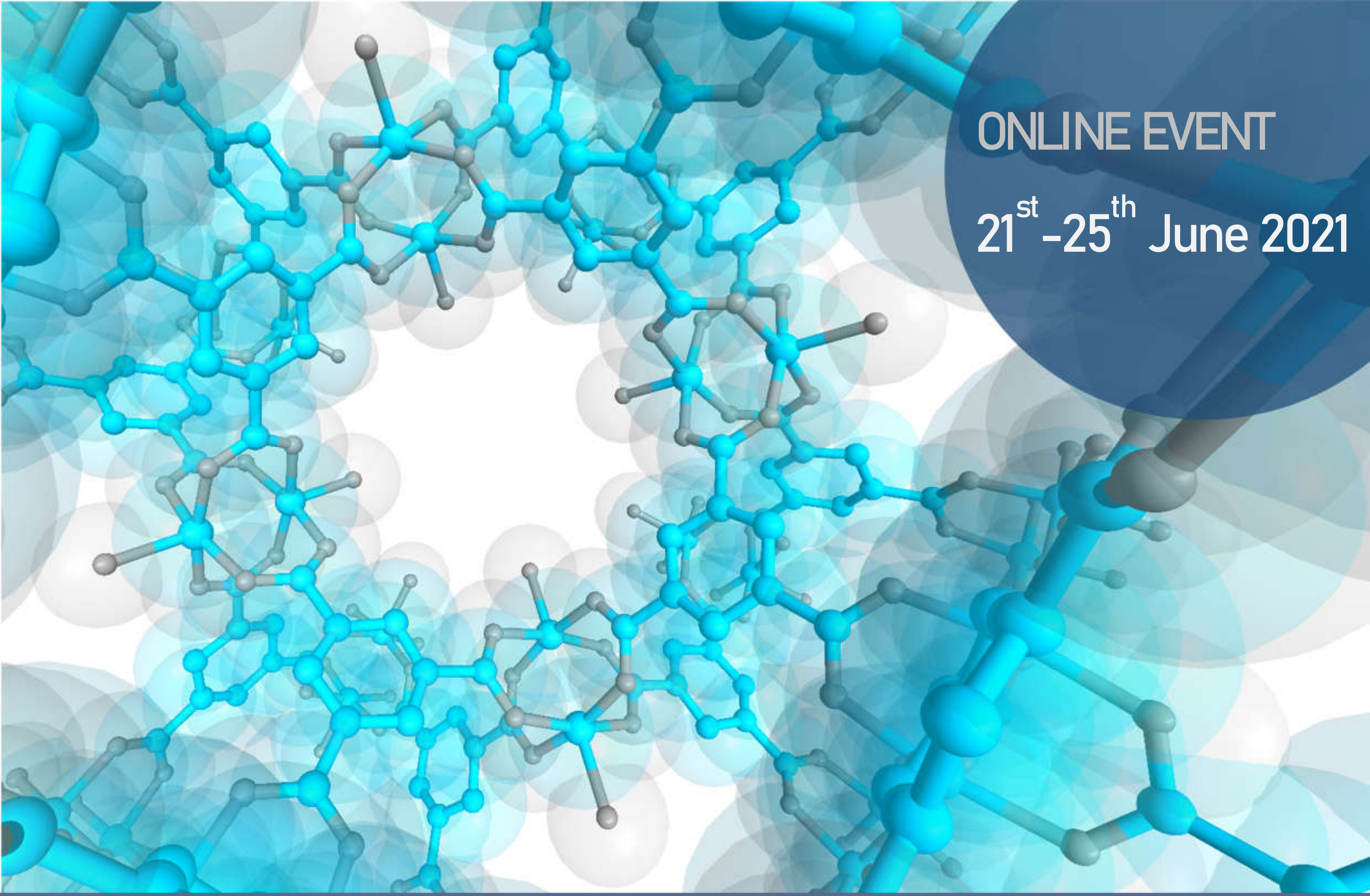

ONLINE EVENT

21st-25th June 2021

2nd International School on Porous Materials

MOFschool2021

Book of Abstracts

It is a great pleasure for us to welcome you to the Second International School on Porous Materials (MOFschool2021)

Metal-organic Frameworks (MOFs) and **Covalent organic Frameworks (COFs)** are advanced porous materials deriving from the linking of (organic/inorganic and organic/organic) building units. In the past twenty years, the broad library of building units and synthetic conditions has allowed the preparation and consequent investigation of a huge number of MOFs and COFs showing intriguing functional properties – adsorption, separation, heterogeneous catalysis, sensing, drug delivery, to list a few – that outperform, in many aspects, those of classical porous materials.

In a number of occasions, the functional properties and potential applications of these non-conventional porous materials has prompted their appearance on the market or testing in technologically relevant devices. Despite this, there still exists a large playground for isolating new substances and/or improving the properties of existing ones.

As this vast and interdisciplinary research field is advancing at a very fast pace, two years after the success of the first International School on Porous Materials we feel that times are mature to propose a second edition of the event, **MOFschool2021**, despite the restrictions imposed by the Covid-19 pandemic.

MOFschool2021 aims to introduce the attendees into the realm of MOFs and COFs: starting from advanced synthetic methods, the School will propose representative examples of up-to-date characterization techniques and cutting-edge applications, up to implementation into devices. To the aim, MOFschool2021 lecturers panel can count on a number of internationally recognized scientists, including Silvia Bordiga, Elisa Borfecchia, Jose Casaban, Valentina Colombo, Mircea Dincă, Roland Fischer, Felipe Gándara, Jorge Gascón, Stuart James, Stefan Kaskel, Piero Macchi, Carlos Martí-Gastaldo, Jorge A.R. Navarro, Davide M. Proserpio, and Omar M. Yaghi.

MOFSchool2021, jointly organized by the Universities of Insubria, Milano La Statale and Granada, has made a great effort to encourage participation of young, enthusiastic scientists from all over the world, for which we are gratefully indebted to our generous funders.

We are looking forward to welcoming you, possibly to Villa del Grumello
and we are convinced you will spend a very fruitful time during the School!

Sincerely yours,

Valentina Colombo, Simona Galli and Jorge A.R. Navarro (School Directors)

Supporting Institutions:

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CULTURA
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LAKE COMO SCHOOL OF ADVANCED STUDIES

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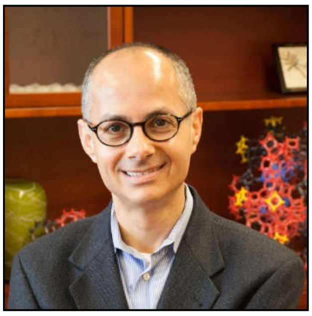

Omar M. Yaghi

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Program Overview:

Monday 21/06/21		
3.00 – 3.30 PM	*Welcome Time*	
3.30 – 5.00 PM	Omar M. Yaghi	Reticular Chemistry I: MOFs, Multi-variation, and Sequences
5.00 – 6.30 PM	Omar M. Yaghi	Reticular Chemistry II: COFs, Linkages, and Molecular Weaving
6.30 – 8.00 PM	*Dinner*	
8.00 – 9.30 PM	Omar M. Yaghi	Reticular Chemistry III: Water Harvesting from Air Anywhere at Anytime *(Evening Lecture)*
Tuesday 22/06/21		
9.00 – 10.30 AM	Stefan Kaskel	Flexibility, Switchability and other Dynamic Phenomena in Porous Metal-Organic Frameworks
10.30 – 11.00 AM	*Coffee Time*	
11.00 – 12.30 AM	Stefan Kaskel	Advanced *in situ*-Characterization Techniques for Porous Metal-Organic Frameworks
12.30 – 2.00 PM	*Lunch*	
2.00 – 3.30 PM	Stuart James	Porous Liquids: A new Phase for Porous Materials
3.30 – 4.00 PM	*Coffee Time*	
4.00 – 5.00 PM	Jorge A. R. Navarro	Metal-Organic Framework Based Materials for Capture, Separation and Degradation of Toxic Gases
5.00 – 6.30 PM	Jose Casaban	*MOF Technologies:* Towards MOFs' Mass Market Adoption
Wednesday 23/06/21		
Poster Session on Twitter (9.00 am – 6.00 pm)		
9.00 – 10.00 AM	Felipe Gándara	Single Crystal X-ray Diffraction with Reticular Materials
10.00 – 10.30 AM	*Coffee Time*	
10.30 – 11.30 AM	Valentina Colombo	*In situ* Powder and Single Crystal X-ray Diffraction with MOFs
11.30 – 12.30 AM	Piero Macchi	Putting MOFs Under Pressure
12.30 – 2.00 PM	*Lunch*	
2.00 – 3.30 PM	Jorge Gascón	MOFs in Heterogeneous Catalysis: Advantages, Limitations and Opportunities
3.30 – 4.00 PM	**Flash Presentations** – session 1	
4.00 – 4.30 PM	*Coffee Time*	
4.30 – 6.30 PM	Davide Proserpio	Topological Analysis of Reticular Framework Materials with ToposPro

Thursday 24/06/21		
Poster Session on Twitter (9.00 am – 6.00 pm)		
9.00 – 10.30 AM	Mircea Dincă	Electrically Conductive MOFs
10.30 – 11.00 AM	*Coffee Time*	
11.00 – 12.30 AM	Mircea Dincă	Site-isolated Catalysis with MOFs
12.30 – 2.00 PM	*Lunch*	
2.00 – 2.30 PM	**Flash Presentations** – session 2	
2.30 – 5.30 PM	Silvia Bordiga & Elisa Borfecchia	Understanding MOFs by Spectroscopic Methods: Fundamentals and Selected Applications to UiO MOFs
5.30 – 6.00 PM	*Coffee Time*	
6.00 – 6.30 PM	**Flash Presentations** – session 3	
Friday 25/06/21		
9.00 – 10.00 AM	Roland Fischer	Photophysical, NLO and Multi-photon Absorption/ Upconversion Properties of MOFs
10.00 – 10.30 AM	*Coffee Time*	
10.30 – 11.30 AM	Roland Fischer	SURMOF-derived Electrocatalyst Materials for OER/ORR (Water Splitting/Fuel cells)
11.30 – 12.30 AM	Carlos Martí-Gastaldo	Charge Transport, Photoactivity and Chemical Reactivity in Metal-Organic Frameworks
12.30 – 1.00 PM	**Poster Prize & Closing Remarks**	

Flash Presentations

Introducing a Cantellation Strategy for the Design of Mesoporous Zeolite-like Metal–Organic Frameworks: Zr-sod-ZMOFs as a Case Study

Norah Alsadun [a],[b], Georges Mouchaham [a], Vincent Guillerm [a], Justyna Czaban-Jóźwiac [a], Aleksander Shkurenko [a],Hao Jiang [a], ,Prashant M. Bhatt [a], Prakash Parvatkar [a] and Mohamed Eddaoudi [a]

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In our continuous quest targeting materials with large pores featuring zeolitic topologies, a series of novel mesoporous Zr-MOFs showing the zeolitic sodalite (**sod**) topology is introduced for the first time.[1] These Zr-**sod**-ZMOFs have been designed and constructed following the molecular building blocks approach, unveiling the cantellation design strategy. Concretely, the organic linkers have been finely designed via derivation from enlarged tetrahedral building units approach, a prerequisite for a zeolite-like net. The two **sod**-ZMOFs in this work are highly porous frameworks with intricate truncated rhombic dodecahedron mesopores of ≈ 43 Å diameter and experimentally measured pore volume of 1.98 $cm^3 \cdot g^{-1}$, regarded as the highest reported exp. pore volume for ZMOFs based on tetrahedral nodes [1].

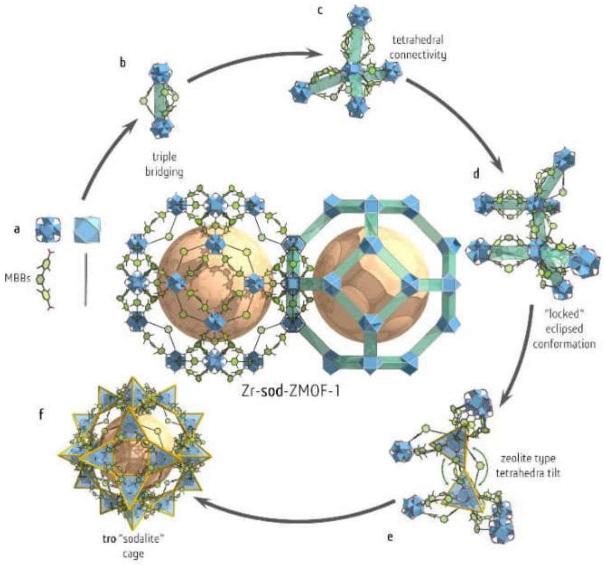

Figure 1. Illustration of the bottom-up construction of Zr-**sod**-ZMOF-1 (center): (a) Organic and inorganic MBBs assemble through (b) the formation of triple bridges. (c) Each MBB connected to four others in a tetrahedral fashion. (d) Tetrahedral MBBs oriented in eclipsed fashion, with (e) a slight tilt characteristic of zeolites, allowing the overall formation of (f) the sodalite type cage.

[1] N. Alsadun, G. Mouchaham, V. Guillerm, J. Czaban-Jóźwiac, Al. Shkurenko, H. Jiang, P.M. Bhatt, P. Parvatkar, M. Eddaoudi, J. Am. Chem. Soc. (2020), 142, 20547−20553

From Cu- complexes to Cu- functionalized ligands to design redox catalysis in MOFs

Barbara Centrella[a], **Gabriele Deplano**[a], **Matteo Bonomo**[a], **Matteo Signorile**[a], **Alessandro Damin**[a], **Claudia Barolo**[a], **Erlend Aunan**[b], **Unni Olsbye**[b], **Karl Petter Lillerud**[b], and **Silvia Bordiga**[a]

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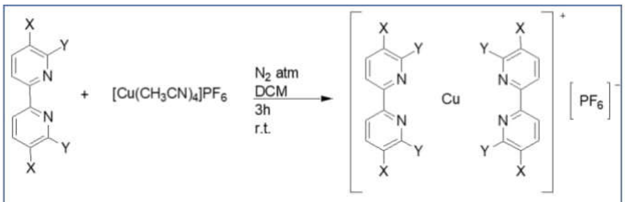
With the aim of inserting a catalytic copper-based center in a Ce or Zr based MOF, e.g. belonging to the UiO-67 family, a set of bipyridine-based ligands has been studied. It is already well known that 2,2'-bipyridine-based ligands are able to firmly complex Cu(I) and are used in many fields of application[1],[2]. In fact, these ligands are easily available, low-cost and easily manageable. By using these ligands, we obtained scalable and cheap Cu complexes in excellent yield with a quick and simple procedure[3] (Scheme 1). Since we want to develop Cu complexes able to catalyze selective oxidation reactions, our focus is on the redox property of the metal center and on the impact of the ligand structure on the latter. In fact, we considered different substituted bipyridine ligands, to test both steric and electronic effects of the substituents and to investigate the Cu(I)/(II) conversion in the respective complexes. We considered 6,6'-dimethyl-2,2'-bipyridine (coded BPA), 5,5'-dimethyl-2,2'-bipyridine (BPB) and 6,6'-dimethoxy-2,2'-bipyridine (BPC), as well as the unsubstituted 2,2'-bipyridine (BPD) as a reference. All the ligands were commercially available except for the BPC, synthetized starting from 2-Bromo-6-methoxypyridine[1]. The synthetized complexes will be chemically oxidized to study the kinetic of the oxidation and the reversibility of the Cu(I)/(II) conversion, to understand how the different substituents on the bipyridine ligands affect their reactivities. Once the desired reversibility is obtained, the ligands could be functionalized in 5,5' position with carboxylic groups to obtain building blocks suitable for a MOF useful to perform the same oxidation reactions in a heterogeneous fashion.



A = 6,6'-Dimethyl-2,2'-bipyridyl (X=H, Y=CH3)
B = 5,5'-Dimethyl-2,2'-bipyridyl (X=CH3, Y=H)
C = 6,6'-Dimethoxy-2,2'-bipyridyl (X=H, Y=OCH3)
D = 2,2'-bipyridyl (X=Y=H)

Scheme 1

Acknowledgments: The work was financially supported by the European Research Council (ERC), under the Horizon 2020 research and innovation program: CuBE ERC-Synergy project (Grant agreement n° 856446).

[1] Fresta E, Volpi G, Milanesio M, Garino C, Barolo C, Costa RD. *Inorg Chem.* 2018;57(16):10469-10479. doi:10.1021/acs.inorgchem.8b01914
[2] Li X, Van Zeeland R, Maligal-Ganesh R V., et al. *ACS Catal.* 2016;6(9):6324-6328. doi:10.1021/acscatal.6b01753
[3] Listorti A, Accorsi G, Rio Y, et al. *Inorg Chem.* 2008;47(14):6254-6261. doi:10.1021/ic800315e

Adsorption Effects of Zn-MOF-74 in Cobalt-Catalyzed Hydroformylation

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Hydroformylation is one of the most important homogeneously catalyzed reactions. Promoted by cobalt or rhodium catalysts, olefins react with a 1:1 mixture of H_2 and CO to form branched and linear aldehydes [1]. We observed that the addition of certain MOFs enhances the branched selectivity by adsorption-driven kinetic modulation (AKM) [2]. We analyzed the impact of the MOF on the product distribution through a conversion vs selectivity study. The branched selectivity increased at higher conversion of the olefin, which is counterintuitive based on the literature [3]. This was explained by the slow adsorption of the cobalt catalyst within the MOFs (Figure 1). Based on that finding, we investigated several approaches to increase the adsorption kinetics.

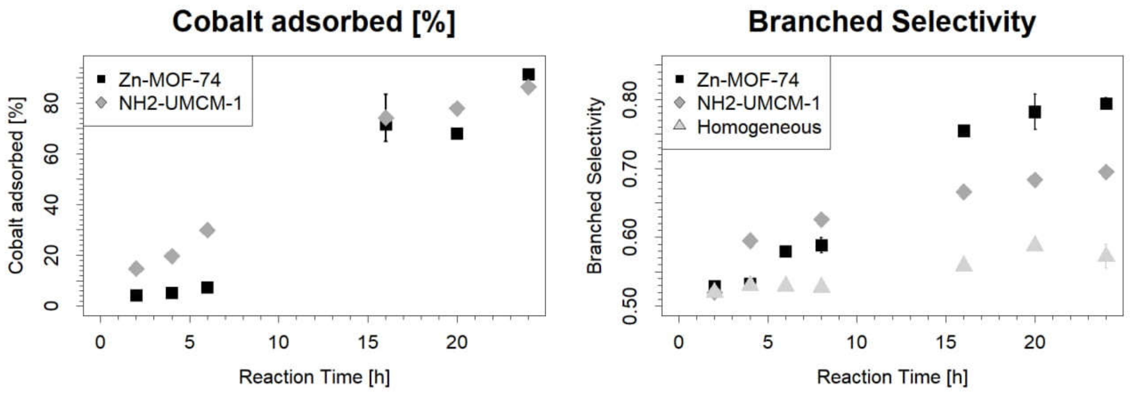

Figure 1. Percentage of cobalt adsorbed to the MOF (left) and corresponding share of branched aldehyde product (right).

Zn-MOF-74 plays also a major role in promoting aldol condensation of the aldehyde products. Our data and simulation [2] suggest that the MOF increases the local concentration of the aldehyde and thus enhances the reaction rate. Zn-MOF-74 therefore promotes aldol condensation by AKM as well. The understanding of AKM will drive the development of even more selective MOF-promoted reactions exploiting kinetic effects.

References

[1] R. Franke, *Chem. Rev.* **112** (2012) 5675. [2] G. Bauer, *Nat. Commun.* **11** (2020) 1059. [3] R. Gholap, *Ind. Eng. Chem. Res.* **31** (1992) 2446.

Higher Valency and Constitutional Dynamics in Covalent Organic Frameworks

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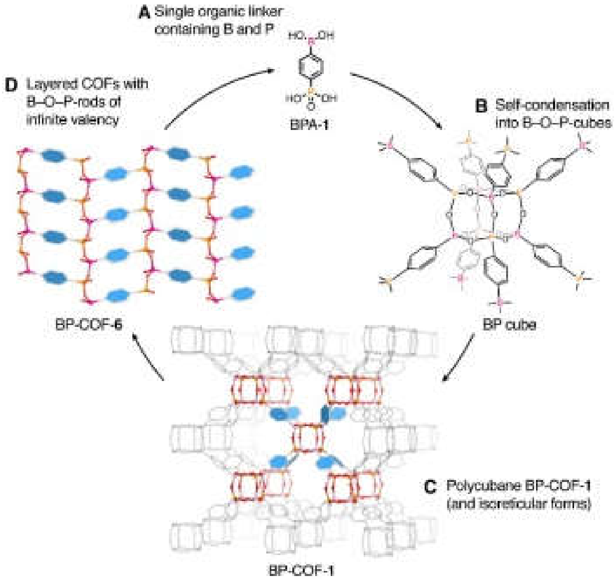
While metal-organic frameworks (MOFs) boast a vast structural diversity[1]—originating from the large variety of metals in the periodic system and their ability to form clusters of different shape and size[2]—covalent organic frameworks (COFs) are predominantly made by connecting preformed carbon-based building units, thus severely limiting their structure space.

We here present an isoelectronic strategy to implement higher valency in COFs by designing molecules capable of forming cubic and infinite linkages through clustering.[3] Specifically, we designed organic molecules based on the main group elements boron (B) and phosphorus (P), which self-condensed into polycubane COFs of valency 8. Upon addition of acid, the polycubic framework rearranged into a layered structure with an unusual infinite rods-within-layer arrangement.



This chemistry breaks with previously pursued synthetic strategies for COFs and opens the doors to new solid-state organic chemistry and its application in materials science.

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[2] M. J. Kalmutzki, N. Hanikel, O. M. Yaghi, Sci. Adv. (2018), 4, eaat9180.

[3] C. Gropp, T. Ma, N. Hanikel, O. M. Yaghi, Science (2020), 370, eabd6406.

Dual Removal and Selective Recovery of Phosphate and Organophosphorus Pesticide from Water by Metal-Organic Frameworks

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One of today's main priorities is the development of environmentally-friendly agricultural practices. In this regard, the accumulation of organophosphorus pesticides is leading to water pollution, causing problems for both human and animal health. Moreover, due to the indiscriminate use of phosphorus, a key component of fertilizers, reserves of this element are expected to be depleted in 50-100 years. In this context, metal-organic frameworks (MOFs) can contribute to water remediation and phosphorous circular economy thanks to their high adsorbent properties.

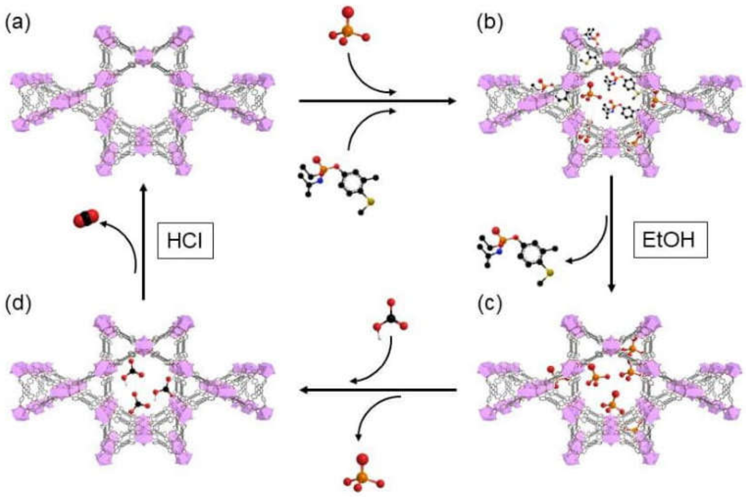

Figure 1. Dual adsorption and selective recovery of both phosphate and fenamiphos using NU-1000. (a) Adsorption process; (b) desorption of fenamiphos using ethanol; (c) desorption of phosphate using sodium hydrocarbonate; (d) recovery of pristine material by treatment with HCl

In this work, metal-organic framework [Zr(μ_3-OH)$_8$(OH)$_8$(TBAPy)$_2$] **(NU-1000)** has been selected due to its large surface area, high density of active sites and good chemical stability in water. The results suggest that this porous material behaves as a dual adsorbent of both phosphorus and fenamiphos (organophosphorus pesticide), enabling the subsequent selective recovery of them (Figure 1). Additionally, static and dynamic adsorption studies have been carried out in the presence of potential interferences typically presented in water.

NEW MULTIMETAL MOFs OBTAINED FROM GROUP 13 ELEMENTS PREASSEMBLED PRECURSORS

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Incorporating multiple metal elements within a same metal-organic framework (MOF)[1] allows the obtaining of materials with new or enhanced properties. One of the most common problems during the synthesis of multimetal MOFs, is the lack of control over the disposition and proportion of the different metal elements. In this work, we report the structural characterization of two new heterometallic MOFs based on group 13 elements, denoted MOF-1071, and MOF-413. Through the adjustment of the initial metal precursors and synthetic conditions, we have been able to obtain heterometallic MOFs where we can control the position and amount of the different metal cations. The specific organic linkers used in this work were benzene-1,3,5-tricarboxylic acid (H_3BTC) and 1,3,5-tris(4-carboxyphenyl)benzene (H_3BTB), which have been combined with gallium and indium, and gallium and nickel, respectively. Single crystal X-ray diffraction has been used to characterize the obtained materials, and their formula was determined to be and $[In_5Ga(BTC)_8]\cdot[DMA]_6$ for MOF-1071, and $[Ga_{3-x}Ni_x(\mu_3\text{-}O)(BTB)_2(Piv)(DMF)]\cdot[DMA]_x$ for MOF-413, where the Piv nomenclature corresponds to a pivalate ligand $[(CH_3)_3CCO_2]$, and DMA to dimethyl ammonium. MOF-1071 belongs to the $I\bar{4}$ tetragonal space group, and it consists of a three-dimensional network, with a previously unreported (3,4)-connected topology. MOF-413 crystallizes in the orthorhombic system, space group *Pnma*, and it exhibits a flexible[2] three-dimensional structure, consisting of two interpenetrated networks. Both MOFs present flexible frameworks, which allows them to expand or shrink, which is a phenomena known as breathing effect. This property makes this MOFs potential candidates for applications such as gas capture.

Acknowledgments: Funding by Spanish "Agencia Estatal de Investigación", projects EUR2019-103824, MAT2016-78465-R and CTQ2017-87262-R is acknowledged.

References:

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Bifunctional MOF-based Catalyst for Cycloaddition of CO_2 to Epoxides under Mild Conditions

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The direct functionalization of metal nodes is one of the strategies of post-synthetic modification of Metal-Organic Frameworks (MOFs) which offers a convenient way of introducing new functionalities into a system.[1] The multifunctional MOF-based catalysts are often regarded as excellent candidates for heterogeneous catalysis.[2] Recently, MOFs have been found to be especially efficient in the cycloaddition of CO_2 to epoxides. However, in most of those examples, the presence of an external co-catalyst is required, and satisfactory yields of cyclic carbonates are achieved only after longer reaction times.[3]

In our work, we have devised a straightforward strategy of tandem post-synthetic modification of metal nodes in selected mesoporous MOFs based on a well-developed solvent-assisted ligand incorporation (SALI) protocol and further extended by subsequent alkylation with selected haloalkyl reagents (Figure 1). As a result, we obtained a series of well-defined *2-in-1* heterogeneous catalytic systems which proved to exhibit high catalytic activity in the synthesis of cyclic carbonates under solvent-free and co-catalyst-free conditions. Our approach allowed us also to investigate the influence of the co-catalyst moieties introduced in close proximity to the inorganic nodes and perform a more detailed analysis of factors governing the structure−reactivity relationship.[4]

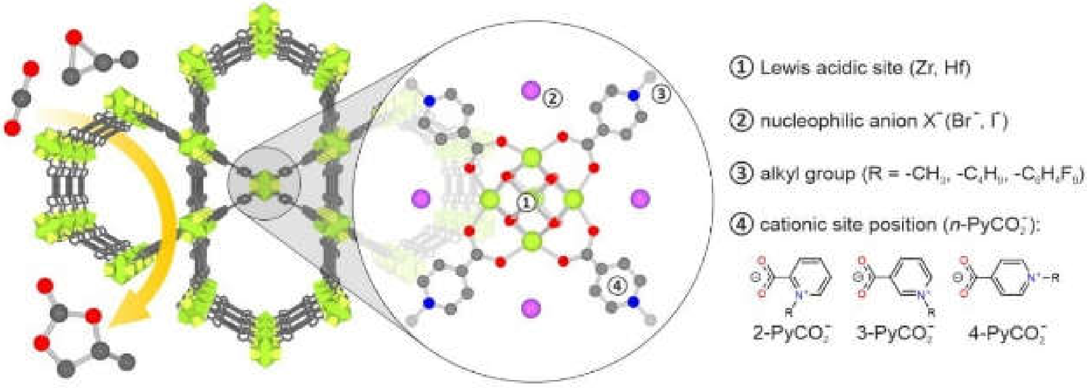

Figure 1. Design of the bifunctional MOF-based catalytic system based on the **NU-1000** platform; the schematic representation of modified inorganic node is presented as an inset.

This work was supported by National Science Center, Poland, Grant No. UMO-2014/14/E/ST5/00652 as a part of the project entitled Development of new strategies for synthesis of inorganic-organic porous materials.

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ADVANCED PROPERTIES OF MOFS: ULTRAFAST DYNAMIC OF MOLECULAR ROTORS AND FAST SCINTILLATION UNDER IONIZING RADIATION EXCITATION

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Metal organic frameworks provide a versatile platform that can generate intriguing behaviours and innovative properties. Specifically, this contribution highlights our recent results related to the installation of highly dynamic molecular rotors in MOFs[1] and the development of fast scintillating MOFs and MOF/polymer composites for fast detection of high-energy radiations[2]. MOFs provide precise spatial disposition of organic struts and enough free volume to preserve the dynamic properties of molecular motors and rotors even in condensed matter. Molecular rotor bicyclo[1.1.1]pentane–dicarboxylate was installed in the 3D cubic structure of a highly porous zinc MOF[1] (figure A,B,C,D). Its dynamic behaviour was investigated with solid state NMR relaxation and muon-spin spectroscopy performed at temperatures as low as 2 K and molecular dynamic simulations, providing clear evidence of very fast molecular reorientation in the GHz regime even at the lowest temperatures, consistent with a low activation energy for rotational motion of 6.2 cal mol^{-1}. High-Z MOFs were generated by coordination of zirconium-based clusters and highly emissive 9,10-bis(4-carboxyphenyl)anthracene (DPA) ligands allowing for the efficient sensitization of the linker fluorescence under high-energy radiation excitation (figure E,F). MOF nanocrystals were embedded in a continuous polymer matrix producing ultra-fast scintillators with rise time of ~ 50 ps and high light yields suitable for application as detectors for time-of-flight positron emission tomography (TOF-PET).

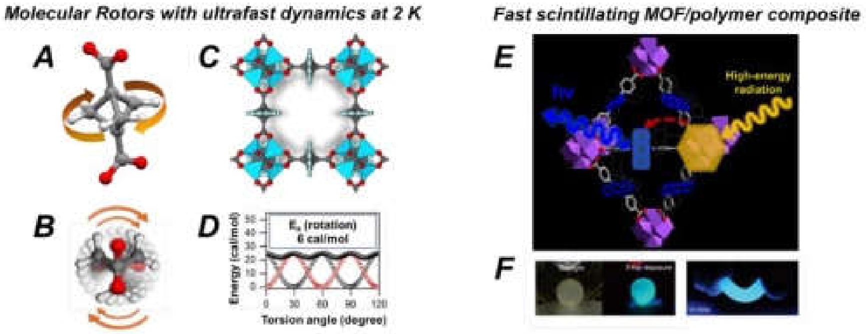

Figure 1. A, B) Rotational motion of bicyclo[1.1.1]pentane–1,3-dicarboxylate strut. C) 3D cubic structure of zinc-based MOF viewed along c axis. D) 12-fold potential for rotational motion of bicyclo units with 6.2 cal mol^{-1} activation energy. E) Schematic representation of the scintillation mechanism inside ZrDPA MOFs F) Digital images of MOF/polymer composites under daylight, x-ray and U.V. light irradiation.

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The development of a comprehensive toolbox based on multi-level, high-throughput screening of MOFs for CO/N_2 separations

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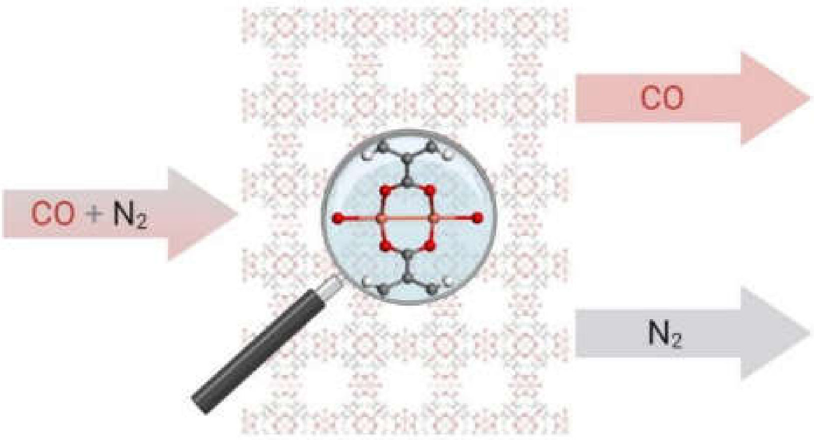
The separation of CO/N_2 mixtures is a challenging problem in the petrochemical sector due to the very similar physical properties of these two molecules, such as size, molecular weight and boiling point. To solve this and other challenging gas separations, requires a holistic approach. The complexity of a screening exercise for adsorption-based separations arises from the multitude of existing porous materials, including metal-organic frameworks. In addition, the multivariate nature of the performance criteria that needs to be considered when designing an optimal adsorbent and a separation process – i.e. an optimal material requires fulfillment of several criteria simultaneously – makes the screening challenging. To address this, we have developed a multi-scale approach combining high-throughput molecular simulation screening, data mining and advanced visualization, as well as process system modelling, backed up by experimental validation. We have applied our recent advances in the engineering of porous materials' morphology to develop advanced monolithic structures. These conformed, shaped monoliths can be used readily in industrial applications, bringing a valuable strategy for the development of advanced materials. This toolbox is flexible enough to be applied to multiple adsorption-based gas separation applications.



Poster Presentations

THE IMPACT OF CRYSTAL SIZE AND MORPHOLOGY ON SWITCHABILITY OF PILLARED LAYER METAL–ORGANIC FRAMEWORK DUT-8(ZN)

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The ability of metal-organic frameworks structurally adopt to the changes in the environment directs the application pathway[1]. One of the crucial factors affecting MOFs properties are chemical composition and topology, however, the crystal size and morphology are also known to uniquely affect the switchability[2].

The strong impact of the crystal size (macro- vs. micron-sized) and morphology (plates vs. rods) on the switching characteristics of pillared layer MOF $[Zn_2(2,6\text{-ndc})_2dabco]_n$, also known as DUT-8(Zn) (DUT = Dresden University of Technology) was discovered recently[3]. The removal of guests from the pores causes phase transition from open (*op*) to closed pore phase (*cp*). Interestingly, the response of the framework towards molecules, triggering phase transition, is strongly particle size dependent. The *cp* phase of DUT-8(Zn) shows no opening upon adsorption of N_2 at 77 K or CO_2 at 195 K, independent of particle size regime. The adsorption of dichloromethane at 298 K, however, allows reopening of the macro-sized (200 µm) crystals, but the micron-sized (0.2-1 µm) crystals remain in the *cp* state. The alcohols, on their part, are able to trigger the *cp* to *op* transition in the micron-sized particles, but not in the macro-sized crystals. In addition, the adsorption of alcohols leads to the so called shape-memory effect[4], rarely observed up to know.

To investigate the impact of morphology on structural dynamic, the plate- (width 1 µm, length 0.2 µm) and rod- (width 1 µm, length 5 µm) shaped crystals were produced by face-selective coordination modulation. The crystals are responsive towards dichloromethane and alcohols, therefore combining the properties of macro- and micron-sized particles. In particular, the morphology determines the critical aspect ratio (length/width) of anisotropic crystals, governing the dynamic properties upon adsorption.

Thus, the crystal size engineering and morphology modification provide an opportunity not only to control the structural dynamics of MOFs, but also to tailor responsivity towards guest molecules.

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CO_2 and SF_6 adsorption on mixed-linker ZIF-7-8s: The effect of linker substitution on gas uptake and selectivity

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A series of mixed-linker Zeolitic Imidazolate Framework(ZIF)-7–8s constructed from varying amounts of benzimidazolate (bIm) and 2-methylimidazolate (mIm) linkers are reported in this study. We demonstrate that the particle morphology and pore size of ZIF-7–8 can be tailored by carefully adjusting the ratios between bIm and mIm linkers in the frameworks resulting in a significantly enhanced CO_2 or SF_6 uptake capacity and selectivity. ZIF-7–8 containing 90% bIm and 10% mIm linkers were shown to have a CO_2 uptake capacity of 1.44 mmol g^{-1} at 293 K (1 bar) and a CO_2/N_2 selectivity of over 30. While ZIF-7–8 with 26% bIm and 74% mIm linkers had a SF_6 uptake of 2.08 mmol g^{-1} at 293 K (1 bar) and a high SF_6/N_2 selectivity of over 40. Isosteric enthalpy of adsorption calculations and cyclic pressure-swing adsorption experiments showed that both CO_2 and SF_6 were physisorbed on ZIF-7–8. The adsorption of CO_2 was also found to occur rapidly on all samples, with over 80% of the total uptake capacity being reached within 30 s. Detailed kinetics analysis concluded that the diffusion of CO_2 and SF_6 in the mixed-linker ZIF-7–8s were governed by a mixture of different mechanisms, including intracrystalline diffusion. The highly tunable sorption properties, uptake capacities and high gas selectivities of ZIF-7–8 render them as interesting candidate sorbents for certain greenhouse gases.

Extended Zr-MOF Monolith for High Volumetric Hydrogen Gas Storage Capacity

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Section: advanced chemical engineering

Keywords: MOF, monolith, DoE target, volumetric adsorption capacity.

The widespread access of hydrogen (H_2) as a clean energy vector is currently hindered by the high energy demand and safety concerns of conventional storage technologies. Subsequently, adsorbed gas storage (AGS) has emerged as a promising technology alternative that operates at relatively low pressure and room temperature. To incentivize research activities towards this direction, the US Department of Energy (DoE) has set an ultimate target for onboard H_2 storage of 6.5 wt.% (50 g/L), that cannot be reached by compressed H_2 storage method. Metal-organic frameworks (MOFs) are an emerging class of crystalline porous materials that have shown potential for H_2 gas storage[1,2] due to their high surface areas and large pore volumes. However, a critical bottleneck hampering the utilization of MOFs in an industrial setting has been the lack of densification methods capable of MOFs shaping into mechanically stable structures. Herein, we report the densification of extended Zr-based MOF, namely UiO-67 and its formulation into a hard monolith. Interestingly, formic acid (FA) modulated UiO-67 monolith recorded a benchmark usable H_2 volumetric adsorption capacity of 53 g/L, exceeding the DoE target. However, when benzoic acid (BA) was used as a modulator, lower H2 uptake (42 g/L) was recorded due to reduced BET area and pore volume. Our findings represent a step forward in the application of MOFs for H_2 gas storage and adds to the security of a cleaner energy sources.

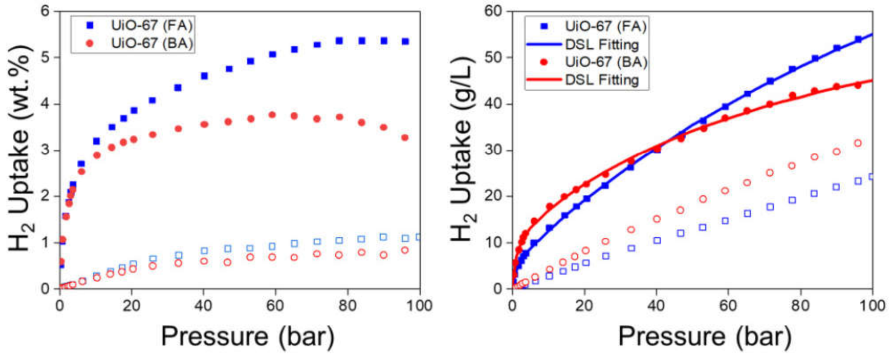

Figure 1. a) H_2 gravimetric uptake; b) H_2 absolute volumetric uptake of H2 at 77 K (closed symbols) and 160 K (open symbols) up to 100 bar.

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IRON(II) AND COBALT(II) SECONDARY BUILDING UNITS FOR NOVEL METAL-ORGANIC FRAMEWORKS

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Metal-organic frameworks are a class of complex and versatile materials. Their modular structure allows a great versatility, like the possibility of tuning their properties through metal choice and linker design. Many works recently are broadening the use of metallo-ligands as secondary building units (SBUs) in MOFs, in particular incorporation of a Ru(II) photocatalytic complex in supramolecular metal-organic architectures has been successfully achieved, opening the path to a new class of heterogeneous photocatalysts[1].

Aiming to explore the supramolecular chemistry of first-row transition metals, we provide an experimental and computational characterisation of Iron(II) and Cobalt(II) carbene complexes[2] as possible SBUs for novel metal-organic frameworks. The electronic properties of these complexes have been investigated through DFT and semi-empirical GFN2-xTB methods[3] and through experimental measurements. Geometry and dimensions of the Iron(II) complex have been determined by single crystal X-ray diffraction, providing useful information on the dimensions of this linker.

These results suggest that these complexes may represent valid SBUs for the synthesis of new metal-organic frameworks, making thus possible to incorporate the electronic properties of metal compounds in a supramolecular architecture.

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HIERARCHICAL FRAMEWORK MATERIALS FOR CO_2 CAPTURE

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The increase in carbon dioxide that has been produced in recent decades has put in the spotlight one of the greatest challenges we will face in the 21st century[1]. Although work is being done to reduce the emissions of this gas, it has been shown that it is not enough, and therefore, it must be combined with other strategies, such as capture and storage. Metal-organic frameworks (MOFs), which are highly porous crystalline materials with uniform structures and high surface area, have been proposed as materials for both capture and storage of carbon dioxide[2]. Even if it is true that today we can find a great variety of these materials in the literature, we are still far from achieving a MOF that has a large storage capacity and, in turn, is selective with respect to other molecules, such as N_2, O_2 or H_2O.

In order to overcome this problem, in this work, we propose the formation of hierarchical framework materials (HFM) based on the combination of high selective and large storage capacity MOF nanoparticles (figure 1). Despite many strategies have been developed, it is still challenging for scientists to reach the hierarchical complexity and advanced functions of even the most simple systems found in nature. These materials can contain hierarchical architecture, porosity or composition and understanding how hierarchy affects properties of bulk materials and how to control it is of vital importance[3].

For that, the synthetic protocols of MOFs were optimize taking into account parameters like the synthetic method (microwave, oven), temperature, time and solvent, among others. For material characterization, powder X ray diffraction (PXRD), scanning electron microscopy (SEM), dynamic light scattering and thermogravimetric analysis (TGA) were applied to analyse structural aspects, size, morphology and chemical composition. Moreover, CO_2 adsorption isotherms were measured also. Finally, the aim is to connect nanoparticles covalently and form hierarchical materials to have a synergistic effect of the single nanoparticles; that is to say, to compare CO_2 adsorption properties of MOF nanoparticles with the adsorption of the hierarchical materials formed after connecting MOFs and prof that the combination of different units would outperform single nanoparticle properties.

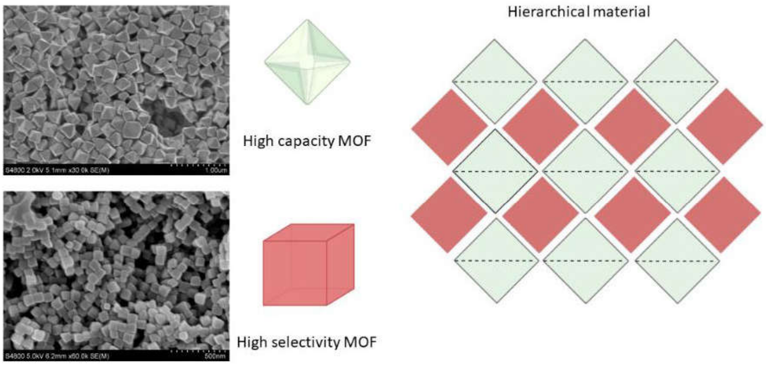

Figure 1. Hierarchical material based on high capacity and high selectivity MOF.

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EFFECTIVE PREPARATION OF MOF-DERIVED NANOPOROUS CARBON SPONGE FOR OIL SPILL REMEDIATION

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Metal-Organic Frameworks (MOFs) are porous materials composed of metal cations and organic linkers. MOFs have enjoyed considerable research attention due to their high specific surface areas and their highly tunable pore sizes and functionalities (through exchange of metals or organic components). In particular, these materials are promising candidates for a vast number of applications, such as environmental ones, including pollutant extraction and degradation.[1] Lately, MOFs have been used as templates to form nanoporous carbons (NPCs), which maintain the morphology from their precursors and own extraordinary physicochemical properties such as better chemical stability, high porosity and hydrophobicity. As a result, MOF-derived NPCs have been used for water treatment and remediation.[2]

In this work, we report on an easy approach to fabricate high hydrophobic/oleophilic hybrid materials, coating commercial melamine-formaldehyde (MF) sponges with a MOF-derived NPC. We selected MIL-100(Fe) as a precursor, synthesized at room temperature. Then, it was directly carbonized to obtain a porous derived carbon, which was supported onto the three-dimensional skeleton of the MF-sponge. The prepared sponge was employed to absorb oils and organic solvents from aqueous solutions, showing high selectivity, excellent oil-absorption capacity and good reusability, always maintaining its properties of hydrophobicity and oleophilicity.[3] Furthermore, when applied in conjunction with a vacuum system, this modified sponge could quickly and continuously separate large amounts of oils from water in a one-step process and demonstrated excellent properties to offer practical applications for the treatment of seawater samples (figure 1).

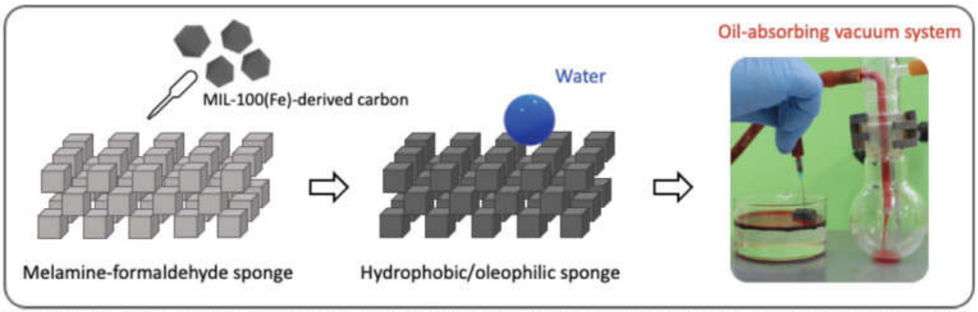

Figure 1. Fabrication of effective hydrophobic/oleophilic sponge for continuous oil-water separation.

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FIRST EXAMPLE OF BIOCOMPATIBLE AND ANTIMICROBIAL Cu-HKUST-1@HYDROXYAPATITE COMPOSITE

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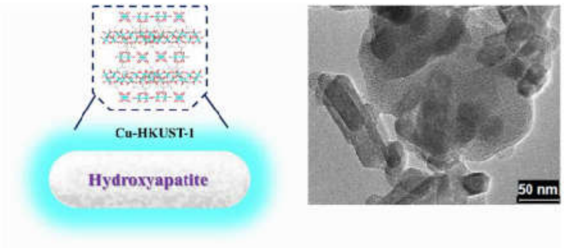
Biocompatible chemically-synthesized hydroxyapatite (HA) is extensively used in bone treatments, controlled drug release, and dental implants.[1] HA coatings on metal alloy substrates have gained much attention for bone replacement because they exhibit high biocompatibility and acceptable mechanical properties, such as high bond strength and an elastic modulus value close to that of the bone. Nevertheless, infection with medical implants and injection materials are still one of the common causes of failure for bone repair.[1] The fabrication of HA composite materials with antibacterial properties could be an intriguing solution. Following this topic, as a promising approach to increase the antimicrobial properties, coating of hydroxyapatite nanoparticles with a Cu-based MOF layer such as Cu-HKUST-1[2] was proposed.

The newly obtained composite was characterized structurally, spectroscopically, and texturally using different techniques such as XRD, IR, TEM, XPS, ICP-OES, TG, and N_2 sorption (77 K) analysis. This MOF coating increased significantly the BET surface area from 40 $m^2\,g^{-1}$, for hydrothermally treated HA nanorods, to 246 $m^2\,g^{-1}$ for Cu-HKUST-1@HA. Cu-based MOF was responsible for the antimicrobial effect of the composite, more against Gram-positive (*S. aureus*) than Gram-negative strains (*E. coli*, *K. pneumoniae* and *P. aeruginosa*). The MIC (minimum inhibitory concentration) value of Cu-HKUST-1@HA against *S. aureus* was found to be 2 mg mL^{-1} while MBC (minimum bactericidal concentration) was 5 mg mL^{-1}.



Scheme and TEM image of Cu-HKUST-1@HA composite.

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Acknowledgement

Financial support of the National Science Center (NCN, Poland) with grant no. 2019/35/D/ST5/02243 is gratefully acknowledged.

Cu- defective sites in HKUST-1: a thorough characterization with *operando* ambient pressure NEXAFS experiments and theoretical calculations

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We investigated the geometry and electronic state of the copper sites present in the HKUST-1[1] MOF pristine and thermally activated, employing ambient pressure near edge absorption spectroscopy (AP-NEXAFS). Interesting, until a few years ago, the collection of Cu L_3 edge was limited to the vacuum condition, which hampered the use of this powerful technique for the investigation of oxidation states *in operando*. Nowadays, the novel AP-NEXAFS technique is a fertile ground to unveil the nature of coordinately unsaturated metal sites in MOFs during adsorption experiments. Here, we demonstrate the powerful use of this technique on the archetypal HKUST-1 MOF with an exclusive investigation of its defective sites. L-edge NEXAFS is a direct probe of the covalence in transition metal coordination complexes because it is sensitive to the 3d orbitals and ligand valence orbitals. Such information are of a great importance in elucidating the nature of the chemical bonds between the active metal site and the ligands. [2] In addition, AP-NEXAFS technique is surface sensitive (<10nm) which is a crucial feature to investigate the defective sites that, predominantly, are on the surface. We find that upon thermal treatment at 160 °C, Cu^+ defective sites are formed due to the loss of one BTC linker, process confirmed by theoretical X-ray absorption calculations. Furthermore, it is shown that the Cu^+ sites easily coordinate CO_2 molecules with a fully reversible process. Intriguingly, the CO_2 interaction with copper sites is regulated by an interesting redox chemistry involving Cu^+/Cu^{2+} species (see Figure). Our results have implications for both the deep understanding of structural defective sites and the electronic features of exposed metal centres into MOFs, through the combination of advanced experimental and theoretical techniques.

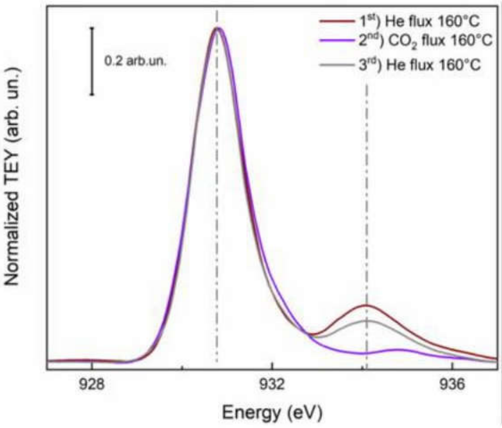

Figure. Cu L_3-edge AP-NEXAFS spectra of HKUST-1 MOF collected at 160°C in 1 bar of He flux before (red line) and after exposure to CO_2 (grey line), and in 1 bar of He flux containing 2% of CO_2 (violet line).

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Use of “shoe-last” solid-state templates in the mechanochemical synthesis of high-porosity RHO-Zinc Imidazolate phases

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In the last decade Zeolitic Imidazolate Frameworks (ZIFs), a subclass of metal-organic frameworks, have been rising in popularity, due to their diverse topologies, good thermal and chemical stability, and large pore volumes, which could enable their use for gas storage, separation of gases, and catalysis.[1] However, traditional methods are energy demanding, use large quantities of organic solvents and expensive organic nitrates, and, above all, are often irreproducible and hard to control, giving mixtures of different ZIF frameworks with different topologies, in often low yields.

To improve the synthetic yield and make the syntheses both more environmentally friendly, and more specific with regards to topological outcome, we have combined mechanochemical synthetic methods[2] with the use of different macrocyclic templates (Cram’s cavitands). We showed that we can reproducibly direct the topological outcome of our syntheses to the desired product by templating a specific topological motif, the *double-eight-ring* (*d8r*).[3,4]

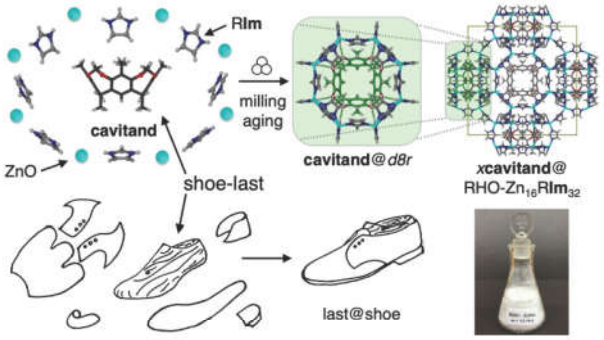

Figure 1. Schematic representation of templation of the *d8r* motif in ZIFs by Cram’s cavitands.

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Probing Zeolitic Imidazolate Frameworks (ZIFs) for heat storage applications

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The ability to supply sufficient energy and heat in an environmentally friendly manner to the rapidly growing population is of great importance. One method that addresses this issue and uses renewable energy is Thermal Energy Storage (TES), which uses the reversible chemical reactions and/or sorption processes of gases in solids or liquids. One major benefit of using this method is that it only shows an insignificant amount of heat loss while reaching a considerably higher energy storage density. Sorption thermal energy storage can be examined using traditional adsorbents (*e.g.* zeolites) or innovative adsorbents (*e.g.* metal-organic frameworks). One of the subgroups of MOFs is Zeolitic Imidazolate Frameworks (ZIFs), which are comprised of transition metal ions (Zn, Co, etc.) and imidazolate linkers. ZIFs are structured similarly to zeolites with where the metal ion replacing the Si/Al and the imidazolate linker replacing the O atoms. The use of ethanol as a sorbate has seldom been explored but may prove to be beneficial for applications at lower temperatures.[1,2]

This poster will show the synthesis, characterisation and ethanol sorption studies of a number of ZIFs (ZIF-71, ZIF-90 and ZIF-93). The materials were synthesised using optimised methods based on literature data. The activation of the ZIFs was achieved using various methods, for example *via* soaking in methanol followed by drying in vacuum oven at 150°C (ZIF-90). Structural properties were checked by XRD, TG, SEM/EDX, and nitrogen physisorption and revealed phase pure products. Ethanol sorption analyses were performed by an IGA-100 gravimetric analyser (Hiden Isochema Ltd.). The isotherms were collected at two different temperatures 25 °C and 30 °C in the relative pressure range from 0 – 0.9 in order to elucidate adsorption enthalpies. The results showed that the capacity up to 35 wt. % ethanol could be reached and that mechanism of sorption of ethanol in selected ZIFs were dominated by diffusion limitations of the molecules through the pores.

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AMINO-DECORATED ZINC BIPYRAZOLATE MOFS FOR CATALYTIC CONVERSION OF CARBON DIOXIDE: AN EXPERIMENTAL AND COMPUTATIONAL STUDY

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Carbon dioxide is the primary greenhouse gas emitted through anthropogenic activities, hence the importance of finding systems capable to reduce its concentration in atmosphere. Porous materials such as Metal-Organic Frameworks (MOFs) seem to be the ideal candidates for that purpose due to the surprising ability of some MOFs in selective adsorption of carbon dioxide, in its storage and also in its conversion in fine chemicals (Carbon Dioxide Capture and Reuse, CCR). Various studies have highlighted the importance of the presence of basic chemical groups (tags) in the MOF pores to improve CO_2 storage thanks to its acidic nature.[1] In this communication, two isomeric forms of diamino-decorated zinc bipyrazolate MOFs Zn(3,3'-L) and Zn(3,5-L) (L=diamino-4,4'-bipyrazolate) have been synthesized by solvothermal route[2] in DMF and characterized by IR, TGA/DTA, EA. Their structure has been solved from XRPD analysis, showing in both cases 3D (4,4)-connected networks with 1D squared channels, isostructural with respect to Zinc MOFs based on 3-amino-4,4'-bipyrazole and 4,4'-bipyrazole linkers previously synthesized;[3],[4] their textural properties (BET surface area, pore size distribution) and their ability as CO_2 adsorbents were investigated through N_2 and CO_2 adsorption. Zn(3,3'-L) and Zn(3,5-L) were subsequently tested as heterogeneous catalysts in the solvent-free conversion of epichlorohydrin or epibromohydrin and carbon dioxide into the corresponding five-membered cyclic carbonates at 393K and p_{CO_2}=5 bar. (Figure 1). In order to better understand the catalytic mechanism, a computational approach has been adopted at PM6 level.

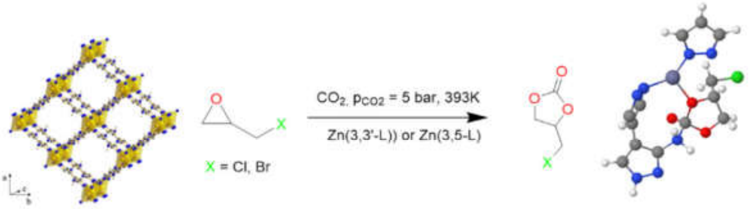

Figure 1. Sketch of Zn(3,3'-L) and Zn(3,5-L) topology, CO_2 catalytic conversion scheme and PM6-optimised intermediate structure corresponding to cyclic carbonate formation.

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HIGHLY SELECTIVE PALLADIUM-P-MOF-CATALYZED MILD SUZUKI REACTIONS

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Cross-coupling reactions are important tools in the synthesis of complex organic molecules. Homogeneous palladium complexes are predominantly used in large-scale production of fine chemicals as well as in pharmaceuticals and agrochemicals[1]. The development of robust and versatile heterogeneous catalysts offers the potential to recycle the catalyst as well as to simplify the purification of the final product from metal residue contaminations[2]. Heterogeneous palladium catalysts based on metal nanoparticles are often applied under conditions that promote a high mobility of the metal species[3]. The use of heterogeneous catalysts may also promote the hydrodehalogenation of the starting material[4]. In this contribution, we present a molecularly defined heterogeneous palladium catalyst based on the phosphine-functionalized metal-organic framework (P-MOF) LSK-15[5].

We studied the catalytic performance of various palladium catalysts in Suzuki cross coupling reactions of 3-bromoanisole with phenylboronic acid under mild conditions. Thereby, we have demonstrated that the presence of a phosphine ligand and the stoichiometry between metal and ligand play a critical role for the product selectivity and the activity of the catalyst. Catalysts based on LSK-15 gave the highest selectivity among all the homogeneous and heterogeneous systems studied. XAFS (X-ray Absorption Fine Structure) characterization at the P and Pd K-edges shows a correlation between the nature of the active site and the selectivity of the system. Our experiments suggest that palladium–phosphine sites promote cross coupling, whereas metal particles are negatively affecting the selectivity via hydrodehalogenation side reaction.

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SYNTHESIS AND CHARACTERIZATION OF SULFONIC-FUNCTIONALIZED MIL-100(Al) METAL-ORGANIC FRAMEWORKS FOR THE EXTRACTION OF DICLOFENAC

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An increasing sensitivity about the negative effects that industrial and human activities have on the environment and public health has led to the development of new strategies to mitigate the impact of these activities, becoming one of the most important social challenges today. Among the strategies proposed with the aid to reduce these effects is possible to find the development of materials that permit the extraction of environmental pollutants.

Metal-organic frameworks (MOFs) are an exciting class of crystalline materials based on the coordination of metals by organic linkers thus creating extended ordered networks.[1] This type of materials has been widely studied for catalysis, gas storage, sensing, and, more recently, for the adsorptive removal of different environmental pollutants. In this application, one of the unique characteristics of some types of MOFs is the existence of open metal sites or coordinative unsaturated sites (CUSs) in which the metal center is not fully coordinated to an organic linker. By post-synthesis modification (PSM), is possible to grafting functional groups on these CUSs, which enhance the interaction with pollutants.[2]

In this context, sulfonic-functionalized metal-organic frameworks were prepared by post-synthesis modification of MIL-100(Al) with Aminomethanesulfonic acid (AMSA) (*Figure 1*).[3] The obtained functionalized material (MIL-100(Al)-AMSA) was characterized and used for the extraction of diclofenac (DCF), one of the main pollutants present in the pharmaceutical industry. The results show that MIL-100(Al)-AMSA exhibited excellent DCF extraction capacity, improving the adsorption capacity of the MIL-100(Al).

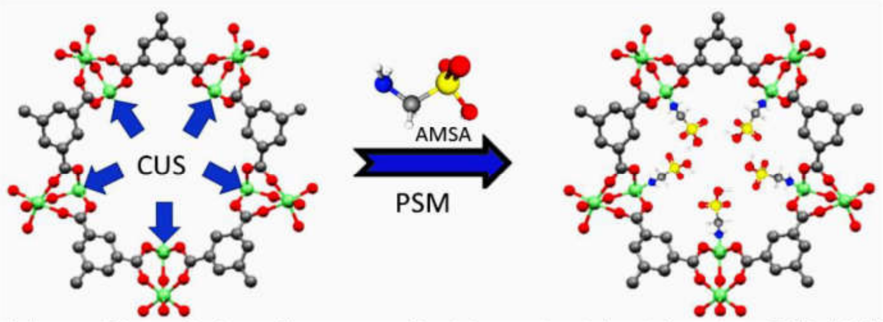

Figure 1: Scheme of the sulfonic grafting on coordinately unsaturated metal centers of MIL-100(Al).

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EXPRESSION OF CHIRALITY IN SELF-ASSEMBLED MOLECULAR NETWORKS INDUCED BY METAL COORDINATION AND HOST-GUEST INTERACTIONS

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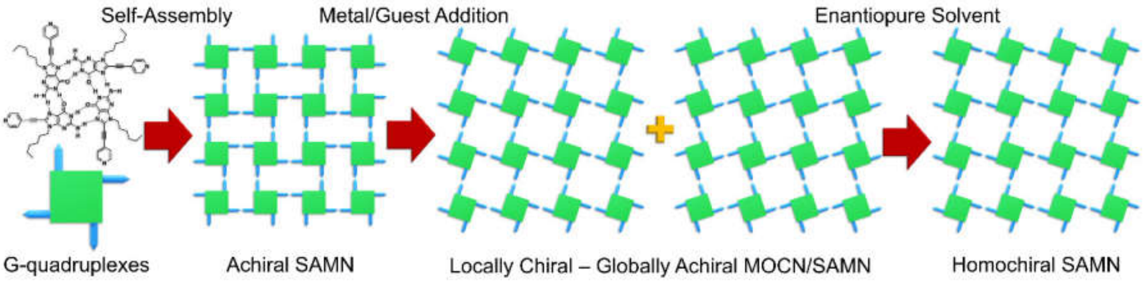
Supramolecular chemistry at interfaces provides the optimal conditions for the fabrication of crystalline self-assembled molecular networks (**SAMNs**), driven by intermolecular interactions and by the chemical properties of the interface itself[1]. Achiral molecules can also form chiral supramolecular patterns following their confinement at a solid interface [2].

Nucleobases are versatile examples of building blocks known to form supramolecular assemblies based on **hydrogen bonding** and they can be further functionalized in order to increase the variety of binding interactions and supramolecular structures. Inspired by the structural and functional tunability of metal-organic frameworks (**MOFs**), derivatives containing an additional coordinating unit have been synthesized[3]. Here, we present a scanning tunneling microscopy (**STM**) study on the metal-organic coordination framework (**MOCN**) formed by a guanine-based **ethynylpyridine nucleobase**. The precursor formed a well-ordered nanoporous supramolecular network, made up of H-bonded G-quadruplexes, which are achiral. The addition of a **Pd(II)** salt induced morphological changes in the MOCN. The metal coordination led to the formation of **enantiomorphous** domains with opposite handedness. The same changes are observed following the introduction of suitable guest molecules, such us a **phthalocyanine**. Furthermore, **homochiral MOCNs** could be fabricated by using chiral **enantiopure solvents**, in which case the surface exclusively contained only one orientation.



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Zirconium-metal-organic polyhedra as dual catalyst and drug delivery systems for detoxification of AChE inhibitors.

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One of the greatest challenges of the 21st century is to increase the production of crops in order to reach the high demand of food of the ever increasing global population (from the current 7.6 billion to the 10 billion expected by 2050). This challenge involves a significant increase of global production and use of agrochemicals, including fertilizers and pesticides. Organophosphates (OPs) are one of the most common classes of pesticides, however, these systems are highly toxic to humans and ecosystems as a consequence of their acetylcholinesterase (AChE) inhibition activity.[1] Noteworthy, AChE plays a major role in the correct neurotransmission process by regulating the concentration of neurotransmitter acetylcholine (ACh) in the neuron synapse.

In this communication, we report on the synthesis and structural characterization of a isoreticular series of robust Zirconium metal-organic polyhedra (MOP) based on butylcyclpentadieny capped zirconium trinuclear clusters connected by benzene-1,4-dicarboxylate (bdc) and biphenyl-4,4'-dicarboxylate (bpdc) spacers yielding tetrahedral MOPs. Noteworthy, the synthesized Zr-MOP systems are able to behave as dual drug delivery systems for AChE reactivating drug pralidoxime (Figure 1) and detoxifying catalysts for the hydrolytic degradation of model nerve agent diisopropylfluorophosphate.

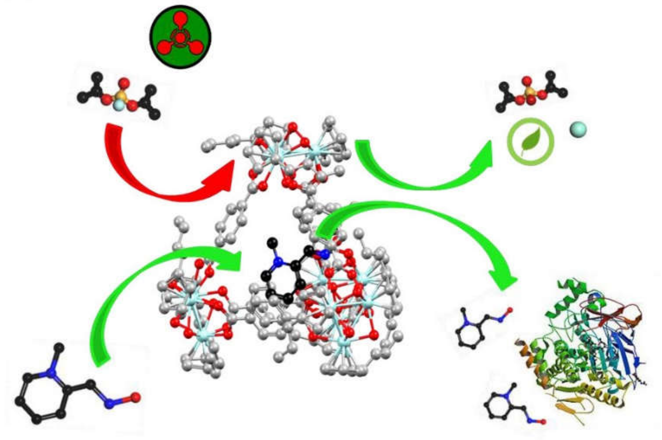

Figure 1. Zr-MOP-1 as a dual system for drug delivery and OPs detoxifying.

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ADVANCES IN MOF-BASED SYSTEMS FOR ENERGY CONVERSION

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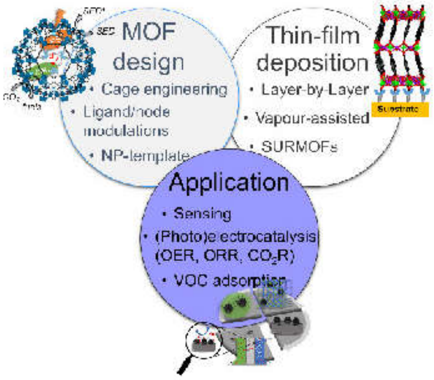
The inherent properties of MOFs, such as tailorable structures and chemical functionalities, high surface areas and pore size tunability, offer high potential for a broad variety of energy conversion purposes. Designing and realizing these systems is what the “e-conversion” subgroup at the TUM Chair of Inorganic and Metal-Organic Chemistry has made their mission. The overarching aims are the transformation of abundant feedstocks such as water, oxygen and carbon dioxide into fuels and electricity, as well as contaminant-sensing and adsorption of volatile organic compounds. Thus, aspired MOF designs range from water-splitting electrocatalysis, photocatalysis and nanoparticle templating to molecular hosting nanoreactors, which is supported by a wide range of *ex-situ* and *in-situ* characterization techniques.



Our recent publications highlight the relevance of MOFs in bottleneck processes for sustainable and environmentally clean energy conversion, involving (photo)electrocatalyzed processes like the oxygen evolution reaction (OER), oxygen reduction reaction (ORR), and carbon dioxide reduction reaction (CO_2R).[1-5] The design of catalytically active systems for these reactions can be accomplished in various fashions. For example, there are several reports on oriented surface-mounted metal-organic framework thin films used for OER and ORR catalysis, which exhibit high density and accessibility of active sites and can be obtained *via* controlled liquid phase layer-by-layer growth under ambient conditions. Another example involved a MOF-templated approach towards developing platinum nanoparticles with a narrow size distribution. The spatial confinement of the Pt clusters in the pores of a MOF effectively prevents their agglomeration even after ligand removal and allows for superior ORR electrocatalytic activities. Furthermore, there are also studies on the synergistic entrapment of a photocatalyst and photosensitizer inside defined MOF cages, which enabled enhanced photocatalytic CO_2R in a controlled molecular environment.

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Multifunctional Fe_3O_4-MOF Core-Shell Nanoparticles for Cancer Therapy

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Severe situations often require new ways of thinking and advantageousness: Recently, the extraordinary approach of utilizing highly toxic arsenic for cancer therapy showed that arsenic trioxide (ATO) actually could be an extremely useful and promising drug in cancer research.[1] However, its high toxicity complicates its usage at higher therapeutic doses and therefore, the treatment of solid tumor entities is more difficult. Hence, we were the first to address this issue with a novel approach: The introduction of highly porous metal-organic frameworks (MOFs), which exhibit manifold functional properties, as a drug delivery system for arsenic-based drugs. We succeeded to integrate high amounts of arsenic-based drugs postsynthetically *via* coordinate bonds into the framework of the three different MOFs, namely MFU-4*l*, Zn-MOF-74 and ZIF-8.[2-4] These three MOF-based drug delivery systems clearly outperform all ATO drug delivery systems reported in literature so far with respect to all the essential criteria: Besides a high drug loading capacity, they also enable a convenient pH-triggered drug release, and additionally, the first *in vitro* cytotoxicity studies revealed promising results. To push the benefits of MOF-based drug delivery systems even further we then developed the first model example of a Fe_3O_4-MOF core-shell nanoparticle, namely Fe_3O_4-ZIF-8, as theragnostic agent for arsenic-based drugs.[5] Due to the MOF shell Fe_3O_4-ZIF-8 turned out to be a suitable pH-sensitive drug delivery system and due to its superparamagnetic Fe_3O_4 core it represents an effective contrast agent for magnetic resonance imaging at the same time. In addition to the characterization by FT-IR, TGA, XRPD, TEM, STEM-EDS, DLS, ICP-OES, CHN-elemental analysis, SQUID and sorption analysis, arsenic release studies are carried out at different pH values as well as *in vitro* cytotoxicity tests with various cancer and non-tumorous cell lines.

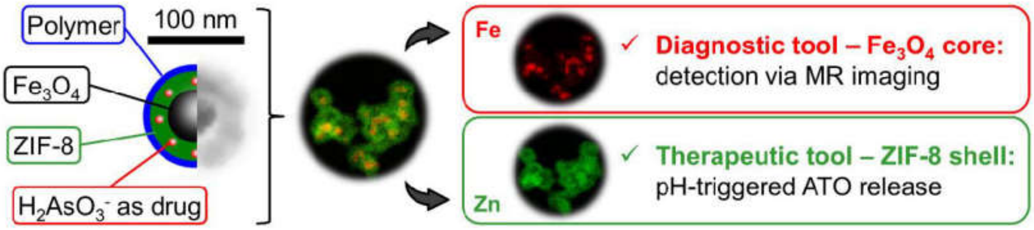

Figure 1: A combination of a schematic representation of a Fe_3O_4-ZIF-8 nanoparticle and its STEM image, and STEM-EDS mappings confirming their suitability as a diagnostic and therapeutic tool.

Financial support by Prof. Dr. Russell E. Morris of the University of St. Andrews is gratefully acknowledged.

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Iron-Nitrogen-Carbon Electrocatalysts Based on Zeolitic Imidazolate Frameworks for Oxygen Reduction Reaction in Alkaline Environment

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Alkaline membrane fuel cells (AEMFCs) can be considered as a viable technology for promoting the transition to a sustainable economy, since these electrochemical devices generate electrical energy at low or zero pollutant emissions [1,2]. The sluggish kinetics of oxygen reduction reaction (ORR) at the cathode and the resulting need of expensive catalysts, such as platinum, hamper the sustainable development of this technology. Hence, a great variety of materials have been developed, including metal-nitrogen-carbon (M-N-C) catalysts as platinum group metal free (PGM-free) materials. Such materials allow achieving ORR rate comparable to Pt, the morphology and structure of the catalysts playing an important role on the efficiency and stability of ORR active sites [3-5]. Despite the promising results reported in the literature, high costs for synthesis, stability and activity issues under operating conditions still limits their applicability in AEMFCs [1-3]. Metal organic frameworks (MOFs) represents a promising approach to obtain atomically dispersed M-N-C active sites in PGM-free catalysts. [6]. High surface area, structured nano and microscale cavities, availability of in-pore functionality and outer-surface modification, and diversity of metal center ions and N-containing ligands are among the properties making MOFs an attractive alternative as M-N-C precursors [7].

In this work, we developed Fe-N-C catalysts derived from Zeolitic Imidazolate Frameworks (ZIFs), by a solvothermal method at room temperature. In our approach, functionalized carbon Black Pearls were used as carbon support and zinc based ZIF as template to incorporate iron (II) ions by wet impregnation and pyrolysis steps in argon atmosphere. The synthesis parameters, including pyrolysis temperature, were optimized to tailor textural properties and electrocatalyticalytic activity towards ORR in alkaline media. Morphology, structure, and thermal properties of the prepared samples were characterized by SEM, FTIR, XRD and TGA, while electrocatalytic activity was assessed cyclic voltammetry and hydrodynamic voltammetry with rotating ring disk electrode. The obtained results indicated that the increase in pyrolysis temperature led to Fe-N-C catalysts with high ORR activity which exhibited similar and even higher performance as compared to Pt-based catalysts taken as reference.

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LAYER-BY-LAYER INTEGRATION OF METAL-ORGANIC FRAMEWORKS INTO ACTIVATED CARBON YIELDING SELF-CLEANING PROTECTIVE SYSTEMS

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Metal-organic frameworks (MOFs) have been widely studied as catalytic platforms for the adsorption and decontamination of highly toxic chemicals used in military and terrorist events.[1] Recent efforts are directed to the integration of MOFs into protective systems [2-3] (garments, mask cartridges) with the aim of improving the protective capacities of traditional systems based on carbonaceous materials. In this work, we combine the adsorptive capacities of activated carbon systems (in the form of fabrics and spheres) with the catalytic properties of two prototypical Zr-MOFs: UiO-66 and UiO-66-NH_2. We performed a layer-by-layer synthetic strategy in order to obtain a thin layer of Zr-MOF of controlled thickness over the carbon surface. In this approach, the substrate was alternatively immersed in two solutions of preformed zirconium cluster and ligand. In this manner, a thin homogeneous layer was obtained in sharp contrast with the heterogeneous layer obtained as a result of a one-pot solvothermal synthesis (*Figure 1*). These composites were tested in the catalytic hydrolysis of a nerve agent simulant (diisopropylfluorophosphate, DIFP). **UiO-66@AC(fabric)** and **UiO-66-NH_2@AC(fabric)** systems are able to block the secondary emission (partial desorption of the contaminant from the carbon surface) thus yielding self-cleaning composites.

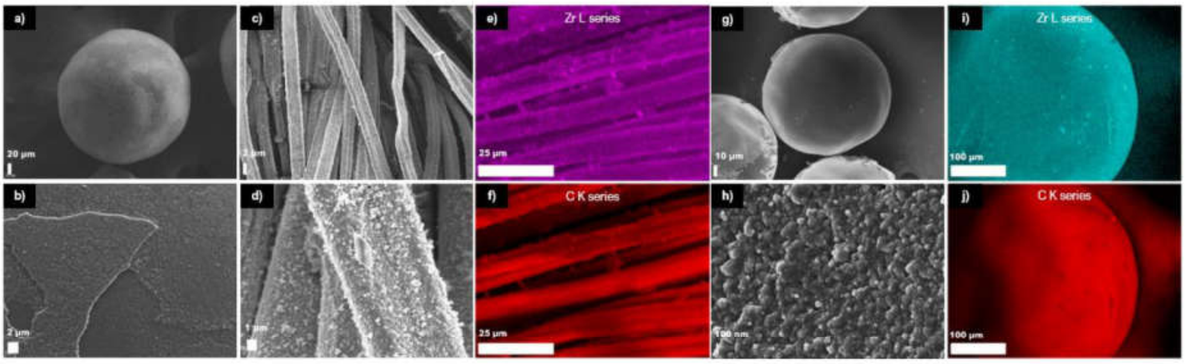

Figure 1. SEM-EDX analysis of (a,b) solvothermally prepared UiO-66@AC(spheres)-st compared to (c-f) layer-by-layer prepared **UiO-66@AC(fabric)** and (g-j) **UiO-66@AC(spheres)**

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SOLVENT INTERACTION AND EXCHANGE WITHIN $M_{12}L_8$ POLY-[*N*]-CATENANES WITH ZN(II) HALIDES AND 2,4,6-TRIS(4-PYRIDYL)BENZENE (TPB)

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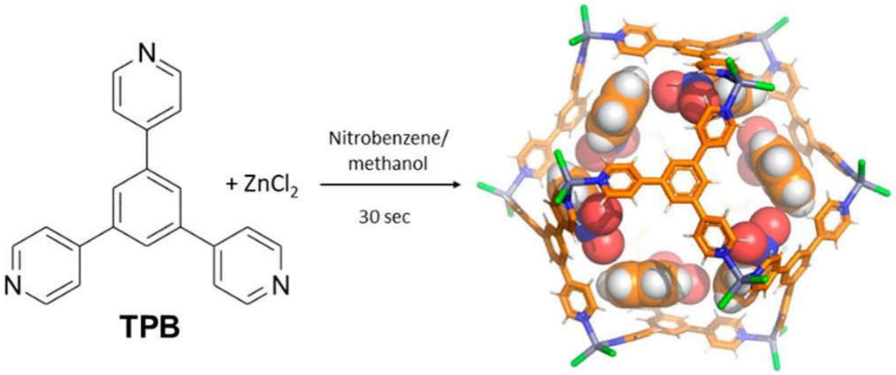

Recently, the synthesis of a $M_{12}L_8$ icosahedral coordination cage was reported which consist of $ZnCl_2$ units (M) and 2,4,6-Tris(4-pyridyl)benzene (TPB) ligands (L).[1] These cages have dimensions in the nanometer range with internal voids of about 2500 Å^3 and are furthermore interlocked to form one-dimensional poly-[*n*]-catenated chains. The essential key in the synthesis is the presence of suitable aromatic templating molecules which enable the kinetic control of the reaction to selectively give only the $M_{12}L_8$ cage instead of the large number of coordination polymers.

The Synthesis of the cage can also be expanded to zinc bromide and iodide giving isostructural compounds. The cell metric of the respective crystal structures show small but significant variations and reveal the influence of the zinc halide incorporated in the cage but, more importantly, of the templating solvent molecule which underlines the importance of the interaction between cage and templating molecule. X-Ray diffraction is used to get a deeper understanding of this interaction and showed the presence of 13 solvent molecules in the case of 1,2-Dichlorobenzene within ZnI_2/TPB-cages as well as strong π-π interactions with the aromatic groups of the cage. Single crystal X-Ray diffraction furthermore revealed that the solvent molecules inside the voids can be exchanged pointing to an inherent flexibility of this compound.

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Topological characterisation of MOFs in the Cambridge Structural Database (CSD)

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Development of metal-organic frameworks (MOFs) created a unique class of crystalline materials based upon the assembly of molecular clusters, as opposed to individual single atom constructions. These molecular clusters, often termed secondary building units (SBUs) can be assembled using organic linkers to create aesthetic periodic structures. The connectivity network, or topology, of these SBUs can be instrumental in the search for new materials.

The topology is a subjective property which can be best described by simplifying the atomic bonds of these structures to map out a simple graph. Graph theory allows for the simplification of these structures into fundamental unit cells which enables the comparison of two very different, but identically connected materials. These simplified graphs are collected in an open-source online database, the Reticular Chemistry Structure Resource (RCSR). The programme Systre is used in conjunction with the RCSR to allocate distinct three-letter network identifiers to a fundamental unit cell. There are several deconstruction programmes which allow a researcher to simplify their chosen material, and have a topology assigned automatically without any extensive knowledge of the subject, however there are limitations to the use of these software and it is easy to return unsuitable results. In some cases, certain representations are actually complex representations of other types of nets themselves, additionally there can be information loss due to oversimplification of certain branches. Notably, cluster type topologies should be discarded when searching for representations of periodic structures, as correct bond assignment is essential when searching for topological networks.

The CSD contains approximately 80,000 MOFs, which have well defined bond assignments. This means that the CSD provides the perfect platform for structure simplification, and subsequent topological assignment by enabling a researcher to bypass any errors produced by their choice of automatic bond assignment software. Development of new tools to return topology of MOF structures has the potential to significantly increase the rate of successful topological assignment.

MECHANOCHEMICAL BALL-MILLING SYNTHESIS OF Mg^{2+} AND Zn^{2+} CARBOXYLATE COORDINATION POLYMERS STARTING FROM ECONOMICALLY FEASIBLE AND BENIGN BUILDING BLOCKS

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Hydrogen is an attractive alternative to fossil fuels, but its low volumetric energy density is a serious drawback when efficient gas storage is required[1]. Among the materials that have been studied for physisorption of hydrogen, Metal-Organic Frameworks (MOFs) reach the most remarkable performance at the temperature of 77 K[2] which makes them great candidates for large-scale hydrogen storage in stationary sources (e.g. for refueling stations). The best porous materials for the cryogenic physisorption of hydrogen have already been identified[3], but they are expensive to produce using traditional solvothermal synthesis, even at large scale[4]. In order to reduce the cost of MOFs solvent-free approaches like mechanochemistry are being studied[5].

In this work, we systematically explored liquid-assisted grinding (LAG) as a mechanochemical approach to obtain Mg- and Zn-based MOFs from relatively cheap organic linkers and environmentally and process benign metallic precursors. Syntheses from $Mg(OH)_2$, $Zn(CH_3CO_2)_2·2H_2O$, and $Zn_5(CO_3)_2(OH)_6$ with trimesic (H_3btc), terephthalic (H_2pbdc), and isophthalic (H_2mbdc) acids were carried out. LAG was conducted by adding small amounts of H_2O, MeOH, EtOH, or DMF in the grinding jars. A Pullverisette 23 vertical miller (Fritsch, Germany) with two stainless steel grinding balls were used to yield ca. 1 g of the final product after 15 min at 50 Hz of milling frequency. Longer grinding time (up to 2 hours) and increased amount of liquid were used when necessary until no-remaining signals from reagents appeared in the PXRD patterns.

The reactions between zinc salts and H_3btc yielded compounds with different dimensionality, according to the information in the CCDC: one-dimensional $Zn_3(btc)_2(H_2O)_{12}$, two-dimensional $[Zn_3(btc)_3(H_2O)_6]·2H_2O$, and three-dimensional $[Zn_6(\mu_3\text{-}OH)_2(btc)_4(DMF)_{2.5}(H_2O)_2][Zn(H_2O)_3(DMF)_3]·3H_2O$ were isolated when H_2O, EtOH, and DMF, respectively, were used as grinding liquids. When using $Mg(OH)_2$ and H_2O as grinding liquid, the reaction yielded zero-dimensional $[Mg(Hbtc)(H_2O)_5]·H2O$ and $Mg(H_2btc)_2(H_2O)_4$, one-dimensional $Mg_3(btc)_2(H_2O)_{12}$, and three-dimensional $Mg(pbdc)(H_2O)_2$ compounds. The mechanochemical synthesis of these compounds has not been reported to the best of our knowledge. Furthermore, four unreported crystalline products can be quantitatively isolated depending on the grinding liquid: one from the mixture of $Zn(CH_3CO_2)_2$ and H_3btc in the presence of MeOH, and three more from $Mg(OH)_2$ and H_2mbdc using either H_2O, EtOH/MeOH, or DMF. These results open the door for the sustainable industrial production of a new set of MOFs from cheap, easily available, benign building blocks, and small amount of solvents.

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Linker substitution in ZIF-8 and its effect on the selective uptake of the greenhouse gases CH_4, CO_2 and SF_6

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Attempts were made to synthesize, pore size tailor, and characterize ZIF-8 and several mixed-linker ZIF structures to improve capture of the greenhouse gasses CH_4, CO_2, and SF_6. Three experimental linkers, 2-methylbenzimidazole, 2-aminobenzimidazole, and 5-nitrobenzimidazole were chosen to gradually substitute 2-methylimidazole as the linker in ZIF-8. This substitution was intended to gradually reduce pore sizes and possibly add functionality to the apertures present in ZIF-8.

ZIF-hybrids were synthesized and characterized using PXRD, FTIR, 1HNMR, SEM, sorption measurements, and subsequent IAST modeling to evaluate these changes. Hybrid ZIFs were mostly XRD-crystalline. Linker incorporation was found to be incomplete, but increasing with added linker. Sodalite topology was confirmed in ZIF-8 samples and confirmed as modified in hybrid ZIFs. The hybrid ZIFs did indeed show altered sorption results and gas selectivity.

Orientation and Thickness Dependence of Thermal Conductivity in COF Thin-Films

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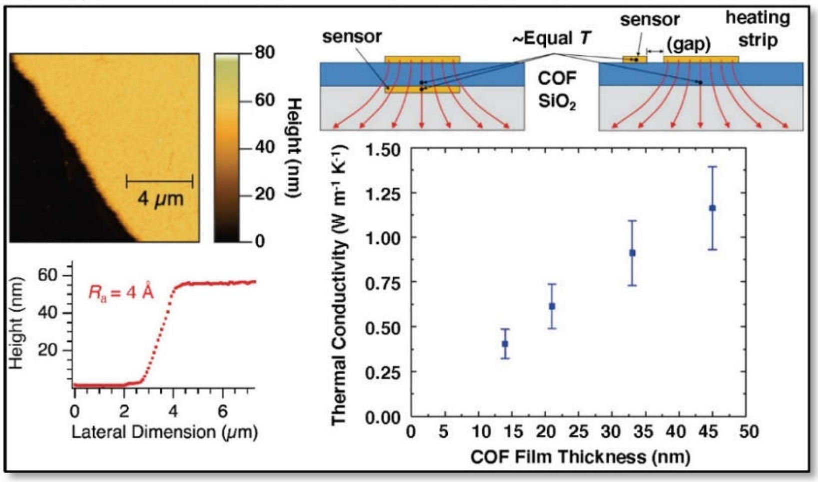
High heat dissipation and low dielectric permittivities are desired properties in next-generation dielectric layers, especially in high-power density chips.[1] Previous studies show the ability to modulate the thermal conductivities of 2D materials by varying the thicknesses in graphene thin-films[2] or by altering the pore sizes and shapes of metal organic frameworks.[3] 2D covalent organic frameworks (2D COFs) are polymer sheets with crystalline lattices and high porosities that should allow relatively high thermal conductivities and low-dielectric constants.[4,5] The combination of these properties position 2D COFs as desirable dielectric layers in electronic devices.

Despite these advantages, 2D COFs are conventionally prepared as insoluble, polycrystalline powers, limiting their integration in devices. A multidisciplinary effort recently reported that 2D COF thin-films have relatively high thermal conductivities (κ = 1 W m^{-1} K^{-1}) and ultra-low dielectric permittivities (k = 1.6) compared to other low density materials.[1] Despite the high quality of these films, their surface roughnesses at varying thicknesses decreased the necessary precision for elucidating structurally relevant trends. Here, we report new colloidal synthesis conditions that produce COF thin-films with thicknesses between 14-50 nm and roughnesses below 2 nm. Time-domain thermoreflectance measurements indicate a thickness-dependent trend in the measured thermal conductivities of thin-films. Atomic-force microscopy and grazing-incidence X-ray scattering data show that these films are homogenous, crystalline, and oriented, leading to enhanced phonon transport. Further linkages and characterization of COF thin-films for integration in electronic devices will be presented.



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FUNCTIONALITY AND FLEXIBILITY CONTROL IN METAL-ORGANIC FRAMEWORKS BY TETRAZINE CLICK REACTION AS COVALENT POST-SYNTHETIC MODIFICATION

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Modern research on the chemistry of metal-organic frameworks frequently focuses on the multifunctionality of these materials. It is often desirable to combine several properties in one material, allowing it to be used in industry or to construct a functional sensor.[1] One way in which a multifunctional material can be obtained is to modify previously obtained frameworks. Among the known classes of post-synthetic modifications, covalent post-synthetic modifications deserve special attention.[2] The variety of functional groups, possibility of influencing on chemical environment of the pores, gentle interference with the crystal structure and other features of these modifications contribute to our special interest in their use in our work.

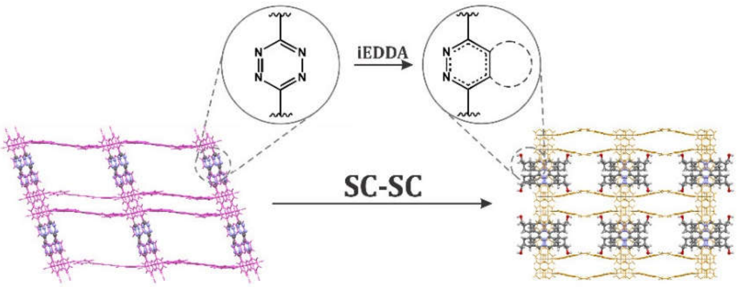

Figure 1. Inverse-electron-demand Diels-Alder reaction on 3,6-disubstituted 1,2,4,5-tetrazine ligand built in a metal-organic framework, carried out on a single crystal.

The inverse-electron-demand Diels-Alder reaction (iEDDA) is a type of well-known organic reaction which has the advantages of mild synthesis conditions, no (or negligible amount of) by-products, or high selectivity of the diene to react with the dienophile. At the same time, this reaction has so far been explored to a very small extent for ligands embedded in metal-organic networks.[3] This work is a compilation of research on a series of new metal-organic frameworks to apply the iEDDA reaction as an underexplored area of covalent post-synthetic modifications of metal-organic frameworks. The work was completed by carrying out the Diels-Alder reaction on single crystals of several MOFs. The reactions were carried out on a ligand containing a 1,2,4,5-tetrazine moiety and a series of dienophiles, differentiated in terms of electron-donor effect, angular strain and applied functional groups.

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Chemically sensitive single-particle imaging for drug delivery processes

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The key challenge of chemotherapy is usually to selectively deliver anti-cancer drugs to diseased tissue. Novel approaches employ nanoparticles that act as nano-carriers encapsulating the drugs and releasing them at the target tissue in a controllable fashion. Despite its many advantages, these systems are no satisfactory solution: Even very tight capping mechanisms or incorporation of the drug into the structure of the nano-carrier cannot guarantee an absence of premature leakage. Furthermore, after release and action at the target site the drugs may induce side effects. An alternative concept for tumor therapy without inherently toxic substances represents the induction of sudden lysosomal bursts that have been shown to lead to cell death [1]. This purely physical effect could be generated by an abrupt increase of molecular building blocks of any kind without involvement of toxic substances. We designed lipid-coated, iron-based poly-carboxylate metal-organic frameworks that offer this unique property: they decompose under acidic conditions of the lysosome and their degradation releases the building blocks of its material at high concentrations leading to the desired enhanced osmotic pressure and cell death [2]. Since current methods were not sufficient to observe the import and degradation in vivo directly, we set out to develop a system capable of revealing the underlying processes.

In this contribution, we discuss our newly developed multi-modal imaging system [3] and present first steps towards the study of uptaken, lipid-coated MIL-100(Fe) nanoparticles, that deliver and release high amount of iron ions into cells. Since the iron release into cells occurs only in slightly acidic extracellular environments, this controlled ion delivery provides a technology for the study of their effect on cellular behavior. Our goal is the development of a correlative and multifunctional imaging approach to monitor the steps of the cellular import of MOF nanoagents in a chemically sensitive manner, the regions of accumulation and the following degradation with their effects on the cell.

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Molecular dynamics simulations of palladium nanocluster formation inside UiO-67

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Metal-organic frameworks (MOFs) are promising materials that represent a new class of porous crystals[1]. Additional useful properties can be achieved by the functionalization of MOFs, which allows obtaining new structures with specific functions. Promising MOFs is the UiO-66/67/68 family, that shows an incredible thermal and chemical stability. Also, in the case of UiO-66/67/68, functionalization has played an important role in enhancing the material potentialities, by insertion of other metals in the inorganic cornerstones and by functionalization of linkers by additional metals.

In the previous work, we characterized the formation and growth of palladium nanoparticles in the UiO-67 structure with using extended X-ray absorption fine structure (EXAFS)[2]. We obtained several important structural results: (i) destruction of Pd-Cl bonds starts in the interval 200 - 300 °C, the decrease in the relative number of Pd-N bonds begins at lower temperatures, but covers a wider temperature range compared to Pd-Cl. The formation of palladium nanoparticles starts above 200 °C, and further heating in hydrogen above 300 °C leads to the formation of larger particles that are no longer limited by the pores of UiO-67.

In the recant work, we combine density functional theory (DFT) and reactive force-field (ReaxFF) calculations to simulate the formation of palladium nanoparticles inside UiO-67 MOF. One of the applications of ReaxFF is molecular dynamics modeling of large systems over big time scales. It can simulate chemical reactions despite traditional force fields. It looks like classic molecular dynamics, but the main difference is that it can break and create chemical bonds.

To describe the UiO-67 MOF functionalized with Pd, the ReaxFF potential was created based on the following potentials:

1.C / H / O / Pd[3] all parameters are used.
2. Li / Na / K / Cs / F / Cl / I / water[4], and the following parameters for Cl were added.

We systematically varied the geometries of big number of structures performing precise DFT calculations, that allowed for further retraining of the potential. To train the potential, the CMA-ES optimization algorithm was used. The CMA-ES evolutionary algorithm allowed us to find the best ReaxFF parameters for describing the values provided in the sample.

We were able to simulate the formation of nanoparticles in the MOF over 1/10 nanosecond and confirmed the formation of palladium clusters with an average interatomic distance of 2.75 Å, which is close to the distance of metallic Pd. The integrated DFT/ReaxFF methodology employed here demonstrates a combined quantum/classical workflow that can give information about evolution Pd nanoparticles inside UiO-67 and provide detail explanation of working mechanisms of MOF functionalizated my nobel-metals.

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A Bilayer Coating Strategy for Metal-Organic Framework with Soybean Lipid and Biosurfactant for Enhanced Stability in Biomedical Applications

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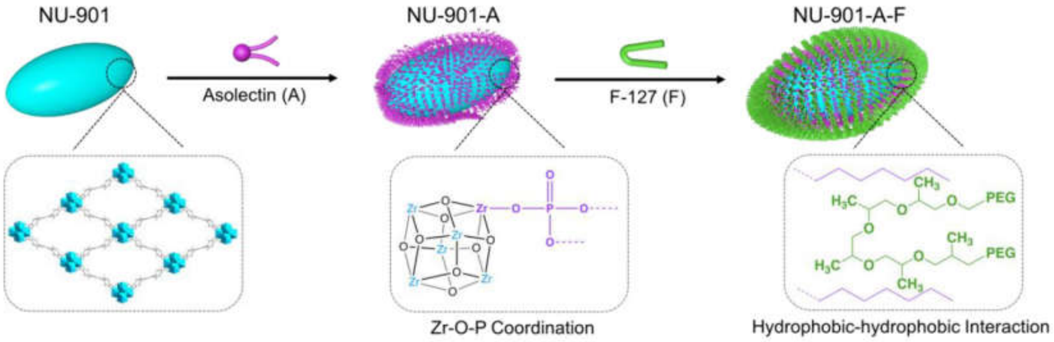
The development of nanoparticle-based drug carriers has yielded opportunities to tackle challenging diseases. Amongst different carriers, zirconium-based metal-organic framework (Zr-MOF) has emerged as a promising candidate in biomedical applications due to the compatible size with intravenous injection and surface functionalization for targeted treatment. However, the aggregation and early drug-release of Zr-MOF nanoparticles in the body fluid remain a key issue, which can diminish their therapeutic efficacy. Driven by this, we have developed a simple and economic bilayer coating strategy in a two-step fashion using soybean lipid (asolectin) and bio-surfactant (F-127) sequentially. The bilayer-coated MOFs remained well dispersed in three different mimicked body fluid: PBS, DMEM and RPMI. The bilayer-coated MOFs also released a licensed chemotherapy drug, pemetrexed, in a sustained and controlled manner, avoiding the burst-release problem. Additionally, the coating assists the long-term storage of drug-loaded MOF in water through preventing the sustained leakage of pemetrexed and the aggregation of MOF particles. We demonstrated the generality and versatility of our approach by extending the coating strategy using two more lipids and four more surfactants. This research highlights a facile bilayer coating, providing new insight into the design of a promising MOF-based drug delivery system.



Eu-doped lanthanide metalorganic frameworks: facile synthesis and luminescent studies

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Recently, the scientific community has focused great attention on the development of new and environmentally friendly strategies for the synthesis of lanthanide metalorganic frameworks (Ln-MOFs) to obtain more and more complex structures with the best properties for a specific application. The use of lanthanide elements as dopants within MOF's structures leads to the acquirement of unique luminescent properties, which can be exploited for the fabrication of optical sensors. Up to now, different Ln-MOFs have been studied for the detection of toxic ions [1-3], heavy metals [4], and small molecules [5]. In addition, Ln-MOFs are also gaining interest for photovoltaic applications [6]. The special feature of these materials refers to the capability of tailoring their properties by simply changing their internal structure, through variation of the organic linkers and the metallic centre or by modifying the operating conditions such as time, temperature and pressure. The most recent applied strategy for the syntheses of Ln-MOFs is the solvothermal reaction which uses organic solvents, high pressure and very long reaction times [7-8].

The challenge in the development of more sustainable synthetic strategies actually leds to the exploration of new and greener approaches. In this context, we propose a one-step synthesis of Eu doped Ln-MOF (Ln = Y, Tb) in water/ethanol solvents, starting from a mixture of 1,3,5-benzenetricarboxylic acid (H_3BTC) as the organic ligand and $Ln(NO_3)\cdot nH_2O$ as a source of Y, Tb and Eu. The powders obtained were characterised by X-ray diffraction (XRD), FT-IR spectroscopy and field emission scanning electron microscopy (FE-SEM) for the investigation of structure and morphology; with Brunauer–Emmett–Teller (BET) method to rationalize the textural properties (surface area) of the system. Finally, preliminary studies were performed in order to investigate the luminescent properties of Ln-MOF doped with Eu ions.

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INDUCING HIGH PROTON CONDUCTIVITY IN METAL-ORGANIC FRAMEWORKS BY MECHANOCHEMICAL APPROACH

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Proton-conducting metal-organic frameworks (MOFs) have been gaining increasing attention for their role as solid-state electrolytes in fuel cells.[1,2] In the literature, several competing methods could be found for inducing proton conductivity in MOFs which generally fall into two main categories –the *de novo* synthesis and post-synthetic modification (PSM).[3] The first approach has serious limitations regarding inducing and control of conductivity in resultant frameworks, but a promising and effective alternative is offered by the second main approach towards proton-conducting MOFs that relies on modifications of pre-assembled frameworks. The aim of the research is to carry out a mechanochemical post-synthetic modification of the family of metal-organic CPO-27/MOF-74 networks, which is expected to lead to systems containing a coordinated thiocyanate and an extraframework NH_4^+ ions. The presence of extraframework Brønsted acid (NH_4^+) makes the obtained networks (CPO-27-NCS) show proton conductivity as high as 10^{-2} S cm^{-1} at high relative humidity (60°C, 90% RH) and 10^{-4} S cm^{-1} already at 30% RH. Interestingly, proton conductivities of CPO-27-NCS can be controlled by mechanochemical stoichiometric dosing of thiocyanate ions within the 6:1 to 6:3 metal-to-thiocyanate ratio range.

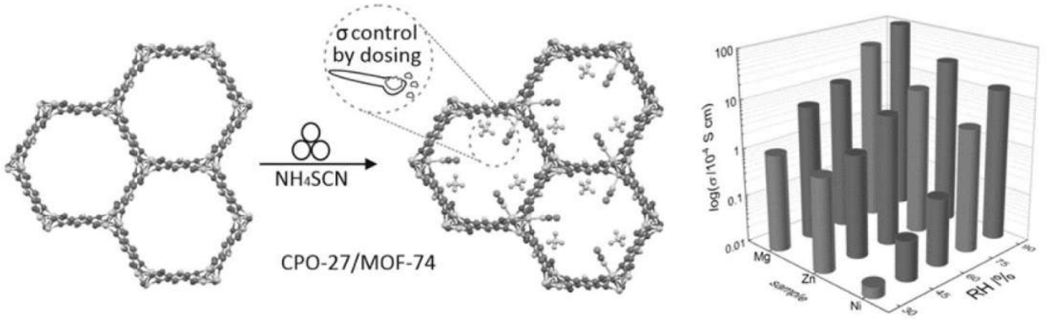

Figure 1. Solid-state reaction of CPO-27 with NH_4SCN; (a) general scheme for the mechanochemical synthesis of CPO-27-NCS; (b) proton conductivities at 60°C and different RH values.

An additional purpose of the work is to replace ammonium ions with other counterparts in order to improve the stability of the modified metal-organic frameworks, without losing high proton conductivity. Another goal is to apply the above-described post-synthetic mechanochemical modification procedure to other metal-organic frameworks.

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Impact of the linker elongation on the flexible adsorption behavior in pillared layer MOFs

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Pillared layer structures based on paddle wheels (PWs) as "soft SBUs" represent a prototypical class of MOFs showing structural flexibility in selected cases. In switchable, microporous DUT-8(Ni) compound, the layers constructed of Ni_2 PWs interconnected by 2,6-naphtalenedicarboxylates (2,6-ndc) are pillared by 1,4-diazabicyclo[2.2.2]octane (dabco) molecules[1]. DUT-8(Ni) has outstanding properties, such as huge volume change upon structural transformation, as well as switching selectivity, useful for sensing,[2] separation, and purification applications.[3]

To make the pores accessible for large molecules, the elongation of the linkers in an isoreticular approach is very powerful strategy. Moreover, the specific functionalization of the framework backbone may lead to tunable switching properties.

Therefore, new MOFs, isoreticular to DUT-8(Ni), were synthesized by substitution of 2,6- ndc by longer linear linkers: 4,4´- biphenyldicarboxylate (in DUT-128(Ni)) or 4,4´-stilbenedicarboxylate (in DUT-131(Ni)).

Investigation of the structural response towards the desolvation and adsorption of the different guest molecules disclosed distinct differences in the flexible behavior of these three compounds.[4]

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ULTRASONICATION: A FEASIBLE ROUTE FOR THE SYNTHESIS OF AN IRON (III) TRIMESATE XEROGEL

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Metal-Organic Frameworks (MOFs) are crystalline porous coordination polymers composed of organic-inorganic building units[1]. Structures built on iron (III) and 1, 3, 5-benzenetricarboxylate (BTC or trimesate), also known as Fe-BTC materials, have attracted enormous attention because of their high biocompatibility, low cost, redox behavior and stability in air, water and organic solvents[2]. All these features have made Fe-BTC MOF a suitable candidate for the application in several fields, including catalysis, gas storage and separation, drug-delivery and protein immobilization[3]. The first type of iron (III) trimesate MOF synthesized was MIL-100(Fe)[4]. The traditional synthesis of this system consists in the solvothermal method, which is time-consuming, expensive and implies the use of large amounts of solvents (e.g. HF)[4]. Hence, several alternative green approaches, including mechanochemical and sonochemical methods, have been proposed in order to obtain this material in a shorter time under mild and low-cost conditions[5]. We present here a green method for the synthesis of a microporous Fe-BTC MOF at room temperature in water, using ultrasonic (US) irradiation. We conducted two groups of experiments using different ultrasonic apparatus to investigate, respectively, the time effect of US irradiation and the influence of pH in terms of microstructure, thermal stability and textural properties of the material. A gel was obtained in all synthesis as the effect of cavitation due to US irradiation. After a drying process, accompanied by a shirking effect, a transparent, glassy xerogel was obtained (Fig. 1). The gel and monolithic states hold great promise for novel application of MOFs, owing to providing a minimal mass transfer resistance and an increased gas adsorption capability, compared to powders[6]. All the samples obtained were characterized by X-ray powder diffraction (XRPD), Fourier transform infrared spectroscopy (FTIR), thermal analysis and nitrogen physisorption. We observed significant differences in surface areas and micropore volume, although the samples showed similar microstructure by FTIR and PXRD.

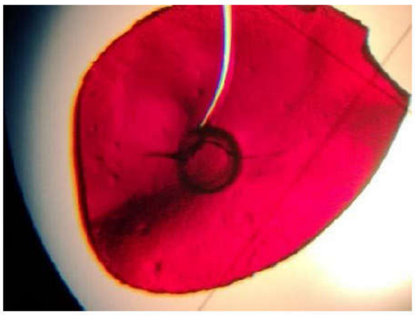

Fig. 1. Fe-BTC xerogel from the shrinking process during slow drying of gel at room temperature observed with an optical microscope.

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COMBINATION OF MECHANOCHEMISTRY AND ELECTRON CRYSTALLOGRAPHY FOR THE DISCOVERY OF NEW METAL-ORGANIC MATERIALS

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Mechanochemistry is an interesting synthetic approach that combines environmental-friendly conditions with rapid and efficient reactions[1]. In the past twenty years, it has found application in the synthesis of new organic and metal-organic materials in the form of molecular crystals, salts, cocrystals and polymeric structures. One of the advantages of this method is that the low amount (or absence) of solvents required leads to synthetic processes characterized by high conversion of reagents, low energy consumption and reduced chemical waste production. Moreover, mechanochemical synthesis can allow the formation of products, polymorphs and topologies different from those obtained in solution.

However, the structural characterisation of the obtained products is one of the main challenges related to this synthetic approach, due to the presence of nanometric crystals that cannot be analysed by conventional single-crystal X-ray diffraction. Furthermore, powder diffraction methods can be extremely difficult to apply in case of large unit cells, low symmetry and polyphasic systems.

Electron crystallography, especially 3D electron diffraction performed in a transmission electron microscope, is an emerging characterisation technique that, due the most recent developments, can be successfully employed to obtain the structure of nanocrystalline species. This has allowed the structural characterisation of different types of materials, spanning from porous MOFs, COFs and zeolites, to pharmaceutical APIs[2-4].

In this contribution, we will show how we have combined mechanochemistry and 3D ED-TEM for the synthesis and characterisation of metal-organic compounds based on 2,6-pyridine dicarboxylic acid and 4,4'-bipyridine as ligands and zinc(II) or copper(II) as metal centers. The successful improvement of the 3D ED model, by using Rietveld refinement on X-ray powder diffraction data, will also be discussed.

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Mechanochemical strategy for controllable encapsulation of fullerene C_{60} within metal-organic framework ZIF-8

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Fullerene and fullerene derivatives show vast potential for application due to their unique physicochemical properties. Functional materials with fullerene embedded in their structure are researched due to their increased stability, conductivity, or catalytic activity compared to their constitutional components. Metal-organic frameworks (MOFs) are crystalline, porous materials that have proven to be excellent host matrices for the encapsulation of various guest molecules.[1] Guest encapsulation into MOFs is mainly done by solution methods that are dependent on the solubility, MOFs aperture size, and competition with the solvent. The main problem with this approach is the lack of control over the encapsulation process.[2] Here, a fast and green mechanochemical approach emerged as a fitting solution as it requires only traces of solvent. Ball milling allowed stoichiometrically controlled encapsulation and provided four C_{60}@ZIF-8 (zeolitic-imidazolate framework) crystalline materials containing 15, 30, 60, and 100 mol % of fullerene entrapped in the available pores of the sodalite ZIF-8 while solution-based experiments resulted in a minimal load of fullerene. The fullerenes contained within the ZIF-8 show properties of isolated molecules.[3] Therefore, this strategy could serve to fit selected endofullerenes into suitable MOFs for use in spintronics.

The work has been supported by the "Research Cooperability "Program of the Croatian Science Foundation funded by the European Union from the European Social Fund under the Operational Program Efficient Human Resources 2014−2020, through grant PZS-2019-02-4129.

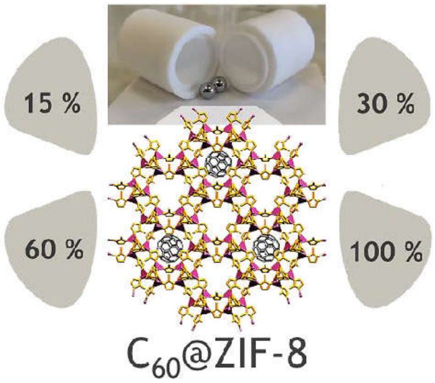

Figure 1. Mechanochemically synthesized C_{60}@ ZIF-8 crystalline materials containing 15, 30, 60, and 100 mol % of Buckminsterfullerene

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ZIRCONIUM METAL-ORGANIC FRAMEWORKS CONTAINING A BISELENOPHENE LINKER: FROM SYNTHESIS TO LUMINESCENT APPLICATIONS

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In recent years Metal-Organic Frameworks (MOFs) have gained great attention for their widespread application in several fields of materials science (catalysis, luminescence, gas storage and separation). Based on versatility in MOFs design, achieved through a tailored combination of organic linkers and inorganic metallic nodes, it is possible to tune pore size and surface areas [1] and to include suitable functional groups on their linkers' skeleton [2]. In this work, we describe the synthesis and characterization of the bicyclic ditopic linker 2,2'-biselenophene-5,5'-dicarboxylic acid (H_2SpSp) specifically designed for MOFs construction, together with the corresponding zirconium MOF $[Zr_6O_4(OH)_4(SpSp)_{3.8}Cl_{4.4}]$ (**1**). The XRPD analysis has shown this MOF being isostructural with its bithiophene and bithiazole analogues. Additionally, three new mixed-linker MOFs have been synthesized (Figure 1), containing biselenophene (H_2SpSp), bithiophene (H_2ThTh) and bithiazole (H_2TzTz) linkers together, in detail the double-mixed $[Zr_6O_4(OH)_4(SpSp)_{2.6}(ThTh)_{1.3}Cl_{4.2}]$ (**2**) and $[Zr_6O_4(OH)_4(SpSp)_2(TzTz)_{1.8}Cl_{4.4}]$ (**3**), as well as the triple-mixed $[Zr_6O_4(OH)_4(SpSp)_{1.6}(ThTh)_{1.2}(TzTz)_{1.4}Cl_{3.6}]$ (**4**). MOFs **1-4** display luminescence in the blue-green visible region under UV irradiation [3].

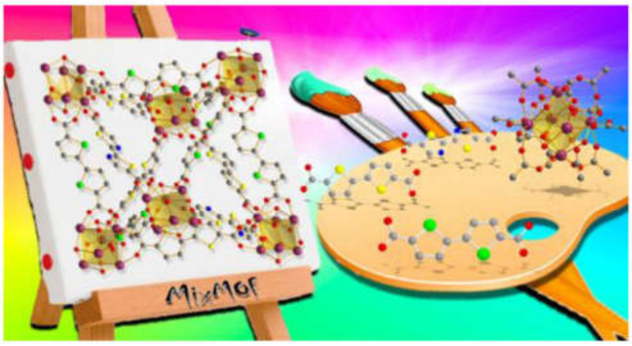

Figure 1

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MERCURY ADSORPTION-PROMPTED PHASE TRANSITION IN LUMINESCENT BIPYRAZOLATE MOFS: A MULTI-TECHNIQUE STUDY

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Water contamination by heavy metals is a contemporary global issue caused by their wide environmental spread, mainly due to anthropogenic activities, and their high toxicity for the living species. Mercury accumulates in the human body through the food chain provoking several health concerns. Among the approaches to detect or remove heavy metals from water, adsorption has emerged for its economy and effectiveness, though the inorganic adsorbents studied so far show a number of limitations[1]. Metal-organic frameworks (MOFs)[2] do possess great potential[3] to overcome these issues.

In this context, the novel MOFs Zn(BPE) and Zn(BPE)·nDMF [**i-Zn** and **ni-Zn**; H_2BPE = 1,2-bi(pyrazol-4-yl)-ethyne; DMF = dimethylformamide], with a ligand skeleton featuring a triple carbon-carbon bond potentially imparting affinity *vs.* mercury to the two materials, were isolated as microcrystalline powders. A multi-technique approach, combining PXRD structural investigations to solid-state UV-Vis absorption, fluorescence emission and fluorescence excitation spectroscopy, as well as theoretical calculations enabled us to study the phase transition selectively prompted by mercury adsorption. The two MOFs show a 3D (interpenetrated, **i-Zn**, or not interpenetrated, **ni-Zn**) network with 1D channels. After 1-day suspension in water, **ni-Zn** interconverts into **i-Zn** which, at variance, is water stable for at least 15 days. **i-Zn** suspension in $HgCl_{2(aq)}$ in the concentration range 10-500 ppm prompts its partial but progressive interconversion into **Hg@ni-Zn** due to $HgCl_2$ adsorption ($HgCl_2$ remaining associated in aqueous solutions). At variance, after **i-Zn** suspension into 500 ppm $HgCl_{2(aq)}$ for increasing amounts of time, the **i-Zn** to **Hg@ni-Zn** transformation reaches equilibrium within 10 min. Finally, no transformation is observed with Group 1 or 2 metal chlorides in the essayed conditions. The excitation spectra of the two MOFs are maximally different in correspondence of a charge transfer band peaking at 365 nm. Upon excitation at this wavelength, an intense fluorescence emission peaked at 470 nm is observed for **ni-Zn**, but partially quenched for **i-Zn**, most likely due to an excitation transfer through the π-π (triple bond-triple bond) stacking interactions present in its crystal structure, as confirmed by TD-DFT calculations. This spectral feature was exploited to *i)* determine the fractional concentration of **Hg@ni-Zn** in the samples recovered from the 10-500 ppm suspensions; *ii)* real-time monitor, on the suspensions, the **i-Zn** to **Hg@ni-Zn** interconversion kinetics at different $HgCl_{2(aq)}$ concentrations in the range 5-500 ppb. Even at the lowest probed concentration a sizeable fluorescence increase was observed within a 1 h time lapse. DFT calculations on model systems representing **i-Zn** and **ni-Zn** suggested the inability of the former to coordinate either Hg^{II} or $HgCl_2$, while both species bind to the triple carbon-carbon bond in **ni-Zn**. The $HgCl_2$ binding energy is estimated to be only a few kJ/mol, the value depending on the number of water molecules in the models.

In summary, our multi-technique approach allowed a comprehensive investigation of a specific case-study contributing to define the chemical and structural features a MOF should possess to be employed as a luminescent sensor in water in straightforwardly accessible experimental conditions.

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Moving from traditional coordination chemistry to MOFs for the investigation of new families of MOFs with unique properties

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Metal-Organic Frameworks (MOFs) is a class of hybrid materials, which have attracted interest as they are promising candidates for a variety of applications, such as gas separation/purification/storage, catalysis, medicine, sensing, imaging, etc. The pores' size, shape and properties of MOFs are affected by the type of the organic linker that is present in their structure. Many organic ligands or their combination have now been used and yielded MOFs with interesting properties (photoluminescent, magnetic,...), including carboxylates, imidazolates, etc.

Herein, the family of pyridyl oximes and pyridine-alcohols are introduced for the first time into the field of MOFs. They have extensively used in the field of single-molecule magnets (SMMs) for the formation of metal clusters, which favours ferromagnetic coupling between the metal centers. Preliminary results include the isolation of new species with interesting magnetic properties and unique metal topologies. [1,2,3] Among them, $[Zn_2(bdc)(hmp)_2]_n \cdot DMF$ and $[Fe_3(bdc)_3(Hhmp)_2]_n$ are the first MOFs bearing Hhmp with the former displaying an unprecedented structural topology. The synthesis, structural characterization and physical properties of the compounds are discussed in detail. [4 ,5, 6,7]

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The study of phase formation upon MW synthesis in UiO-66/MIL-140A system.

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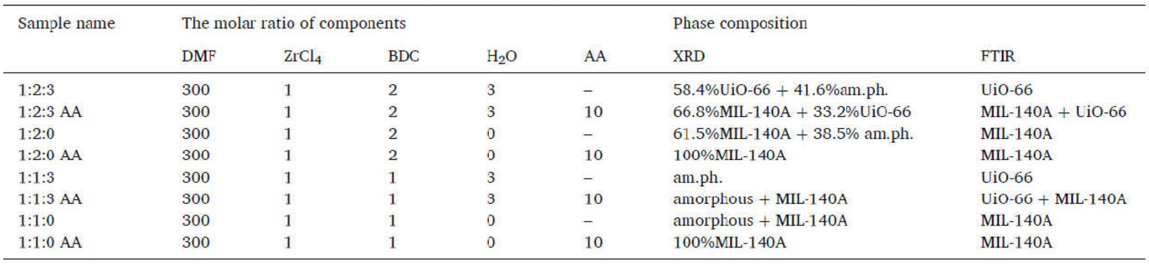
In the recent work by Butova et. al., [1] it was reported that water could play a role of structure driving agent from MIL-140A phase (in the absence of water) to UiO-66 (in the presence of water). It is expected that MW synthesis provides the list of features, which could have their effect on the phase formation process. In particular we have observed that precipitate could be obtained after 0.5 h of MW heating or 3 h of conventional heating, while a product with proper crystallinity forms after 2h and 24 h for MW and conventional heating respectively [2]. Moreover, utilization of acetic acid as a modulator could also result in some deviations in phase formation [2].

To unravel the phase formation process in the investigated systems upon MW synthesis the obtained samples has been characterized by laboratory XRPD, FTIR, TEM microscopy, BET analysis as well as synchrotron Zr K-edge XAS spectroscopy. The MW synthesis method employed in this work described in detail in Ref. [2]. The phase composition analysis has been performed qualitatively on the basis of FTIR data and quantitatively on the basis of full profile analysis performed by means MAUD software [3]. The details of the full profile analysis as well as an estimation of the averaged crystalline size within isotropic and anisotropic model for crystalline shape can be found in ref. [2], while the analysis of FTIR data has been performed based on fingerprint features of UiO-66 and MIL-140A MOFs earlier reported in the literature [4,5,6]. The obtained results are summarized in Table 1.

Table 1. Molar ratio of precursors and phase compositions obtained according to XRD and FTIR data.



Sample name	The molar ratio of components					Phase composition	
	DMF	$ZrCl_4$	BDC	H_2O	AA	XRD	FTIR
1:2:3	300	1	2	3	–	58.4%UiO-66 + 41.6%am.ph.	UiO-66
1:2:3 AA	300	1	2	3	10	66.8%MIL-140A + 33.2%UiO-66	MIL-140A + UiO-66
1:2:0	300	1	2	0	–	61.5%MIL-140A + 38.5% am.ph.	MIL-140A
1:2:0 AA	300	1	2	0	10	100%MIL-140A	MIL-140A
1:1:3	300	1	1	3	–	am.ph.	UiO-66
1:1:3 AA	300	1	1	3	10	amorphous + MIL-140A	UiO-66 + MIL-140A
1:1:0	300	1	1	0	–	amorphous + MIL-140A	MIL-140A
1:1:0 AA	300	1	1	0	10	100%MIL-140A	MIL-140A

In overall full profile XRD analysis confirm that at 200 ºC fast MW heat transfer obstructs formation of high symmetric UiO-66 phase, while MIL-140A constructed from Zr-O chains do not need any particular nuclei for crystal growth and can be willingly crystallized under investigated conditions. Moreover, addition of acetic acid (AA) enhances the observed trend due to efficient adsorption of MW irradiation. MW synthesis and AA additive lead to the predominant formation of MIL-140A phase with high crystallinity and specific surface area. XRD based findings have been further qualitatively confirmed by FTIR. Due to the presence of not negligible contribution from amorphous fraction in few synthesized samples, in addition to short-range order probed by FTIR spectroscopy from the linker side, Zr K-edge XAS were aimed to trace different local environment of the metal sites in SBUs of UiO-66/MIL-140A being able to account for the contributions both from crystalline and amorphous phases. Indeed, FT-EXAFS analysis allows to get some useful insights, particularly providing an estimation of the contribution from the UiO-66/MIL-140A amorphous parts. Moreover, comparison of the experimental XANES collected for the sample representatives of UiO-66/MIL-140A morphologies accompanied by XANES simulations allowed to derive some structure-driven modifications in the XANES region. This finding can be useful for the analysis of local atomic arrangement in SBUs in the amorphized components or for monitoring the synthesis process by means *in situ* XAS experiment.

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Extra-framework zirconium clusters in MOF DUT-67 controlled by the choice of the metal precursor

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DUT-67, where DUT stands for the Dresden University of Technology, is a more recent addition to the family of Zr-MOFs, with composition $Zr_6O_8\ (TDC)_4\ (OAc)_2\ 2H^+$, where TDC is 2,5-thiophenedicarboxylate and OAc is a carboxylic acid. The structure of DUT-67 is formed by 8-connected Zr_6-clusters $[Zr_6(\mu_3\text{-}O)_6(\mu_3\text{-}OH)_2]^{10+}$ bridged by TDC linkers in **reo** topology [1]. The DUT-67 structure, in the $Fm\bar{3}m$ (225) space group, presents two large microporous cavities: an octahedral cavity a cubo-octahedral cavity. Catalytic metal active sites can be introduced in DUT-67 via impregnation [2]. The improvement of the environmental impact and the scalability of Zr-MOF syntheses has received wide attention, notably implying microwave heating in an aqueous solvent and continuous synthesis in microfluidic systems [3] [4]. In this context of growing interest, virtually no attention has been given to the nature and formation of EFCs, despite their potential relevance for the properties of the materials, from the porosity to the affinity for adsorbed species in separation and catalysis processes. In a first attempt to assess the variability of EFCs in Zr-based MOFs as a function of the preparation conditions, the present study is focused on the assessment of the nature of EFCs formed in DUT-67 synthesized from different metal precursors in the presence of a formic acid modulator. DUT-67 MOFs have been synthesized in the presence of formic acid from different zirconium precursors and the EFCs formed have been characterized by X-ray diffraction. Rietveld structure refinement has permitted to localize inside the microporosity zirconium and oxygen atoms of extraframework clusters (EFCs), whose conformation depended on the nature of the zirconium precursor. Dissolution-condensation processes of $ZrCl_4$ and $ZrOCl_2$ during the synthesis gave rise to Zr_6 EFCs in one every six cuboctahedral pores. Less numerous zirconia-like Zr_{12} oxo-clusters were formed from Zr isopropylate, whereas characteristic Zr_8 nitro-clusters were formed from Zr oxonitrate.

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Hierarchical Iron-Nitrogen-Carbon Nanostructured Electrocatalysts for Oxygen Reduction Reaction

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COFs (covalent organic frameworks) are organic polymers known for their great surface area making them strategic materials in applications such as catalysis, chemical separation, and gas storage.[1] Tuning synthesis parameters allowed obtaining different structures and morphology leading to extraordinary electrocatalytic performance and stability toward oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). In this context, the preparation of carbonaceous systems with nitrogen atoms that coordinate metals, such as iron (Fe-N-C), with high catalytic performance is fundamental to achieve new generation energy systems.[2,3]

In this work the synthesis of a class of COFs with a 3D spherical hierarchical structure has been developed and optimized. The synthesis takes place through the polymerization reaction of two monomers, such as phenol (P) and melamine (M), followed by hydrothermal treatment. During this process, a soft template, Pluronic F127 (F127), is added to modulate the microporosity [4]. After that, the phenolic resin has been impregnated with different amount of iron and pyrolyzed at 900 °C in NH_3 atmosphere. Changing the mass ratio of P, M and F127, nanostructured samples with different morphologies have been obtained (Figure 1a,1b and 1c). The prepared materials showed a large specific surface area (around 850-1100 m^2/g) and hierarchical porosities composed of mesopores and micropores. Furthermore, due to its structure, chemical composition, porous structure and high specific surface area, these materials exhibited a good electrocatalytic performance and stability toward ORR in alkaline electrolyte, with an onset and half-wave potential of 1.087 V and 1.016 V vs RHE, respectively, which are comparable to commercial Pt/C catalyst.

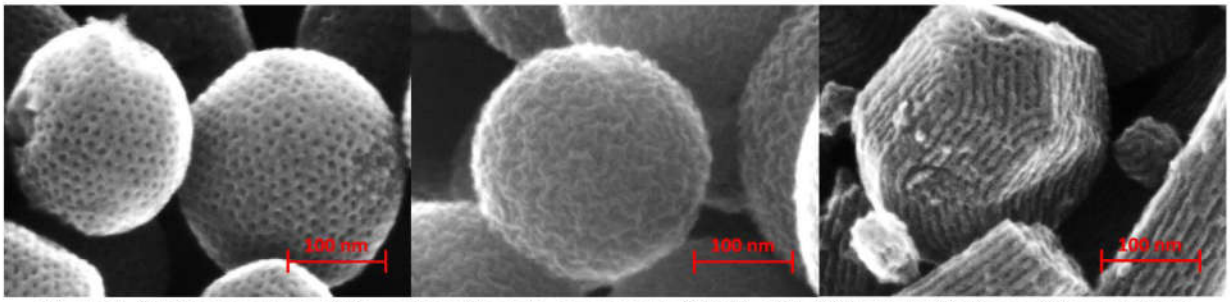

Figure 1. SEM comparison of three phenolic resin compounds (PMR) with different synthetic conditions a) PMR homogeneously distributed micropores; b) PMR without micropores and c) PMR asymmetric structure with pores and linear grooves.

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STUDY OF THE BENZENE/CYCLOHEXANE SORPTION BEHAVIOR OF IMINE-BASED COFs

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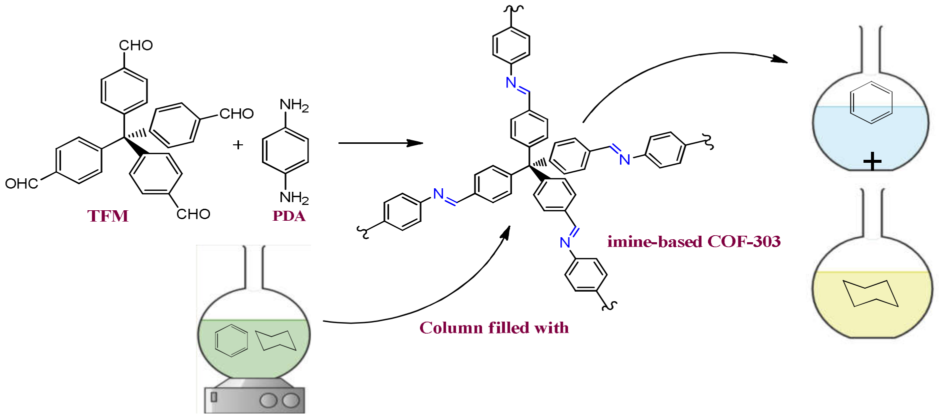
COFs (Covalent Organic Frameworks) represent a new and interesting class of porous crystalline materials with a wide range of potential applications[1] including catalysis, separations and gas storage. These materials, which are built up through covalent connections among light elements (e.g. C, H, Si, N), present different structures, types of channels and properties depending on the organic building blocks used in their synthesis.[2]



In this communication, we present a preliminary study of the benzene/cyclohexane sorption behavior of four different imine-based COFs (COFs-300, 303, LZU-111 and its carbon analog),[3] which highlighted a high adsorption capacity for these gases. These COFs are composed by the combination of tetrahedral-tetrahedral or tetrahedral-linear aromatic building blocks connected through a condensation of amine and aldehyde groups (imine bond). Thanks to the high density of aromatic rings in their structures, they should exhibit more affinity for benzene than for cyclohexane. Our aim is to take advantage this useful property to properly separate benzene/cyclohexane mixtures.

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PHOTORESPONSIVE METAL-ORGANIC ROTAXANE FRAMEWORKS

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The use of rotaxanes as ligands for the preparation of metal-organic frameworks (MOFs) leads to materials that combine mechanically interlocked molecules chemistry and reticular chemistry. By incorporating the intertwined structures into these structures, the Brownian motion of the components in solution is restricted, which could facilitate the motion switching.[1]

The incorporation of rotaxanes into MOFs has allowed to study the large amplitude motions of the interlocked components at the solid state, including rotational[2] and translational motion.[3]

Herein, the preparation of MOFs using interlocked fumaramide and maleamide bearing carboxylic acid groups at macrocyclic positions as organic ligands, and copper(II) as metal node.[4] The difference in the configuration of the photoactive olefinic thread afforded materials with different porosities. These functional materials operate as photoresponsive molecular dispensers of quinone derivatives, taking advantage of the changes that the photoisomerization of the thread cause in the properties of these MOFs.

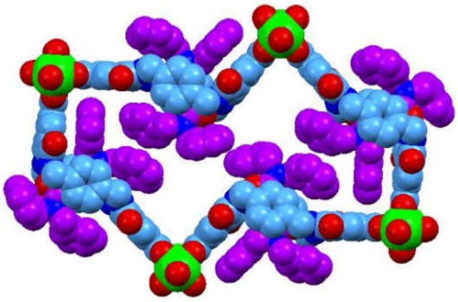

Figure 1. Spacefill representation of a 2-periodic *sql* net in an interlocked fumaramide-based MOF.

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The Hydrolytic Activity of Bimetallic Zr/Ce-MOF-808 Nanozymes Towards Peptides

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Metal Organic Frameworks (MOFs), which are formed of metal-oxo clusters bound by organic linker molecules are proving to be a very promising new class of catalytic material. MOFs show potential for site specific catalysis of various substrates through targeted design and many, such as Zr-UiO-66 show exceptional thermal and chemical stability, as well as being reusable for many catalytic cycles. We have previously demonstrated that a selection of Zr-MOFs (NU-1000, UiO-66 and MOF-808) show superior activity as artificial proteases.[1–3] For example, Zr-MOF-808 reduces the half-life of the peptide bond in a simple dipeptide from 600 years in nature, to just 0.72 h. As cerium salts have been shown to be more efficient at hydrolyzing peptide bonds that zirconium salts, by incorporating cerium into the MOF-808 structure the MOF is expected to also increase in activity towards peptide bond hydrolysis.[4]

Through a detailed experimental and computational study, we present the effect of incorporating cerium into the Zr_6 metal clusters in MOF-808, on the hydrolytic performance of the materials toward simple peptides. The series of MOF-808 containing 0-69% cerium in place of zirconium showed moderate reactivity towards peptide bond hydrolysis but revealed the significant effect of the presence of cerium on the interaction of the dipeptide substrate and MOF. Supported by computations, the increase in cerium reduces this interaction, and indeed, hinders the reactivity of the MOF due to unfavorable interactions between MOF and substrate. However, the presence of small amounts of cerium shows a positive effect on the reactivity as a balance between the strongly favorable interaction of Zr and dipeptide is balanced by the unfavorable interaction with Ce.

Additionally, we also show that the presence of small amounts of cerium in the synthesis promoted formation of highly crystalline MOF materials, with large surface areas, during very short synthesis times. Therefore, in this work we demonstrate a two-fold benefit to incorporating small amounts of cerium into the synthesis of hydrolytically active MOF-808.

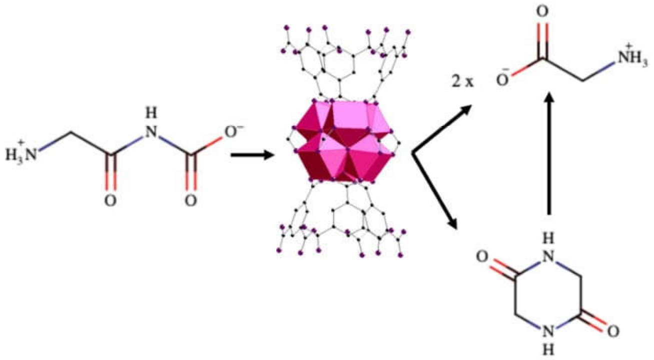

Figure 1. Hydrolysis of the simple dipeptide glycylglycine to glycine and cyclic glycylglycine in the presence of MOF-808 (pink polyhedra = M)

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IMPACT OF PORE SIZE AND DEFECTS ON NICKEL(II)-PYRAZOLATE BASED MOFs

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C_2H_2/CO_2 separation is a highly challenging process due to their similar physicochemical properties. It has recently been shown that acetylene can selectively interact with alkyne residues located on the pore walls of metal-organic frameworks, leading to enhanced gas separation.[1] Taking into account these premises, we have selected two isoreticular robust Ni-fcu pyrazolate-based MOFs[2], $[Ni_8(L_4)_6]$ and $[[Ni_8(L_5)_6]$ containing a high concentration of alkyne residues on the organic linker backbone defining their pore structure [Figure 1][3].

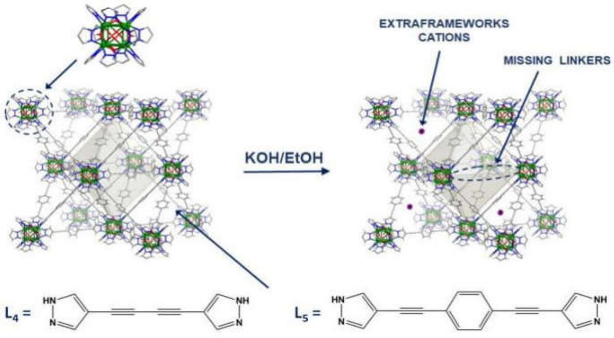

Figure 1. Schematic representation of post-synthetic treatment with KOH to yield defective materials.

Noteworthy, these systems are amenable to further pore surface tuning by post-synthetic modification with KOH ethanolic solutions.[4] This treatment leads to enhanced acidic gas adsorption as a consequence of missing linkers defects, incorporation of extraframework K^+ ions and basification of the $[Ni_8(OH)_6]$ metal clusters. We have investigated the impact of these structural features on the separation of C_2H_2/CO_2 gas mixtures by a combination of static gas sorption techniques, dynamic pulse gas chromatography, breakthrough experiments and computational modelling. The results have revealed high adsorption capacity and selectivity for C_2H_2 over CO_2 gas molecules on the $[Ni_8(L_4)_6]$ and $[Ni_8(L_5)_6]$ systems which can be attributed to the selective interactions of the adsorbate molecules with metal cluster hydroxide, aromatic and alkyne residues and extraframework within the structure [Figure 2]. All these results exemplify the high impact of targeted functionalization of MOFs for specific adsorption properties, as well as highlight the importance of post-synthetic modification leading to the creation of defects to further fine tune the adsorptive properties of this class of robust MOF materials.

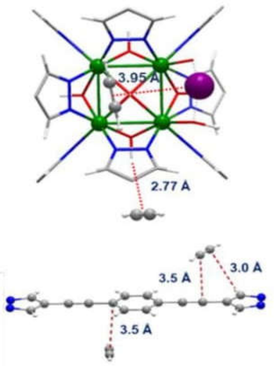

Figure 2. C_2H_2 interaction with $[Ni_8(L_5)_6]$ framework.

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TOWARDS ENHANCING CATALYTIC ACTIVITY – FROM 3D MOF TO 2D NANOSHEETS

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In recent years, Metal-Organic Nanosheets (MONs) have attracted increasing scientific interest due to their remarkable features combining all significant properties of MOFs and nanostructures. Up to date, various synthetic strategies of delamination processes were investigated using as starting material layered Metal-Organic Frameworks (MOFs) materials[1]. One of the examples of those materials are MOFs which contain *paddlewheel* secondary building unit (SBU) and were proved to easily undergo post-synthetic modification, i. e. using SALE technique[2]. Thanks to their unique MONs can find many potential applications, one of which could be catalysis[3]. Moreover, the improved accessibility of inorganic nodes in obtained monolayers can enhance the catalytic activity of those material in comparison with the bulk MOFs[4].

The aim of this work was to study the intercalation and exfoliation processes on the model *paddlewheel*-type MOF, $[Zn_2(TBAPy)(H_2O)_2]$, incorpsing the Zn nodes and $TBAPy^{4-}$ linkers[5]. We probed the possibility to coordinate various alkyl-DABCO ligands to metal centers of the material. As a result we obtained intercalated material $[Zn_2(TBAPy)(RDABCO^{+}I^{-})_2]$. In the next step, we investigated exfoliation process of this material. The efficiency of intercalation and exfoliation processes was monitored with various analytical techniques, including SEM, ^{1}H NMR, PXRD and DRIFT analysis. The presence of both Lewis acid sites and tetraalkylammonium halides moieties in resulting material prompted us to further challenge it as a bifunctional catalytic system for cyclic carbonate formation. As a result, the material exhibited high catalytic activity in cycloaddition of CO_2 to selected epoxides in mild reaction conditions.

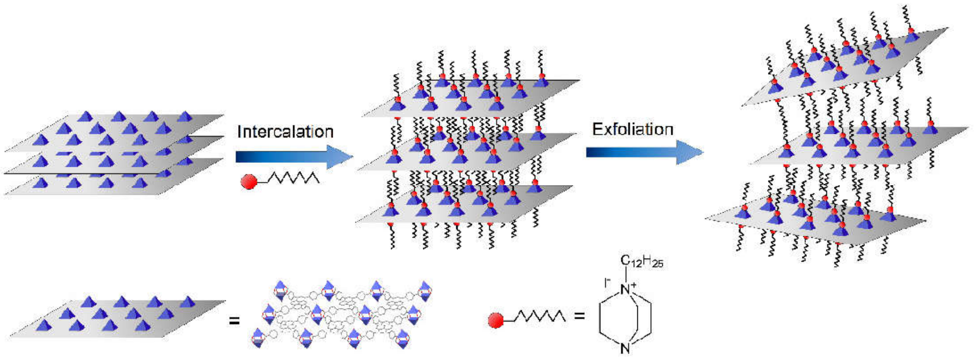

Figure 1. Schematic representation of the proposed strategy of the metal-organic nanosheets (MONs) preparation.

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INCORPORATING PENDANT SULFONIC ACID GROUPS INTO METAL-ORGANIC FRAMEWORKS USING SULFONYL CHLORIDE DERIVATIVES OF 4,4'-OXYBISBENZOIC ACID

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Metal-organic frameworks are porous materials, which can be proton conductors. Good proton conducting MOFs should have Brønsted acid moieties that are essential elements of a conduction pathway. One of such moieties are sulfonic acid groups which, however, show strong coordination ability, thus their intact incorporation into a framework is difficult.[1],[2] Sulfonic acid groups can be inserted into frameworks by post-synthetic modifications,[3] but such a treatment is typically energy consuming, generates extra waste and requires harsh conditions.

Here, we present a strategy that relies on incorporating pendant sulfonic groups by using sulfonyl chloride precursors of organic linkers (Fig. 1a).

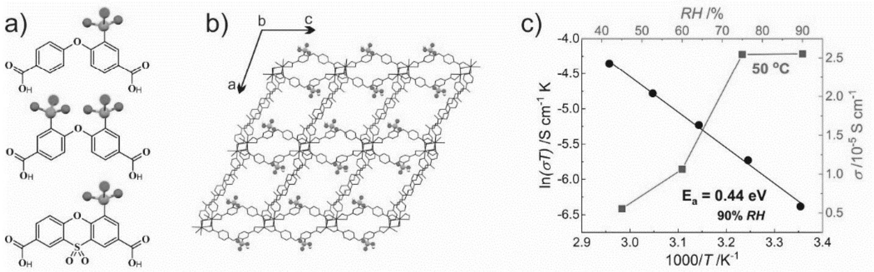

Figure 1. a) Linkers used for synthesis of MOFs with pendant SO_3H groups, b) crystal structure of JUK-13-SO3H, c) proton conductivity of JUK-13-SO3H.

In order to synthesize new metal-organic frameworks with uncoordinated sulfonic groups, three sulfonyl chloride derivatives of 4,4'-oxybis(benzoic acid) were prepared. Metals selected for exploration are lanthanides, zirconium and cadmium.

A new MOF (JUK-13-SO3H, Fig, 1b) is representative of the strategy. It was obtained by concerted deprotonation-metalation-hydrolysis reaction.[4] This coordination polymer contains a sulfonated linker, a diacylhydrazone as a colinker and is capable of proton conduction according to the Grotthuss mechanism and achieves its maximum conductivity values on the order of 10^{-5} S·cm^{-1}, (Fig. 1c).

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SiO_2@FLEXIBLE MOFs: THE ROLE OF FUNCTIONALIZED LINKERS, HETEROGENEITY AND DEFECTS

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Flexible metal–organic frameworks (MOFs) can present large structural flexibility as a result of different stimuli (temperature, gas pressure variation, *etc.*)[1], which can lead both to interesting properties and applications of technological relevance[2]. Most of the work on "breathing" MOFs is related to gas-storage and selective adsorption/separation applications[3]; however, only in recent years it was recognized that the flexibility of MOFs may influence the efficacy of catalytic reactions[4]. In this regard, it has been shown that encapsulation of nanoparticles (NPs) into porous MOFs can lead to enhanced stability and selectivity in catalysis. Most of the recent studies, however, are focused on the effect of NPs encapsulation on rigid MOFs, ignoring the possible role of structural flexibility in this process[5]. It is indeed true that embedding of NPs into a porous framework can lead to the modification of the rigid/flexible behavior of the crystal structure and to the generation of structural defects[6]. Since the mechanical and flexible properties of these porous materials are deeply related to the concentration, size regime and type of defects, understanding the connection between flexibility, disorder and defects is of great importance for the design of superior materials for catalytic applications.

In this study a series of flexible pillared-layered MOFs of formula: $Zn_2(fu\text{-}bdc)_2(P)$ ($fu\text{-}bdc^{2-}$ = functionalized 1,4-benzene di-carboxylate; P = dabco or bipy) is presented[7], in which fluorescent silica NPs were embedded. It is well known that this MOF family, undergoes to guest- and temperature-induced reversible phase transitions between a narrow pore (*np*) and a large pore (*lp*) form[8]. Here, the fluorescent silica NPs represent the "heterogeneity" of the system and the result is a group of NPs@MOFs hybrid materials.

This work is indeed focused on the deep understanding of the difference in flexibility/responsivity of the parent flexible MOFs with the hybridized NPs@MOFs through their detailed characterization, to gain a deeper understanding of their mechanical, chemical and structural properties.

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UPGRADING VITAMIN BASED METAL-ORGANIC FRAMEWORKS

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Bioapplications are an emerging field of metal-organic frameworks' (MOF) utilization. In the design of bioMOF systems, biocompatibility of the frameworks constituents is required[1,2]. Herein we present the first example of a Zn(II) bioMOF based on vitamin C as a sole ligand (bioNICS-1 – National Institute of Chemistry Slovenia), with a unique three-dimensional chiral framework. Inorganic building unit of bioNICS-1 has a diverse Zn(II) coordination geometry forming an infinite 3-dimensional building unit bridged through ascorbate ligands, resulting in permanently microporous framework, with a BET surface area of 552 m^2/g.

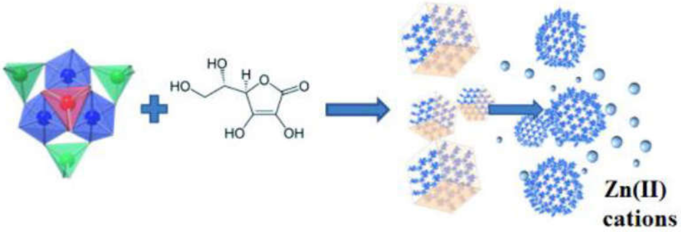

Figure 1. A graphical representation of thebioNICS-1 components and degradation process.

Comprehensive tests of structure stability in aqueous media at different pH values (3.5, 7.4 and 9) were performed in static and dynamic conditions demonstrating high resistivity of the framework, retaining up to 68% of its parent specific surface area within 24 hours of exposure. Furthermore, slow degradation process confirmed by kinetic studies enables controllable release of bioactive components rating the bioNICS-1 as an excellent candidate for creating a small drug molecule delivery system, which was demonstrated by a successful loading and release of urea.

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BIS(PYRAZOLATO)-BASED METAL-ORGANIC FRAMEWORKS OF COPPER(II) AND ZINC(II) DISPLAY ANTIMICROBIAL ACTIVITY

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In recent years pathogens are becoming resistant towards large use antibiotics, thus creating increasing difficulties in the treatment of infections. Research is increasingly moving towards the development of new antimicrobial agents that act through mechanisms other than those of widely used antibiotics.[1] In this regard, metal-organic frameworks (MOFs) have shown to be successfully employed as antimicrobial materials for food, medical, and environmental fields. They are hybrid porous materials with uniform structures, high specific surface area and tunable physical and chemical properties. MOFs can also act as antimicrobial agents by releasing metal ions, such as Ag(I), Cu(II), Co(II), and Zn(II), or by oxidizing the protein and fatty acids on the bacterial membranes without the release of metal ions.[2] Moreover, MOFs nanoparticles with suitable size can cross the bacterial cell membranes resulting in their destruction. Starting from this assumption, we have decided to investigate the antibacterial activity of copper and zinc MOFs based on different bis(pyrazolyl)-tagged ligands such as $[M(BPZ)]_n$ (M = Zn(II), Cu(II), H_2BPZ = 4,4′-bipyrazole),[3] $[M(BPZ\text{-}NH_2)]_n$ (M = Zn(II), Cu(II); H_2BPZNH_2 = 3-amino-4,4’-bipyrazole)[4] and $[Zn(Me_4BPZPh)]$, $[Cu_2(Me_4BPZPh)]$ (H_2Me_4BPZPh = bis-4′-(3′,5′-dimethyl)-pyrazolylbenzene)^5 (Figure 1). Their antimicrobial activity has been be tested against Gram-negative (*P.s aeruginosa*, *E. coli*), Gram-positive (*S. aureus*) bacteria and also against fungi (*C. albicans*), as representative agents of infections.

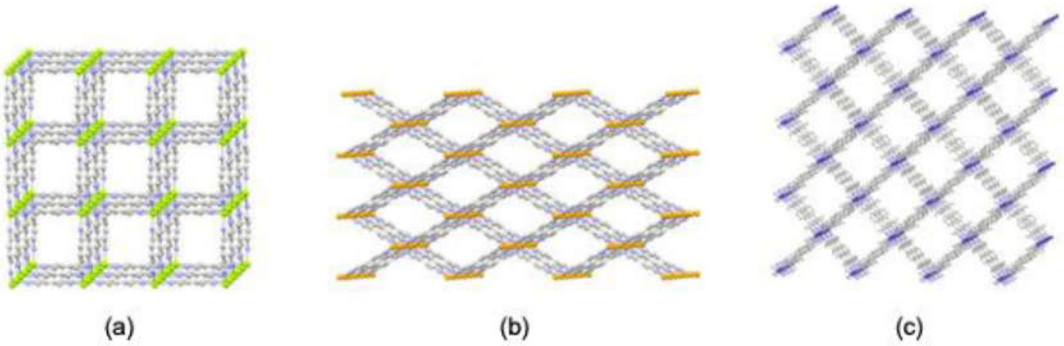

Figure 1 Representation of the crystal structure of (a) [Zn(BPZ)]n (b) [Cu(BPZ)]n and (c) [Zn(Me4BPZPh)].

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CO ADSORPTION-INDUCED SPIN TRANSITION IN MOFS WITH UNSATURATED Fe^{2+} SITES

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Metal–organic frameworks are a class of permanently porous materials exhibiting impressive chemical tunability and high internal surface areas.[1] An important subset of MOFs features high densities of exposed metal cation sites that typically act as Lewis acids, able to accept electron density from easily polarized gas molecules, such as CO2.[2] This electrostatic interaction is at the basis for a wide variety of potential applications in gas storage and separations.[3] Moreover, MOFs featuring π-donating exposed metal sites acids can display unprecedented selectivity in separations with gas molecules that can behave as π-acids, such as CO and other small molecules with low-lying π* orbitals. Exceptional adsorption performances have been indeed observed in MOFs with coordinatively unsaturated Fe^{2+} sites that undergo a transition from high to low spin upon binding CO. The framework Fe-BTTri (H_3BTTri = 1,3,5-tris(1H-1,2,3-triazol-5-yl)benzene) exhibits extremely steep yet reversible CO uptake.[3] Moreover, a cooperative spin transition mechanism for CO uptake on Fe^{2+} sites has been reported for Fe_2Cl_2(btdd) (H_2btdd = bis(1H-1,2,3-triazolo[4,5-b],[4′,5′-i])dibenzo[1,4]dioxin).[4] In this contribution we report our work on the characterization of these adsorption processes with X-ray absorption spectroscopy (XAS) experiments in operando conditions (Figure 1). These experiments are able to provide a direct and highly sensitive measure of the electronic processes behind the CO adsorption induced spin transition, providing valuable electronic structure details about the underlying mechanism.

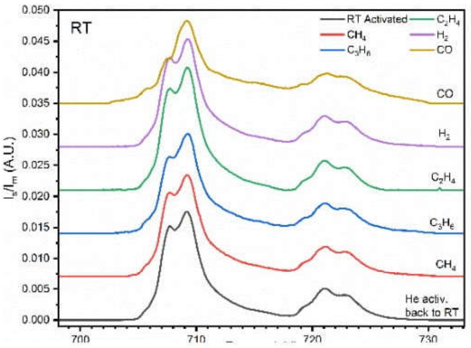

Figure 1. Fe $L_{2,3}$-edge spectra for FeBTTri under different gas atmosphere, showing the CO-induced spin-transition (orange line)

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UNDERSTANDING THE IMPACT OF THE CRYSTALLIZATION MECHANISM ON A BIMETAL METAL-ORGANIC FRAMEWORK FAMILY

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Over the past decades, in the quest for innovative multifunctional materials, the attention has gravitated towards metal-organic frameworks[1] (MOFs) due to their hallmark features: robust crystalline structure, tailored permanent intrinsic porosity and versatile chemical composition. These features make them widely used in many applications, such as adsorption or catalysis,[2] and they depend to a large extent on the metal ions of the MOF. When incorporating various metal ions into a framework, its properties are enhanced; however this field still remains fairly unexplored as monometallic MOFs have gathered more attention.

In previous reports of our group, we found that an initial metal combination can result in the formation of different atomic sequences within the same SBU, and the crystallization mechanism of the material can also be altered depending on the metals it contains.[4,5] Bearing this in mind, we carried out a study of an array of factors that lead to the formation of different types of atomic sequences in a multimetal MOF family with a rod-shaped SBU, with the idea of achieving a higher control over the distribution of the metal atoms. Firstly, after analyzing different initial combinations and different ratios of lanthanides, we found that the topology of the MOF is not altered in none of the cases, however some cations have a prevailing effect on the crystallization mechanism, and therefore on the morphology of the crystals and the atomic distribution within the SBU. Furthermore, this competitive crystallization mechanism gives different outputs when tested in a slightly different reaction media or with extended reaction times.

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EVALUATING THE ROLE OF PORE PLASTICITY IN BENZENE/CYCLOHEXANE SEPARATION BY Zr^{IV} MOPS AND MOFS

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One of the challenging separation processes in the future hydrogen economy is the resolution of benzene (BEN) / cyclohexane (CH) mixtures. Liquid organic hydrogen carriers (LOHCs) can be used for hydrogen storage and release through hydrogenation-dehydrogenation cycles.[1] After the catalytic hydrogenation process, the unreacted aromatic hydrocarbons must be removed to recover pure aliphatic hydrocarbons.

Since BEN and CH possess similar physical properties [T_b(BEN) = 350 K vs T_b(CH) = 351 K], energetically costly distillation processes are used for their selective separation. The use of porous materials as shape-selective molecular sieves is less energy demanding but require an optimal balance between selectivity and diffusion kinetics. In this work, we evaluated how the framework stiffness and pore size in porous materials affect the molecular diffusivity and the efficiency of the separation process.

Two systems were investigated: *i)* novel isoreticular Zr^{IV} metal organic polyhedra (MOPs),[2] as examples of soft and processable porous materials, and *ii)* Zr^{IV} metal-organic frameworks (MOFs) of the UiO family,[3] as structurally related extended and stiff porous networks. Linkers of different length were employed to unveil the impact of pore size and framework rigidity on guest dynamics.

Experimental and computational studies were carried out to evaluate the vapor-solid interactions, as well as the dynamics and efficiency of the BEN *vs* CH separation process. Static vapor adsorption isotherms and dynamic adsorption breakthrough curve experiments, to quantify the adsorption capacity and the separation efficiency, were coupled to powder X-ray diffraction and molecular dynamics simulations, to locate the adsorbate in the loaded systems. Thanks to this multi-technique approach, the preferential adsorption sites and molecular dynamics of the adsorbed molecules in both soft-pore materials (MOPs) and rigid-framework materials (MOFs), as well as the impact of pore plasticity and size on the ambient temperature efficiency of the title separation process, were unveiled.

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Metal influence on the gate opening in zeolitic imidazolate frameworks

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The pressure-induced rotation of the imidazolate in Zeolitic Imidazolate Frameworks (ZIFs) is accompanied by an increase of ZIF pore openings, affecting ZIFs performance in separation processes. This phenomenon is known as the gate opening or the swing effect [1,2].

We show by using periodic Kohn-Sham density functional calculations that metal substitution (Mg, Fe, and Zn) is a very effective way to tune the flexibility of ZIF-8 materials. For both the magnesium- and the iron-based system the gate opening phenomenon requires half and a fourth of the energy than for the zinc material, respectively [3]. The metal determines also the most stable phase of the material. Because of the importance of ZIF-8 among porous materials and because the gate opening is its most studied property, our results strongly call for future high-pressure diffraction studies aimed at the experimental verification of the present findings.

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DESIGNING MAGNETIC FRAMEWORK COMPOSITES FOR CARBON CAPTURE

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Rising carbon dioxide (CO_2) concentrations in our atmosphere due to human activity is well known to have strongly negative implications for the environment and our society.[1] An effective action to decrease emissions is to capture the CO_2 from its largest sources, power plants, preventing it from entering the atmosphere. However, the current aqueous amine absorption/scrubbing technologies have very high energy requirements for regenerating the absorbent and separating CO_2, increasing a power plant's energy demand by 25-40%. This equates to an increase in electricity cost of $0.06 per KWh.[2]

Metal-organic frameworks (MOFs) are porous lattices of metal ions/clusters connected by organic linkers. MOFs are excellent materials for carbon capture due to their tunable structures and properties and high porosities, resulting in very high capacities and selectivities for CO_2.[3] Despite this, CO_2 regeneration can be challenging at scale due to their thermally insulating natures. Our work seeks to develop composites of the highest performing MOFs for carbon capture and magnetic materials to enable rapid and highly energy efficient CO_2 regeneration by localized induction heating.[4] The magnetic materials investigated are porous and non-porous microspheres prepared from our novel flame-spheroidisation process.[5] In addition to providing the magnetic property benefits, the microspheres may also form hierarchical porosity with the MOFs, improving mass transfer rates for CO_2 through the composite material.

In this presentation, we discuss the synthesis and characterization of the porous and non-porous microspheres, including surface functionalisation and induction heating studies. The synthesis and characterization of some of the highest performing MOFs reported for post-combustion CO_2 capture will also be presented. We then look at how these promising early results pave the way for various experimental studies to form magnetic framework composites with leading profiles and processing capabilities for capturing CO_2 before it enters the atmosphere.

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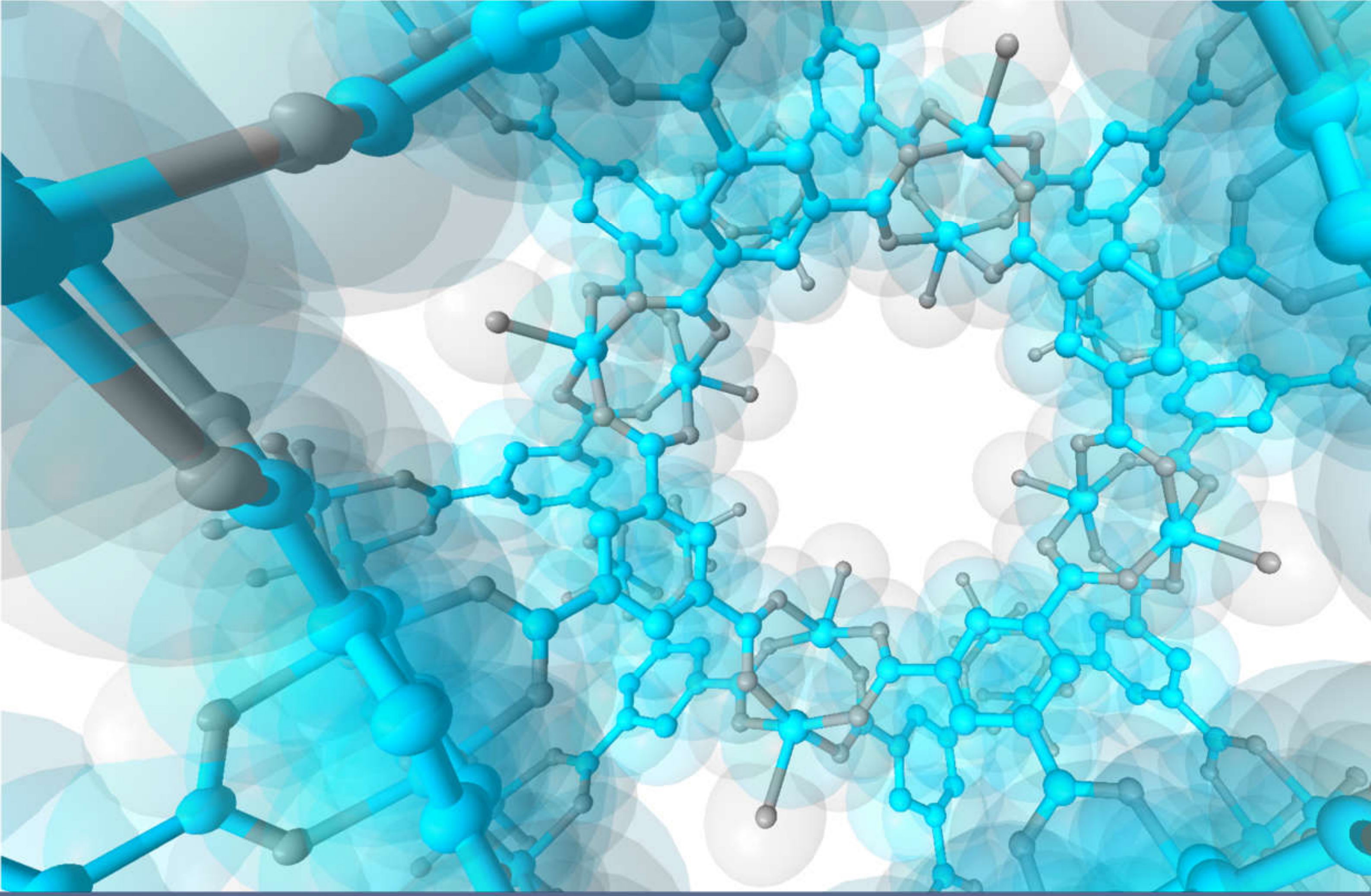

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