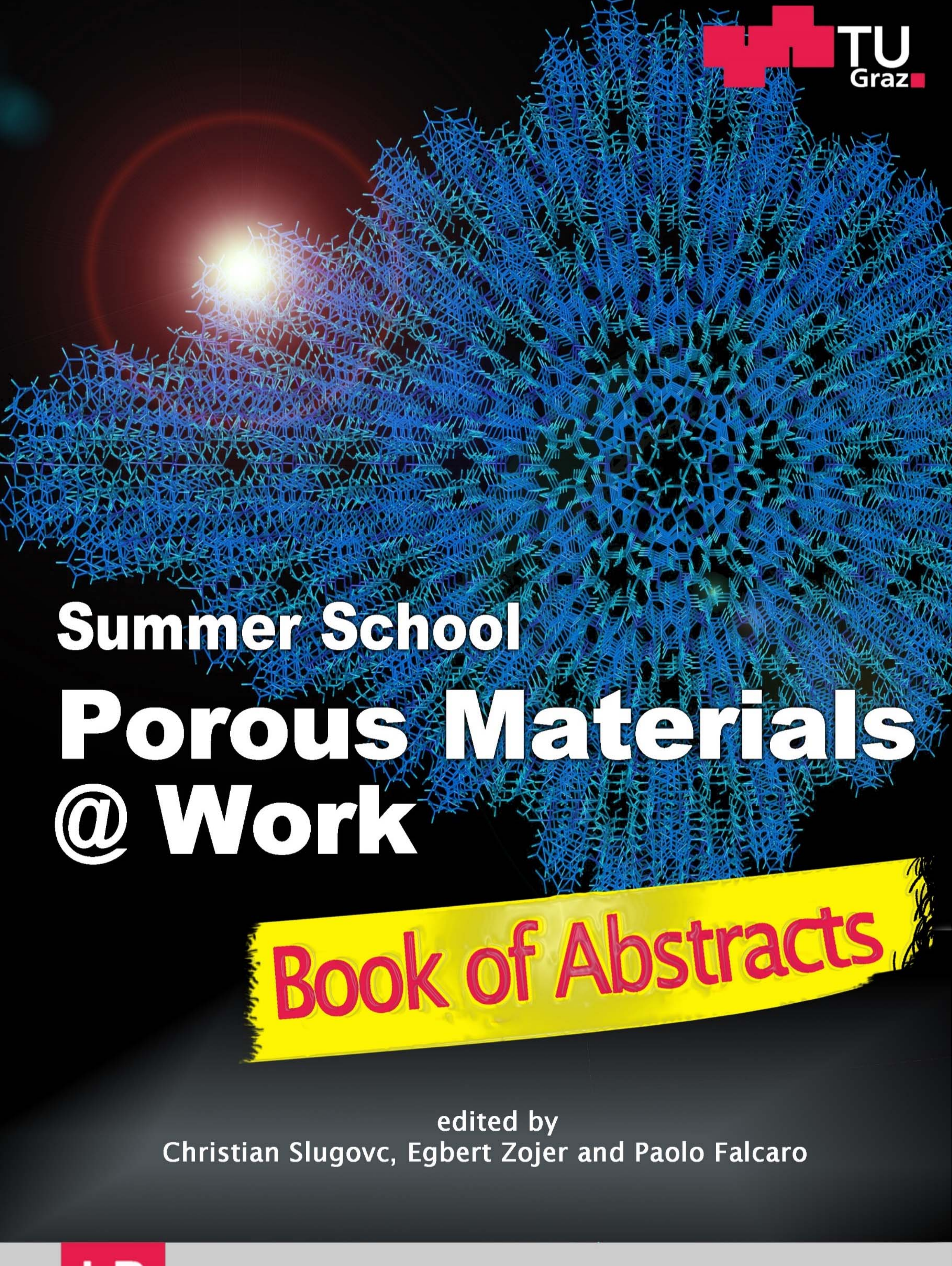

Summer School

Porous Materials @ Work

Book of Abstracts

edited by
Christian Slugovc, Egbert Zojer and Paolo Falcaro

LP 03
Leadproject initiative of
Graz University of Technology

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Foreword

Nano- and micro-porous materials are technologically relevant solids as they offer unique properties with respect to their denser counterparts. However, the successful integration of nano- and micro-porous materials as functional components of real-world systems requires precise control of the physical form of the material across all dimensions. Despite the advances that have been made over a short period of time, there are common challenges faced by the community to bring materials with exceptional properties from the lab bench to real devices.

This summer school covers diverse aspects of chemistry and materials science ranging across synthesis, modelling, processing, characterization and applications of nano- and micro-porous materials.

Internationally renowned leading experts in the field of porous materials will discuss preparation protocols for the fabrication of porous films, patterns, monoliths and composites. The class of materials that will be examined are Metal-Organic Frameworks (MOFs), Metal-Organic Polyhedra (MOPs) and mesoporous materials prepared via the Sol-Gel method. Recent progress in the applications of porous materials from thermoelectric MOF-based devices to microelectronics will be illustrated. Their physical, structural and chemical characteristics will also be discussed.

This educational event will provide necessary skills for researchers interested in the application of porous materials, their design and synthesis. Learning about the current research directions discussed by participants of all levels can concurrently identify trends in problem solving and facilitate future scientific collaborations.

More than 55 participants from different institutions in Japan, Spain, Italy, France, Germany, Belgium, Czech Republic, Slovenia, Poland, Croatia and Austria have registered for this summer school. The invited speakers have been asked to present lectures on cutting edge research on porous materials to inspire all participants about their research directions. Each participant has the opportunity to give either an oral or a poster presentation.

Finally, we acknowledge TU Graz for supporting this initiative (LP-03).

Paolo Falcaro, Christian Slugovc and Egbert Zojer

Timetable

	Mon. 16.9.	Tue. 17.9.	Wed. 18.9.	Thu. 19.9.
09:00		Lisa Vaccari	Rob Ameloot	Natalia Bedoya-Martinez
09:20				
09:40				
10:00		Michal Bláha	Marianne Kraeuter	E. Vakalopoulou
10:20		Coffee	Coffee	Coffee
10:40				
11:00		Rocio Semino	Nicola Hüsing	Raffaele Ricco
11:20				
11:40				Miriam de J. Velásquez-Hernández
12:00		Sandro Wieser	Lunch	
12:20		Lunch	Excursion	Lunch
12:40				
13:00	Welcome			
13:20	Shuhei Furukawa	Christof Wöll		Sebastijan Kovačič
13:40				
14:00				
14:20	Hidetsugu Shiozawaa	Christoph Gadermaier		Francesco Carraro
14:40				
15:00	Coffee	Coffee		
15:20				Farewell
15:40	Vincent Guillerm	Engelbert Redel		
16:00				
16:20				
16:40	Poster short talks	Alexander Knebel		
17:00		Coffee		
17:20	Poster session	Carlos Martí-Gastaldo		
17:40				
18:00				
18:20				
18:40			Dinner	
19:00				

🟥 invited lecture & tutorial
🟨 topical lecture
🟦 oral presentation
🟩 poster presentation

Programme

Monday, September 16, 201

	13:00- 13:20	Welcome
Paolo Falcaro	13:20- 14:20	**Functionally gradient porous soft materials** Alexandre Legrand Gavin Craig, Mickaele Bonneau, Shuhei Furukawa *Kyoto University, Japan*
	14:20- 15:00	**Molecular doping of Metal-Organic Frameworks** Shiraz Ahmed Siddiqui,[a] Michal Bláha,[b] Hidetsugu Shiozawaa,[b] [a] *University of Vienna, Austria;* [b] *Czech Academy of Sciences, Czech Republic*
	15:00- 15:40	Coffee
Roland Resel	15:40- 16:40	**Geometry mismatch & reticular chemistry for the assembly of Metal-Organic Frameworks** Vincent Guillerm,[a] Borja Ortín-Rubio,a Hosein Ghasempour,[a] Thais Grancha,[a] Inhar Imaz and Daniel Maspoch[a,b] [a] *ICN2, CSIC and The Barcelona Institute of Science and Technology,* [b] *ICREA, Spain*
	16:40- 17:20	Poster - short presentations
	17:20- 19:00	Posters session & snacks

Tuesday, September 17, 2019 - Morning Session

Heinz Amenitsch	9:00 - 10:00	**FTIR spectroscopy, microscopy and imaging for porous material chemical characterization** Lisa Vaccari,[a] Giovanni Birarda[a] *Elettra Sincrotrone Trieste, Italy*
	10:00-10:20	**Raman spectroscopic investigation of M-MOF-74 doped with 7,7,8,8-tetracyanoquinodimethane** Michal Bláha,[a] Hidetsugu Shiozawa[a,b] [a] *Czech Academy of Sciences, Czech Republic;* [b] *University of Vienna, Austria*
		Coffee
Anna Coclite	11:00-12:00	**Modeling polymers and MOF/polymer composites** Rocio Semino *Université de Montpellier, France*
	12:00-12:20	**Understanding the bottlenecks of thermal transport in Metal-Organic Frameworks** Sandro Wieser,[a] Tomas Kamencek,[a] Egbert Zojer,[a] and Natalia O. Bedoya-Martínez[a,b] [a] *Graz University of Technology;* [b] *Materials Center Leoben, Austria*
		Lunch

Tuesday, September 17, 2019 - Afternoon Session

Egbert Zojer	13:20-14:20	**Fabricating designer solids: the SURMOF approach** Christof Wöll *[a] Karlsruhe Institute of Technology, Germany*
	14:20-15:00	**Strong light-matter interaction in tungsten disulfide nanotubes** Bojana Višić,[a] Lena Yadgarov,[b] Stefano Dal Conte,[c] Giulio Cerullo,[c] Reshef Tenne,[b] Christoph Gadermaier[c] *[a] University of Belgrade, Serbia; [b] Weizmann Institute of Science, Israel; Politecnico di Milano, Italy*
		Coffee
Sergey Borisov	15:40-16:40	**Electric and Thermoelectric Properties of SURMOFs** Zeinab M. Hassan,[a] Xin Chen,[b] Vincent Linseis,[c] Helmut Baumgart,[c] Engelbert Redel[a] *[a] Karlsruhe Institute of Technology, Germany; [b] Old Dominion University, USA; [c] Linseis Messgeraete GmbH, Germany*
	16:40-17:00	**Make MOFs “real” molecular sieves by electroshock treatment** Alexander Knebel,[a,b] Benjamin Geppert,[b] K. Volgmann,[b] Daniil I. Kolokolov,[c,d] Alexander G. Stepanov,[c,d] Jens Twiefel,[e] Paul Heitjans,[b] Dirk Volkmer,[d] Jürgen Caro[b] *[a] Karlsruhe Institute of Technology; [b,e] Leibniz University Hannover; [f] Augsburg University, Germany; [c] Siberian Branch of Russian Academy of Sciences; [d] Novosibirsk State University, Russia*
		Coffee
R. rschum	17:20-18:20	**Chemical stability in MOFs: challenges and advantages of titanium organic frameworks** Natalia M. Padial, Javier Castells-Gil; Neyvis Almora-Barrios, Carlos Martí-Gastaldo *Universidad de Valencia, Spain*

Wednesday, September 18, 2019

Gregor Trimmel	9:00 - 10:00	**Porous crystalline materials in microelectronics** Rob Ameloot *KU Leuven, Belgium*
	10:00-10:20	**Vapour deposition of ZIF-8 thin films with preferred orientation** Marianne Kraeuter,[a] Alberto Perrotta,[a] Julian Pilz,[a] Rob Ameloot,[b] Timothée Stassin,[b] Alexander Cruz,[b] Roland Resel,[a] Anna M. Coclite[a] [a] *Graz University of Technology, Austria;* [b] *KU Leuven, Belgium*
		Coffee
R. Schennach	11:00-12:00	**Hierarchically organized porous metal oxides, carbons and hybrids: Non-Conventional Sol-Gel Precursors and Processes** Andrea Feinle, Michael S. Elsaesser, Nicola Hüsing *Paris-Lodron-University of Salzburg, Department of Chemistry and Physics of Materials, Salzburg, Austria*
	12:00-12:20	Lunch - takeaway
	12:20-20:00	Excursion and Dinner

Thursday, September 19, 2019

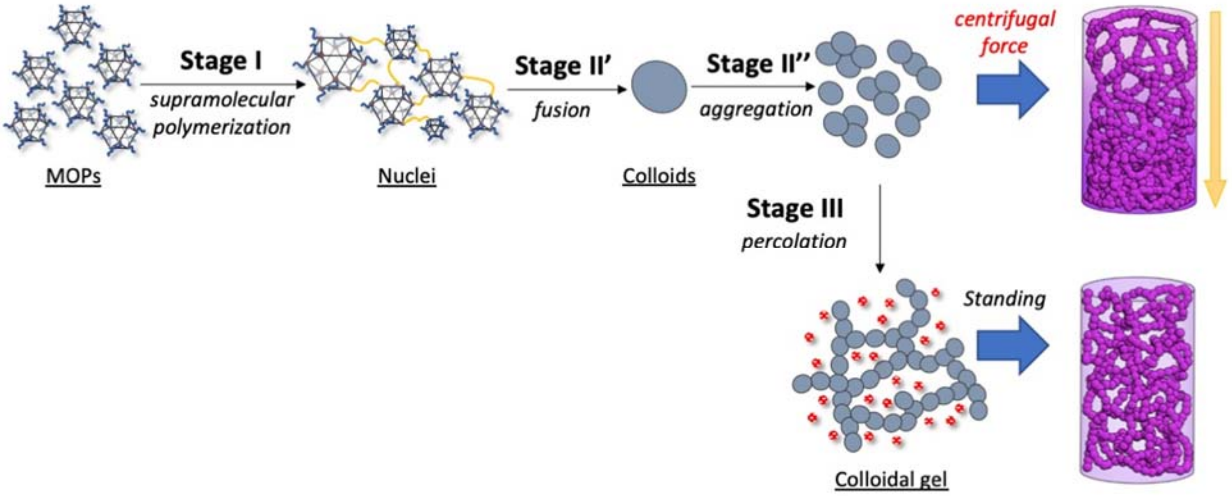
Anne-Marie Kelterer	9:00 - 10:00	**Calculating thermal transport properties of MOFs: methods, challenges and examples** Natalia Bedoya-Martinez *Materials Center Leoben Forschung GmbH, Austria*
	10:00-10:20	**Metal xanthates: a route to porous metal sulfide thin layers** Efthymia Vakalopoulou, Gregor Trimmel *Graz University of Technology, Austria*
		Coffee
Eva-Maria Steyskal	11:00-11:40	**From copper-based substrates to Metal-Organic Frameworks** Raffaele Ricco,[a] Paolo Falcaro,[a] Masahide Takahashi,[b] Christian Doonan[c] *[a] Graz University of Technology, Austria; [b] Osaka Prefecture University, Japan; [c] The University of Adelaide, Australia*
	11:40-12:20	**Degradation of ZIF-8 in phosphate buffered saline media** Miriam de J. Velásquez-Hernández,[a] Raffaele Ricco,[a] Francesco Carraro,[a] Ted Limpoco,[f] Mercedes Linares-Moreau,[a] Erich Leitner,[c] Helmar Wiltsche,[c] Johannes Rattenberger,[d] Hartmuth Schröttner,[d] Philipp Frühwirt,[a] Eduard M. Stadler,[a] Georg Gescheidt,[a] Heinz Amenitsch,[e] Christian J. Doonan,[b] Paolo Falcaro[a,b] *[a,c,e] Graz University of Technology, Austria; [b] The University of Adelaide, Australia; [d] Graz Centre for Electron Microscopy, Austria; [f] Oxford Instruments GmbH Asylum Research, Germany*
		Lunch
Christian Slugovc	13:20-14:20	**Functional Pickering foams produced by polymerization of nanoparticle-stabilized emulsions** Matjaž Mazaj,[a] Nataša Zabukovec Logar,[a,b] Ema Žagar,[c] Sebastijan Kovačič[c,d] *[a,c] National Institute of Chemistry; [b] University of Nova Gorica; [d] University of Maribor, Slovenia*
	14:20-15:20	**Metal-Organic Frameworks (MOFs) position technology** Francesco Carraro, Paolo Falcaro *Graz University of Technology, Austria*
		Farewell

Functionally gradient porous soft materials

Alexandre Legrand Gavin Craig, Mickaele Bonneau, Shuhei Furukawa*

Institute for Integrated Cell-Material Sciences, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan

Spatial heterogeneity and gradients within porous materials are key for controlling their mechanical properties and mass/energy transport, both in biological and synthetic materials. However, it is still challenging to induce such complexity in well-defined microporous materials such as crystalline Metal-Organic Frameworks (MOFs). Here we show a method to generate a continuous gradient of porosity over multiple length scales by taking advantage of the amorphous nature of supramolecular polymers based on metal-organic polyhedra (MOPs).[1,2] First, we use time-resolved dynamic light scattering (TRDLS) to elucidate the mechanism of hierarchical self-assembly of MOPs into colloidal gels and to understand the relationship between the MOP concentrations and the architecture of the resulting colloidal networks. These features directly impact on the viscoelastic response of the gels and their mechanical strength. We then show that gradients of stiffness and porosity can be created within the gel by applying centrifugal force at the point of colloidal aggregation.[3]



Schematic illustration of preparing functionally gradient porous gels based on MOPs.

References:

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Geometry mismatch & reticular chemistry for the assembly of Metal-Organic Frameworks

Vincent Guillerm,[a,*] Borja Ortín-Rubio,[a] Hosein Ghasempour,[a] Thais Grancha,[a]
Inhar Imaz, Daniel Maspoch[a,b*]

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[b] ICREA, Pg. Lluís Companys 23, 08010 Barcelona, Spain
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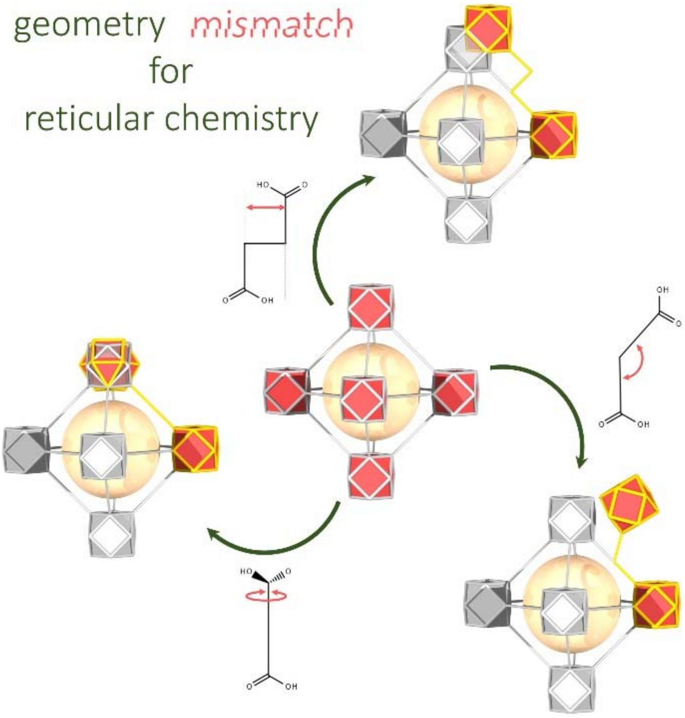
Understanding and controlling the assembly of molecular building blocks is of a prime importance for the fabrication of tailored made porous materials. In our work, we take advantage of the *geometry mismatch*[1] induced by the use of zigzag ligands to study their topological influence in the assembly of Zr(IV) metal–organic frameworks (MOFs).[2] Through a transversal design strategy using reticular chemistry, we were able to synthesize a family of isoreticular Zr(IV)-based MOFs exhibiting the **bcu** topology. Our work has revealed that the transversal parameter in organic ligands can be modulated for reticular synthesis of MOFs, as demonstrated in our rational synthesis of four isoreticular Zr-**bcu**-MOFs using zigzag ligands. This parameter provides an additional degree of structural fine-tuning in MOFs by reticular chemistry, enabling deviations from default structures such as the **fcu** topology typically observed for Zr(IV) MOFs with 2-connected, linear ligands. By reducing the connectivity of the inorganic building blocks from the ideal 12 down to 8 to create ordered defects, our approach could become complementary to -or even substitute- the classical monotopic ligand (modulator) addition for MOF synthesis.



Schematic of the concept of geometry mismatch

References:

1 Guillerm, V.; Maspoch, D. **2019**, *submitted*
2 Guillerm, V.; Grancha, T.; Imaz, I.; Juanhuix, J.; Maspoch, D. *J. Am. Chem. Soc.* **2018** *140*, 10153; highlighted in *Science* **2018**, *361*, 889.

FTIR spectroscopy, microscopy and imaging for porous material chemical characterization

Lisa Vaccari, Giovanni Birarda

Elettra Sincrotrone Trieste, S.S. 14 Km 163.5, Basovizza, Trieste, Italy

The no-damaging nature of the infrared (IR) light is a unique feature in Synchrotron Radiation (SR) facilities, which allows the safe investigation of vibrational and vibro-electronic transitions for a wide variety of materials. Hence, the applications of IR spectroscopy cover a wide range of research fields including biochemistry, cultural heritage, forensics, geology, polymer-science, in-vitro live cell analysis, biomedical diagnostics, and many others.

The present lecture is intended to present Elettra Synchrotron radiation facility, focusing on the most relevant characteristics of IR synchrotron radiation and associated instrumentations, through exemplary experiments on diverse porous systems with different functionalities.

The chemical sensitivity and versatility of Attenuated Total Reflection (ATR) Fourier Transform Infrared (FTIR) spectroscopy will be highlighted in the study of the encapsulated enzymes in Hydrophilic Metal–Organic Frameworks,[1] as well as in the investigation of lyotropic liquid-crystalline nanosystems exploitable as drug delivery agents.[2]

The ability to correlate morphological features of the investigated porous material with its local chemical nature through vibrational analysis with micrometric lateral resolution will be exemplified considering two case studies on Zeolitic Imidazolate Frameworks (ZIFs)[3] and Tetraethyl orthosilicate (TEOS) devices fabricated by Deep X-ray lithography.[4] In addition, the possibility to analyse the efficiency of porous materials applied as rigid supports to solid phase peptide synthesis by FTIR microspectroscopy will be illustrated.[5]

Finally, the most recent infrared instrumentation, capable to provide vibrational information at the nanoscale level, will be shown, highlighting the potential of the technique to bridge molecular properties to functional behaviour through mesoscale analysis.

References:

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Modeling polymers and MOF/polymer composites

Rocio Semino

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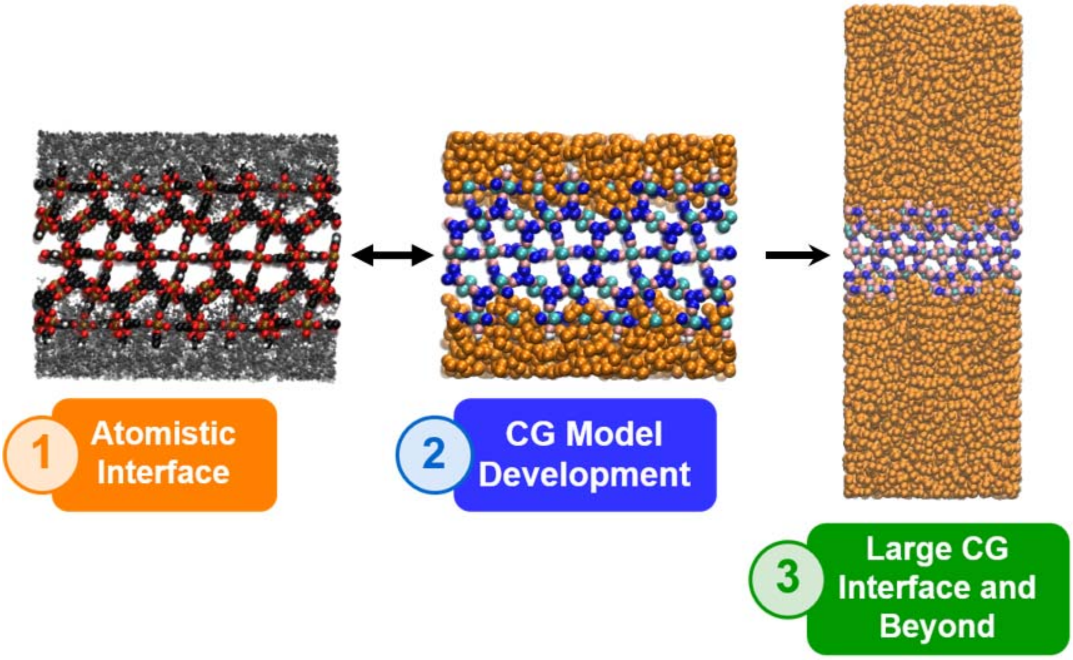
In this talk, I will first introduce the basic workflow of molecular dynamics simulations and discuss the challenges that need to be sorted out when applying this technique to model polymers. Subsequently, I will present a methodology to model the Metal-Organic Framework (MOF)/Polymer interface.[1] MOF/Polymer Mixed Matrix Membranes (MMMs) have attracted great interest in the last few years as a promising alternative to the polymer membranes currently used for gas separations.[2] Although many experimental studies have been published on the elaboration of such MMMs and on their efficacy for specific gas separations, both the interfacial structure of these composites, and their mechanism of action are still not completely understood. Our modeling methodology has allowed us to shed light on the microscopic and mesoscopic structure of MOF/polymer interfaces, and to correlate this information with the MOF/polymer compatibility. These studies pave the way towards understanding interfacial phenomena of paramount importance such as aggregation and phase separation in these mixed matrix systems.



Summarized workflow of our multiscale study of a MOF/Polymer interface

References:

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b) Semino, R.; Dürholt, J. P.; Schmid, R.; Maurin, G. *J. Phys. Chem. C* **2017**, *121,* 21491.

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Fabricating designer solids: the SURMOF approach

Christof Wöll

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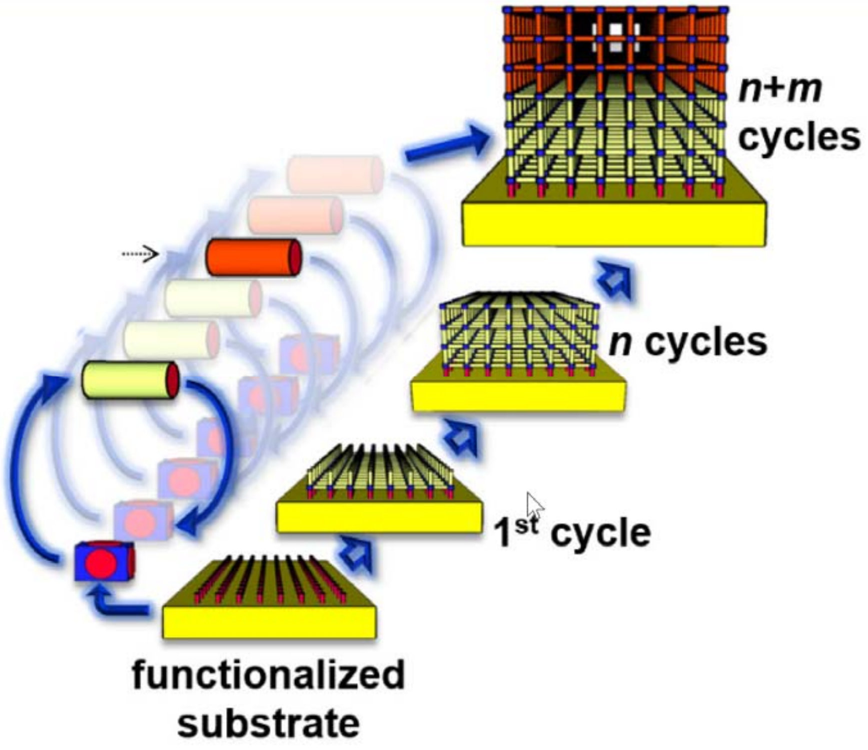
Realizing molecular "Designer Solids" by programmed assembly of building units taken form libraries is a very appealing objective. Recently, Metal-Organic Frameworks (MOFs) have attracted a huge interest in this context. Here, we will focus on the programmed assembly of porous, molecular solids using MOF linkers and the integration of specific functionalities, e.g. molecular switches. We will also briefly discuss several applications based on these highly versatile crystalline materials. For numerous MOF-based applications the conventional solvothermal synthesis yielding powders is not well suited, e.g. in optics the powder particles cause strong scattering which makes a reliable determination of photophysical parameters difficult. To overcome these problems, we have developed a layer-by-layer (lbl) deposition method to produce well-defined, highly oriented and monolithic MOF thin films on a number of different substrates. The resulting films are referred to as SURMOFs.[1,2] The fabrication of hetero-multilayers (see Figure) is rather straightforward with this lbl method. In this talk, we will describe the principles of SURMOF fabrication as well as the results of systematic investigations of electrical and photophysical properties exhibited by empty MOFs and after loading their pores with functional guests. Subsequently we will focus on the implementation of molecular switches into SURMOFs, and the application for a variety of purposes.



Layer by layer scheme to fabricate SURMOFs

References:

1 Liu, J.; Wöll, C. *Chem. Soc. Rev.* **2017**, *46*, 5730.
2 Heinke, L.; Wöll, C. *Adv. Mater.* **2019**, *31*, 1970184.

Electric and thermoelectric properties of SURMOFs

Zeinab M. Hassan,[a] Xin Chen,[b] Vincent Linseis,[c] Helmut Baumgart,[c] Engelbert Redel[a,*]

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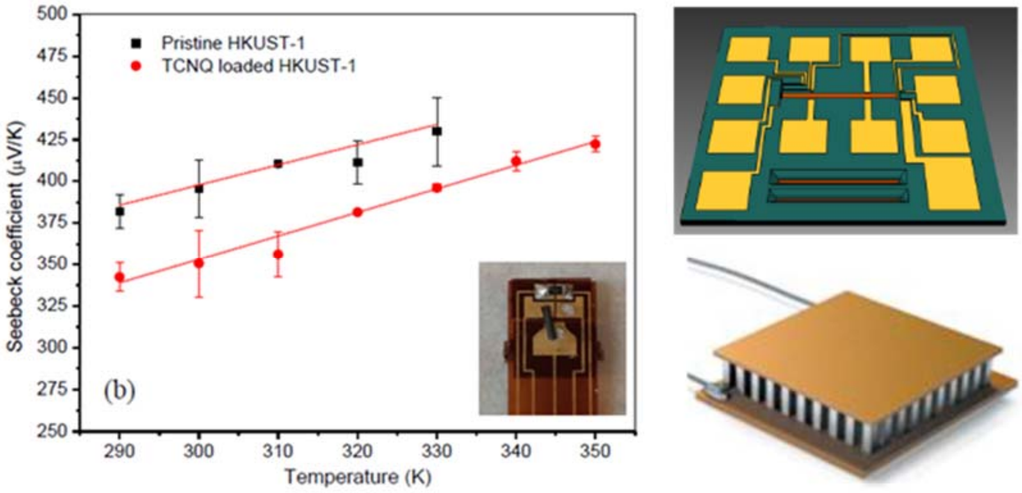
The general topic introduction, will present basic knowledge in electric and thermoelectric properties of SC (Semiconductors). Based on this principles a new class of thermoelectric materials termed surface-anchored (Metal-Organic Frameworks and coordination network compounds) SURMOFs thin films materials will be introduced. SURMOFs thin films demonstrates promising application potential of organic porous thin films in future thermoelectric and electronic devices working highly efficient in the RT (Room Temperature) region. In our first studies we have characterized the Seebeck coefficient of polycrystalline and highly-ordered SURMOF thin films.[1,2]



Electric and Thermoelectric Characterizations of SURMOFs.

Since SURMOFs are highly porous and the size of their pores are highly adjustable, they can be further functionalized and tailored due to their electrical and thermal conductivity properties. SURMOFs can be therefore regarded as tailorable organic Thermoelectric Material of the future. An outlook will be given on their further electronic characterization, Hall measurements and thermal conductivity as well as on first *ZT* Chip measurements.[3]

References:

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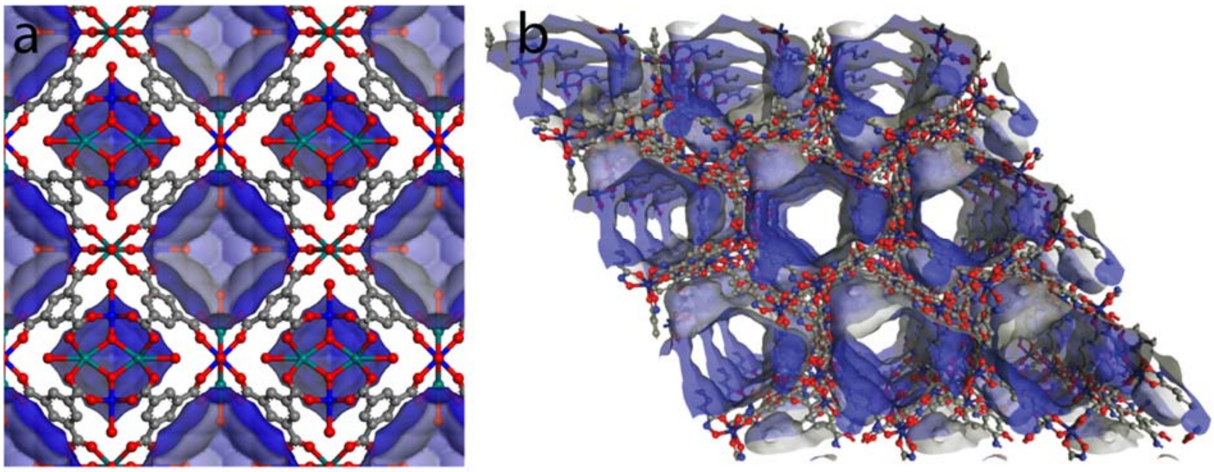
Chemical stability in MOFs: challenges and advantages of titanium organic frameworks

Natalia M. Padial, Javier Castells-Gil; Neyvis Almora-Barrios, Carlos Martí-Gastaldo*

Functional Inorganic Materials Team, Instituto de Ciencia Molecular, Universidad de Valencia, Catedrático José Beltrán, 2, 46980, Spain; e-mail: carlos.marti@uv.es

The synthesis of crystalline, open titanium frameworks remains still very challenging due to the high reactivity of the reagents used and the difficulties in controlling the formation of persistent Ti(IV) secondary building units with predetermined directionality, amenable to the isoreticular approach. Common precursors are prone to hydrolysis in the solvothermal conditions used in the synthesis of Metal-Organic Frameworks (MOFs) leading to uncontrolled precipitation of amorphous oxides or hydroxides. As result, only a few porous Ti(IV)-MOFs have been reported thus far.[1] Compared to other highly charged metals like Zr(IV), more generally used for the synthesis of chemically stable MOFs, titanium is naturally more abundant and offers advantageous features like low toxicity, redox versatility and photoactivity.



Structure of Ti-MOFs: a) heterometallic MUV-10 and b) homometallic MUV-11.

After introducing the different strategies used for endowing MOFs with chemical stability toward water degradation, we will describe our recent results in the synthesis of new titanium organic frameworks by using high throughput methodologies.[2,3,4] Our approach permits producing porous crystals of homo and heterometallic Ti-MOFs at high scale from multiple precursors. We will also discuss the interest of these families of micro and mesoporous materials in the context of photocatalysis and water sorption and how their function can be manipulated by metal doping or defect engineering for more precise control over their electronic properties, photoactivity and porosity.

References:

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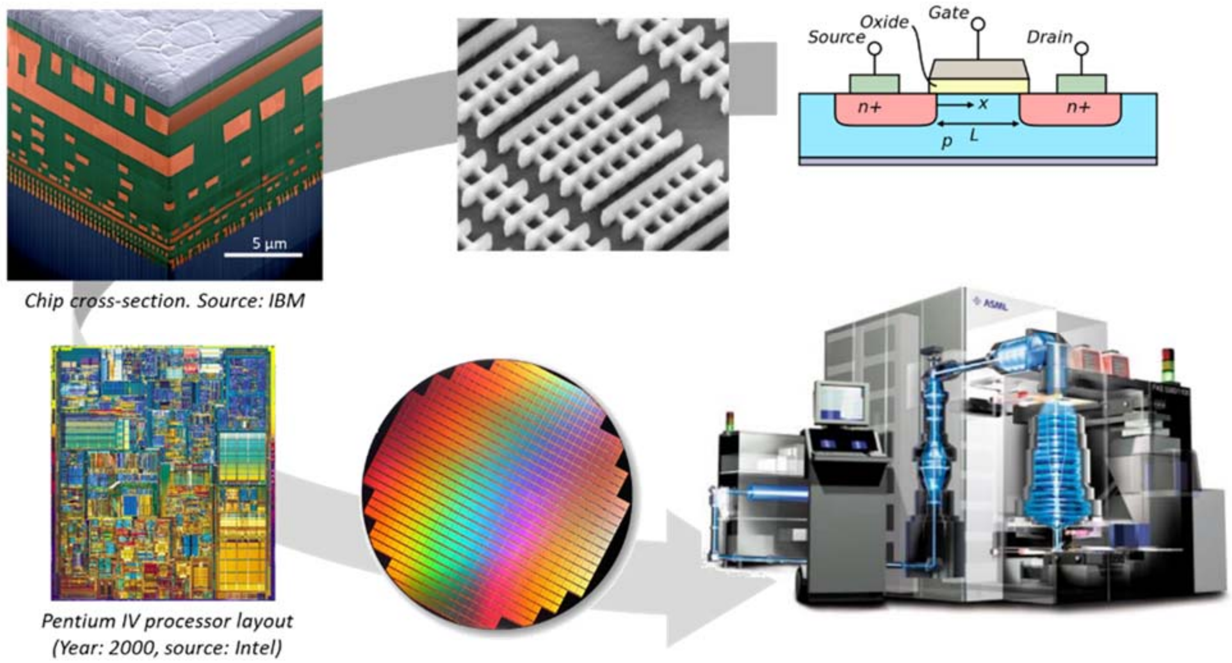
Porous crystalline materials in microelectronics

Rob Ameloot

cMACS - Centre for Membrane Separations, Adsorption, Catalysis & Spectroscopy,
KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium.

Since the invention of integrated circuits (ICs) 60 years ago, there has been a persistent incentive towards the miniaturization of IC components. In this talk we will look at how ICs are made and how molecular self-assembly and porous materials can play a role in microelectronic devices. Particular focus will be on Metal-Organic Frameworks (MOFs), an intriguing class of porous crystalline materials with record internal surface areas. There is tremendous potential for integrating MOFs into microelectronics, e.g. as active sensor coatings or dielectrics.[1] Key enabling steps in leveraging the properties of MOFs in microelectronics will be (1) developing robust thin film deposition methods[2] and (2) solving technological issues that are hard to tackle with existing materials.[3] We will look in detail at how MOF dielectrics could help to enhance the speed of signal propagation and lower the power consumption of ICs.



Different length scales in microelectronics production. Porous materials could aid in realizing faster and more power-efficient chips.

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Hierarchically organized porous metal oxides, carbons and hybrids: Non-Conventional Sol-Gel Precursors and Processes

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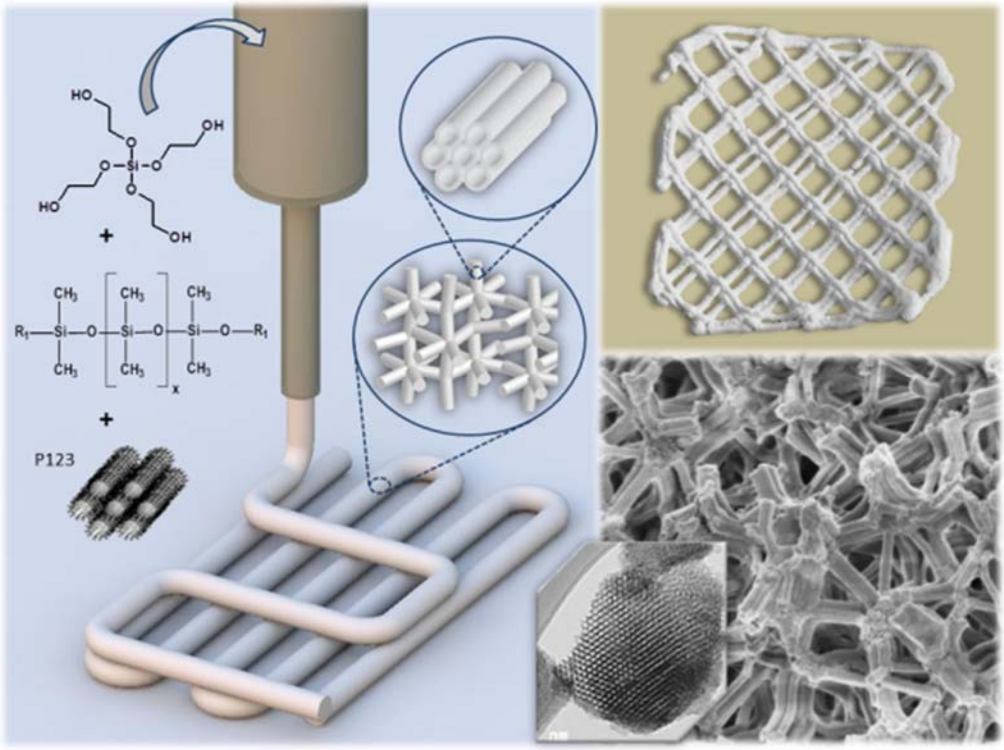
A deliberate control over the pore architecture including pore sizes, pore connectivity and tortuosity as well as pore shape is in many cases a prerequisite for their applicability, however often difficult to achieve in a laboratory.[1] Simple and general methods to prepare (functional and/or monolithic) materials with well-controlled pore architectures, composition and surface functionality are therefore highly desired.

In this presentation, sol-gel processing towards highly porous monoliths by using non-conventional sol-gel precursors and processes will be presented. This includes the application of glycolated precursors, such as tetrakis(2-hydroxyethyl)orthosilicate and the corresponding metal derivatives with and without organic monomers, as well as a discussion of the advantages but also challenges resulting from substitution of the alkoxy groups by glycoxy moieties.[2]



3D printed hierarchically structured silica using glycolated silanes

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Calculating thermal transport properties of MOFs: methods, challenges and examples.

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The versatile structure of MOFs could in, principle, allows for the design of nearly unlimited number of new materials with specific properties. The implementation of MOFS in real applications, however, crucially depends on their ability to transport heat. For example, thermal transport is crucial to exploit the porous structure of these systems in applications dealing with the capture, storage and separation of gases: Capture and release processes are exothermic and endothermic, respectively, heating or cooling the device during operation. Thus, MOFS with good thermal conductivities are desirable to either maintain isothermal conditions, or to impose temperatures that enhance the device performance during operation

To fully realize the potential of MOFs, an in depth understanding of how the fundamental structural characteristics of individual building blocks, as well as their interconnection, impact the thermal transport properties of these systems is necessary. Developing such structure-to-property relationships for heat-transport, by means of atomistic simulations, is in the focus of our investigations.

In the first part of this tutorial, I will give an overview of the most standard methods for calculating thermal conductivities of crystalline solids. I will discuss about the challenges behind this kind of calculations in the case of MOFs, and I will present some examples where we have used these methodologies to study their thermal transport properties.

Functional Pickering foams produced by polymerization of nanoparticle-stabilized emulsions

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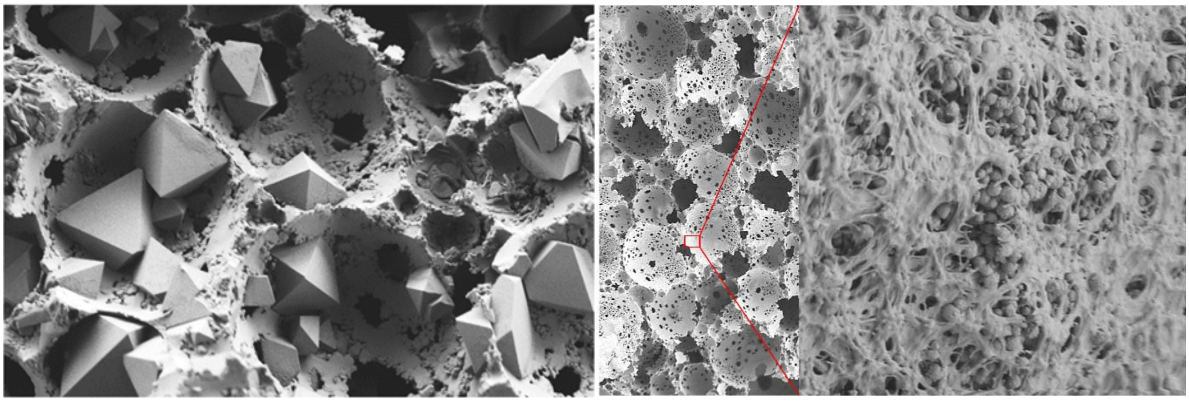
Embedding microporous nanoparticles (e.g. MOFs or zeolites) into the polymeric matrices is an appealing combination since the resulting nanocomposites maintain the shape and flexibility of the polymeric supports and exhibit microporosity and high surface area of microporous nanoparticles. Among the methodologies available for the preparation of polymeric matrices, high internal phase emulsion (HIPE) templating and polyHIPEs thereof are especially intriguing as their macroporous structure serves as "highways", providing an unobstructed flow towards the active (Lewis acids) sites of the microporous nanoparticles.



Scanning electron micrographs of HKUST-1@polyHIPE (left) and β-zeolites@polyHIPE (right).

Among the others synthesised,[1] two examples of nanoparticles@polyHIPE heterostructure designs will be presented; (1) the confined re-crystallization of MOFs and (2) incorporation of β-zeolites within the polyHIPE's macroporous matrix. In both cases, MOF and zeolite phase were successfully immobilized within the polyHIPE matrix (Figure 1), retaining their high accessibility of sorption and catalytic sites.[2]

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Metal-Organic Frameworks (MOFs) position technology

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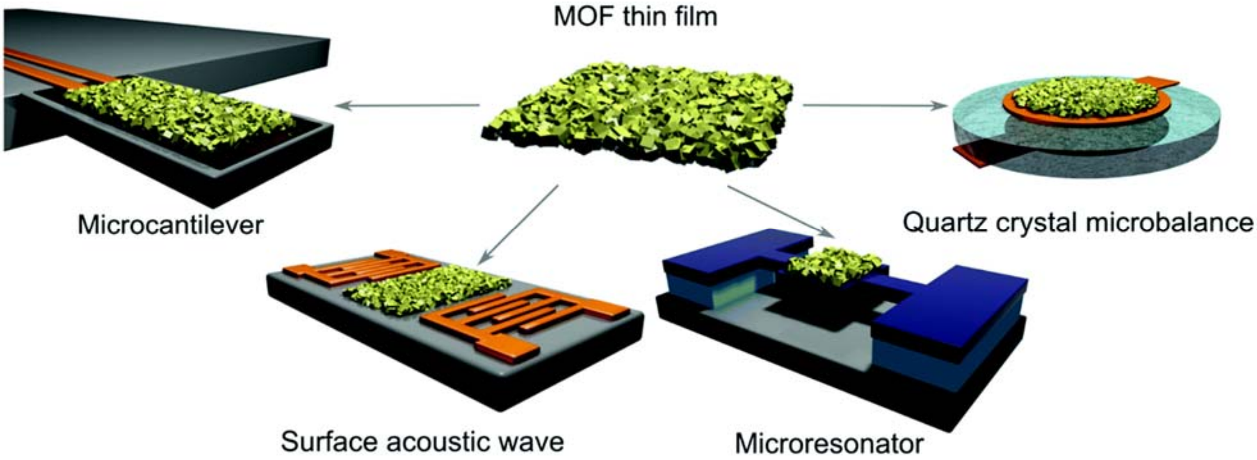
Metal-Organic Frameworks (MOFs) are a class of ultra-porous materials with exceptionally high accessible surface area due to the framework produced by inorganic nodes coordinated by organic ligands.[1] An increasing number of studies are investigating MOFs for a variety of functional applications including sensing, microelectronics, energy production, drug delivery and microfluidics.[2] However, MOF-based device fabrication requires synthetic protocols for the controlled functionalization of the porous crystals and their integration in suitable platforms.[3] Both Bottom-up and Top-down processes could be employed to position porous materials on a device[3] and different possibilities will be discussed during the presentation. For example, conversion of ceramics have been recently employed for the synthesis,[4] functionalization,[5] patterning[6] and orientation[7] of MOF crystals. This presentation will summarize the recent progress in this emerging field.



Example of MOF films used for different applications, from ref. 8

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Molecular doping of Metal-Organic Frameworks

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Coordination polymerization leads to various metal–organic frameworks (MOFs) with unique physical properties with permanent porosity. Molecular doping can further improve the MOF's properties.[1-3] Here we show that the M-MOF-74, a honeycomb nano–framework with one-dimensionally arranged metal atoms, change its colors and electrical conductions by accommodating tetracyanoquinodimethane (TCNQ), an acceptor molecule. It is found that strong intermolecular charge transfer reduces the optical band gap down to 1.5 eV of divalent TCNQ, leading to the enhanced electrical conduction, which allowed the MOF to be utilized for resistive gas- and photo-sensing.

This work was supported by the Austrian Science Fund (FWF) P30431-N36 and the Czech Science Foundation (GACR) project 19-15217S.

References:

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Strong light-matter interaction in tungsten disulfide nanotubes

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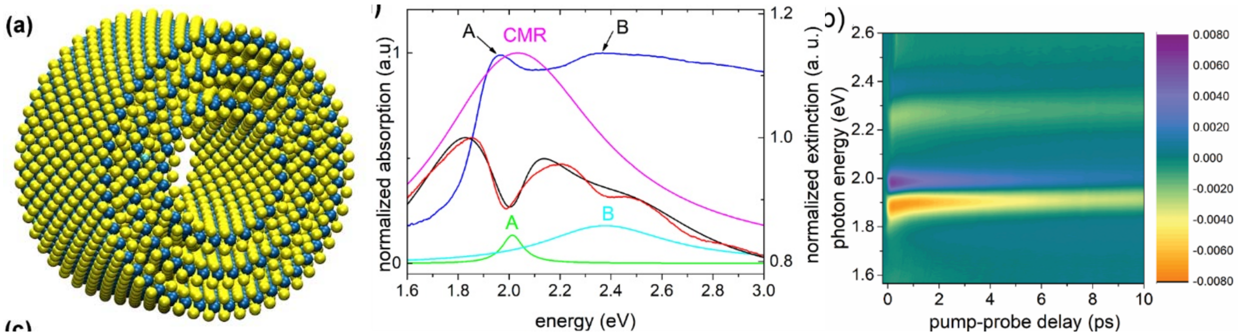
Exceptionally strong light-matter interaction combined with flexible processing and fabrication techniques moved semiconducting layered transition metal dichalcogenides (TMDs), in particular MoS_2 and WS_2, into the focus of optoelectronics, nanophotonics, and energy harvesting research. Besides the two-dimensional platelets, TMDs also form closed-cage fullerene-like structures and nanotubes (NTs). NTs provide an intrinsic optical cavity mode which strongly couples to the excitonic resonance of nanotubes, crucially altering the extinction spectrum compared to the layered counterparts.[1] We model the extinction of dispersed WS_2 NTs with a phenomenological coupled oscillator (PCO) model involving two excitonic resonances and the optical cavity mode. To understand the electronic processes behind the NTs' functional properties, we investigate the non-equilibrium light-matter interaction in WS_2 nanotubes in the time domain using femtosecond transient extinction spectroscopy.[2] We describe the transient extinction spectra with the PCO model with time-dependent parameters, allowing us to disentangle the interplay of population dynamics and many-body effects and discuss analogies with the corresponding behaviour in the layered compounds, for which a more comprehensive knowledge base has been assembled.



Left: Schematic representation of a three-walled WS2 NT. Centre: Normalized pure absorbance (blue) and extinction (red) spectra of WS2 NT presented together with a PCO fit (black) and its constituent peaks (A, green; B, cyan and CMR, magenta). Right: Contour plot of the transient differential extinction spectrum.

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From copper-based substrates to Metal-Organic Frameworks

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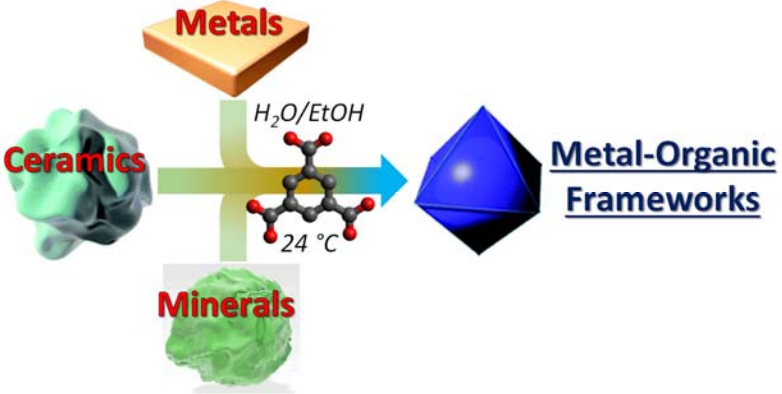
Metal-Organic Frameworks (MOFs) have huge surface area and tuneable porosity,[1] with potentials in applications like storage, separation, drug delivery, and catalysis.[2] MOFs can be directly obtained from ceramics, for example alumina,[3] and zinc oxide.[4] This presentation summarizes the collaborative efforts obtained in the recent past by our groups for the conversion of copper-based metals,[5] ceramics,[6] and carbonates[7] into $Cu_3(BTC)_2$ (HKUST-1, BTC = trimesic acid ligand), a MOF with excellent gas adsorption and catalytic activity.[8] The simple process requires hydro-alcoholic solution of the ligand and room temperature. In particular, we found that carbonate feedstock can be also derived from natural sources (malachite and azurite). The catalytic properties of HKUST-1 synthesized with this efficient technique were successfully proved, with similar performance to the MOF synthesized by classic method. This promising pathway can lead to new development of porous sorbents obtained via eco-friendly and sustainable processes.



Schematic way of the conversion of various substrates into MOFs

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Degradation of ZIF-8 in phosphate buffered saline media

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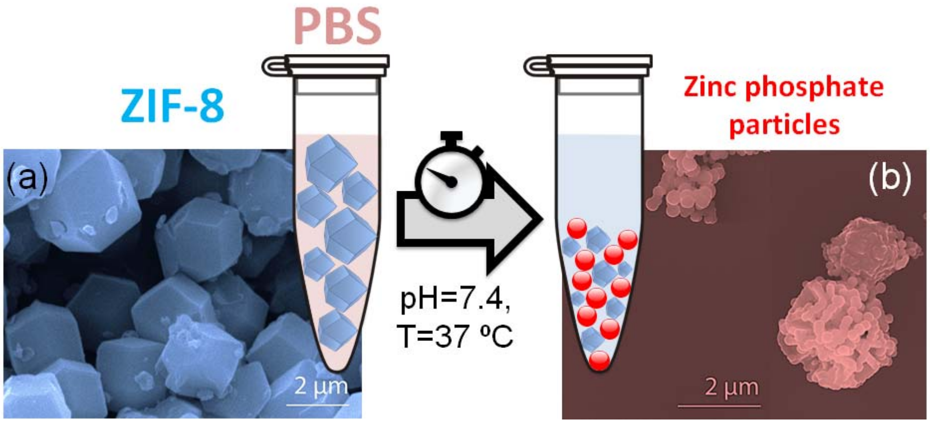
Zeolitic imidazolate framework-8 (ZIF-8) is one of the most studied MOF for bio applications such as drug delivery, bio-storage, and bio-catalysis.[1] The widespread interest in ZIF-8 depends on its high potential for the encapsulation of a wide variety of biotherapeutics. ZIF-8 biocomposites can be prepared under mild reaction conditions affording high encapsulation efficiencies.[1] However, for drug delivery applications, the biodegradation properties of the drug carrier control the pharmacokinetic and biodistribution of the material in *in vivo* trials.[2] Thus, to shed light on the kinetics of biodegradation of ZIF-8 we present a comparative study on the stability of pure micro- and nano-ZIF-8 particles using a PBS medium under physiological pH and temperature. The stability of these particles was evaluated in terms of crystallinity, morphology, and chemical composition, using PXRD, IR, and SEM/EDS. Further, the decomposition of micro-ZIF-8 particles was monitored by *in situ* AFM and GC-MS. Our results indicate that ZIF-8 is not stable in 1X PBS. NMR suggests the formation of zinc phosphate byproducts.



Incubation process of ZIF-8 particles in phosphate buffered saline media (PBS) under physiological conditions. (a) SEM image of as-synthesized micro-ZIF-8 particles. (b) SEM image of micro-ZIF-8 particles after being soaked in PBS for 24h.

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Understanding the bottlenecks of thermal transport in Metal-Organic Frameworks

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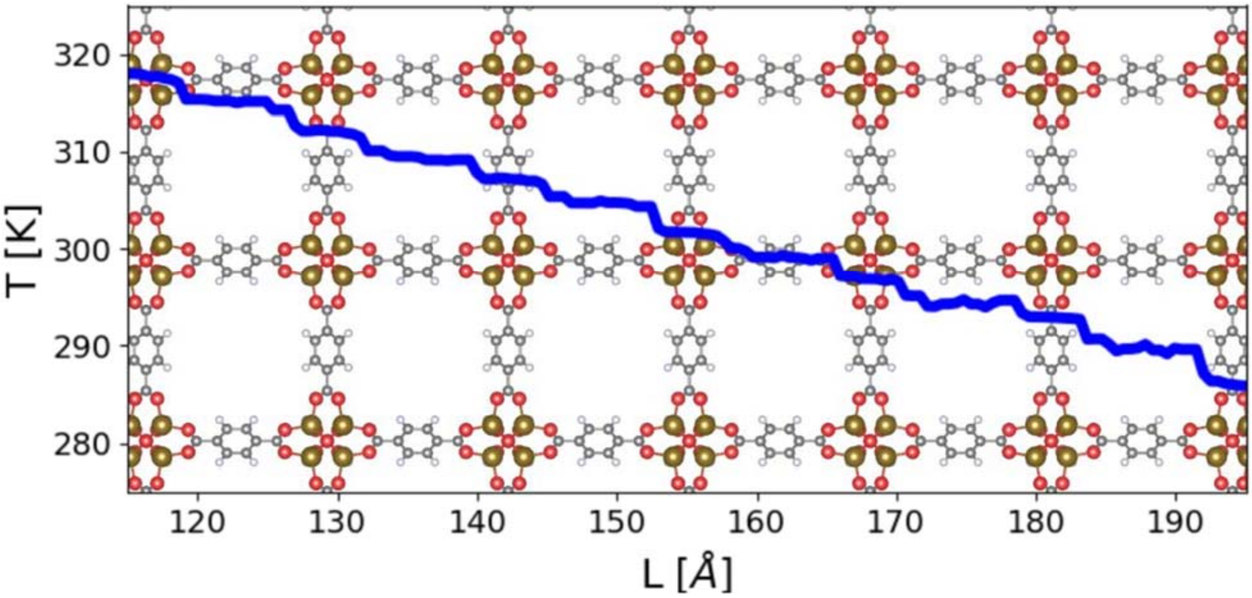
Many of the applications for metal-organic frameworks (MOFs), like gas storage and catalysis, rely on the effectiveness of heat dissipation. Therefore it is crucial to investigate their thermal transport properties. As MOFs allow for easy modifications in their composition and architecture, an in-depth understanding of the structure-to-property relationship will allow a precise tailoring of the material to meet specific requirements. Here we apply classical molecular dynamics (MD) simulations, in combination with the MOF-FF[1] force field potential, to investigate the heat transport properties of MOFs with different composition. For determining the thermal conductivities of the observed systems both equilibrium and non-equilibrium molecular dynamics approaches have been applied. The initial focus is on the isoreticular family of MOFs (IRMOFS) where different combinations of metallic nodes and organic linkers are investigated. Special care is taken to analyze the node-linker interfaces occurring in MOFs, as they are identified as a major limiting factor for heat transport. Vibrational properties have also been investigated in the framework of density-functional-theory, in order to provide additional insight. We show that using lighter metallic nodes or smaller linkers can significantly increase thermal conductivity and that the nature of the organic-inorganic interface severely impacts thermal transport.



Temperature profile of a non-equilibrium molecular dynamics simulation of MOF-5 showing poor thermal conductance across the node-linker interface.

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Raman spectroscopic investigation of M-MOF-74 doped with 7,7,8,8-tetracyanoquinodimethane

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Coordination polymerization leads to various metal–organic frameworks (MOFs) with unique physical properties and chemical functionalities. One of the challenges towards their applications as porous materials is to make MOFs optimally conductive to be used as electronic components.[1-4] It has been previously shown that a Co-MOF-74, a honeycomb nano–framework with one–dimensionally arranged cobalt atoms, advances its physical properties by accommodating tetracyanoquinodimethane (TCNQ), an acceptor molecule.[5] Strong intermolecular charge transfer reduces the optical band gap down to 1.5 eV of divalent TCNQ and enhances the electrical conduction, which allowed the MOF to be utilized for resistive gas- and photo-sensing.[5]

Within this contribution, we study charge transfer and delocalization in M-MOF-74 materials doped with TCNQ by means of resonance Raman scattering.

This work was supported by the Czech Science Foundation (GACR) project 19-15217S and the Austrian Science Fund (FWF) P30431-N36.

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Make MOFs “real” molecular sieves by electroshock treatment

Alexander Knebel,[a,b] Benjamin Geppert,[b] K. Volgmann,[b] Daniil I. Kolokolov,[c,d] Alexander G. Stepanov,[c,d] Jens Twiefel,[e] Paul Heitjans,[b] Dirk Volkmer,[d] Jürgen Caro[b]

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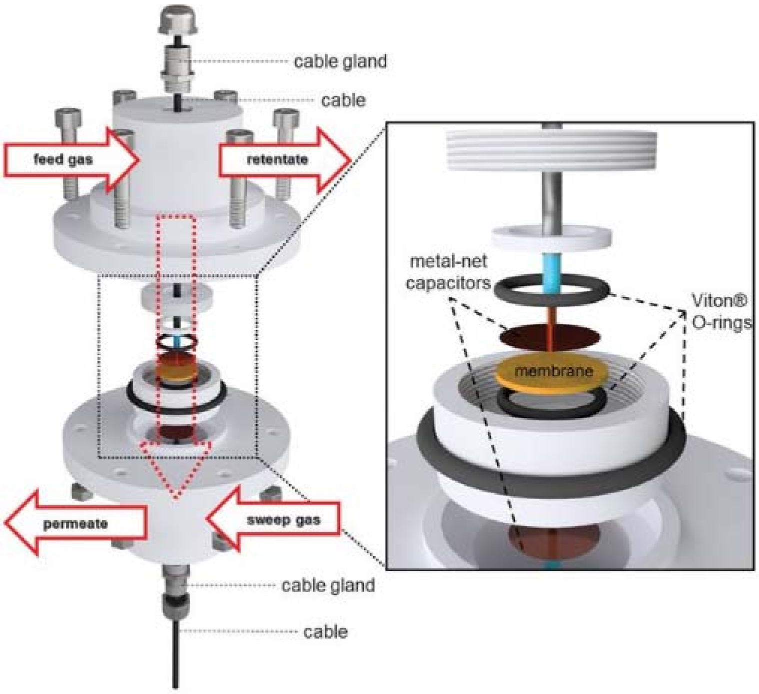
MOFs and the class of ZIFs (zeolitic imidazolate framework) are well recognized in membrane science to be molecular sieves. Following the definition of a molecular sieve, regarding only a pore-window size below 1.5 nm, this might be true. Experimental findings show that the molecular sieving performance of ZIF-8 is far behind calculated, theoretical values.[1] This is due to the fact that MOFs in general and ZIF-8 especially exhibits thermally induced flexibility, such as gate-opening and shear deformation, as shown in Thz spectroscopy.[2] We could show that the lattice of ZIF-8 in a gas separation membrane undergoes polarization induced polymorphic phase transitions at 500 V/mm in a dc-electric field. We measured *in-situ* that the molecular sieving performance in the case of C3 separation increases significantly by 33%. Theoretical calculations, dielectric and NMR spectroscopy and also polarization experiments reveal an underlying mechanism.[3]



Setup of the permeation cell with in-situ applied electric dc-field for separation of e.g. propylene/propane by electric-field induced polymorphs of ZIF-8 [Ref3]

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Metal xanthates: a route to porous metal sulfide thin layers

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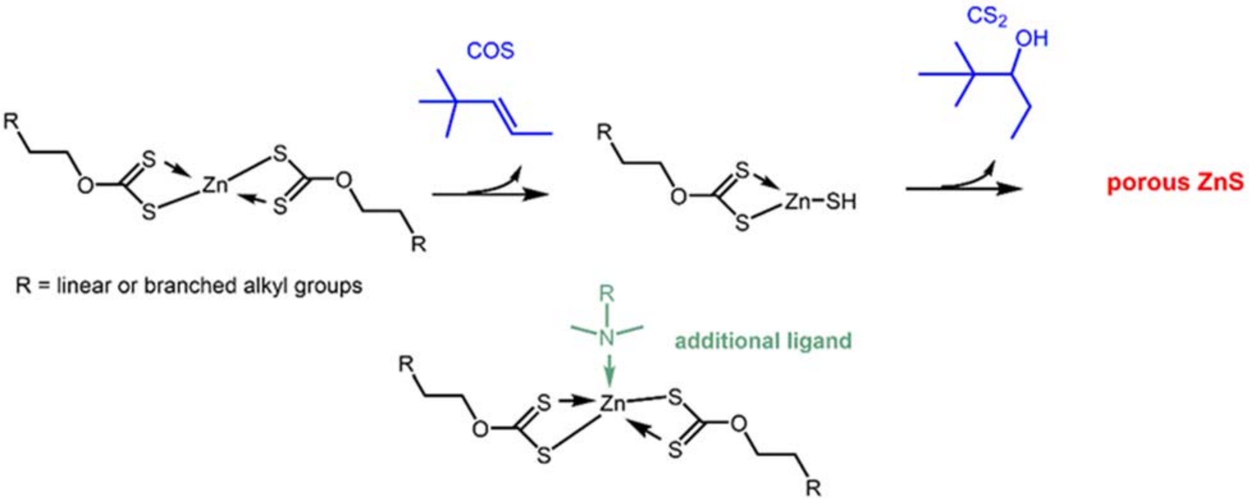
Many metal sulfides are of interest in various applications comprising luminescent devices, sensors, solar cells and many more. Among the various routes towards metal sulfides, we focus on a single source precursor route using metals xanthates. These are metal-organic compounds exhibiting a sulfur-metal bond, which decompose at relatively low temperatures (< 200°C) resulting in highly pure metal sulfides via a mechanism called Chugaev elimination. Another advantage is the ability to control their properties (decomposition temperature, solubility) by changing the structure of the organic moiety of the xanthate group[1] and/or of adding additional ligands.

Our research is focused on the synthesis of hierarchically structured metal sulfide thin layers (ZnS, SnS_2) via metal xanthates, where the porosity is influenced by altering the chemical structure of the metal xanthate. As shown in figure below, this can be achieved either by introducing longer alkyl-groups into the xanthate group or by attaching additional ligands to the metal center. During the thermal decomposition of the xanthates, porous films are generated. The properties and features of the layers before and after xanthates' decomposition are studied via several techniques such as FT-IR and, UV-Vis spectroscopy, X-ray reflectivity and X-ray diffraction.



Schematic representation of reaction taking place towards the formation of porous ZnS.

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Vapour deposition of ZIF-8 thin films with preferred orientation

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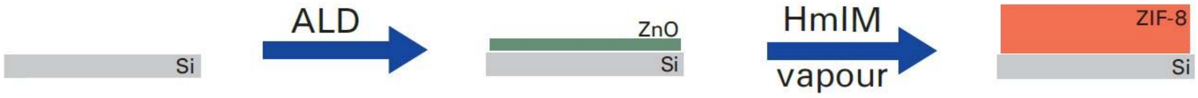
Metal organic frameworks are known for storage and release of gases, catalysis and molecular separation due to their intrinsic nanoporosity and high internal surface area. ZIF-8 (zinc atoms linked via methyl imidazole) stands out due to additional advantageous properties, e.g., resistance to thermal changes and high chemical stability. However, classical synthesis methods are not compatible with device integration or large area deposition, calling for a viable alternative.

For our studies we employed a two-step chemical vapour deposition process that allows for the delivery of high-quality thin films of ZIF-8 with uniform and controlled thickness. First, an ultrathin ZnO seed layer is deposited via plasma-enhanced atomic layer deposition. Acting on the substrate temperature, ranging from room temperature to 200°C, the preferred crystal orientation can be switched from (100) to (002). ZIF-8 thin films are subsequently grown by subjecting the ZnO-layer to a 2-methyl imidazole vapour, following the method presented by I. Stassen, et al.[1] The resulting ZIF-8 thin films were thoroughly investigated in regard to their chemical, crystalline and morphological properties to gain insight into their orientation and growth. Synchrotron radiation studies showed a (100) preferred orientation for the resulting ZIF-8 films with a powder like structure underneath and led to the proposition of a growth model.



Schematic way of preparing ZIF-8 via vapour deposition: ZnO is deposited onto the Si substrate via atomic layer deposition and subsequently subjected to a 2-methyl imidazole vapour at elevated temperatures leading to the formation of ZIF-8.

References:

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Alignment study of epitaxially grown Cu(BDC)-MOFs via X-ray pole figure technique

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Aligned metal organic frameworks (MOFs) are interesting for usage in optical, sensor and microelectronic application.[1] Recent works demonstrated how MOFs can be epitaxially grown on a copper hydroxide surface.[2,3] In this work, copper-based MOFs linked in two dimensions by 1,4-benzenedioic acid (BDC) are grown on $Cu(OH)_2$ nanobelts. The nanobelts, with dimensions of several µm in length, and approximately 20 nm in width, are deposited on silicon surfaces by solution processing. It is apparent that the alignment of the $Cu(OH)_2$ nanobelt substrate is an important parameter for the controlled, oriented growth of the MOF. Samples are investigated using rotating grazing incidence X-ray diffraction (GIXD), probing a large volume of reciprocal space by rotation of the sample around its surface normal. This data then allows the determination of the nanobelt alignment by calculation of pole figures. Applying the same approach to the MOF, we studied the degree of alignment of the substrate transferred to the MOF. In a subsequent step, the crystal structure of the MOF can be compared to known crystal structures from literature.[4] Interestingly, we found that none of the known crystal structures is matching the experimental peak pattern, i.e. Cu-BDC can form a new crystal structure when grown on $Cu(OH)_2$ nanobelts.

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Phonon-related properties in Metal-Organic Frameworks

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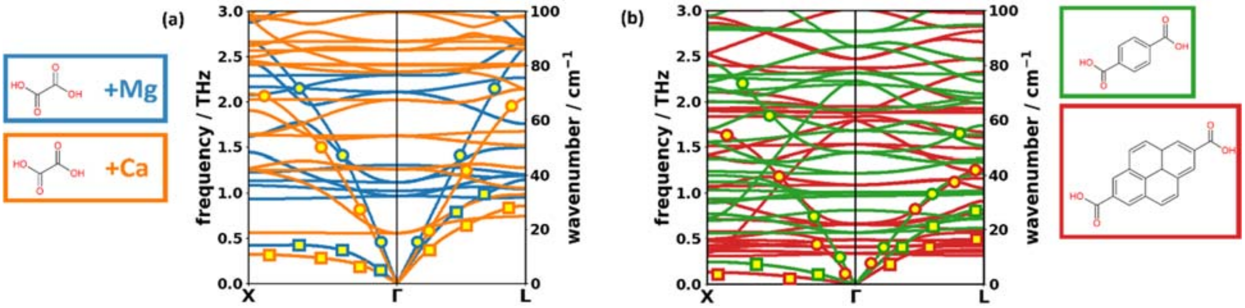
Metal-Organic Frameworks (MOFs) have been extensively studied during the last years due to their numerous possible applications exploiting the large internal surface area (e.g. catalysis, storage, capture and separation of gases). Due to the relatively new trend to employ MOFs in functional devices[1-3], researchers have been gradually becoming more interested in their properties, many of which are typically dominated by contributions of phonons. However, vibrational properties in MOFs, despite their importance for describing practically relevant quantities like thermal conductivity[4], mechanical behaviour[5], or thermal expansion[6], are still largely unexplored. Here, the phonon picture provides a convenient framework to associate various materials properties with individual vibrational modes and helps to understand why certain properties can be observed. By exploiting knowledge about the phonons, specific building blocks can be combined to engineer phonon band structures and the resulting properties. Therefore, we studied the influences of different constituents on the (an)harmonic vibrational properties of a variety of MOFs by means of atomistic simulations. We systematically varied the constituents in isoreticular MOFs (IRMOFs) to separately explore their influence on the phonon dispersion. The goal of our study is to deduce structure-to-property relationships for phonon-related properties (thermodynamic quantities, elastic constants, etc.) in MOFs. Our simulations have been performed in the framework of density functional theory using the PBE functional[7] and self-consistent charge density functional tight binding[8].



Manipulating the phonon band structure by (a) replacing the metal by a heavier one, and (b) exchanging the linker in the typical IRMOF geometry. The markers highlight the acoustic bands.

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MOF as a preorganizing scaffold for heterogenized olefin metathesis catalyst

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Metal Organic Frameworks offer a unique opportunity for rational design of catalytic systems encapsulated in programmable confined spaces. Controlling the physical environment of a catalytic molecule may be vital in suppressing certain decomposition pathways and bringing about desirable selectivity.[1] In recent years, it was found that quaternary ammonium tagged olefin metathesis catalysts have a high affinity towards nanoporous MIL-101(Al)-NH_3Cl.[2] We used this trait to impose a steady stabilization of transient ruthenium methylidene species by a recurring styrene ligand (boomerang effect)[3] upon the heterogenized catalyst and tested the catalytic properties of thus obtained system in batch and flow reactions.

The „Catalysis for the Twenty-First Century Chemical Industry” project is carried out within the TEAM-TECH programme of the Foundation for Polish Science co-financed by the European Union under the European Regional Development Fund.

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How to convince industry to use immobilised ruthenium metathesis catalyst

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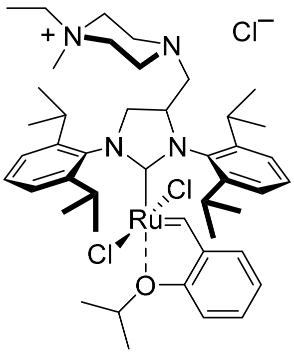
Olefin metathesis is a very elegant tool for reorganisation of carbon-carbon multiple bonds, which makes it a very useful method to construct advanced molecules, like natural products, active pharmaceutical ingredients or polymers, in an efficient and green way.[1,2] The potential of this methodology has also been recognised by pharmaceutical and petrochemical companies,[3] although its wider industrial application will be possible if selective, active, and long-lived catalysts will be widely available, also as a heterogeneous systems. Unfortunately, current research are mostly focused on influence of immobilisation on catalysts recyclability which from industrial point of view is not of the highest importance.[4]

In our research we focused on easy, non-covalent immobilisation of ruthenium complexes and its implications on stability, selectivity and effectiveness of *N*-tagged catalysts, both commercially available (e.g. Figure 1) and obtained by us. As a support different porous materials such as silanes and zeolites were used. After careful selection of reaction condition we could perform self cross-metathesis reactions of easily isomerised substrate with high selectivity.



FixCat

One of N-tagged catalyst used in our research.

Acknowledgements: The „Catalysis for the Twenty-First Century Chemical Industry" project is carried out within the TEAM-TECH programme of the Foundation for Polish Science co-financed by the European Union under the European Regional Development Fund.

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Porous materials under high hydrostatic pressures

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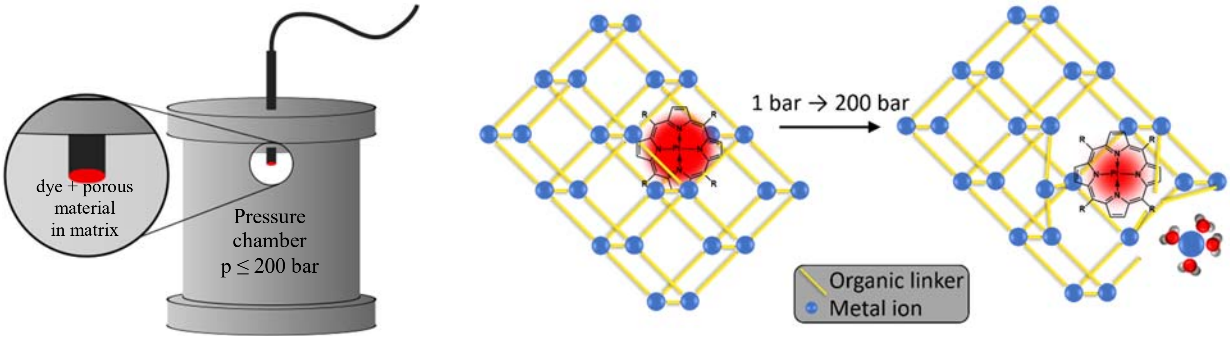
As a greenhouse gas, the global warming potential of methane is ~28 times higher than that of CO_2.[1] Apart from being released from fracking, coal mining or cattle farming, huge amounts of methane are stored as methane hydrates on the ocean floors. Therefore, detection of dissolved methane is of high importance to monitor the release from these storage sites. Their tunable pore size and chemistry makes Metal-Organic Frameworks (MOFs) promising materials for pre-concentration of methane in sensing applications.[2] While various porous materials have been developed that are highly stable in solution, extreme pH values, under high pressure or temperature,[3] there are no studies that investigate the stability of porous materials under high hydrostatic pressures as would be needed in marine applications at great depths.



left: Schematic representation of the pressure chamber; right: Lattice distortion due to high pressure causing change in luminescence properties of dyes molecule

In this study, different porous materials have been equipped with an oxygen indicator dye and dispersed in a hydrophobic polymeric matrix as well as in hydrogel as a water permeable reference. The stability of the porous host material under high hydrostatic pressures has been investigated in a specially designed pressure chamber. The luminescence of the O_2 sensitive dye was logged during the pressurization and depressurization process to detect possible reversible and irreversible changes in the host geometry. The structure of the samples was also investigated with powder XRD and compared before and after the pressurization. This way, the stability of common MOFs (MOF-5, ZIF-8 and UiO-66) as well as that of other porous materials (porous silica, PIM 1, poly(siloxanes) and reduced poly(TMSP)) was investigated and compared.

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Why are charge carrier mobilities in organic semiconductors typically low? Are COFs and MOFs the solution?

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A crucial factor determining charge transport in organic semiconductors is the electronic coupling between the molecular constituents, which is heavily influenced by the relative arrangement of the molecules. To systematically investigate this interplay between transport relevant parameters, energetic stability, and the crystal structure we performed first principles calculations for the instructive example of quinacridone. For this material one finds three polymorphs with fundamentally different packing motifs. Additionally, based on the α-polymorph, an artificial coplanar quinacridone crystal can be constructed. The latter allows correlating electronic properties like transfer integrals t and band-widths with the total energy of the crystal. This way we identify the combination of Pauli repulsion and orbital rehybridization as driving force steering the system towards a structure in which the electronic coupling is minimal, resulting in poor transport properties. The general nature of these observations is supported by equivalent trends for an analogous pentacene model system. Thus, one can conclude that the electronic interaction between neighboring molecules provides a driving force towards structures with low transfer integrals and band-widths, resulting in reduced transport properties.

This also means that the design of high-performance materials cannot rely on the "natural" assembly of the π-conjugated cores of the semiconducting materials into their most stable configurations. Rather, it must include the incorporation of functional groups that steer crystal packing towards more favorable structures. Freezing certain degrees of freedom by interconnecting the molecular building blocks, i.e. building COFs and MOFs, might also provide a design handle to prevent the materials from adapting structures with low intermolecular electronic couplings and band-widths.

Porphyrin-based porous materials

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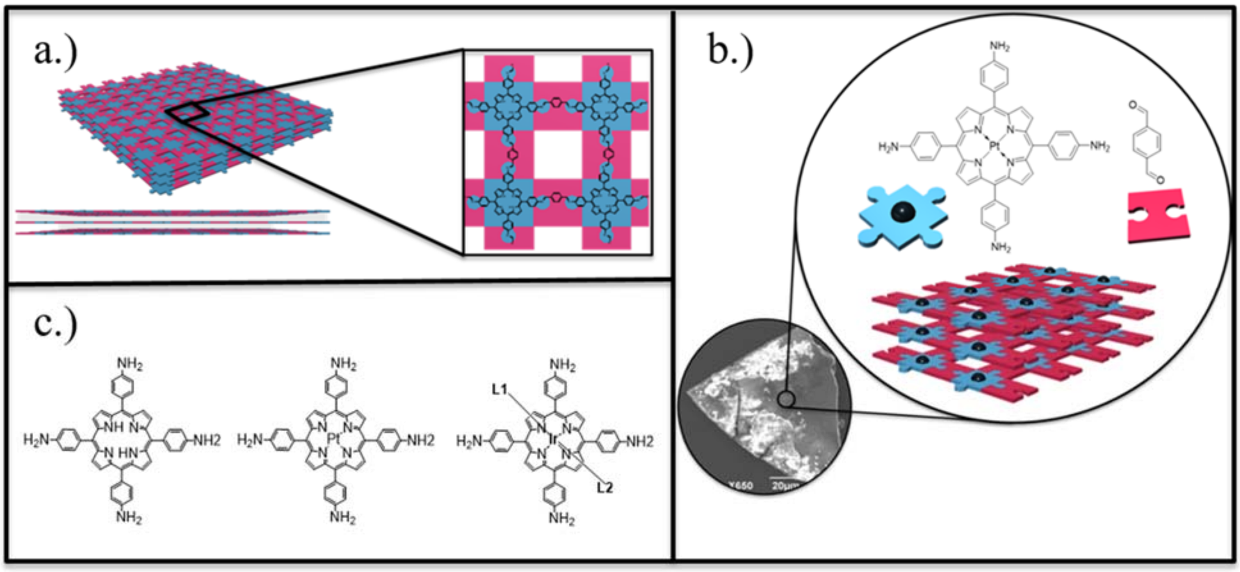
Porphyrins and related macrocycles such as tetrabenzoporphyrins and phthalocyanines are ideal building blocks for porous Metal-Organic Frameworks (MOFs), covalent-organic frameworks (COFs) and ionic crystalline materials.[1] Their versatility regarding metalation of the macrocycles allows addition of additional features. To use such materials as active elements in electronic devices, coplanar stacking of the aromatic macrocyclic units is required, as this should lead to high charge carrier mobility.[2] As interacting units, Pt(II)-porphyrins are incorporated into the framework in order to optimize the crystal structure towards coplanar stacking. Covalent organic frameworks containing porphyrins and Pt(II)-porphyrins have been prepared and are currently under investigation. Additionally, application of Ir(III) porphyrins for this purpose is currently investigated. With these porphyrins, which are bearing two axial ligands, tuning of the inter-planar distance of the covalent organic framework may be possible to achieve. This can be done by ligand exchange reactions or via reduction towards porphyrin-Ir-porphyrin double decker systems.[3] The latter could minimize the inter-planar distance of two coplanar arranged layers further.



a.) Schematic representation of porphyrin-based COFs. b.) SEM image of Pt(II) porphyrin based COF and schematic representation of porphyrin and linker. c.) Selected porphyrins to be used in COFs.

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Synthesis and spin crossover properties of $[Fe(Htrz)_2(trz)](BF_4)$

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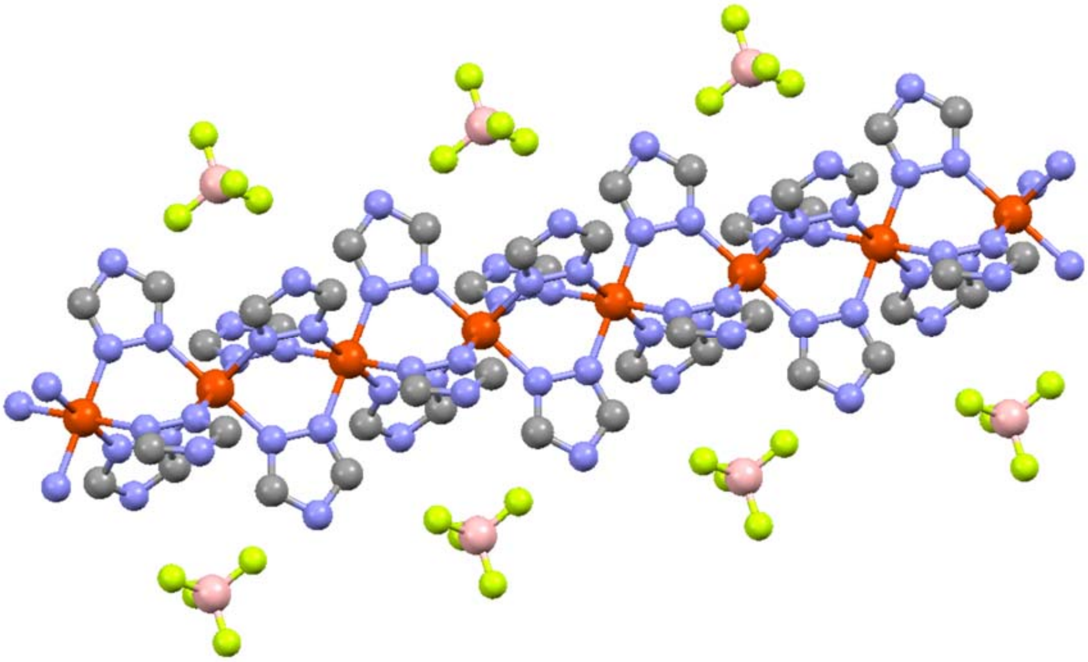
The spin crossover (SCO) phenomenon has been reported for a number of coordination complexes, mostly for Fe(II) molecular species, whose spin state can be reversibly switched between high-spin (HS) and low-spin (LS) configurations by a change of temperature, pressure or by the application of an external perturbation as light illumination[1]. SCO materials can be used as elemental components in electronic applications such as switches, data storage and optical devices[2].

In this contribution, the elaboration of spin crossover crystals of $[Fe(Htrz)_2(trz)](BF_4)$ (Htrz) = 1,2,4-1H-triazole)[3,4] is discussed regarding their synthesis and crystal size-dependent properties as elucidated by means of optical microscopy, X-ray diffraction, optical spectroscopy and Raman spectroscopy.

This work was supported by the Czech Science Foundation (GACR) project 19-15217S and the Austrian Science Fund (FWF) P30431-N36



Polymeric structure of $[Fe(Htrz)_2(trz)](BF_4)$

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Nanostructured hydrogel for humidity sensing layers

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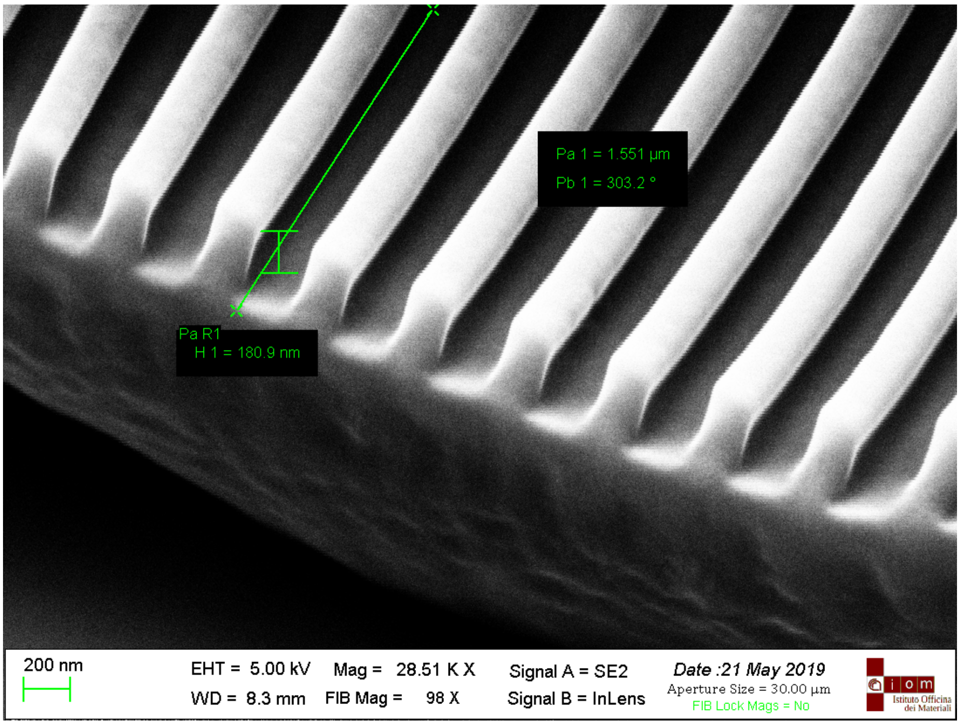
Hydrogels are polymeric networks with the ability to swell after changing different ambient properties (e.g. humidity, temperature, pH-value…).[1] In a previous work a hydrogel-based optical sensor was developed to measure the change of relative humidity in air. Beside of the new optical readout principle, this work especially highlighted the response time of the sensing layer, which was 3X faster compared to commercial humidity sensors.[2] A possible way to further improve the response time of the system could be to nanostructure the sensing layer. This would result in a faster water take-up due to the better volume to surface ratio. To test this idea, the hydrogel layer was patterned by an optimized thermal imprinting technique, which yielded large and homogenous nanostructured areas without damages to the sensitive hydrogel thin film. The swelling of such nanostructured hydrogel is currently under investigation.



SEM image of the periodic nanostructured hydrogel thin film.

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Theoretical investigation of excited state formation and electronic coupling in a Zn-SURMOF

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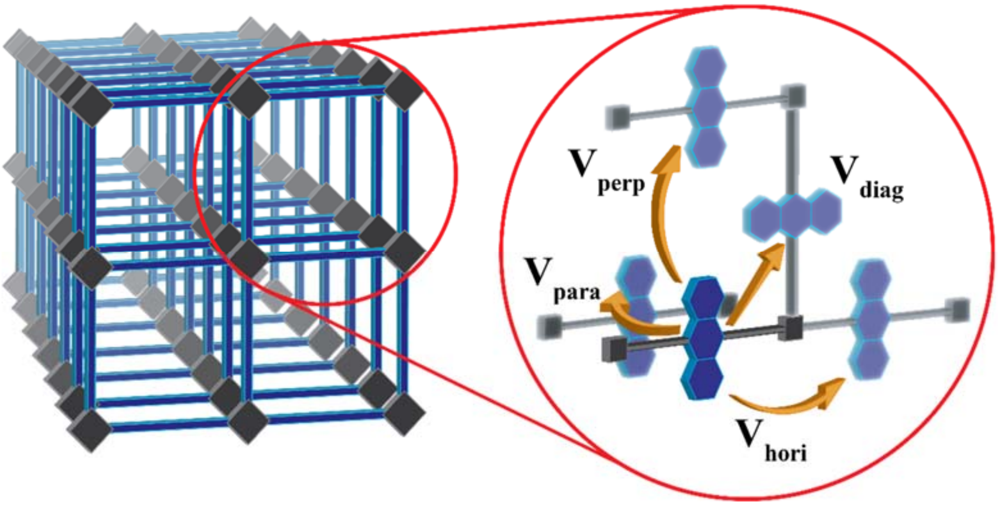
Metal organic frameworks are promising materials for the design of artificial light-harvesting systems as they provide control of distances and relative orientations of optically active molecules. Their defined geometries allow for sequential migration of photoinduced energy (exciton) over long distances. For instance, Haldar et al.[1] recently showed an efficient anisotropic energy transfer in a Zn-SURMOF containing anthracene-dibenzoic acid as organic linker and Zn^{2+} as metal node.

In this study we aim to provide a deeper understanding of excited state formation and Förster energy transfer in Zn-SURMOF2.

Here, an approach is chosen that combines periodic, molecular, and cluster-based density functional theory calculations. First, the geometric structure of the MOF is obtained from periodic calculations. From the relaxed structure suitable linker-node units are extracted to perform quantum chemical simulations of the ground and first excited state. The Coulombic coupling as a measure of the energy transfer rate is then obtained applying the Transition-Density-Cube (TDC) method, as presented by Krueger et al.[2] This allows us to study the electronic coupling along several directions in Zn-SURMOF2. (Fig. 1)



Four possible energy transfer paths in the general structure of Zn-SURMOF 2.

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Postsynthetic treatment of mesoporous FAU type zeolite with zinc(II), iron(II) and iron(III) ions

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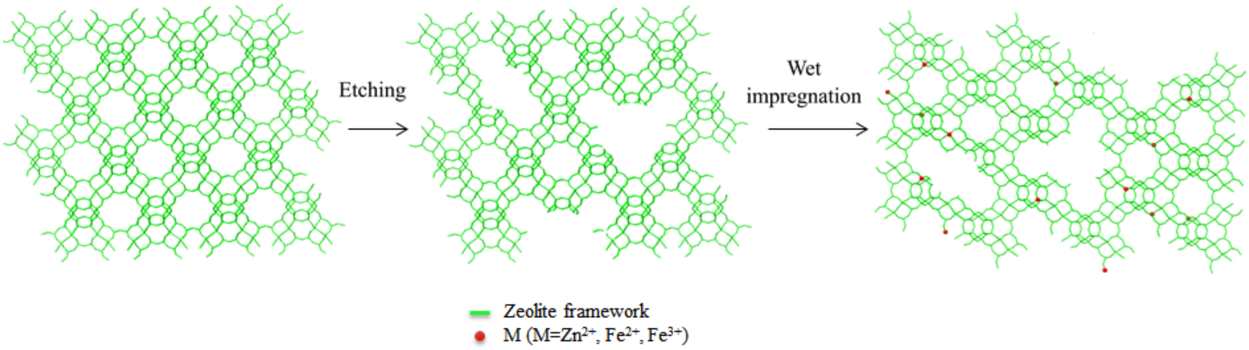
Faujasite type zeolites (FAU) showcase properties that make them great potential catalysts for methanol-to-olefins (MTO) conversion.[1] Their catalytic properties can be further enhanced by creating mesopores using surfactants, such as cetrimoium bromide (CTAB) or etching the crystals with NH_4F in order to facilitate intercrystal diffusion.[2] Thus prepared materials are then further modified by wet impregnation with various zinc(II), iron(II) and iron(III) salts.[3] Incorporation of the transition metal ions in the zeolite framework creates larger number of Brønsted's and Lewis's acid sites that are catalytic canters for MTO conversion.



Schematic way of preparing functionalized MTO catalysts from FAU type zeolite

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Tuneable emission in Ln-SURMOF heterolayer thin films

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I will present oriented and crystalline Ln-SURMOF for the first time in a layer-by-layer (LbL) fashion fabricated by liquid phase epitaxy (LPE) hetero-epitaxy process. Eu/Tb Ln-SURMOF on quartz, have been prepared with outstanding tuneable photoluminescence properties. The thickness of the Ln-SURMOFs can be easily controlled, thereby maintaining its transparent properties, which makes them attractive for the field of optical coatings. Moreover, employing a hetero-epitaxy process, we demonstrated that Eu-SURMOF can be deposited on the top of Tb-SURMOF, maintaining the crystallinity and orientation. The hetero-epitaxial bilayer architectures of Eu/Tb-SURMOF reduced the efficient energy transfer from Tb(III) to Eu(III) and optimized the fabrication of Ln-MOF thin film with a straightforward modulation of the emission color. These novel hetero-epitaxial Ln-SURMOF architectures, possess a bright future in the field of optics, photonics and optoelectronics.

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Coordination polymers with a ROMP-able moiety

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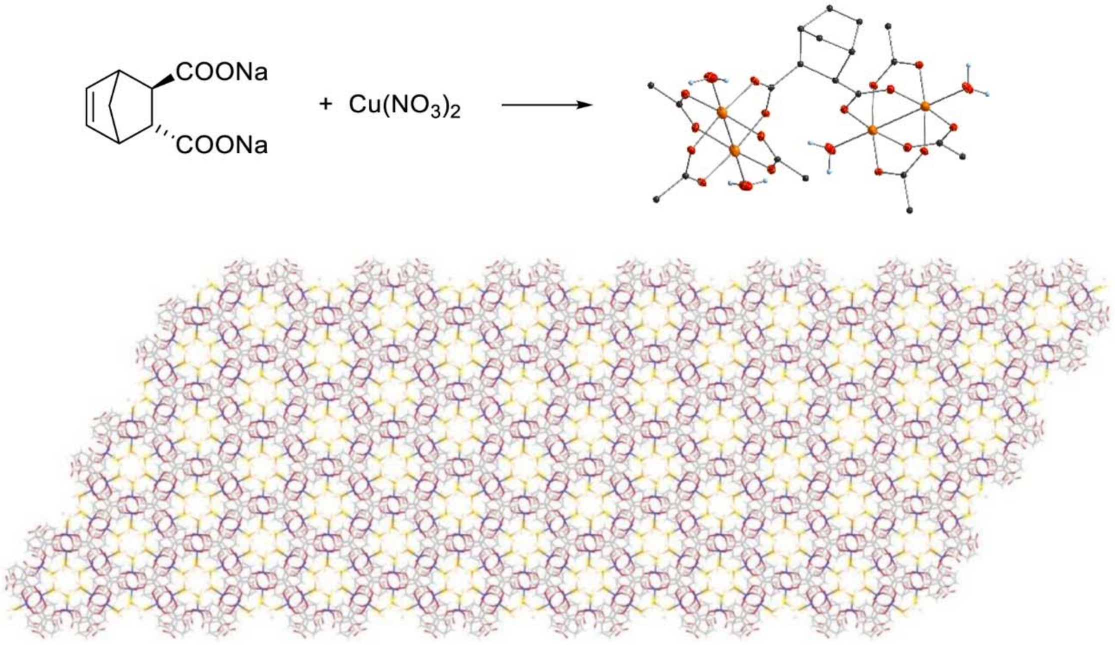
Metal-Organic Frameworks (MOFs) typically consist of a metal ion and a rigid linker enabling the formation of open pores and high internal surface areas. Despite many advantages of these materials, their brittleness and poor processability remains a problem especially in membrane preparation.[1] Thus, MOF-polymer composites have been studied intensively to exploit both the permeability of Metal-Organic Frameworks and the mechanical strength of polymers.[2] In this context, metal-organic polyhedra (MOPs) are of special interest. These porous coordination nanocages are soluble, stable entities, which can be functionalized post-synthetically to form a cross-linked product that can be processed more easily.[3]

In this work, we tried to synthesize MOPs containing a norbornene moiety which can potentially be functionalized or cross-linked. The disodium salt of *endo*,*exo*-5-norbornene-2,3-dicarboxylic acid was mixed with various metal ions including (among others) the nitrate and acetate salts of copper and zinc in aqueous solution. Up to now only the product resulting from the reaction of the linker and copper(II)nitrate is structurally characterized as a 3D coordination polymer with a surface area of 18.2 m^2/g and an average pore size of 68.4 Å.



3D coordination polymer resulting from the reaction of $Cu(NO_3)_2$ and the linker

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Enzyme encapsulation with hydrophilic mesoporous coordination polymers

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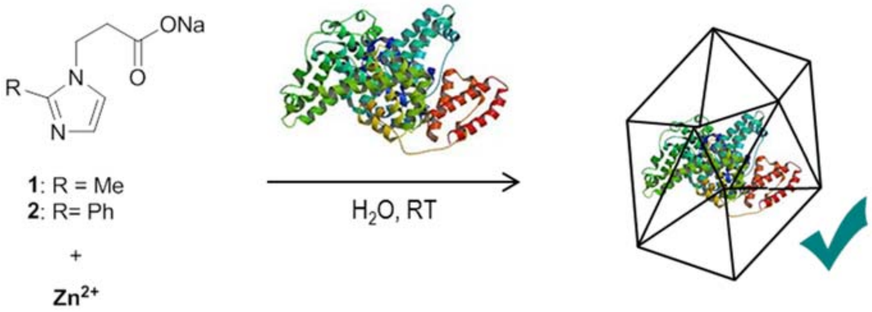
The durability of enzymes under harsh conditions can be enhanced by encapsulation within Metal-Organic Frameworks (MOFs). Hereby the protective capacity and possible applications are strongly dependent on the localization of the biomacromolecules and the topology of the coating.[1,2] The most widely studied MOF for biomimetic mineralisation is so far the hydrophobic zeolitic imidazolate framework-8 (ZIF-8). It is known that proteins tend to have a greater affinity for hydrophobic surfaces, but also that hydrophobic interactions often engender conformational changes that denature the protein and lead to loss of activity.[3] Furthermore, ZIF-8 features micropores of 11.6 Å allowing only small substrates to reach the encapsulated enzyme.



Enzyme encapsulation within hydrophilic coordination polymers

To overcome these limitations we introduce a series of imidazole-carboxylate based hydrophilic coordination polymers of Zn^{2+} which feature mesoporous channels in the range of 46-56 Å. The biocomposites are formed by simply incubating proteins in (buffered) aqueous solution containing the ligand and the Zn-salts under mild conditions, which is important to maintain protein activity.[4] We demonstrate that encapsulated proteins were not degraded upon addition of trypsin (EC 3.4.21.4) to the supernate and can be again released from the composite by dissolving it.
This contribution will deal with the synthesis, the structural description and the properties of the materials. Furthermore results on the encapsulation of proteins will be discussed.

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Adsorption and desorption of L-cysteine on nanoporous gold monitored by in-situ resistometry

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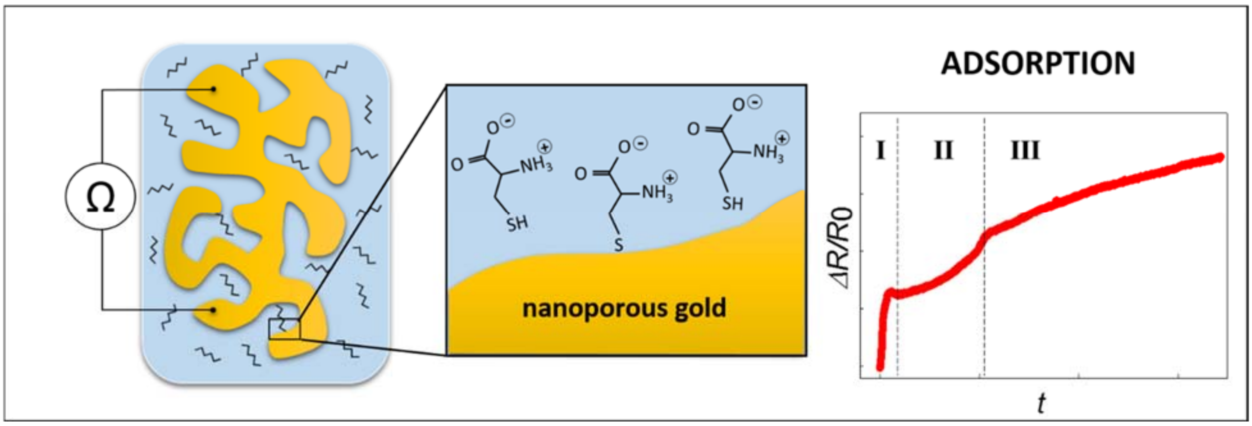
Surface modifications of nanoporous metals have become a highly attractive research field as they exhibit great potential for various applications, especially in biotechnology. Using self-assembled monolayers is one of the most promising approaches to modify a gold surface, however, only few techniques are capable of characterizing the formation of these monolayers on porous substrates.

Here, we present a method to in-situ monitor the ad- and desorption of self-assembled monolayers on nanoporous gold by resistometry, using cysteine as example. During the adsorption an overall relative change in resistance of 18% is detected which occurs in three different stages. First, the cysteine molecules are adsorbed on the outer surface. In the second stage, they are adsorbed on the internal surface and in the last stage the reordering accompanied by additional adsorption takes place. The successful binding of cysteine on the Au surface was confirmed by cyclic voltammetry, which showed a significant decrease of the double layer capacitance. Also, the electrochemically controlled desorption of cysteine was monitored by concomitant in-situ resistometry. From the desorption peak related to the (111)-surface of the structure, which is associated with a resistance change of 4.8%, an initial surface coverage of 0.48 monolayers of cysteine could be estimated.



Thin-layer zeolitic imidazolate frameworks as host for metal nanoparticles

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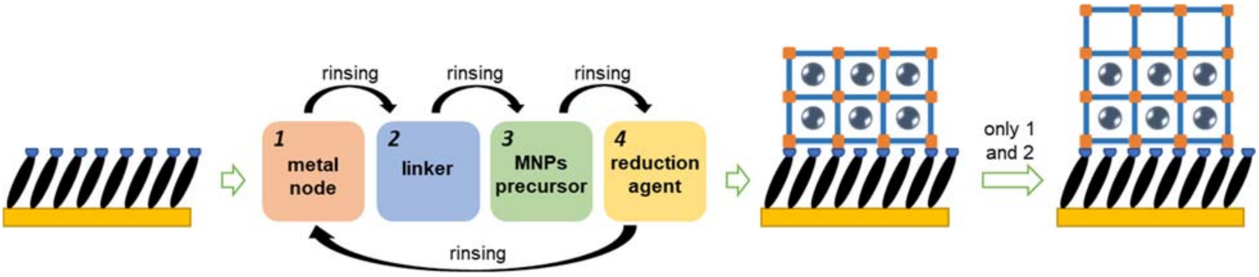
Metal-Organic Frameworks (MOFs) are perspective supports for different guest species such as gas molecules, ions, bioactive compounds, nanoparticles, enzymes, and many others due to their fascinating properties.[1] Among all the MOFs, zeolitic imidazolate frameworks (ZIFs) are promising hosts for monometallic and bimetallic nanoparticles (MNPs) given their known water stability, crystallinity and small pore sizes.[2] For many applications, the achievement of smooth and defect-free MOF thin films is required. For such needs, highly oriented surface-mounted MOFs (SURMOFs) can be produced by liquid-phase epitaxy (LPE) using layer-by-layer (LBL) approaches on various substrates.[3] Hereby, we show that SURMOF-ZIFs can be successfully loaded with monometallic nanoparticles using the LPE-LBL liquid impregnation technique via dipping (Figure 1). We have demonstrated the versatility of this technique and prepared various MNPs@SURMOF composites on different supports. Such LBL deposition of MNPs offers the possibility of creating sandwich-type structures with precisely localized MNPs inside the MOF, something not yet achieved using powder MOFs. Likewise, high catalytic activity of MNPs@SURMOF composites in organic reactions could be demonstrated.



Schematic way of preparation of MNPs@SURMOF composite by LPE-LBL technique

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Porous materials characterization

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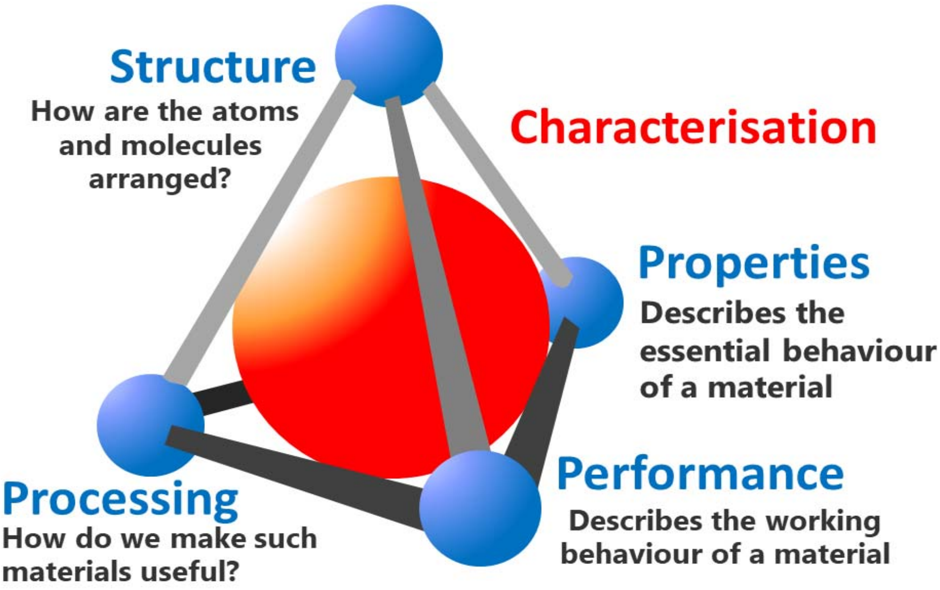
Good characterization techniques are fundamental for the development of advanced materials. Our laboratory houses state-of-the-art devices which have provided crucial insights into materials we have developed – in particular their crystallinity,[1] morphology,[2] microstructure and porosity.[3] In this presentation, we profile the instrumentation in our laboratory for both the *in-* and *ex-situ* characterization of porous and ceramic materials. We illustrate how each device has been used to elucidate important properties of porous materials and the ramifications for the scientific literature.



The materials science paradigm[4]

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Fatty acids as biomimetic replication agents for luminescent MOF patterns

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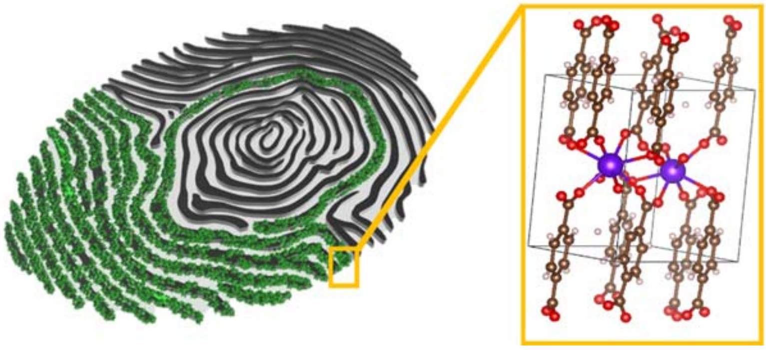
Biomimetic replication is a process that exploits the interaction of specific biomolecules and precursors of Metal-Organic Frameworks (MOFs) to control the MOF crystal positioning and patterning. The understanding of this self-assembly process is crucial for the fabrication of MOF-based devices (i.e. sensors). In the biomimetic replication process, the biomolecules act as heterogeneous nucleation seeds for the crystallisation of MOFs.[1–3] In our study, we employed fingerprint residues (*fpr*) as seeds for the growth of a luminescent Terbium-based MOF (Tb-MOF). The Tb-MOF grows exactly on *fpr*, paving the way for applying MOFs to forensic science.[4,5] In our study, we analysed the effect of the different chemical components of the *fpr* on the Tb-MOF growth, and we identified the key-role of different biomolecules as seeding agents. Finally, we exploited the mechanism for the fabrication of different Tb-MOF patterns.



Schematic of the biomimetic replication of Tb-MOF on fingerprint residue

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Metal-Organic Frameworks acting as enzyme carriers

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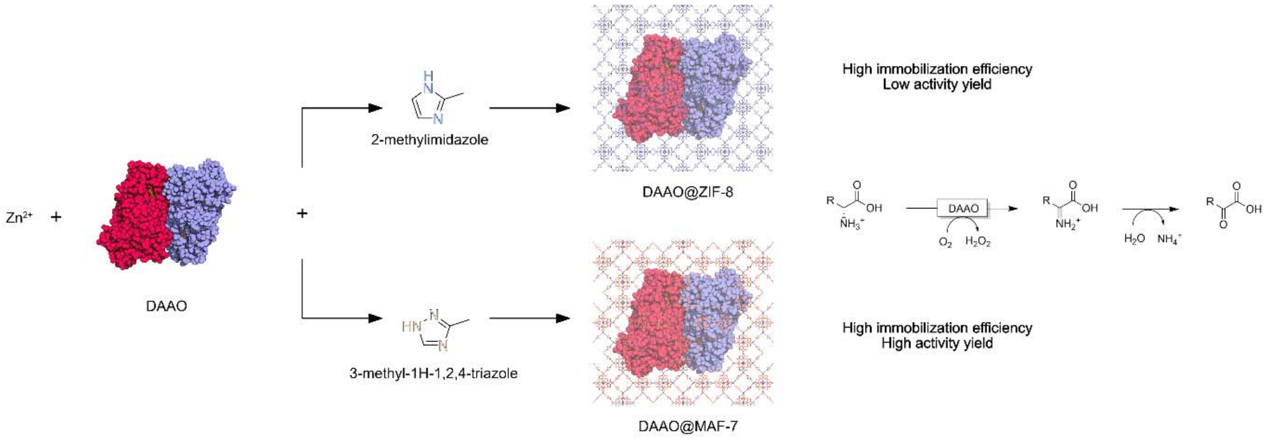
Metal-Organic Frameworks (MOFs) are a class of materials which can act as immobilization carriers for many different biocatalysts.[1,2] In addition to protecting the biocatalysts from harsh conditions, they may also increase their long term stability and enable biocatalyst recycling.[3,4] In particular, zeolitic imidazole framework-8 (ZIF-8) and metal-azolate framework-7 (MAF-7) have recently gained increasing attention as protein carriers, nevertheless little is known on the in operando stability of these materials.[5,6] Herein, we describe the encapsulation of two proteins; the D-amino acid oxidase (DAAO) from *Trigonopsis variabiilis* and the green fluorescent protein variant sYFP from *Aequorea victoria*.[7] Characterization of the obtained material revealed high protein loading for DAAO@MAF-7 and the retention of activity. Using sYFP we were able to assess the stability of MAF-7. Thus, MAF-7 was confirmed to be an interesting MOF for biotechnological applications.



Schematic of the preparation of DAAO@ZIF-8 and DAAO@MAF-7

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Carbohydrates@ZIF-8

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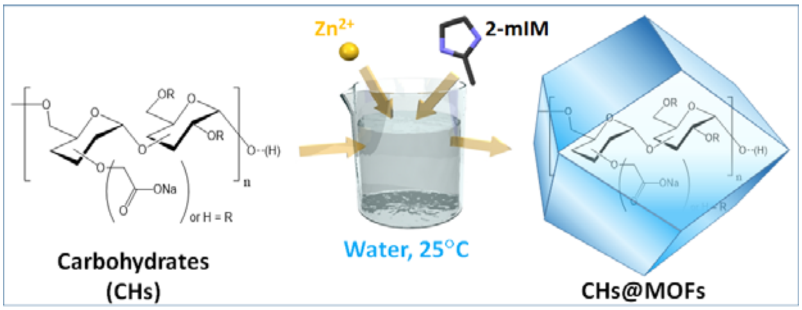
Metal-Organic Frameworks are a class of porous materials that are promising for applications in areas such as gas storage, separation, catalysis and biotechnology.[1] A recently disclosed method named *biomimetic mineralization* uses biomacromolecules to enhance the MOF self-assembly process for the encapsulation of proteins, DNA, enzymes, viruses, living yeast cells and bacteria in MOFs.[2] Carbohydrates, as pure molecules or as a component of proteins and cells, perform essential biological functions; nevertheless, a reliable/reproducible preparation protocol was missing. The successful preparation of carbohydrates@MOFs and the understanding of the proper conditions for the preparation of such MOF biocomposites could result in new biomedical applications.[8]

In this work, we disclose how carbohydrate@MOF biocomposites can be reliably prepared.[8] We found that chemical functionalizations, such as carboxylation, leads to an enhancement of the metal cation concentration at the surface of the molecule and triggers the rapid self-assembly of ZIF-8. We determined the encapsulation efficiency and measured the release of the encapsulated carbohydrate. Our findings demonstrates that ZIF-8 and related polymorphs can be used to prepare ZIF-based biocomposites for the delivery of carbohydrate-based therapeutics.[3]



biomimetic mineralization of ZIF-8 triggered by carbohydrates

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Atomic Force Microscopy for in-situ characterization of porous crystals

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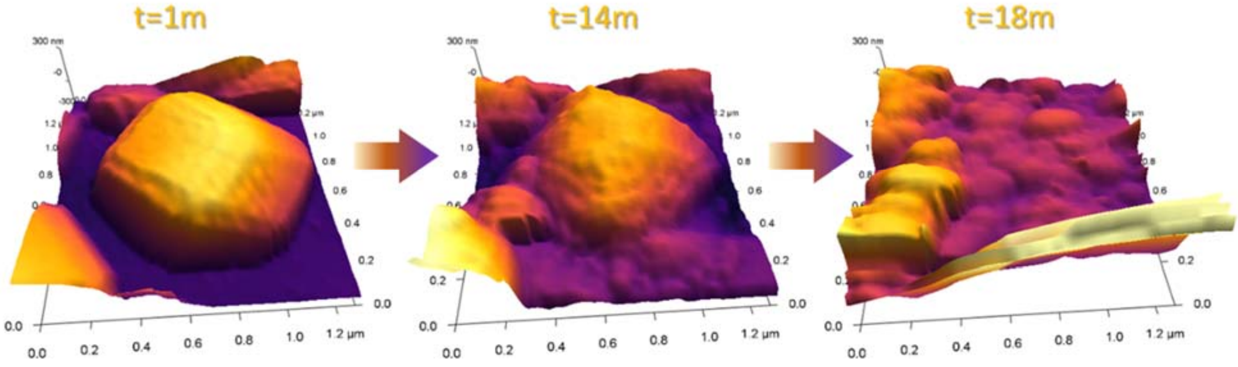
Metal-Organic Frameworks (MOFs) have been proposed as active materials for a wide scope of applications related to their high specific area, tuneable pore size and surface chemistry[1]. The relevant functional properties of MOF materials and composites are often related to the structural and morphological characteristics of these porous crystalline materials. However, it is fundamental to understand and further control their properties, such as crystal size and structure, surface area, defects, chemical composition, nanoscale structure, porous arrangement and mechanical properties. In this context, Atomic Force Microscopy (AFM) is an excellent tool to provide information about morphology and nano-scale properties of MOFs and composites. AFM and other Scanning Probe Microscopy (SPM) techniques can provide information not only about the topography but also about nanomechanical properties and other local characteristics (electrochemical, magnetic) with outstanding resolution, down to the atomic scale.[2] More specifically, in-situ AFM measurements performed in a closed liquid cell provide the possibility to study chemical reactions and the evolution of crystal growth and dissolution. Moreover, the advent of ultra-fast scanning AFMs has recently enabled the study of dynamic processes relevant to these materials. In this work we demonstrate these exciting possibilities by monitoring in-situ growth and decomposition of MOFs.[3,4]



AFM topography images showing the dissolution of a ZIF-8 crystal immersed in a 10mM PBS solution, taken at three different times during the process.

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Macroporous poly(norbornadiene) is a fast oxygen scavenger material at room temperature

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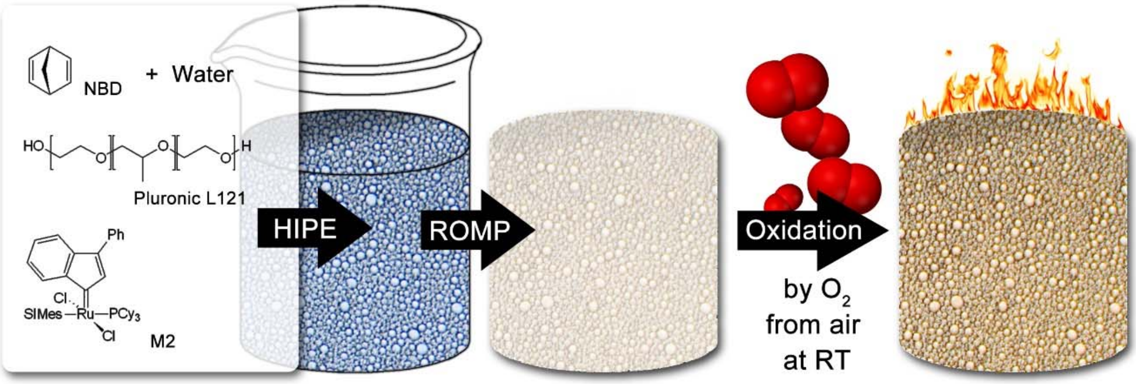
Oxygen can have considerable detrimental effects on goods prone to oxidization, in particular food. Oxygen scavengers are therefore a mean to maintain food product quality. Most oxygen scavengers are based on iron powders containing catalysts, which react with some water from the surroundings to produce a reactive hydrated metallic reducing agent that scavenges oxygen and irreversibly converts it to a stable oxide. Such oxygen scavengers are capable of reducing oxygen levels to less than 0.01% (100 ppm(v)). As an alternative, in particular for protecting liquids, various non-metallic reagents and organometallic compounds that have an affinity for oxygen have been used but speed and capacity of such oxygen scavenging plastic films and laminated trays are considerably lower compared to iron based oxygen scavenger sachets or labels.[1]



Schematic preparation of the oxygen scavenger material

Herein, a hitherto unprecedented polymeric material for oxygen removal, namely a macroporous poly(norbornadiene) foam is reported. Emulsion templated norbornadiene is cured via Ring-opening Metathesis Polymerization (as it is described in Ref 2 for dicyclopentadiene) yielding macroporous poly(norbornadiene) foams of 76% porosity exhibiting appealing stiffness combined with considerable ductility. The foams are readily oxidized in air at room temperature. Their oxygen uptake capacity amounts to more than 300 mg O_2/g foam. A final oxygen level of a maximum of 0.0005 vol%, i.e. 5 $\text{ppm}_{(v)}$ can be achieved in closed volumes after several hours at room temperature. The synergism of the chemical nature of the polymer and the porous morphology allows for the first example of a purely organic oxygen scavenger material with properties distinctly surpassing the state-of-the art in the field.[3]

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