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The Dynamic Materials, Crystals and Phenomena conference will take place in Fribourg, Switzerland from the 22nd to the 24th of March 2023.

Amphidynamic materials have emerged as a unique category of condensed phase matter that combine crystalline lattice formation with the components that display dynamic behavior in the solid state. This has so far involved a range of materials incorporating dynamic functional units in the form of stimuli-responsive molecular switches and machines with functionalities that are preserved in the solid state. In particular, this has been possible by relying on porous framework materials, metal-organic frameworks (MOFs) and covalent organic frameworks (COFs), as well as other hybrid and bio-inspired materials that have demonstrated potential for serving as dynamic scaffolds. While these unique properties of dynamic materials often inspired by nature increase the level of complexity in understanding their properties and functions, they also open the way for innovative applications.

The aim of this symposium is to bring together experts from different disciplines and provide an unprecedented forum for open discussion towards deepening the understanding of dynamic materials across different material classes and length scales, including responsive molecular switches and machines, porous dynamic materials (MOFs, COFs), as well as emerging hybrid dynamic materials, such as hybrid perovskites and others. Beyond materials design and synthesis, the discussion will address critical experimental and theoretical techniques for assessing structural and in particular dynamic properties of this unique class of materials on a spatial-temporal level.

<u>Conference organizers</u>

Jovana Milic

Soft Matter Physics

University of Fribourg, Adolphe Merkle Institute, CH

Simon Krause

Nanochemistry Department

Max Planck Institute for Solid State Research, DE

#DynaMIC23	
Keynote Speakers	
Andrew Goodwin	Inorganic Chemistry Laboratory University of Oxford, GB
Stephen Loeb	Department of Chemistry and Biochemistry University of Windsor, CA
Monique van der Veen	Chemical Engineering Department of Chemical Engineering, Delft University of Technology Van der Maasweg, NL
Invited Speakers	
Tessel Bouwens	Yusuf Hamied Department of Chemistry University of Cambridge, GB
Stefano Canossa	Nanochemistry Max Planck Institute for Solid State Research, DE
Angiolina Comotti	University of Milano-Bicocca, IT
Jack D. Evans	University of Adelaide, AU
Nicolas Giuseppone	University of Strasbourg, France., FR
Sebastian Henke	Technische Universität Dortmund, GE
Claire Hobday	School of Chemistry, University of Edinburgh, GB
Susumu Kitagawa	Institute for Integrated Cell-Material Sciences Kyoto University, Japan, JP
Dominik Kubicki	University of Warwick, GB
Veronique Van Speybroeck	Center for Molecular Modeling Ghent University, BE
Omer Yaffe	Weizmann Institute of Science, IL
Local Coordinators	
Jessica M. Clough	Assistant Professor, Polymer Chemistry & Materials Group, Adolphe Merkle Institute
José Augusto Berrocal	Group leader, Polymer Chemistry & Materials, Adolphe Merkle Institute

001 ORAL

Dynamic disulfide chemistry in polymers and crystals

Zhang, Qi

University of Groningen (NL)

Understanding dynamic chemistry systems in Nature inspires chemists to design biomimetic synthetic materials. Disulfide bonds, the bonds that tie peptides, feature their dynamic covalent nature, that is reversible covalent bonds. Here we propose that making polymers with disulfide bonds can be a solution towards intrinsically dynamic materials. Unlike traditional plastics and noncovalent (supramolecular) polymers, poly(disulfides) can simultaneously exhibit chemical recycling ability and excellent mechanical performances. We will focus on the poly(disulfides) derived from thioctic acid, a natural small molecule, to show the promising applications of these intrinsically dynamic materials in self-healing elastomers, adhesives, and actuators [1-5]. Then I will move to our recent discovery that hydrogen bonds are essential in the control of disulfide chirality and enable stereodivergent chirality transfer. We find that the formation of S−S---H−N hydrogen bonds in solution can drive conformational adaption to allow intramolecular chirality transfer, while the formation of C=O---H−N hydrogen bonds results in supramolecular chirality transfer to form antiparallel helically self-assembled solid-state architectures [6].

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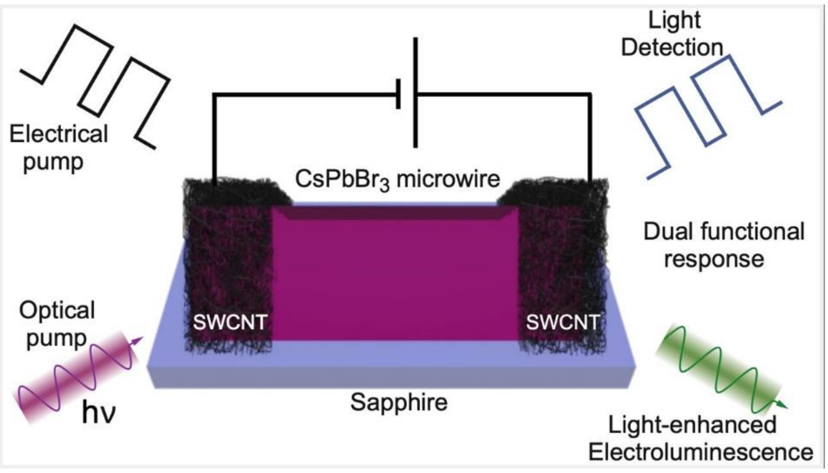
003 POSTER

Mixed Ionic-Electronic Conduction Faciliates Halide-Perovskite Light-Emitting Photodetector

Marunchenko, Alexandr

ITMO University, St. Petersburg, Russia (RU)

Light emission and detection are the two basic elements in optoelectronic communication systems. Generally, both functions have been demonstrated using the p-n diode structure which is used for wide range of optoelectronic applications. However, the processes of carrier injection and photocarrier collection have competing carrier dynamics, where in order to implement both functions, the direction of the applied electrical bias should be switched. In current work we demonstrate that the concept of mixed ionic-electronic conduction in halide-perovskites is beneficial in demonstrating the novel effect: light-emitting photodetection without switching applied electrical bias. The device consists of a lateral structure where CsPbBr3 microwire is connected to single-walled carbon nanotube (SWCNT) thin film electrodes. Both functionalities of light detection and light emission come from the modulation of an energetic barrier caused by the cooperative effect of mobile ions and the photogenerated charge carriers at the CsPbBr3/SWCNT interface. We additionally see the electroluminescence enhancement by optical light. Such dynamic and complex behaviour governed by mixed ionic-electronic conduction in halide-perovskites will be in demand in multifunctional optoelectronic devices searching for complex multifunctional materials.



004 INVITED SPEAKER

Benchmark Rotor Dynamics and Light-Driven Motors Engineered in 3D Porous Architectures

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Bracco, Silvia [a]
Perego, Jacopo [a]
Bezuidenhout, Charl X. [a]
Piva, Sergio [a]
Daolio, Andrea [a]
Prando, Giacomo [b]
Rosa, Ilaria [a]
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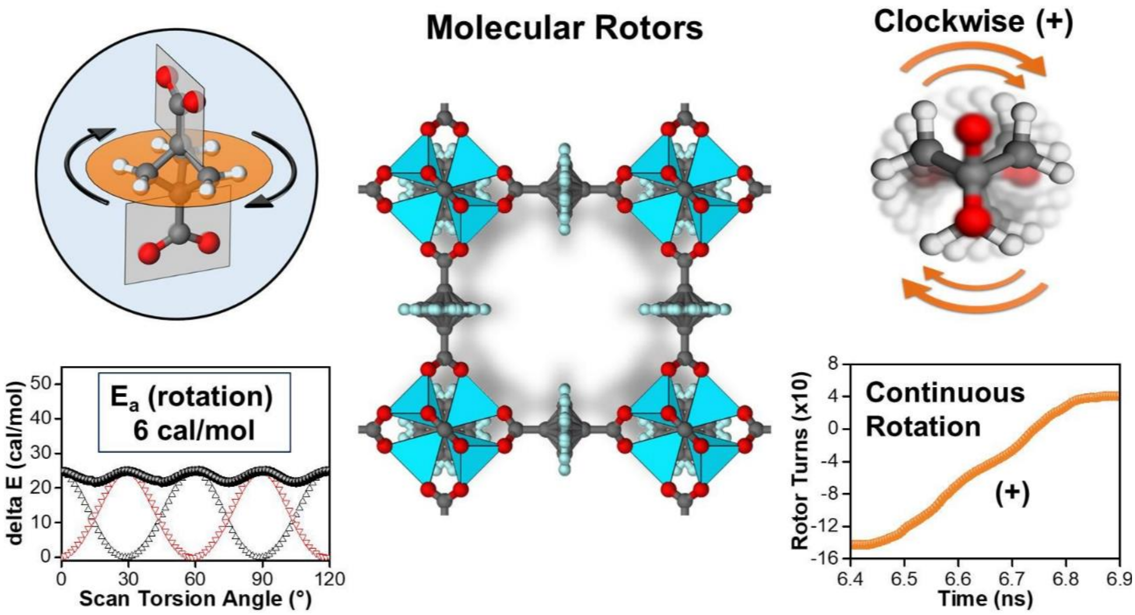
Rotors, motors and switches in the solid state find a favorable playground in porous materials, especially in Metal Organic Frameworks (MOFs), thanks to their large free volume, which allows for fast dynamics. We focused on dynamic materials endowed with high responsiveness and under limited thermal noise conditions which enable the fabrication of molecular machines with low energy dissipation and controllable dynamics.

We have realized a fast molecular rotor in the solid state whose rotation speed approaches that of unhindered rotations in organic moieties even at very low temperatures (2 K) [1,2]. The three-fold bipyramidal symmetry of the rotator conflicts with the four-fold symmetry of the struts within the cubic crystal cell of the zinc metal–organic framework, frustrating the formation of stable conformations. This allows for the hyperfast rotation of the bicyclic units persistent for several continuous turns, with an energy barrier of 6.2 cal mol−1 and a high frequency even at very low temperatures (1010 Hz below 2 K).

Geared molecular rotors with negligible energy-requirements in MOFs enabled fast yet controllable and correlated rotary motion[3]. A MOF architecture was capable of supporting fast motional regimes (107 Hz), even at extremely cold temperatures, of two distinct and hypermobile rotors arranged in pillar-and-layer 3D arrays. The rotors explored multiple configurations of conrotary and disrotary relationships, switched on and off by thermal energy, an unprecedented cascade mechanism modulated by distinct energy barriers. Notably, fluorinated Metal-Organic Frameworks (MOFs), comprising a wheel-shaped ligand with geminal rotating fluorine atoms, produced a benchmark mobility of correlated dipolar rotors at 2 K, with practically null activation energy (Ea = 17 cal/mol), as supported by 1H T1 relaxation NMR, synchrotron radiation X-ray diffraction at 4 K and DFT modeling (Angew. Chem. Int. Ed. 2023 in press). Gas accessibility, shown by hyperpolarized-Xe NMR, allowed for chemical stimuli intervention: CO2 triggered dipole reorientation, reducing their collective dynamics and stimulating a dipole configuration change in the crystal.

Furthermore, motors were inserted into porous frameworks and metal-organic frameworks wherein two distinct linkers with complementary light absorption-emission properties were integrated into the same material. Unidirectional motion was achieved by exposure to sun-light of the solid particles, which thus behave as autonomous nanodevices.[4] The visible-light-driven rotation of an overcrowded alkene-based molecular motor strut in a dual-function metal–organic framework (MOF) was realized by the use of two types of functional linkers. Visible light-driven rotation of the molecular motor was proved to be in the solid state at rates similar to those observed in solution.[5]



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005 ORAL

Toward the spatiotemporal design of the switchable Metal-Organic Framework DUT-8

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Bon, Volodymyr [a]
Kaskel, Stefan [a]

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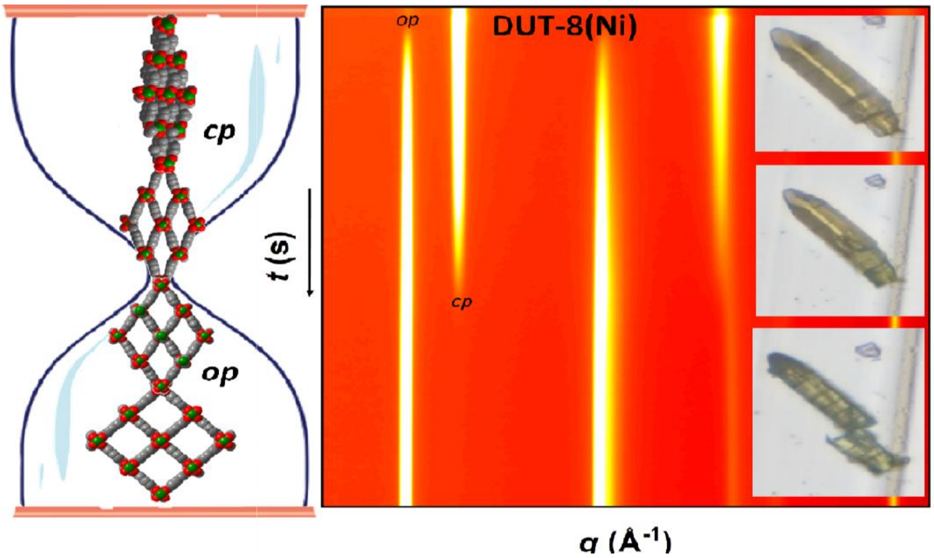
Switchable metal-organic frameworks change their structure in time and selectively open their pores, adsorbing guest molecules, leading to highly selective separation, pressure amplification, sensing, and actuation applications. While numerous studies have addressed the function of switchable MOFs under quasi-equilibrium conditions, only a few studies have addressed their dynamic response and spatiotemporal evolution experimentally. The energetic landscape and transition paths characterising the switching process of dynamic MOFs, are virtually unexplored. The three-dimensional engineering of metal-organic frameworks has reached a high level of maturity, but spatiotemporal evolution opens a new perspective towards engineering materials in the fourth dimension (time) by t-axis design, in essence exploiting the deliberate tuning of activation barriers.

This work demonstrates the first example in which an explicit temporal engineering of a switchable, gate pressure MOF (DUT-8, [M1M2(2,6-ndc)2dabco]n, 2,6-ndc = 2,6,-naphthalenedicarboxylate, dabco = 1,4 diazabicyclo[2.2.2]octane, M1= Ni, M2 = Co) is presented. Spatiotemporal response of DUT-8 is governed by an activation barrier reflected in the gate opening pressure and the activity of the pore opening stimulating guest molecule. It can be deliberately tuned by adjusting the stiffness of the metal node. Finally, we used the variation in metal and metal content to tune the gate opening rates.

Various in situ time-resolved techniques, ranging from ensemble adsorption and advanced synchrotron X-ray diffraction experiments to individual crystal analysis, were applied to analyse the switching kinetic stimulated by vapour adsorption.

Individual crystal transformation rates are orders of magnitude faster than rates estimated based on ensemble methods. However, slow-transforming ensembles show a delayed induction of individual crystal transformations. Differences in the spatiotemporal response of crystal ensembles originate from induction times that vary statistically. In DUT-8(Co/Ni) it widens characteristically with increasing cobalt content, reflecting increasing activation barriers



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006 POSTER

A postsynthetically Modified Amphidynamic Metal Organic Framework

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Torres Huerta, Aaron [a]
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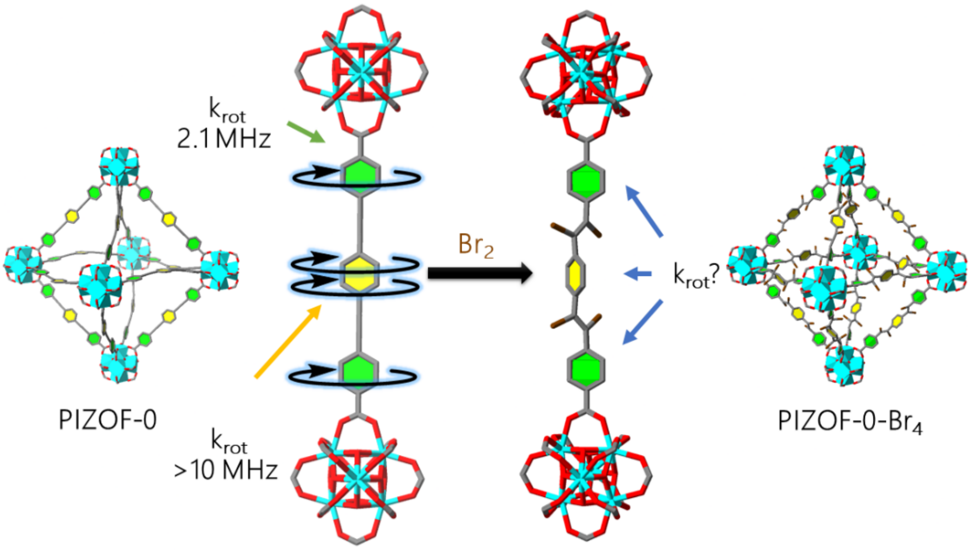
Including Artificial Molecular Machines (AMMs) in densely packed and ordered matrices is a crucial step for developing molecular architectures with sophisticated functionalities. In this way, we develop metal-organic frameworks (MOFs) with amphidynamic properties: fast rotational frequency of specific molecular components embedded within an open, rigid framework. We previously demonstrated that a water-stable MOF named PEPEP-PIZOF-0, exhibits multiple rotational rates due to the electronic structure of the linker, with and without the presence of highly interacting molecular guests.[1]

Controlling dynamics is a crucial step towards functional advanced materials; for this reason, we decided to modify the linker through a Post-synthetic Modification with Bromine.[2] Subsequently, the internal dynamics were studied through solid-state NMR (13CPMAS and 2H echo spin), using deuterated isotopologues with 2H enriched samples showing significant changes in the motion. This work opens the way to develop materials with chemically modulated local dynamic properties aimed to generate coupled and organized AAMs as in an Artificial Molecular Factory (AFM).[3]



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007 INVITED SPEAKER

Static and Dynamic Conformational Freedom of ZIF-90 Revealed by Single Crystal Diffuse Scattering

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Frison, Ruggero [c]
Bürgi, Hans-Beat [d]

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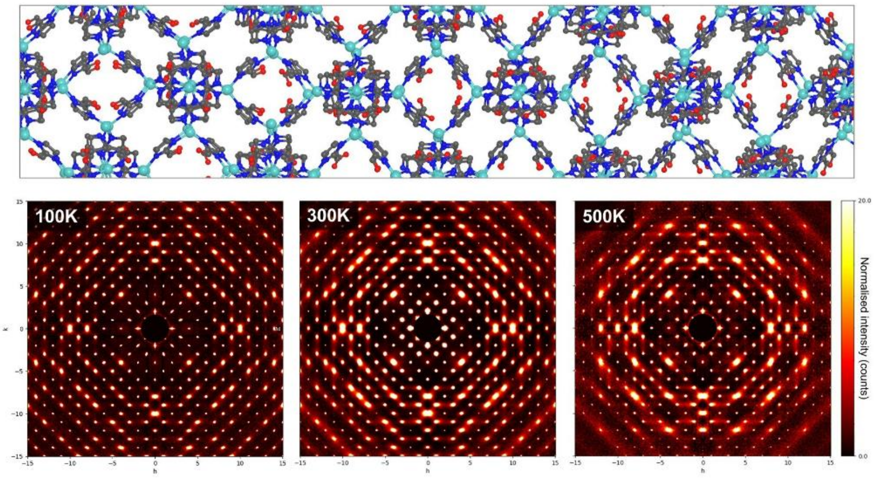
“Perfect crystals” are a human-made concept. Indeed, any crystalline material has some degree of aperiodicity in the form of defects, distortions, etc. In this regard, metal–organic frameworks (MOFs) are among the least periodic, most importantly due to their structure flexibility. Whether this manifests as static distortion or vibrations, characterizing the structural aspects of MOFs flexibility is a long-lasting challenge as conventional crystallography focuses on extracting from diffraction data only the average crystal structure. In this way, local deviations from idealised average models are systematically overlooked. While several complementary spectroscopy, imaging, or powder diffraction techniques provide valuable pieces of information on the complexity of real MOF structures, the use of diffuse scattering present in single crystal diffraction data can allow an actual determination of their 3D aperiodicity.1 Hereby, I will show how this technique afforded a detailed atomistic picture of the unexpectedly complex aperiodic structure of the MOF ZIF-90.2 A combination of Monte Carlo aperiodic crystal simulations and variable-temperature diffuse scattering analysis on single crystals revealed a hidden diversity of framework distortions involved in a temperature-induced phase transition. Our results shed light on a poorly known and uncontrolled degree of freedom in MOF chemistry with inspiring implications for the rational design of their aperiodicity, and highlighting the importance of a meticulous crystallographic inspection of disorder in framework structures.



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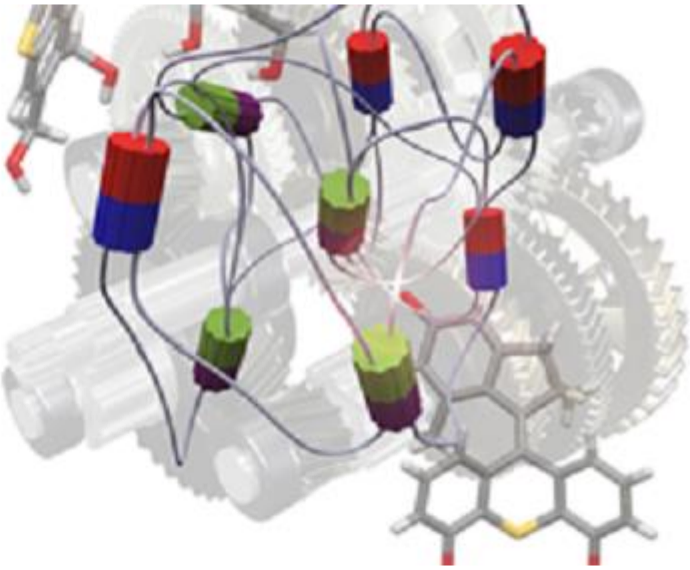
010 INVITED SPEAKER
Artificial molecular machines that work on all scales

Giuseppone, Nicolas

University of Strasbourg - Institut Charles Sadron

Making molecular machines that can be useful in our macroscopic world is a challenging long-term goal of nanoscience. Inspired by the protein machinery found in biological systems, and based on the theoretical understanding of the physics of motion at nanoscale, organic chemists have developed a number of molecules that can produce work when triggered by various external chemical or physical stimuli.[1] In particular, basic molecular switches that commute between (meta)stable states, and more advanced molecular motors that produce unidirectional cyclic motions out-of-equilibrium when fueled with external energy, have been reported. However, the integration of individual molecular motors in a continuous mechanical process that can have measurable effects at various length scales and up to the macroscale remains an important objective. We will discuss advances developed by our group on artificial molecular machines, which involve their mechanical coupling with polymer systems. We will show how it becomes possible to integrate them and to make use of their mechanical work going from individual molecular devices to macroscopic materials.



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011 INVITED SPEAKER
Chemistry and Application of Soft Porous Crystals from PCPs/MOFs

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Metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) possess inherent voids that allow the storage, delivery, and separation of substances, particularly gases. Among them, 3rd generation MOFs, called flexible MOFs or soft porous crystals (SPCs),[1-3] exhibit a structural change from crystal to crystal in response to physical and crystalline stimuli. This feature distinguishes them from other porous materials, reminiscent of the induced fit mechanism of bioenzymes and the cooperative phenomenon of hemoglobin. In contrast to rigid materials showing a Langmuir type I isotherm, SPCs possess a sigmoidal isotherm and higher usable capacity and efficient recognition of guest species. The flexibility depends not only on the binding ability and mobility of unit ligands and metal ions but also on other factors, including the deformation of the entire framework as a result of the guest molecules in the pores. Strategies using ligand functionalization have been developed to investigate the properties but have mainly focused on discovering and understanding SPC phenomena in SPCs. This trend has now shifted towards controlling the adsorption properties for practical applications. This talk provides an essential and accessible overview of the historical background of the chemistry of SPCs, their features, and outlook as 4th generation MOFs,[2,3] in particular, design and synthesis, dynamic structure analysis, flexibility and function, and theoretical treatment and interpretation of the mechanism, as well as their applications.[4,5]

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012 KEYNOTE
Dynamics and Correlated Disorder in some Framework Materials

Goodwin, Andrew
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While framework materials such as MOFs and coordination polymers are often represented as possessing highly-crystalline, ordered structures, in practice many such systems are actually very disordered — and sometimes in particularly interesting ways. Our own interest is in understanding the various kinds of correlated (i.e. non-random) disorder that emerge in framework materials, with the view of learning how to link disorder to different kinds of materials properties. The key experimental tool we use is that of diffuse scattering measurements (X-ray and neutron; powder and single-crystal), and we couple these measurements with simple simulations that help capture the key physics at play. In this talk, I will summarise our recent work with three disordered framework structures: Cd(CN)2 [1], DUT-8(Ni) [2], and TRUMOF-1 [3]. In each case there is an unusual interplay between structural disorder and dynamical or elastic phenomena, and these various relationships will be introduced and discussed. The talk is likely to present more questions than answers.

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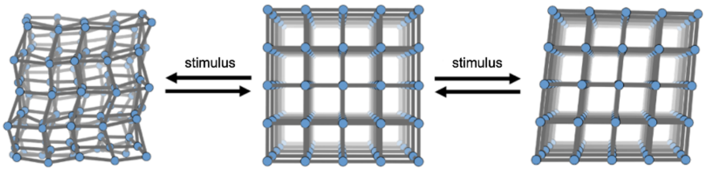
013 INVITED SPEAKER
Non-Crystallinity and Disorder in Dynamic Metal-Organic Frameworks – Responsiveness, Melting and Glass-Formation

Henke, Sebastian
Technische Universität Dortmund (GE)

Metal-organic frameworks (MOFs) are an emerging family of porous solid-state materials exhibiting huge potential for various technological applications (gas storage/separation, catalysis, drug delivery, sensing, etc.). Even though research has primarily focused on the crystalline state of these materials, non-crystalline or amorphous MOFs have received increasing attention recently. This is because of the emergence of novel properties associated to the non-crystalline state, such us meltability and glass formation or unusual structural responsiveness. This talk will cover our recent investigations in the area of non-crystalline and highly disordered MOFs.

Firstly, the phenomenon of frustrated flexibility in MOFs based on the renowned [Zn4O(O2C)6] building unit is introduced. An incompatibility of intra-framework dispersion forces with the geometrical constraints of the [Zn4O(O2C)6] building units results in a new type of guest-responsive structural flexibility of the frustrated MOFs, characterized by reversible loss and recovery of crystalline order under full retention of framework connectivity and topology.[1] A combination of global and local structure techniques reveals stimuli-dependent aperiodic deformations of the inorganic building units as the origin of the unique structural behavior of these MOFs. Some of those materials additionally display a unique thermal behaviour, where increasing the temperature increases the crystalline order of the aperiodically distorted frameworks. This unprecedented entropy-driven disorder-order transition will be discussed in detail.

Secondly, our recent work on liquid and glassy MOFs of the family of zeolitic imidazolate frameworks (ZIFs) is presented. We outline chemical design rules for the systematic modulation of the ZIFs thermal and mechanical properties,[2,3] including tuning the melting point and the corresponding glass transition temperature of the derived glasses. First insights into the intrinsic porosity of the ZIF glasses and how the porosity depends on the choice of the molecular building blocks are introduced.[3,4] Our results set the stage for the application of such MOF glasses as novel functional amorphous materials in kinetic gas separation, solid-state ionic conduction and optics.



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014 ORAL

Dual-Motion Molecular Motors for Advanced Applications

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Crespi, Stefano [a]
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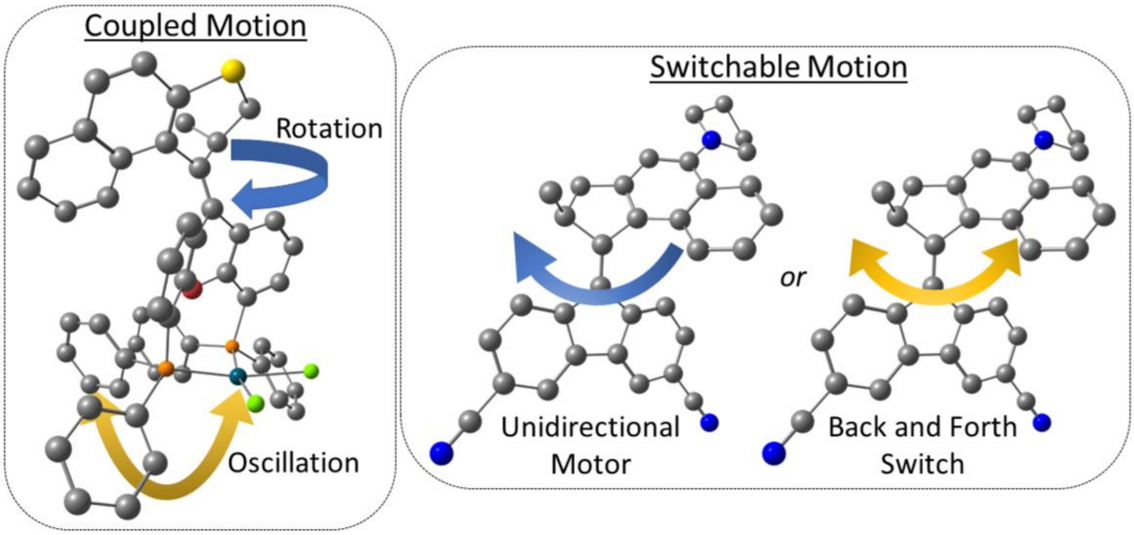
Light-driven, artificial rotary molecular motors have captured the imagination of many chemists and materials scientists with their successful application in a plethora of areas, ranging from catalysis to smart materials and surface science.[1] Overcrowded alkene-based motors are designed to perform a unidirectional rotary motion around the central double bond axle following photoexcitation.[2] In order to achieve a 180° rotation, these compounds first undergo a photochemical E/Z isomerization to reach a metastable isomer from which they relax to a second stable isomer via thermal helix inversion. Repeating this sequence completes a full 360° rotation leading back to the starting isomer. Combining this basic property with additional functionalities is key for unlocking many exciting opportunities for more advanced applications by, for example, allowing us to readily detect these motors in-situ, or adapt the kind of motion they perform.

Here we present two 2nd generation rotary molecular motors which, in addition to their rotation, also perform a second kind of photostimulated motion. In both cases, decorating the motor core with specific substituents was crucial for introducing these additional functionalities. Our experimental results are backed up by in-depth computational studies, revealing the motors’ fundamental modes of operation.

The first example is a Pd complex of a diphosphine substituted motor whose $PdCl_2$ moiety undergoes an oscillation which is coupled to the motor’s rotation.[3] Due to the plane of the $PdCl_2$ group being oriented at an almost 90° angle relative to the lower motor half, rotation of the upper half brings the two into close contact, pushing the Pd centre to the other side. The activation barriers along the trajectory of this induced oscillation are small compared to the rate limiting step of the thermal helix inversion, so the speed of rotation remains unaffected.

The second motor is substituted with electron withdrawing cyano groups in the lower and an electron donating amine in the upper half leading to the formation of a push-pull system.[4] One consequence of this is a pronounced redshift of the absorption spectrum of this compound allowing its rotation to be powered with low-energy orange light. This is coupled with a distinct solvent dependence of the absorption spectrum with the lowest-energy absorption maximum being red-shifted by 49 nm going from pentane to DMSO. In addition, we observe a change in the photostimulated motion from the unidirectional rotation of a 2nd generation molecular motor to a back and forth-type switching motion upon increasing solvent polarity. This is due to a lowering of the activation barrier of the thermal E/Z isomerization of the metastable isomer, reversing the initial photochemical E/Z isomerization. Suppressing the push-pull effect via protonation of the amine leads to recovery of rotary motion in polar solvents.

In short, we present two artificial rotary molecular motors capable of performing two distinct mechanical tasks following photoexcitation. In the first example, an oscillation at the motor's periphery is coupled to the rotation of the motor core, while in the second example the compound's mode of operation can be toggled between that of a unidirectional motor and that of a back and forth-type switch by changing its chemical environment. These principles can be exploited for the design of more complex molecular machines.



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015 KEYNOTE

Designing Mechanically Interlocked Molecules to Function in the Solid-State

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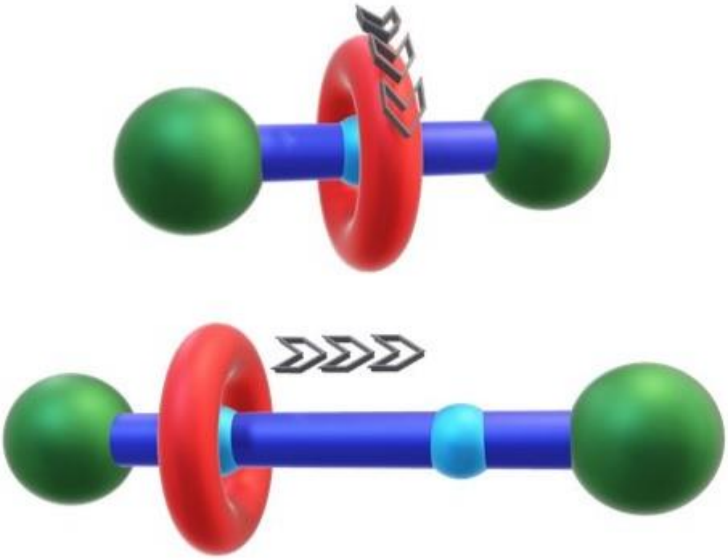
Mechanically interlocked molecules (MIMs) consist of multiple molecular components held together by mechanical bonds. The large amplitude motion of one component relative to the other can be used to design a variety of molecular switches and molecular machines. These molecules are almost exclusively designed to function in solution where their dynamics can occur unimpeded by structural constraints or close contacts between MIM molecules. This is very important for low energy processes but severely limits cooperativity amongst MIMs. This presentation will outline how the mobile components of MIMs can be designed for organization into the porous crystalline lattices of metal-organic framework materials and made to function in the solid-state where there is a much higher degree of organization and potential for interaction and cooperative behaviour.[1] The focus will be on (i) macrocyclic ring rotation [2], (ii) large amplitude translation [3], (iii) molecular switching [4], and (iv) the precise placement and interaction between components with different dynamics [5].



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016 INVITED SPEAKER

Using Supramolecular Machinery to Enhance the Efficiency of Photoelectrochemical Cells

Bouwens, Tessel

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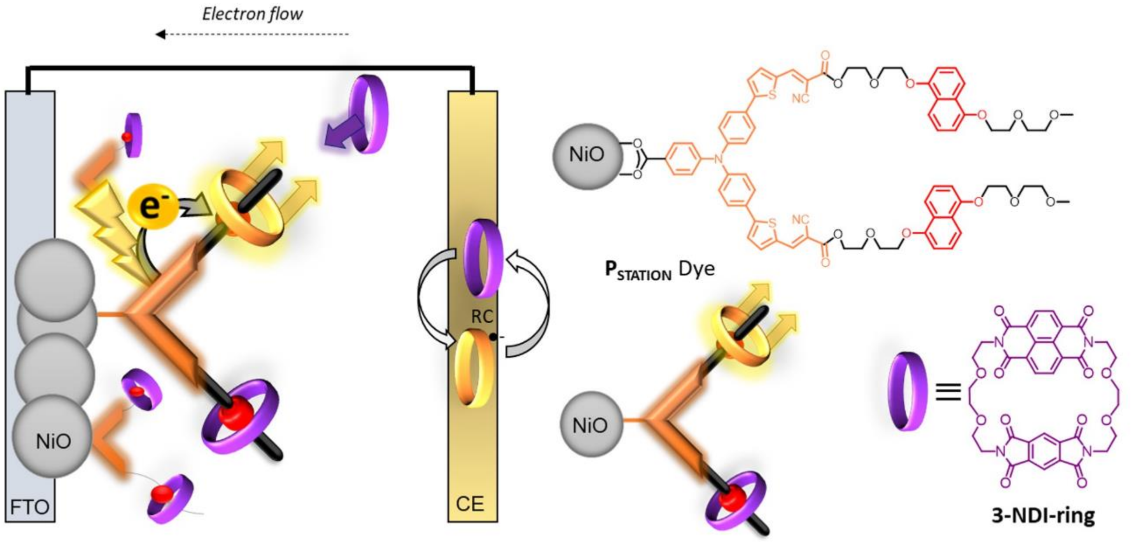
Harnessing solar energy under diffuse light conditions is a challenge that can be addressed with photoelectrochemical cells (PECs). However, PECs suffer from efficiency losses due to electron-hole recombination. Inspired by natural photosynthesis, we demonstrate the use of supramolecular machinery with a pseudorotaxane topology as a strategy to inhibit recombination through an organization of molecular components that enables unbinding of the final electron acceptor upon reduction. We show that preorganization of a macrocyclic electron acceptor to a dye yields a pseudorotaxane that undergoes a fast (completed within ~50 ps) ‘ring launching’ event upon electron transfer from the dye to the macrocycle, releasing the anionic macrocycle and thus reducing charge recombination.. The PECs based on supramolecular machinery demonstrated a 16-fold and 5-fold increase in power conversion efficiency compared to devices featuring two control dyes that do not facilitate pseudorotaxane formation. This bio-inspired approach to integrate supramolecular machinery in PECs demonstrates the impact of molecular organization on the performance of devices for solar conversion technologies.



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017 INVITED SPEAKER

The Dynamics of Pressure Driven Phase Transitions: A Look into the Future of Solid-State Refrigeration

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Heating and cooling processes are responsible for 78% of the UK's environmentally damaging fluorinated gas emissions, primarily due to the employment of hydrofluorocarbon (HFC)-based refrigerant gases.[1] Such compounds are being phased out due to their devastating environmental impact, notably very high global warming potentials (GWP) (~2000 times that of CO_2). This has created a major technological and scientific challenge to find new types of refrigeration materials which are made from sustainable resources, have increased efficiency and are environmentally friendly throughout their entire lifecycle. There is now a strong focus on developing solid-state materials, which are easier to recycle, that demonstrate caloric effects. These have been shown to out-perform vapour compression technology in domestic refrigeration, additionally resulting in lower energy costs.[2] Caloric effects rely on the reversible thermal response of solids to an externally applied field (magnetic or electric field, or hydrostatic pressure) to give rise to magnetocaloric (MC), electrocaloric (EC) or barocaloric (BC) materials.

This talk focusses on understanding the barocaloric effect via study of order-disorder transitions in organic ionic plastic crystals (OIPCs). OIPCs provide a rich parameter space in which to explore the tunability of the BC effect experimentally. This class of materials are comprised completely of ions and at room temperature are solids with significant disorder in the crystal lattice.[3] The disorder comes from the rotational, translational and conformational motions which allows them to flow under stress and increases their conductivity, which has rendered them desirable solid-state electrolytes that can be used in batteries, fuel cells and solar cells.[4] OIPC's inherent order-disorder phase change properties are ideal as potential candidates for BC refrigerants; however, little is known about how to maximise their ionic conductivity, ability to flow and change phase. This talk describes the use of high-pressure DSC and in-situ crystallographic studies under pressure and temperature to understand the reversibility of the process and the cyclability of the materials.

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018 INVITED SPEAKER

Approaches To Describe the Dynamics of Molecular Motors Embedded in Framework Materials

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The incorporation of molecular machines into the structure of porous frameworks facilitates the exciting potential for enhanced molecular transport, nano actuation and other out-of-equilibrium host-guest phenomena [1]. Recently, a diamine-based light-driven molecular motor has been incorporated into a series of imine-based polymers and covalent organic frameworks (COF) [2]. In this work, we extend advanced simulations to understand the structural and dynamic properties of this molecular motor building unit and its derived self-assembled solids.

Models of a crystalline 2D COF with stacked hexagonal layers were produced to match experimental reports. This COF contains ~20 mol-% molecular motors and features significant pore space with an experimentally determined pore volume of up to 0.45 cm3 g−1. We examined the ground state potential energy surface and how this is affected by the framework environment, given the molecular structure and bulkiness of the diamine motor. Our simulations demonstrate that intermolecular interactions from adjacent layers may not necessarily hamper or restrict motor movement and could even lead to fast rotor dynamics.

There are increasing reports of dynamic host-guest properties caused by the responsive dynamics of framework-embedded molecular motors. The simulation approach and in-depth structural characterization demonstrated here provide important access to the dynamics of these exciting materials. These findings are crucial to probe design criteria for the operation of molecular motors in porous solids to produce novel transport phenomena.

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019 INVITED SPEAKER

Recent Advances in Understanding Structural Dynamics in Metal Halide Perovskites Using Solid-State NMR

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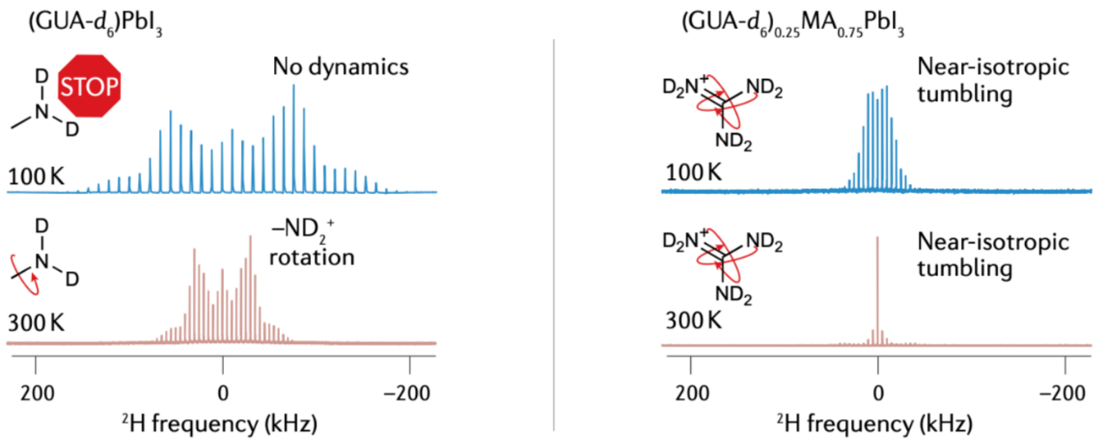
Solid-state NMR is one of the most versatile methods to study dynamics in solid materials, covering processes occurring on timescales from picoseconds to seconds, in an element-specific manner [1]. In metal halide perovskites, the dynamic processes include tumbling of the organic A-site cation in 3D materials, librations of the organic spacer cations in layered (2D/3D) materials and halide diffusion. These processes can affect optoelectronic properties in a variety of ways. For example, photogenerated charge carriers are stabilized as polarons on the inorganic metal halide sublattice, and the dynamics of that sublattice (phonons) is strongly coupled to the motional degrees of freedom of the A-site cation [2,3,4]. The motional degrees of freedom of organic spacer cations have been explored as a proxy for structural adaptability, a key concept in supramolecular chemistry [5]. Finally, halide diffusion gives rise to pernicious phenomena, such as light-induced halide segregation and voltage-current hysteresis [6,7].

I will discuss how solid-state NMR can be used to study these types of phenomena and give an overview of the most recent studies of A-site cation, spacer and halide dynamics in metal halide perovskites.



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020 KEYNOTE

Coupled linker and electric field induced dynamics in metal-organic frameworks

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The structure of metal-organic frameworks is all but static. Rotational dynamics of linkers and guest-induced deformations are very prevalent. Awareness about their potential impact in gas adsorption, sensors and as stimuli-responsive materials[1] and crystalline molecular machines is growing.[2]

Recent achievements in rotor-MOFs include engineering ultrafast rotation by decreasing the rotation energy barrier via molecular design, and ample free space in the MOF structure to avoid steric hindrance.[3] Yet, MOFs have, in fact, the potential of displaying much more intricate dynamics, similar to other dynamic materials containing closely interacting molecules, such as crowded movement of proteins in lipid bilayers, or concerted molecular motion in liquid crystals. MOFs in fact provide an exceptional playing ground, as they are offer a regular arrangement of rotors with defined intermolecular distances that can be tuned through the choice of building blocks. This means that the free pore space and inter-rotor distance can be tuned to a desired level of “crowdedness” of the rotors for cooperative motion.

Here, we present how correlated motions emerge in linker dynamics as the steric environment of the rotors is gradually modified. We use linker functionalization in the MIL-53 family of materials to tune both the pore dimensions and the rotor–rotor interactions. Via a combined experimental and computational approach, including broadband dielectric spectroscopy, solid-state 2H NMR, DFT calculations, and molecular dynamics simulations up to 6x3x3 supercells, we comprehensively determine the linker dynamics. For steric interactions that inhibit independent but do not prohibit rotor motion, we identify the emergence of correlated rotation modes between different linkers, as well long range A-B-A-B-A-B… conformational ordering.

Metal-organic frameworks could be very promising, yet are hardly explored, for harvesting mechanical energy through their piezoelectric properties. Indeed, the energy harvesting efficiency, which scales with 1/ ε_r, should indeed be boosted by the very low dielectric permittivity ε_r MOFs can have due to the porosity.[4] Moreover, their structural variability should allow for optimization of the piezoelectric constant ‘e’ and ‘d’. While it can be expected that these properties would make them competitive with the materials mostly studied nowadays, namely ferroelectric ceramics, polymers and composites, very few studies have studied the piezoelectric response of MOFs.[5]

To understand the structure-property relationship of piezoelectric constant ‘e’ in MOFs, we perform high throughput DFT calculations for ~1500 non-centrosymmetric MOFs starting from a computational ready, experimental MOF database (QMOF database).[6] Key factors that can influence the piezoelectric constant ‘e’ are Born effective charges, symmetry, coordination environment around the metal node and the presence of polar linkers and counterions. For the MOFs which show the highest piezoelectric constant ‘e’ we discuss in detail the key factors contributing to their high performance. For some structures we found values of ‘e’ of the same order of magnitude as those of the best performing ceramics. MOFs have higher elasticity due to their flexible frameworks and orders of magnitude lower dielectric constant of MOFs compared to ceramics. This means that piezoelectric metal-organic frameworks should be able to outperform existing piezoelectric materials for mechanical energy harvesting.

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021 INVITED SPEAKER

Challenges in modeling spatiotemporal phenomena in metal-organic frameworks

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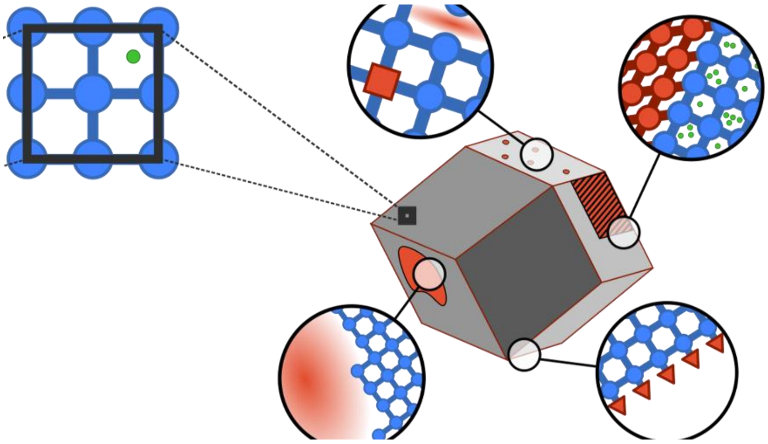
In this contribution, the question is addressed in how far current modeling strategies are capable of modeling spatiotemporal response in MOFs. The terminology spatiotemporal processes refers to the entanglement between the dynamics of the material and its spatial heterogeneities, where spatial heterogeneities from the subnanometer to the micrometer scale in real crystal particles with a finite size and morphology, impact the material's dynamics.[1] Currently there exists a huge length-time scale gap between attainable theoretical length-time scales and experimentally relevant scales. Various challenges are ahead for modelers to bridge this length-time scale gap. First of all, systematic algorithms are needed that enable building atomistic models of realistic MOFs at the mesoscopic scale. Second methods are needed that allow evaluation of interatomic forces with quantum mechanical accuracy albeit at much lower computational cost than currently used Density Functional Theory methods. Third, methods are needed that allow to evaluate the kinetics of phenomena taking place in a multi length-time scale window to obtain an overall view of the dynamics of the process. With this contribution, I will highlight some of our recent efforts where we extended accessible length-time scales by exploited the massive parallelism of state-of-the-art GPUs using the OpenMM software package allowing to simulate MOFs having about a million number of atoms.[2] The simulations necessitated to port our classical force fields to a GPU based framework and a new barostat had to be implemented that allowed to simulate anisotropic cell fluctuations. Despite the success of these simulations, showing how one can push the limits of currently accessible length and time scales, one loosed "quantum accuracy" when using classical force fields. Inspired by this defeat, we recently developed a new active learning based algorithm for developing machine learning potentials of activated processes.[3] Within this framework a numerical potential is derived that can represent the interatomic forces with similar accuracy than the underlying quantum mechanical training data from which it was derived. This MLP based framework allows to simulate flexible behavior in MOFs in a much more efficient way. Our proof-of-concept results show that it is possible to train so-called universal MLPs which are viable for a class of materials. Furthermore, we have recently explored algorithms that allow to generate MLPs for defective materials by adding training data of some well chosen defective clusters. The illustrated methods show great potential to model spatiotemporal processes in realistic MOFs. As will become clear, to further progress in this field a close interaction loop with the experimental community on imaging, spectroscopy and characterization will be of utmost importance.



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022 POSTER
The Interplay Between Local H-bond Vibrations and Lattice Dynamics in Organic Crystals

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In a hydrogen bond (H-bond), adjacent electronegative atoms/groups share a proton that has two distinct equilibrium positions. Though H-bonds are abundant in organic crystals, there is little understanding of how their local dynamics influence the collective lattice motion. We expect H-bonded crystals to have inherent metastable states that stem from the proton motion between its equilibrium positions. In this project, I test the hypothesis that H-bonded crystals have unique structural dynamics that combine the proton's motion and the crystal's lattice dynamics. Using state-of-the-art THz-Raman spectroscopy, I investigate the temperature evolution of both inter- and intra-molecular modes in alpha-glycine crystals. Despite the simple structure and absence of known phase transitions, I show that specific lattice modes behave anomalously with temperature. These anomalies are absent in Anthracene that is bound only by Van der Waals interactions. My study is a first step towards elucidating how metastable states in the macroscopic system emerge from fundamental interactions such as the H-bond.

023 POSTER

Synthesis, structural analysis and dynamics of 3- and 4-fold interpenetrated Zn-Metal-Organic Frameworks

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Canossa, Dr. Stefano [a]
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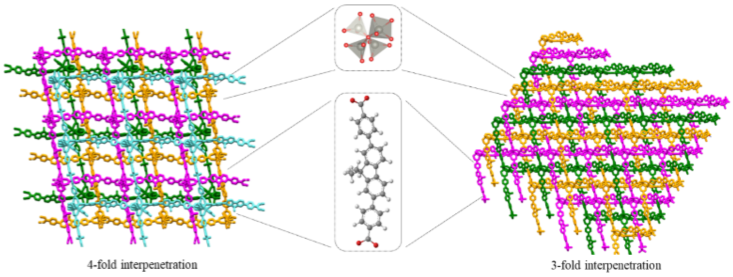
Structural dynamism of interpenetrated Metal-Organic Frameworks (MOFs) due to twisting and sliding of the network in response to temperature change [1,2] or incorporation of small molecules [2,3] has been reported previously. Herein, we investigate solvent mediated dynamic behavior of two new Zn(II) MOFs and establish structure-property relationship in response to external stimuli. The Zn(II) MOFs in question are synthesized using 4,4'-(9,9-dimethyl-9H-fluorene-2,7-diyl)dibenzoic acid ligand. Variation in the reaction conditions led to 3-; and 4-fold interpenetrated structures with the same parent network. Synchrotron single-crystal X-ray diffraction (SCXRD) analysis of both the 3-; and 4-fold interpenetrated structures shows that the Zn forms a ZnO_4 secondary binding unit (SBU). Three of the O atoms come from the completely deprotonated ligands, whereas the last O atom connects to three other Zn^{2+} ions forming an octahedral $Zn_4(O)(CO_2)_6$ cluster. The 3-fold network crystallizes in the trigonal $P31c$ space group, while the 4-fold network crystallizes in the triclinic crystallographic system, space group $P\bar{1}$.



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024 POSTER

Stimuli-responsive behavior of mixed-linker Zr-based MOFs with molecular photoswitch backbones

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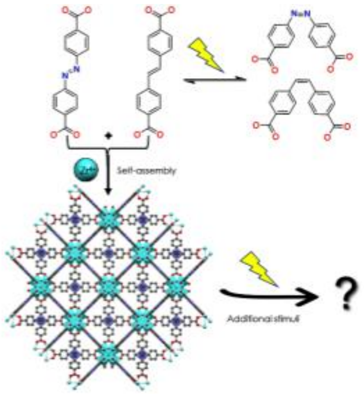
The investigation of Metal-Organic Frameworks (MOFs) structural responsive behavior to external stimuli such as light, temperature, and pressure has been growing over recent years.[1] Indeed, controlling the adsorption, transport, and release properties of gases and fluids in the framework materials by modulating their porosity via light provides exciting possibilities. Azobenzene is a molecular photoswitch that can go through light-activated E-Z isomerization and has been used in light-responsive materials.[2] Due to geometrical constraints, light-responsive properties of azobenzenes are subject to change when used as a linker in the MOF backbone. It has been shown that the photoswitching ability is either quelled as a result of the framework constraints or causes structural degradation when used in the framework backbone.[3, 4] However, by exploiting an additional external stimulus, the MOF's framework can undergo structural transition, as has been revealed before in the flexible DUT-163 material[5], where applying the light and adsorption stress in parallel, a cooperative gas release by a buckling contraction mechanism through the framework backbone was observed.

Herein, we report the synthesis of mixed-linker Zr-based UiO MOFs based on azobenzene dicarboxylic acid along with stilbene dicarboxylic acid. Stilbene and its carboxylic acid derivatives are also photoswitches that can undergo trans-cis interconversion through excitation with irradiation in different wavelengths than azobenzene, and together they can provide an interesting system to probe the possible isomerization or buckling of the constraint linker, and even possibly discover unknown alternative photoswitching pathways. The mixed-linker Zr-MOFs with different linker ratios were synthesized, and their structural features were investigated through various methods, including powder X-ray powder diffraction (PXRD) and scanning electron microscopy (SEM) as such. Future studies aim to determine whether molecular photoswitches can exhibit reversible or irreversible photoisomerization while being constrained in the framework and, if switching could not occur, what effects would arise regarding adsorption or mechanical pressure.



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025 POSTER

Synthesis and swelling behaviour of MIL88B and MIL88D as dynamic framework platforms

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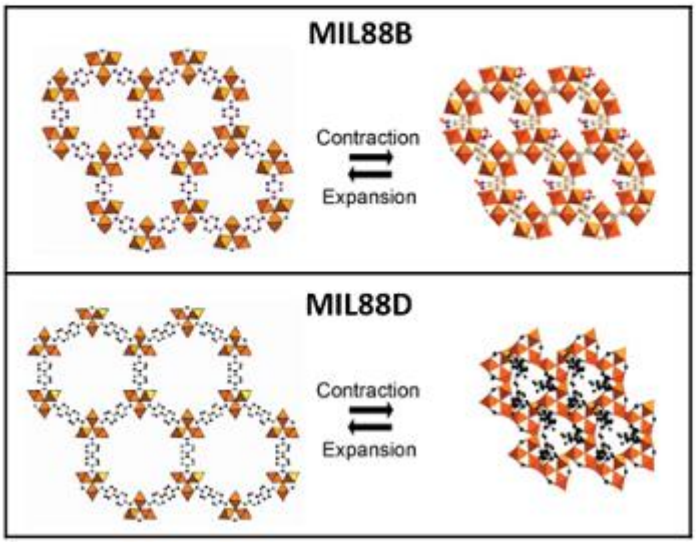
Due to the nontoxic and highly flexible properties, iron(III)-based MOFs received considerable interest, especially MIL-88 [1]. The capacity of the MIL-88 frameworks to swell and contract reversibly under the influence of an external stimulus (temperature, pressure, chemical coupling etc.) without damaging the framework topology is a unique property [2]. In this study, we reported the solvothermal synthesis of isoreticular [3] flexible MOFs, MIL-88B-Fe and MIL-88D-Fe using benzenedicarboxylic acid (BDC) and 4,4'-biphenyl dicarboxylic acid (4’4-BPDC) linkers, respectively (MIL stands for Material from Institut Lavoisier) [4]. We observed swelling behavior of the MIL-88B-Fe and MIL-88D-Fe frameworks in various polar and nonpolar solvents and the unit cell parameters changed after the crystals were dispersed in different solvents. We characterized the MOFs by powder X-ray diffraction and scanning electron microscopy (SEM) analysis. The reversible swelling and contraction without disintegration of the crystal lattice makes MIL-88-Fe an important material for dynamic confinement and responsive behaviour.



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026 POSTER

Swelling of MIL-88 A (Fe) as a function of solvent composition and crystal size

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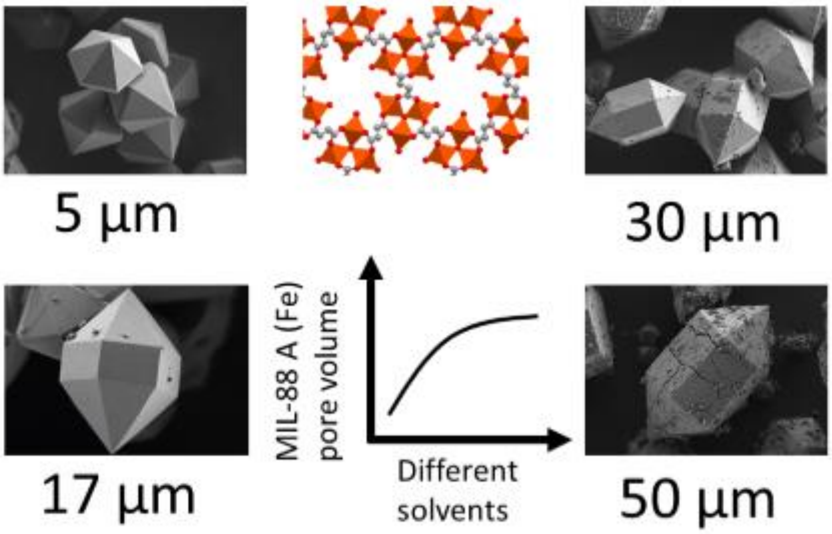
The MOF MIL-88 A was first described in 2004.[1] It consists of an trinuclear iron cluster and fumaric acid as linker and forms a porous structure with hexagonal pores. MIL-88 A crystals have a hexagonal bipyramidal shape, which is also described as diamond shape, spindle-like, or rod-like, depending on the length. The flexibility of MIL-88 A is known since 2005.[2] The volume of the unit cell can change by up to 85% depending on the pore loading with different solvents or as a function of temperature. Even though the system has been known for a long time, many questions remain unanswered about the dynamic behavior. One of these open questions is the study of flexibility and the influence of crystal size on the lattice deformation. Similar effects have already been observed in the flexible MOF DUT-49 systems.[3]
Here we show the synthesis of MIL-88 A crystals with different crystal size distributions by variating the reaction time and temperature of the solvothermal reaction. We present crystals from 5 up to 50 µm, as shown in the scanning electron microscopy (SEM) images. We studied some of the larger single crystals by single crystal X-ray analysis (XRD), and refined the crystal structure. MIL-88 A crystallizes in the hexagonal space group P63/m with lattice parameters of a=b=12.69 Å, c=13.71 Å and a volume of V=1909.54 $Å^3$. Upon solvent exchange, crystals decompose. We observed this behavior for various organic solvents.
In order to investigate the swelling behavior of the network, as a function of solvent, we attempt solvent exchange in the pores. We analyzed the observed changes in the unit cell parameters upon solvent exchange by powder x-ray diffraction (PXRD) and Pawley refinement and calculated volume ranges from 1804 cm^3 (DMSO) to 2107 cm^3 (Water). Analyzing the obtained information from various samples, we present a correlation between the crystal size and swelling behavior.



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026 POSTER

Swelling of MIL-88 A (Fe) as a function of solvent composition and crystal size

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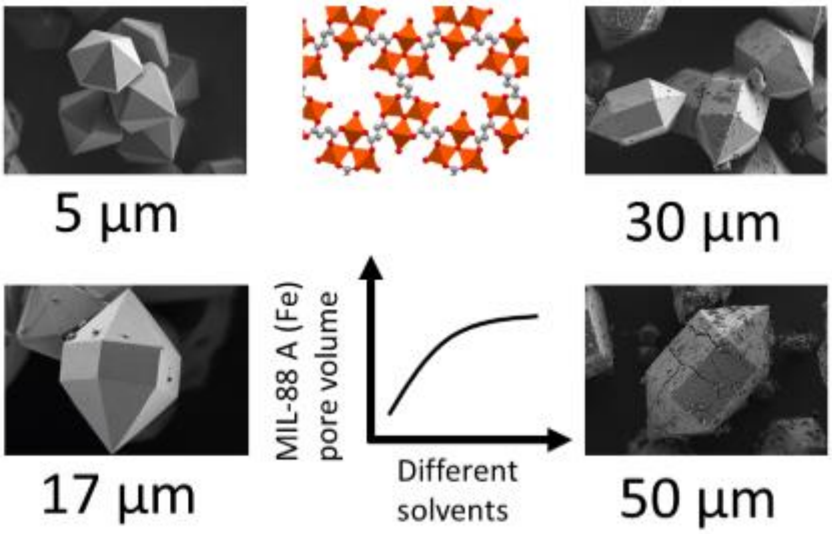

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027 INVITED SPEAKER

Shedding light on phase transformations in amphidynamic crystals

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My group uses Raman spectroscopy to study the interaction between intermolecular vibrational modes in crystals.

Interactions between thermally activated vibrational modes (i.e., anharmonic interactions) cause thermal expansion, heat transport, and phase transformations.

Phase transformations in amphidynamic crystals are fascinating because they involve both the rigid scaffolds' small-amplitude vibrations and the mobile elements' large-amplitude motion.

In my talk, I will present a study where we identify the vibrational modes associated with the phase transition by following the position and width of the Raman peaks with temperature. We compare two amphidynamic crystals that show distinct behavior.

In one crystal, strong damping of a single vibrational mode is responsible for the phase transition and the 'unlocking' of large amplitude motion of the mobile element in the crystal. Therefore, its behavior follows an analytical model that offers predictive power.

In the second crystal, a few lattice modes are simultaneously involved in the phase transition leading to much more complex behavior.

Our study offers insight into the design of tailor-made amphidynamic crystals.

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028 ORAL

Synergistic Exclusive Discrimination Gating for CO2 Recognition using Flexible Porous Coordination Polymers with Narrow Soft Corrugated Channels

Otake, Ken-ichi * a
Gu, Yifan a
Zheng, Jia-jia a
Kitagawa, Susumu * a

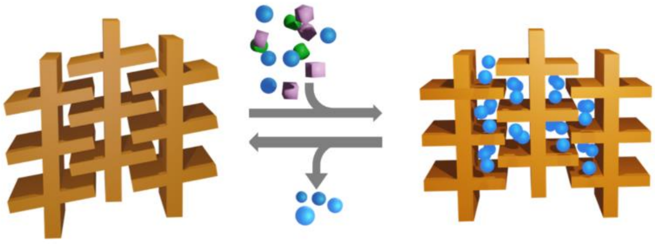
Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University

Porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) are a class of crystalline framework materials that are constructed from the coordination bonds of metal ions/clusters and organic linkers. Since their discovery of being porous, PCPs have been thoroughly investigated as promising adsorptive materials. Among them, structurally responsive PCPs, or flexible PCPs, often exhibit fascinating structural properties because they can have different interconvertible structures depending on external parameters. [1-2]

However, developing artificial porous systems that exhibit high molecular recognition performance is still a significant challenge. Achieving selective uptake of a specific component from a mixture of many similar species, regardless of their size and affinity, is a difficult task. Therefore, a porous platform that integrates multiple recognition mechanisms working cooperatively for highly efficient guest identification is desired. [3-4]

To address this challenge, we designed a flexible porous coordination polymer (PCP) that features a corrugated channel system. This system cooperatively responds only to target gas molecules by taking advantage of its stereochemical shape, location of binding sites, and structural softness. Compared to known molecule recognition strategies, including molecular sieving and functional interacting sites, the proposed intelligent host-responsive molecular recognition mechanism based on the narrow-corrugated channel structure brings unprecedented recognition efficiency. This study successfully demonstrates that unique molecule recognition performance can be achieved through the deliberate organization of pore geometry, structure softness, and binding sites at the molecular-level precision in a defined molecular structure.

In this symposium, the details of the syntheses, crystal structures, in situ X-ray investigations, as well as theoretical studies on the mechanism of exclusive sorption behaviors are discussed.



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029 INVITED SPEAKER

Systematic exploration of stimuli-responsive materials: multi-scale modelling and machine learning

Coudert, François-Xavier

CNRS, Paris, France

The past few years have seen a rapid increase in the use of machine learning (ML) approaches to the fields of chemistry and materials science, in particular in the prediction of physical and chemical properties of existing and novel compounds. Databases of experimental structures — in particular, crystalline structures — continue to grow at a steady pace and are complemented with larger and larger databases of physical and chemical properties. We present here several examples of a multi-scale computational methodology to this problem, by combining the existing tools of theoretical chemistry (i.e., quantum chemical calculations and classical molecular simulations) with statistical learning approaches. [1] We show how these have been integrated together in our group and allow not only the prediction of properties, but also a deeper understanding of the structure/property relationships that can provide chemical insight. [2] We focus in particular on how these tools can accelerate the discovery of materials with stimuli-responsive properties (whether thermal or mechanical). [3]

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