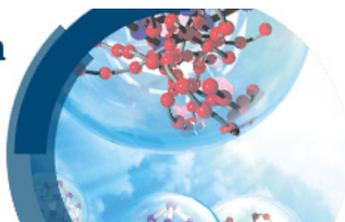


## Cooperative phenomena in framework materials

Faraday Discussion



13-16 October 2020  
Online

Dear Colleagues

We are thrilled to be welcoming you to the Cooperative phenomena in framework materials: Faraday Discussion as an online event.

Meeting in a virtual space brings with it many benefits and opportunities, and we encourage you – as you would do in a physical meeting – to participate fully in the discussion by contributing to the discussion and sharing research, asking questions and networking with each other.

We really look forward to engaging with the audience in inspiring and exciting discussions, giving a glimpse of the future for density-functional and related methods.

Over the years, the unique nature of the Faraday Discussions has led to great scientific debate, great collaborations and great friendships, we are sure this will be true for our community in the virtual space.

On behalf of the Organising Committee, we wish you a very enjoyable and engaging Faraday Discussion.

Susumu Kitagawa, co-chair, Kyoto University, Japan  
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## Meeting information

**Cooperative phenomena in framework materials: Faraday Discussion** is organised by the Faraday Division of the Royal Society of Chemistry.

This e-book contains abstracts of the posters presented at **Cooperative phenomena in framework materials: Faraday Discussion**. All abstracts are produced directly from typescripts supplied by authors. Copyright reserved.

All sessions, including the posters, are available to access via the virtual lobby. Further information on how to join the meeting and best practice for an online event is detailed in the [joining instructions](#).

### Oral Presentations and Discussions

All delegates at the meeting, not just speakers, have the opportunity to make comments, ask questions, or present complementary or contradictory measurements and calculations during the discussion. If it is relevant to the topic, you may give a 5-minute presentation of your own work during the discussion. These remarks are published alongside the papers in the final volume and are fully citable. If you would like to present slides during the discussion type 'question', 'comment', or 'reply' into the chat box at the relevant point during the session.

### Networking sessions

There will be regular breaks throughout the meeting for socialising, networking and continuing discussions started during the scientific sessions. During the networking sessions you will be able to join existing networking rooms or initiate one-to-one chats. Existing networking rooms will be visible from the virtual lobby. To create a one-to-one chat, simply click on the name of the person you would like to speak to and select if you would like to have a private or public conversation. For a public conversation, other delegates can join your chat room. You can participate in the networking sessions with other delegates in the InEvent app.

On the web version, you can only be in one session at a time (this includes networking rooms). It is recommended to use the app if you want network during the sessions.

### Posters

The posters will be available to view throughout the discussion by clicking on the link in the virtual lobby. The dedicated poster session will take place on

Wednesday 14 October 14:55 – 15:55

Thursday 15 October 10:10 – 11:10

During these times, the presenters will be available for live chat and outside of these times, a direct message can be sent to the authors and they can respond when available.

### Poster Prize

The Faraday Discussions Poster Prize will be awarded to the best student poster as judged by the committee.

### Faraday Discussion Volume

Copies of the Discussion Volume will be distributed approximately 6 months after the meeting. To expedite this, it is essential that summaries of contributions to the discussion are received no later than **Friday 23rd October** for questions and comments and **Friday 6th November 2020** for responses. A copy of the publication may be purchased at a reduced price of £70, only for orders placed at the meeting; please email [events@rsc.org](mailto:events@rsc.org) if you would like to purchase a copy.

### Exhibitor



Please visit Surface Measurement System's room in the virtual lobby to find out more about the company.

### **Supporting organisation**

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Andrew Cooper  
University of Liverpool, United Kingdom

Christian Doonan  
University of Adelaide, Australia

Stefan Kaskel  
TU Dresden, Germany

Masako Kato  
Hokkaido University, Japan

## **Invited Speakers**

Omar Farha, Introductory Lecturer  
Northwestern University, United States

Thomas D Bennett  
University of Cambridge, United Kingdom

William Dichtel  
Northwestern University, United States

Satoshi Horike  
Kyoto University, Japan

Jianwen Jiang, Closing remarks  
National University of Singapore, Singapore

Amanda Morris  
Virginia Tech, United States

Rochus Schmid  
Ruhr-Universität Bochum, Germany

Veronique Van Speybroeck  
Ghent University, Belgium

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Stockholm University, Sweden

# Faraday Discussions Forum

[www.rscweb.org/forums/fd/login.php](http://www.rscweb.org/forums/fd/login.php)

In order to record the discussion at the meeting, which forms part of the final published volume, your name and e-mail address will be stored in the Faraday Forum. This information is used for the collection of questions and responses communicated during each session.

After each question or comment you will receive an **e-mail** which contains some keywords to remind you what you asked, and your password information for the forum.

The e-mail is not a full record of your question. You need to **complete your question in full on the forum**.

The deadline for completing questions and comments is **Friday 23<sup>rd</sup> October**.

The screenshot shows the 'Faraday Discussions Online Comment Collection' form. At the top left is the Royal Society of Chemistry logo. The title 'Faraday Discussions Online Comment Collection' is centered. Below this is a dark bar with the text 'Faraday Discussion comment collection'. There are links for 'FAQ' and 'Log out', and a note 'Not in multiple discussions.'. A dark bar contains the heading 'Question or comment'. A grey box contains a note: 'Please note that you are also required to complete the conflicts of interest question that will appear at the bottom of the page under the heading 'These questions have been addressed to everyone''. The form fields include: 'YOU ARE:' with a note 'You must log in to post material.'; 'QUESTION NO:' with a text input box and a note 'To submit a question/comment that was not asked at the discussion meeting and does not have a question number, please e-mail the Editorial Office at [faraday@rsc.org](mailto:faraday@rsc.org)'; 'Q/C:' with a dropdown menu set to 'Question'; 'WHICH DELEGATE ARE YOU ADDRESSING?' with four dropdown menus; 'DURING DISCUSSION OF PAPER:' with a dropdown menu and a note 'You must address your question to somebody.'; and 'YOUR QUESTION OR COMMENT:' with a rich text editor toolbar (italic, bold, super, sub) and a large text area. A keyboard shortcuts legend is visible on the left side of the text area.

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Once we have received all questions and comments, **responses will be invited by e-mail**. These must also be **completed on the forum**. The deadline for completing responses is **Friday 6<sup>th</sup> November**.

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## **Key points:**

- The e-mail is not a full record of your comment/question.
- All comments and responses must be completed in full on the forum

## **Deadlines:**

Questions and comments  
Responses

**Friday 23<sup>rd</sup> October**  
**Friday 6<sup>th</sup> November**

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*Bundesanstalt für Materialforschung und -prüfung, Germany*

**Quantifying the likelihood of structural models through a dynamically enhanced powder X-ray diffraction protocol**

Borgmans, Sander  
*Ghent University, Belgium*

**A Structural Study of Zeolite Merlinoite: Cations, CO<sub>2</sub> and Cooperativity**

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*University of St. Andrews, UK*

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Doan, Huan  
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Edward, Ailsa  
*University of St Andrews, UK*

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Evans, Austin  
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*University of Kent, UK*

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*Hokkaido University, Japan*

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*University of Bremen, Germany*

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*IISER BHOPAL, India*

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*University of Johannesburg (UJ), South Africa*

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*The University of Oxford, UK*

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# A Mechanistic Perspective on Plastically Flexible Coordination Polymer

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Biswajit Bhattacharya<sup>2</sup> and Adam A. L. Michalchuk<sup>1</sup>

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Mechanical flexibility in single crystals of covalently bound materials is a fascinating and poorly understood phenomenon.<sup>1-2</sup> We present here the first example of a plastically flexible one-dimensional (1D) coordination polymer. The compound  $[\text{Zn}(\mu\text{-Cl})_2(3,5\text{-Cl}_2\text{Py})_2]_n$ , is flexible over two crystallographic faces.<sup>3</sup> Remarkably, the single crystal remains intact when bent to 180°. Through the combination of microscopy, diffraction, and spectroscopic studies we probe the structural response of the crystal lattice to mechanical bending. Deformation of the covalent polymer chains does not appear to be responsible for the observed macroscopic bending. Instead, our results suggest that mechanical bending occurs by displacement of the coordination polymer chains. Based on experimental and theoretical evidence, we propose a new model for mechanical flexibility in 1D coordination polymers. Moreover, our calculations propose an origin for the different mechanical properties of this compound and a structurally similar elastic material. The results presented here offer novel insight into the mechanism of mechanical flexibility in coordination polymer crystals and the potential of tuning their physical properties by mechanical force.

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# Quantifying the likelihood of structural models through a dynamically enhanced powder X-ray diffraction protocol

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Sander Borgmans<sup>1</sup>, Sven M.J. Rogge<sup>1</sup> and Veronique Van Speybroeck<sup>1</sup>

<sup>1</sup>*Ghent University, Belgium*

The targeted construction of hypothetical materials with specific functionalities has been the epitome of the design-based approach in material science. However, as building units grew more versatile the number of materials that can be formed has grown correspondingly. While this greatly expands the area of applicability, this also complicates the rationalization of the inner workings for the application at hand. As such, a protocol is required to obtain accurate structural models that provide a microscopic understanding of the formed material structure and yield atomistic insight in how this structure endows the material with specific functionalities at operando conditions.

Many experimental characterization techniques exist to construct and discern between structural models. One of the leading techniques is powder X-ray diffraction (PXRD)<sup>[1]</sup>. During these measurements, the three-dimensional reciprocal space is non-injectively projected onto a one-dimensional Bragg angle, making the determination of the original structure from this projection alone impossible without an initial model. Our three-step protocol reverses the current experimental approach to identify the correct structural model. Instead of extracting initial models from the available peaks, in the first step a large set of possible structures is generated from the building blocks which make up the structure. Then the corresponding PXRD patterns are calculated using either a static or dynamic approach and finally a heuristic is derived and applied to order the proposed structural models as a function of their likelihood to recreate the experimental diffraction pattern. Such a protocol has the added benefit of replacing the ad hoc visual analysis by a well defined metric, allowing quantitative statements on how good the model performs.

Covalent organic frameworks (COFs)<sup>[2]</sup> are ideal materials to test our protocol, as their structural characterization remains a difficult challenge, owing to a lack of crystallinity in most experimental samples. In general, these materials can be subdivided into 3D COFs, which are completely connected by strong covalent bonds, and 2D COFs, which form layered structures whose stacking order is determined by much weaker forces, such as dispersion and Coulomb interactions<sup>[3]</sup>. From our results, it is clear that while the static approach is effective for the strongly connected 3D COFs, the lack of temperature effects and dynamic information prohibits an accurate reproduction of the experimental pattern when dealing with weakly interacting layers of 2D COFs. However, the dynamic approach allows for the prediction of accurate structural models regardless of the topology, validating the general applicability of our protocol.

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# A Structural Study of Zeolite Merlinoite: Cations, CO<sub>2</sub> and Cooperativity

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Elliott Bruce<sup>1</sup>, Veselina M. Georgieva<sup>1</sup>, Ruxandra G. Chitac<sup>1</sup>, Anna M. Hall<sup>1</sup>,  
Clare Murray<sup>2</sup>, Alessandro Turrina<sup>3</sup> and Paul A. Wright<sup>1</sup>

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<sup>3</sup>Johnson Matthey Technology Centre, United Kingdom

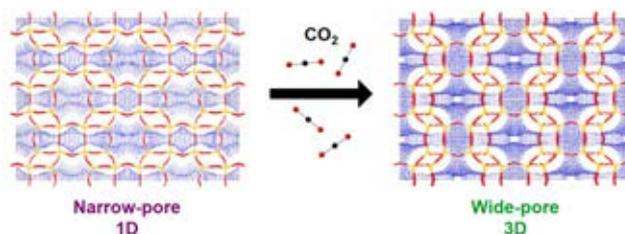


Figure 1. MER materials expand upon CO<sub>2</sub> adsorption from narrow- to wide-pore structures, accompanied by increased connectivity from 1 to a 3D channel systems.

Zeolites find a wide range of applications in commercial gas separation, including CO<sub>2</sub>/H<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub>.<sup>1-3</sup> These materials typically possess Type I adsorption isotherms, in IUPAC nomenclature, with uptake reaching an asymptote at high pressure as pore volume fills. More exotic isotherms are well known for metal organic frameworks, such as stepped adsorption observed in MIL-53.<sup>4,5</sup> More recently, such behaviour has been observed in zeolites, including ZSM-25 and gismondine.<sup>6,7</sup>

We have observed stepped adsorption in zeolite merlinoite (framework type MER),<sup>8</sup> which XRD and subsequent Rietveld refinement has revealed to be due to a phase change from narrow- to wide-pore structures. This transition is greatly affected by cation content, with cations dictating the nature of framework distortion and altering relative favourabilities of narrow- and wide-pore structures. Upon transition, site energetics change causing cation migration, enhancing diffusion in wide-pore structures.

Recently we have examined Li-containing materials exhibiting extreme framework distortion upon dehydration. Modelling shows greatly increased pore volume and channel connectivity for these materials, from 1- to 3-dimensional, upon transition. Variable pressure data suggests expansion to the wide-pore form may proceed via an intermediate phase in a cooperative manner, with local transitions causing neighbouring regions to follow suit.

The variety of behaviour in MER materials suggests judicious selection of cations may allow tuning of adsorption properties for application in gas separation technologies.

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# Investigating the Melting Behaviour of Polymorphic Zeolitic Imidazolate Frameworks

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Alice Bumstead<sup>1</sup> and Thomas Bennett<sup>2</sup>

<sup>1</sup>University of Cambridge, CB3 0FS, United Kingdom and <sup>2</sup>University of Cambridge, United Kingdom

There is a growing interest in the field of metal–organic frameworks (MOFs) towards defective and flexible materials as well as structural transitions from the crystalline to the amorphous state.<sup>1–3</sup> The zeolitic imidazolate framework (ZIF) family are of particular interest due to recent reports of melting and glass formation.<sup>3</sup> Molecular dynamics simulations and X-ray total scattering have revealed that melting occurs through rapid de-coordination of an imidazolate linker from a metal centre followed by re-coordination of a new linker in its place.<sup>4</sup> However, not all ZIFs melt and the influence of linker chemistry and crystal structure on the thermal response of these materials is still not well understood.

To investigate this, a number of ZIFs were selected based on their chemical or structural similarities. TIF-4 and ZIF-UC-5 are structural isomorphs. They both contain Zn<sup>2+</sup> ions, imidazolate and substituted benzimidazolate linkers and crystallise in an orthorhombic *Pbca* space group with the **cag** topology.<sup>5,6</sup> However, in TIF-4 the linker substituent is a methyl group whilst in ZIF-UC-5 it is a chlorine atom. Comparison of these materials allowed the influence of linker chemistry to be studied. It was found that the presence of a more electron withdrawing chlorine substituent lowered both the melting and glass transition temperature.<sup>7</sup>

In contrast, ZIF-76-mblm contains the same metal ion and organic linkers as TIF-4 but crystallises in a more porous, cubic framework with the *P-43m* space group and the LTA topology and does not melt on its own.<sup>7,8</sup> However, the presence of a small quantity of dense phase impurity in ZIF-76-mblm can assist melting of the porous framework.<sup>7</sup> This is believed to occur through a phenomenon termed flux melting whereby the dense ZIF first melts and acts as a solvent, facilitating melting of the second framework.<sup>9</sup> This opens up the rich polymorphic landscape of ZIFs to melting by providing a strategy to prepare novel functional glasses from ZIFs that do not melt on their own.

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# A Functionalized Zr(IV) Metal-Organic Framework: Emission Quenching in the Presence of Nitrophenols in Aqueous Media

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Luminescent Metal Organic Frameworks (LMOF) have recently attracted great attention due to their ability to respond to the encapsulation of various guest species within their structure's pores by changing their emission characteristics. Therefore, these materials have emerged as a highly promising class of luminescent sensors.<sup>[1,2]</sup> Nitroaromatic compounds are known environmental pollutants in addition to their explosive properties which pose a risk for safety and national security. Consequently, there is a great need to develop efficient sensors for the determination of nitroaromatic analytes.<sup>[3]</sup> In this work, we study the synthesis of a Zr(IV) UiO-66-type MOF based on a strongly fluorescent dicarboxylic ligand with a pendant electron rich aromatic group, which shows sorption capacity for 2,4-dinitrophenol (DNP) and 2,4,6-trinitrophenol (TNP). The MOF is characterized by IR spectroscopy, powder X-ray diffraction, thermogravimetric analysis and NMR analysis of digested samples. The surface area according to the BET model is determined by analysis of the N<sub>2</sub> sorption isotherm. Fluorescence titration experiments have shown that the material responds to small concentrations of TNP and DNP by displaying strong emission quenching.

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# Crystal Melting and Vitrification Behaviors of the Three-Dimensional Nitrile-Based Metal–Organic Framework

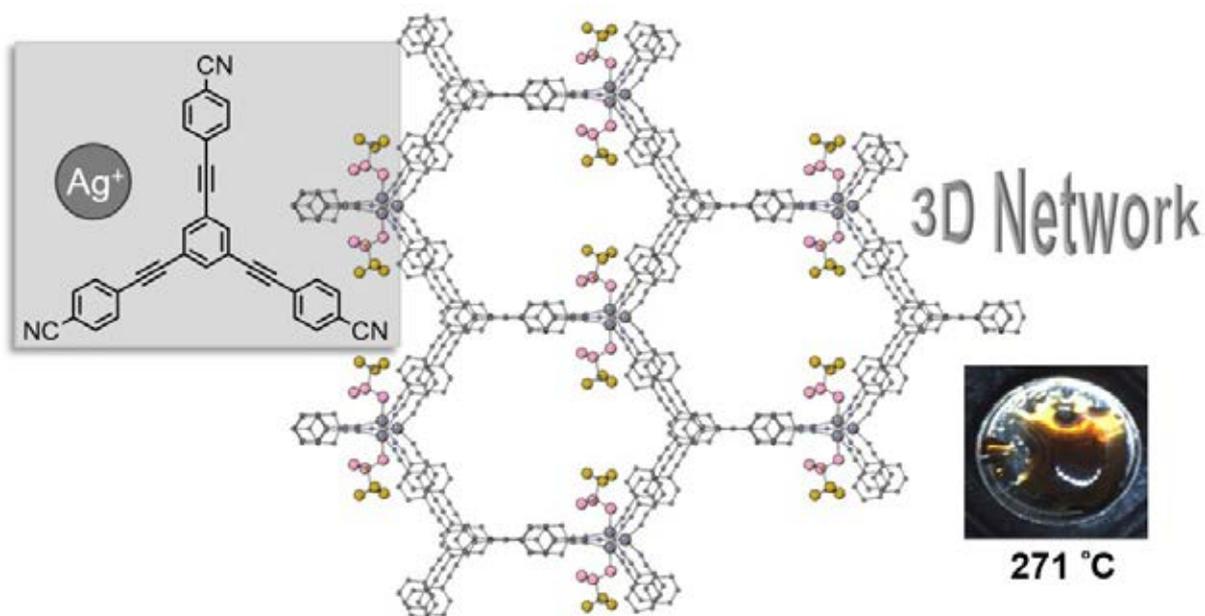
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Crystal melting and vitrification behaviors were investigated in a three-dimensional (3D) metal–organic framework  $[\text{Ag}(\text{pL}_2)(\text{CF}_3\text{SO}_3)] \cdot 2\text{C}_6\text{H}_6$  ( $\text{pL}_2=1,3,5\text{-tris(4-ethynylbenzonitrile)benzene}$ ), composed of  $\text{Ag}^+$  and tripodal nitrile ligand. The benzene-free state showed a crystal melting at  $271^\circ\text{C}$ , and the liquid state transformed into a glassy state *via* cooling. The vitrification of the crystalline compound into an amorphous glassy state was also obtained by mechanical hand-grinding. The 3D networked structure of the glassy state was retained which was confirmed by FT-IR, X-ray absorption, and total scattering measurements. The mechanically induced glass showed a small uptake of  $\text{CO}_2$  gas and a strong affinity for benzene and  $\text{H}_2\text{O}$  vapors, confirmed by gas sorption isotherms. Studies on powder X-ray diffraction have revealed that a vitrified structure returns to the original 3D crystalline structure by exposure to these vapors.

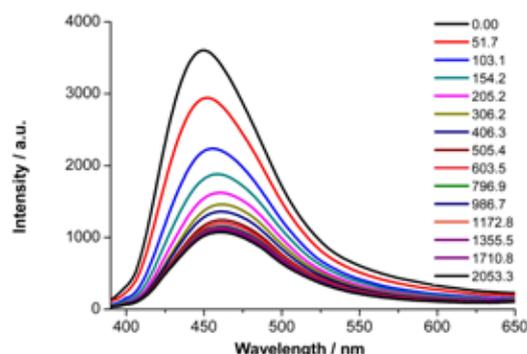


# Fluorescence sensing and sorption of Pb<sup>2+</sup> and Cu<sup>2+</sup> in water by two functionalized Zr<sup>4+</sup> Metal-Organic Frameworks

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Heavy metal ions constitute a class of non-biodegradable pollutants affecting the global environment. As a result, there is an ever-increasing need to identify and constantly monitor these chemical species. Towards this end, analytical techniques based on luminescence are attracting increasing interest due to their high sensitivity and their ability to be incorporated in portable devices for in-field use. Luminescent MOFs show great potential as sensory materials<sup>[1,2]</sup> because they possess highly regular porous structures able to host various chemical species which may induce changes in their emission characteristics, thereby generating a detection signal. In this contribution, we describe two Zr<sup>IV</sup> MOFs based on bridging ligands bearing pendant chelating side groups. Fluorescence studies on the MOFs themselves and on model compounds revealed that these materials exhibit exceptional ability for real-time detection of Pb<sup>2+</sup> and Cu<sup>2+</sup> ions in ppb levels in drinking water, showing high sensitivity and selectivity for these species even in the presence of various competitive ions. Moreover, batch sorption studies have shown that these MOFs exhibit exceptional sorption capacity allowing the efficient removal of these contaminants from water.



**Figure 1.** Fluorescence titration of a MOF material ( $\lambda_{\text{exc}} = 360 \text{ nm}$ ) suspended in water upon addition of Pb<sup>2+</sup>. The numbers correspond to total Pb<sup>2+</sup> in ppb.

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# Disorder in Barocaloric Frameworks

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Cooling is vital to the modern world, from food storage to quantum computing, consuming upwards of 10% of the world's energy and producing many tons of CO<sub>2</sub><sup>[1]</sup>. Typical refrigeration methods still rely on antiquated vapour-compression cycling, which can release damaging gases into the atmosphere. Caloric effects are changes in entropy that occur when materials are exposed to an externally applied field, making them a promising energy-efficient solid-state alternative to gas refrigeration. There is great potential for such entropic switching in metal-organic frameworks, since structural order-disorder phase transitions, especially involving the rearrangement of guest molecules or ions, are common in these materials; their flexibility allows vibrational contributions to the entropy; and their extended network structure encourages cooperative behaviour and hence a sharp switch between high and low-entropy states.

The coordination framework material tetrapropylammonium manganese dicyanamide (TPrAMn(dca)<sub>3</sub> or TPrAM) has generated a lot of interest due to its 'giant' barocaloric effect of 37.0 J kg<sup>-1</sup> K<sup>-1</sup> for small changes in pressure and around room temperature<sup>[2]</sup>. This value places it among the best barocalorics known, making it an ideal material for commercial refrigeration.

Single crystal measurements of TPrAM at ambient pressure and temperature reveal the average structure can be described by a large and highly disordered unit cell. The phase diagram as a function of temperature and pressure is rich in phase transitions further enriched when the tetrapropylammonium or manganese ions are substituted. From ambient temperature to 330 K TPrAM undergoes a first order phase transition to a smaller and more disordered unit cell, accompanied by a large change in entropy dependent on the applied pressure. The relative importance of structural and dynamic contributions to the entropy is currently unclear.

Aiming to improve the barocaloric properties by introducing structural disorder, we have explored the synthetic analogues of TPrAM<sup>[3]</sup>. Here we present the average and local structure of TPrAM under ambient and high pressure conditions. Neutron scattering measurements are the obvious choice for probing the structure and dynamics of TPrAM and its analogues, due to their sensitivity to smaller atoms, local structure and vibrations. The ultimate aim of our research programme is to understand structure-property relationships in these materials and hence to optimise the behaviour of new barocaloric materials.

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# Engineering hierarchical pore structures for improving catalytic performance of metal-organic frameworks

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Introducing additional meso- or macroporosity into traditionally microporous metal-organic frameworks (MOFs) is a very promising way to improve the catalytic performance of these materials, mostly due to the resultant reductions of diffusional barriers during reactions. Here we show that HKUST-1 can be successfully synthesised *via* in situ crystallisation (by exposing the MOF precursor solution to supercritical CO<sub>2</sub>, referred to here as “HKUST CO<sub>2</sub>”) to produce hierarchically porous structures that are highly beneficial for catalysis. This hierarchical MOF was characterised by powder X-ray diffraction (PXRD), scanning electron microscopy (SEM) and gas sorption to confirm the preservation of the microporous structure and the appearance of macropores in the crystallites. More importantly, the benefits of introducing a hierarchical porous structure into this MOF for improving the diffusion accessibility of reagents to the sample in catalysed liquid- and gas-phase reactions were quantified for the first time. It was found that the hierarchical pore structure helped to improve the catalytic performance in CO oxidation, which is evidenced by the greater extent of the reaction over HKUST CO<sub>2</sub> compared to the commercial HKUST-1 sample over the same time period, at temperatures between 220 and 260 °C. The hierarchical porous structure proved even more beneficial in liquid phase reactions where more bulky molecules were involved; here the conversion of styrene oxide in methanolysis was used as an example. These findings serve to demonstrate the advantages of using such hierarchical porous MOFs in catalysis.

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# Particle-surface-functionalisation of sub-micron Metal-Organic Frameworks

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Metal-organic frameworks (MOFs) are highly porous, complex 3D structures with flexibility in their chemical nature, which have become an immensely prevalent area of materials science over the past few decades.<sup>1,2</sup> On reducing the particle size of these materials to the nanoscale, MOF nanoparticles (MOF NPs) can also incorporate the inherent benefits of nanomaterials, such as their controllable outer surface properties and high external surface-area-to-volume ratio.<sup>1</sup> This affords the opportunity to tune the architecture of the MOF NPs by selectively utilising properties from both the MOF- and nano-fields. In particular this is useful in controlling the outer surface modification of MOF NPs providing access to a range of applications. With the ability to incorporate different chemical entities either directly through the diverse chemical building units, or post-synthetically by covalent modification of the linker and/or coordination to the metal, MOF NPs have the ability to introduce many functional groups into their structure.<sup>2</sup>

One such functionalisation is the introduction of 'gated' or 'switchable' behaviour and involves the controlled opening/closing mechanism of MOF pores by some external or chemical stimulus. This enables the ability to control the loading and release of cargoes into and out of the pores of the MOF. Previous approaches to this have seen a focus on using 'capping' units which can be removed by external triggers such as competitive ion binding, temperature or pH changes or in using functional groups which switch between molecular states upon application of a stimulus.<sup>3,4</sup> One scarcely researched area in MOF NPs is the introduction of dynamic covalent chemistry (DCvC), such as those introduced onto the surface of monolayer-stabilised gold nanoparticles.<sup>5</sup>

In this work, we aim to incorporate the concept of DCvC onto the surface of MOF NPs, with the goal of controlling access to the internal pore surface of the MOF. We have first synthesised MOF NPs of UiO-66 with reactive capping units which should allow the introduction of DCvC functionality. We then carried out extensive dynamic light scattering studies to investigate their colloidal stability in various solvents.

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# Thermally Induced Buckling in 2D Covalent Organic Frameworks

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Two-dimensional covalent organic frameworks (2D COFs) are periodic, permanently porous, and lightweight solids that are polymerized from topologically designed monomers. The predictable design and structural modularity of these materials make them promising candidates for applications including catalysis, environmental remediation, chemical separations, and organic electronics, many of which will require stability to mechanical and thermal stress. Generally, the covalent connectivity of these lattices is thought to confer high thermal stability, which is typically evaluated via thermogravimetric analysis (TGA). However, TGA measures the temperature that volatile degradation products are liberated and is insensitive to changes of the periodic structure of the COF. Here, I will describe the variable-temperature X-ray diffraction response of 2D COFs to thermal and mechanical stresses, which reveals that the periodic COF structure is lost at a lower temperature than is observed via TGA. Through an extensive exploration of many chemical structures, I offer design trends that lead to thermally robust 2D COFs.

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# Exploring symmetry and dimensionality in low dimensional Metal-Organic Frameworks as frustrated magnets

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In recent years, low dimensional magnets have sparked a huge interest in the scientific community due both to their unconventional behaviour as well as their potential applications such as magnetic cooling<sup>[1]</sup> and spintronics<sup>[2]</sup>. The sensitivity of low dimensional magnets to small perturbations results in complex magnetic structures and a great variety of phase transitions, i.e. different ordering of the electron spins in the system. Therefore, there is a strong interest in obtaining low dimensional structures, such as those featuring one-dimensional magnetic chains along a given direction of the crystal.

More recently, Metal-Organic Frameworks (MOFs) have proved to be excellent candidates for the realisation of low dimensional magnets. In MOFs, magnetically active transition metals or rare-earth ions are bridged through organic ligands allowing for the formation of a wide variety of 3D framework structures and the incorporation of low-dimensional motifs. The resulting magnetic structures can be studied by means of neutron scattering techniques.

In particular,  $\text{Tb}(\text{HCO}_2)_3$  has shown a range of phase transitions at  $T_N = 1.6\text{K}$ , including a state related to the Triangular Ising Antiferromagnet (TIA)<sup>[3]</sup> due to the geometric frustration induced by the arrangement of the chains in a triangular lattice.

Our main goal is to synthesise and explore the dependence of the TIA state in MOFs containing rare-earth metals, analogous to  $\text{Tb}(\text{HCO}_2)_3$ , upon changing the metal cations, doping the compound both with magnetic and non-magnetic species, varying the ligands - therefore influencing both the distance between the metal cations and the symmetry of the structure. Moreover, the influence of applied magnetic fields on the TIA will be probed.  $\text{Ln}(\text{HCO}_2)_3$  and  $\text{Ln}(\text{HCO}_2)(\text{C}_2\text{O}_4)$  pure structures have been synthesised so far with excellent phase purity and the magnetic properties of these compounds will be studied using magnetometry techniques and further explored in the future using neutron scattering as a technique to probe their magnetic structure.

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# Adjacent cationic-aromatic sequences yield strong electrostatic adhesion of hydrogels in seawater

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Developing adhesives functioning in the marine environment is a great challenge. Mimicking sessile marine organisms is an efficient way. For example, catechol-based adhesives inspired by mussel have been extensively developed in the last decade.<sup>[1-2]</sup> However, the performance of such adhesives in marine environments is still barely satisfactory, because the catechol group is easily oxidized to lose adhesion.<sup>[3]</sup> In an aqueous environment, many solid surfaces, including rocks, glasses, and metals, are negatively charged. Thus, as an alternative strategy, electrostatic interaction could be utilized as a major mechanism for adhesives to these surfaces. However, the electrostatic interaction between oppositely charged surfaces normally diminishes due to the Debye screening effect in high ionic-strength environments.<sup>[4]</sup> Biosystems can use this interaction through adjacent cationic–aromatic amino acids sequence of proteins even in a saline medium.<sup>[5]</sup> Application of such specific sequence to the development of cationic polymer materials adhesive to negatively charged surfaces in saline environments is challenging due to the difficulty in controlling the copolymer sequences.<sup>[6]</sup>

In this study, we discovered that a series of copolymers with adjacent cation–aromatic sequences can be synthesized through cation–p complex-aided free-radical polymerization at an equimolar ratio. There are two prerequisites for the formation of such poly(cation-adj- $\pi$ )s with controlled sequences: formation of cationic/aromatic complex by cation– $\pi$  interaction in the precursor solution of polymerization, and the same reactive vinyl head of cationic and aromatic monomer pairs. The application of this rule to diverse pairs of cation and aromatic monomers is studied in this work. The poly(cation-adj-p) series with adjacently located cationic and aromatic residuals is water-soluble and can form physical hydrogels in seawater. The hydrogels are strong and self-recoverable, exhibiting strong but reversible adhesion to negatively charged surfaces in seawater. The aromatics are found to enhance the electrostatic interactions of their adjacent cationic residues with the counter surfaces in a high ionic-strength medium that usually screens the electrostatic interaction completely for common synthetic polyelectrolytes. This work opens a pathway to develop novel adhesives using in saline water.

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# Random vs. cooperative distortions in a prototypical zeolite framework containing double four-ring cages – The role of framework composition and organic guests

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The “fluoride route”, synthesis in the presence of fluoride anions, is a versatile strategy for the synthesis of zeolites and zeotypes.<sup>1</sup> Fluoride anions tend to stabilise building units containing small rings, such as double four-ring (*d4r*) cages. The presence of small rings often leads to open frameworks with large pores that are able to adsorb relatively large guest molecules, enabling potential applications in catalysis or adsorption. In as-synthesised materials with *d4r* units, diffraction investigations have typically located the fluoride anions at or near the centre of the cage.<sup>2,3</sup> However, crystallographic methods deliver only the average long-range structure, and cannot give insights into the local structure and its variation over time. In previous work, molecular dynamics (MD) simulations based on density functional theory were employed to study the preferred (Si,Ge) configurations of the *d4r* cages and the dynamic behaviour of the fluoride anions in AST-type silicogermanates.<sup>4</sup>

The present contribution uses an analogous computational approach to study the local structure of the *d4r* cages and the dynamics of fluoride anions in AST-type zeotypes having different framework compositions (SiO<sub>2</sub>, GeO<sub>2</sub>, AlPO<sub>4</sub>) and containing different organic structure-directing agents (OSDAs), namely tetramethylammonium (TMA) or quinuclidinium (QNU). An analysis of the MD results shows that SiO<sub>2</sub>-AST contains undistorted *d4r* cages where the fluoride anions oscillate about the centre of the cage. This behaviour is hardly affected by the nature of the OSDA. In GeO<sub>2</sub>-AST, the fluoride anions remain near the cage centre in GeO<sub>2</sub>-AST, but the *d4r* cages are distorted to a “pyritohedron-like” shape (pyritohedron = distorted pentagonal dodecahedron). These distorted cages can assume two different orientations. While both orientations occur randomly in the TMA-containing system, the presence of QNU cations, which are hydrogen-bonded to framework oxygen atoms, induces an ordered arrangement of the distortions. In AlPO<sub>4</sub>-AST, the fluoride anions tend to form bonds to one of the surrounding Al atoms, with Al-F distances of ~1.9 Å. Again, the direction of the fluoride displacements is random in AlPO<sub>4</sub>-AST\_TMA, but tends to be ordered in AlPO<sub>4</sub>-AST\_QNU. At and above room temperature, the MD simulations indicate a significant mobility, with fluoride anions hopping between different Al sites at the picosecond timescale.

First, the results demonstrate that the framework composition governs the propensity of a system towards distortions of the fluoride-containing *d4r* unit. Second, cooperative effects that are due to framework-OSDA interactions can, at least in an idealised system, induce a strict ordering of such distortions. Judicious choice of the OSDA might stabilise such ordered distortions, which could, in turn, lead to a modulation of material's properties.

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# Observation of photoinduced phase transition of organic conductor (EDO-TTF)<sub>2</sub>PF<sub>6</sub> by time-resolved photoelectron microscopy

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In this contribution, we introduce the imaging of photo-induced phase transition on an organic conductor, (EDO-TTF)<sub>2</sub>PF<sub>6</sub> (Figure 1), using time-resolved photoemission electron microscopy (TR-PEEM) (Figure 2) [1,2]. (EDO-TTF)<sub>2</sub>PF<sub>6</sub> is a quasi-one-dimensional conductor at room temperature by forming unoccupied states due to the overlapping of the pi orbitals of EDO-TTF and the charge transfer from EDO-TTF to PF<sub>6</sub><sup>-</sup>. However, it becomes insulator below 280 K due to the interaction between electrons and lattices. Furthermore, it has been reported that the insulator to metal transition occurs by light irradiation [3,4]. The transition is observed by monitoring the volume change of molecules and also the change of the density of conducting electrons.

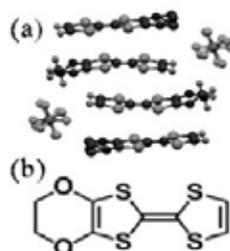


Figure 1: (a) crystal structure of (EDO-TTF)<sub>2</sub>PF<sub>6</sub>. (b) Molecular structure of EDO-TTF.

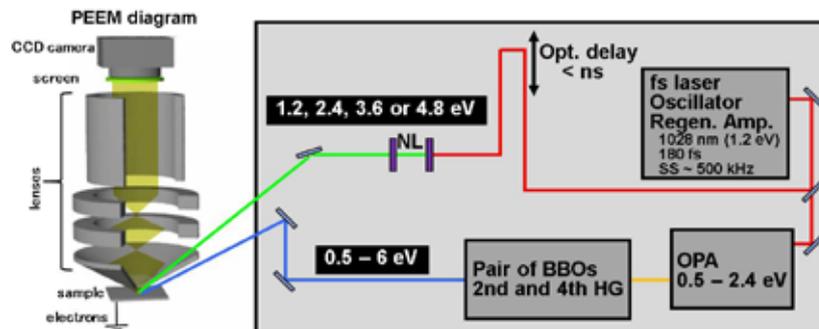


Figure 2: Schematic of TR-PEEM equipment.

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# Correlating Charge Transport and Photocatalytic Hydrogen Evolution Efficiency of Covalent Organic Frameworks

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Visible light driven hydrogen evolution from water is a promising strategy to convert and store solar energy as chemical energy.<sup>1</sup> Covalent organic frameworks (COFs) are front runners among different classes of organic photocatalyst, owing to their tunable porosity, crystallinity, optical and electronic properties. Photocatalytic activity of COFs depends on numerous factors such as band gap, crystallinity, porosity, exciton migration, stability of transient species, charge separation and transport.<sup>2</sup> However, it is challenging to fine tune all these factors simultaneously to enhance the photocatalytic activity. Here, we have established a correlation between charge transport and photocatalytic hydrogen evolution through structure–property–activity relationship combined with microwave spectroscopy and first–principles calculations. Careful molecular engineering allowed us to tune the light absorption (i.e. band gap), crystallinity, porosity, layer stacking and charge carrier generation and transport of a series of isorecticular COFs. We have assessed how these properties and the interplay between them impact photocatalytic activity of studied COFs. From the structure–property–activity relationship, we found that light absorption and charge carrier generation and transport are the prime factors, which influence the photocatalytic H<sub>2</sub> production of COFs in much greater extent than other factors.<sup>3</sup>

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# Multifunctional porous composites: A synergistic influence of ZnO and ionic frameworks for CO<sub>2</sub> conversion and combating microbes

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Porous organic frameworks (POFs) with heteroatom decorated ionic backbone have emerged as advanced materials for a gamut of applications ranging from heterogeneous catalysis to charge-selective molecular separation.<sup>1</sup> On the other hand, metal and metal oxide nanoparticles are well-explored for catalytic, and antimicrobial applications. The incorporation of Lewis acidic metal centre in POF is likely to enhance the catalytic activity and imparts specific interactions with microbial membranes.<sup>2</sup> However, the development of the recyclable material with superior activity as well as low toxicity is a challenge. Herein, we developed ZnO-loaded ionic networks involving triaminoguanidinium for heterogeneous catalysis and combating microbes with superior activity as well as low cytotoxicity to mammalian cells. Triaminoguanidinium chloride-based ionic POFs (BET specific surface area, POF-1: 200 ± 20, POF-2: 470 ± 30 m<sup>2</sup> g<sup>-1</sup>) were fabricated through simple Schiff base condensation.<sup>3</sup> Owing to the highly chelating ionic guanidinium core, and high porosity, the frameworks afford excellent metal [Zn(II): 47.2%] loading capacity. Mesoporous Zn/POFs exhibited pronounced activity towards catalytic fixation of CO<sub>2</sub> into cyclic carbonates under solvent-free, mild-reaction conditions with excellent recyclability. The synergistic influence of infused zinc oxide and ionic POFs led to robust antibacterial activity (Gram-positive, *Staphylococcus aureus* and Gram-negative, *Escherichia coli*) which was used for antibacterial surface coating and decontamination of water through gravimetric column filtration. Moreover, for the first time, we demonstrated the antiviral activity of composite porous organic frameworks towards HIV-1 and VSV-G enveloped lentiviral particles. A brief appraisal of multifunctional applications of triaminoguanidinium-based POFs and Zn/POFs and the future scope of the composite framework materials in environmental remediation and biomedical applications will be presented.

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# Pressure-induced spin crossover at room temperature in a nanoporous host-guest framework structure

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Host-guest chemistry has received enormous attention in recent years, including nanoporous metal-organic framework (MOF) exhibiting spin crossover (SCO) phenomena. The reversible inclusion of guest molecules within the MOF pores enables the control of the MOF functionality. In this study, the single crystals and/or polycrystalline powders of the two-dimensional (2D) MOF  $\{[\text{Fe}_2(\text{azpy})_4(\text{NCS})_4]\cdot\text{G}\}$  (azpy is trans-4,4'-azopyridine, NCS is thiocyanate and G is guest) is pressurized with included guest as a pressure transmitting media (PTM), i.e. ethanol (EtOH) and isopropanol (iPrOH). Room temperature conversion of metal-ion sites from high-spin to low-spin states under high-pressure driven guest-exchange is investigated.

The introduction of a guest is usually reserved for framework structures which are porous and can accommodate a guest species within. MOF's is an example of such a compound where organic linkers between metal ion centers form pores which guest molecules can occupy. Halder *et al.*<sup>1</sup> presented the first evidence of a MOF with guest-dependent SCO capabilities in the 2-dimensional structure  $\{[\text{Fe}_2(\text{azpy})_4(\text{NCS})_4]\cdot\text{G}\}$  which shows reversible uptake and release of guest molecules (guest exchange). Mössbauer effect and magnetic susceptibility measurements showed 50 % SCO when a guest was present (sorbed state), compared to no spin-crossover when no guest was present (desorbed state) with a transition temperature of 150 K.

Upon iPrOH guest-PTM, spin conversion of ~66 % low-spin abundance is attained by ~3 GPa. With an EtOH guest-PTM, SCO progression is more sluggish and ~56% low-spin abundance is attained by ~5.5 GPa. This pressure facilitated guest-specific triggering of SCO is suggestive of guest-molecule interactions with the local co-ordination network of the Fe(II) core, which increases the ligand field. Appreciably, low-spin abundances attained at room temperature upon pressurization are comparable to maximal ~50 % spin conversions only attainable below ~150 K at ambient pressure. This study also shows the increase in guest density within the MOF pores facilitates guest-to-ligand interactions and allows tunability in the SCO transition raising the transition temperature towards room temperature and have potential real-life applications such as switchers and sensor devices.

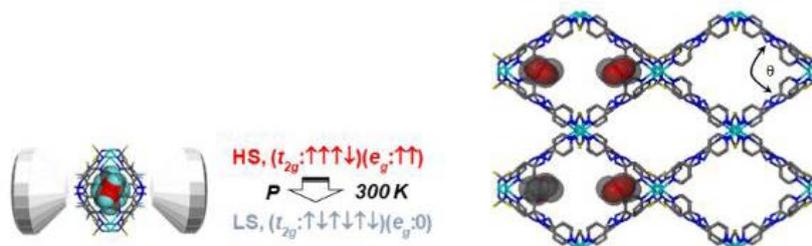


Figure 1: Pressurization of  $\{[\text{Fe}_2(\text{azpy})_4(\text{NCS})_4]\cdot\text{G}\}$  leads to room temperature SCO.

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# Heterometallic MOFs materials: tunable energy transfer process, solid-state lighting and near-infrared luminescence thermometry

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Trivalent lanthanide ions (Ln<sup>3+</sup>) are used to prepare a plethora of coordination compounds; metal-organic frameworks (MOFs) being amongst the most sought-after in recent years.<sup>[1],[2]</sup> The porosity of Ln-MOFs is often complemented by the luminescence imparted by the metal centers, making them attractive multifunctional materials.

Here, we report a class of 3D MOFs obtained from solvothermal reaction between 2,6 naphthalenedicarboxylic acid (H<sub>2</sub>NDC) and lanthanide chlorides yielding three types of compounds depending on the chosen lanthanide: [LnCl(NDC)(DMF)] for Ln<sup>3+</sup> = La<sup>3+</sup>, Ce<sup>3+</sup>, Pr<sup>3+</sup>, Nd<sup>3+</sup>, Sm<sup>3+</sup> (type 1), [Eu(NDC)<sub>1,5</sub>(DMF)]·0.5DMF (type 2), and [Ln<sub>2</sub>(NDC)<sub>3</sub>(DMF)<sub>2</sub>] (type 3) for Ln<sup>3+</sup> = Tb<sup>3+</sup>, Dy<sup>3+</sup>, Y<sup>3+</sup>, Er<sup>3+</sup>, Yb<sup>3+</sup>.<sup>[3]</sup> Photoluminescent properties of selected phases were explored at room temperature. The luminescence thermometry capability of Yb<sup>3+</sup>-doped Nd-MOF was fully investigated in the 15-300 K temperature range under 365 and 808 nm excitation. To describe the optical behavior of the isolated MOFs, we introduce the *total energy transfer balance* model. Therein, the sum of energy transfer rates is considered along with its dependence upon the temperature: sign, magnitude, and variation of this parameter, permitting to afford a thorough interpretation of the observed behavior of the luminescent species of all materials presented here. The combination of novel theoretical and experimental studies presented herein to describe energy transfer processes in luminescent materials can pave the way towards the design of MOF-based chemical and physical sensors working in an optical range of interest for biomedical applications.

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# High-pressure behaviour of DUT-8 via single crystal X-ray diffraction

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MOFs represent a step beyond other microporous inorganic materials with the ability to explore a wide variety of structures and selectively tune the properties of the frameworks. One such interesting property is flexibility, whereby a MOF can change its conformation upon external stimuli such as guest, pressure or temperature. These properties could be harnessed in industrial sectors such as sensing or pressure monitoring.<sup>1,2</sup>

A fundamental technique used to understand the phase behaviour of crystalline materials is high-pressure single crystal X-ray diffraction (HP SCXRD).<sup>3</sup> We focus on using HP SCXRD to understand the pressure response of a flexible MOF, DUT-8. DUT-8 is a pillared-layer MOF comprising of  $M_2$  (where, M = Co, Ni, Cu or Zn) paddlewheels, dabco pillars and naphthalene dicarboxylate (ndc) linkers which can crystallize in many conformational isomers that depend on the orientation of the non-linear ndc linkers with respect to each other. While the open pore form (DUT-8-op) is compatible with several conformation isomers, there is only a unique isomer, with alternating linker orientations, that is stable as a closed pore form (DUT-8-cp).<sup>4,5</sup>

In this study, we focus on the effect of changing the pressure transmitting media (PTM) and the metal-centre of the MOF on the high-pressure phase. DUT-8 was loaded into a diamond anvil cell with a variety of PTMs and its response to pressure was determined. Previously DUT-8 has been shown to be structurally sensitive to different solvents.<sup>6,7</sup> In this study, we could take advantage of high-quality single crystal X-ray data to understand in detail solvent interactions and structural changes of the framework.

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# Structure Determination of Framework Materials by Rotation Electron Diffraction Methods

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Metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) are attracting increasing scientific and technological interest because they are capable of interacting with ions and molecules not only at their surfaces, but also in the entire material through the open channels. They have particular high performance in catalysis, gas storage, ion exchange, fuel cells, supercapacitor, etc. A crucial problem in the study of MOFs is to determine the structure, more specifically, the atomic positions. The novel properties of MOFs and COFs can be revealed by knowing the atomic positions, and then specific applications could be designed.

Diffraction method is the most popular way for structural determination of crystalline materials for more than one century. However, challenges are still remaining on the structural analysis of nanocrystalline materials which are too small to be studied by single crystal X-ray diffraction. X-ray and neutron powder diffraction are the alternatives, but additional challenges rise as reflection peak overlaps and the coexistence of multiple phases.

Electron crystallography has developed rapidly in recent years for structural determination of nano-sized crystals using transmission electron microscopy (TEM) by taking the advantages of the short wavelength of electrons. Rotation electron diffraction (RED) is a semi-automatic technique developed for collection and processing of 3-dimensional electron diffraction (ED) data<sup>[1,2]</sup>. Nowadays, a complete continuous rotation electron diffraction (cRED) data can be acquired in 15-150 seconds using continuous goniometer tilt<sup>[3]</sup>, and the electron dose can be limited to below 0.1 e/Å<sup>2</sup>. Thus, one major problem in electron diffraction, the beam damage, could be minimized. This is crucial for the study of MOFs and COFs, which are always suffered from severe beam damage. As a consequence, more structural details, such as guest molecules, H-bonding, can be revealed, and thereby provides critical insights for developing new functional materials. To further automate the data collection, we have developed SerialRED for automated data collection, processing, and structure solution<sup>[4]</sup>. The large number of particles makes it possible even for quantitative phase analysis, and for detection of minor phases that may not be detectable by X-ray diffraction.

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# Development of picosecond time-resolved X-ray crystallography for observing photoinduced structural change of softcrystals

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We developed picosecond time-resolved X-ray crystallography for observing the photo-induced structural change of luminescent softcrystals using synchrotron X-ray source and an MHz fiber laser system. The luminescence function of softcrystals can be controlled by the specific wavelength<sup>[1]</sup>. The short-lived photo-induced transient structures of them associated with their luminescence process are not yet thoroughly understood at the atomic level. In order to reveal their transient structure of them, the time-resolved X-ray crystallography system has been implemented at the synchrotron facility of the Photon Factory, High Energy Accelerator Research Organization. Using the MHz fiber laser to excite the softcrystals, each X-ray pulse which is operated with 794 kHz synchronized with each laser pulse. The X-ray pulse width and wavelength are 100 ps and 0.8 Å. We synchronized a fiber laser (Pharos, Light Conversion Co. Ltd.) with the synchrotron ring: the wavelength, pulse width, and intensity are 200 fs, and 343 nm by a third harmonic generation (THG), and about 80 mW. The frequency of this laser system is controllable with the luminescence decay time of softcrystals. We use a 2 dimensional X-ray detector (Pilatus3 2M, Ductris Ltd) of 253.7×288.8 mm to record X-ray diffraction images. Using gate signals synchronized with the laser pulse, the reading time of the X-ray detector also synchronized with the laser frequency. We demonstrated to observe the photo-induced structural change of 6-cyano-2-(2'-hydroxyphenyl)imidazo<sup>[1,2-a]</sup>pyridine associated with the excited-state intramolecular proton-transfer process<sup>[2,3]</sup>.

This development provides an opportunity to understand the detailed transient structure of softcrystals after photoexcitation.

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# Chiral Supramolecular Nano-Architectures from Macroscopic Mechanical Rotations

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Vortex motions are inherently chiral. Although it has been believed that the macroscopic vortex motion could not influence the nanoscale molecular chirality because of the difference in scale, fluid dynamics, resulting from the macroscopic mechanical rotation of a rotary evaporator or a magnetic stirrer, has been shown to selectively induce one of two enantiomers (mirror-image structures) in certain nanoscale supramolecules.<sup>1-3</sup> This has attracted considerable attention from the viewpoint of novel synthetic methods for chiral molecules and provides a clue to explain the biased distribution of L-amino acids and D-sugars in biological systems (the homochirality of life).<sup>4</sup> As an alternative to giving a chiral twist to synthesized supramolecules or polymers, it is a challenge to reproducibly prepare chiral species only by macroscopic mechanical rotations. We demonstrate a method for highly reproducible rotary evaporation-induced chiral H-aggregates from achiral phthalocyanines, and propose chiral induction mechanisms by using the chiroptical sign-based absolute structures.<sup>5,6</sup> Here, the stable chiral thin films based on H-aggregates of MPcs (M = H<sub>2</sub> or Pd) were prepared on the bottom of the flask by concentration of the monomeric solution with a rotary evaporator. The chirality is shown to reproducibly depend on its rotational direction for the first time. We propose that these results will provide insight to the origin of the homochirality of life, and this will be a pioneering study in a novel scientific field in terms of admixing nanoscale molecular chemistry and macroscopic fluid dynamics.

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# Cu(II)-based metal-organic framework as electro-active materials in carbon paste electrodes: Evaluation of methanol electro-oxidation and sensing application.

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Metal-organic frameworks (MOFs) are porous polymeric materials elaborated with metal-nodes and organic ligands. The presence of metallic centers with redox-active properties, specific pore size and an elevated surface area makes them attractive materials for electrochemical applications <sup>[1]</sup>, which are mainly focused in designing energy storage devices <sup>[2]</sup>, supercapacitors and electrochemical sensors for biomolecules <sup>[3]</sup>; however, their applicability on methanol electro-oxidation and methanol sensing is recent and growing.

Herein, the synthesis and characterization of copper benzenetricarboxylic metal-organic framework (Cu-BTC) and its electro-catalyst properties were evaluated. The Cu-BTC was novelty synthesized in mild condition at room temperature, and the obtained crystals were characterized by SEM, EDS, XRD. The MOF was incorporated at diverse ratios (7-30 wt %) in carbon paste electrodes for determinate its electrocatalytic activity in the absence and the presence of methanol. The electrodes were characterized by cyclic voltammetry (CV), diferential pulse voltammetry (DPV) and chronoamperometry (CA). A response toward methanol was presented at pH 13 (NaOH 0.1M) with a maximum current density of 10 mA, LOD of 0.0718 mM and a selective oxidation toward methanol in presence of high concentrations of ethanol that was tested by amperometric experiments, obtaining a limit of detection of 0.1134 mM. The capacity of the modified electrode in methanol detection was evaluated in Vodka by differential pulse voltammetry.

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# Molecular Correlated Rotation in Solid State via Stadium Shaped Hexa-arylbenzene

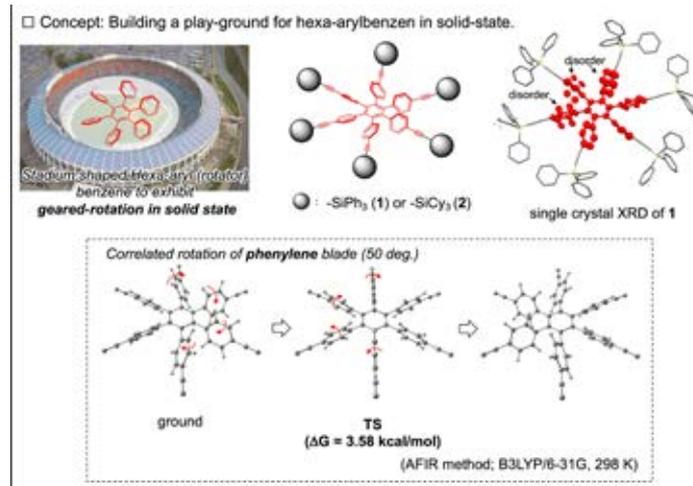
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Molecular dynamics in solid-state have attracted much attention because of the high potential on application to a molecular machine or solid-state functional materials.<sup>1</sup> Recently, molecular rotations in solid-state have been intensely studied using amphidynamic crystals which shows molecular rotations in highly ordered crystalline media. Most of their molecular rotations are Brownian jump via thermal energy, and a correlated-dynamics such as gearing motion in solid state has been known as a challenging subject. Hexa-alkylbenzene moiety has been treated as a candidate template to study molecular correlated motion, and attract much attention because of its through-shape delocalized electronic environment which highly correlated to the phenylene motions and photoluminescent properties.<sup>2</sup> To take advantage of the features of hexa-arylbenzene moiety to develop a novel template for studying molecular correlated motion with photoluminescence in solid state, we designed stadium shape molecules **1** and **2** bearing hexa-arylbenzene and investigated the molecular motion in the crystals and those photoluminescent properties.

The wall-side of molecules is implanted using tri-phenyl or tri-cyclohexyl silyl groups as shown in the below figure. Single crystal XRD analysis confirmed the structure of **1** and **2**, and its packing structure, revealing that the hexa-arylbenzene domain has a reasonable packing environment to show molecular rotations in crystals. Solid-state <sup>2</sup>H- and <sup>13</sup>C-CPMAS NMR measurements under variable temperature indicate that the phenylene blades show molecular rotations in the crystals. Furthermore, calculation studies using Artificial Forced Induction Reaction (AFIR) method revealed that the phenylenes rotate in two different correlated manners with having rotation barriers as c.a. 8.0 kcal/mol and 38 kcal/mol. The crystal **1** and **2** shows blue emission under UV light (365 nm), and the emission intensity was enhanced by lowering the temperature. And applying isotropic pressure (100 MPa) to the crystal **2** induced emission enhancement. In fact, hexa-phenylbenzene is as well known as Aggregation Induced Emission (AIE) chromophore which the emission is quenched by molecular motion. In other words, it is suggested that the emission of crystal **2** is well correlated with the phenylenes correlated motion in terms of the emission enhancement via cooling and applying pressure the crystal. The detail of molecular dynamics and photoluminescence of crystal **1** and **2** will be described in the presentation.



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# Where do reactions occur in metal-organic frameworks with incorporated molecular catalysts? A quantitative kinetic study of bulk vs. surface reactivity

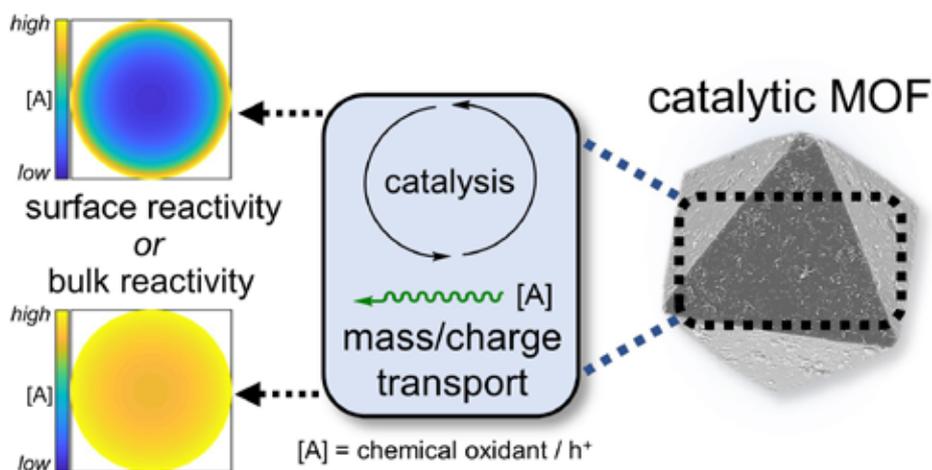
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Metal-organic frameworks (MOFs) are becoming popular heterogeneous support matrices in which to incorporate discrete molecular catalysts capable of carrying out a variety of transformations. One side effect of the heterogenization of molecular catalysts within a finite 3D porous structure is that reactants/substrates and possibly even electrons/holes must be transported through the MOF particles as the reaction proceeds.<sup>1</sup> The catalytic reaction can then take place within the bulk of the material or in a thin layer near the surface of the particles if transport limitations interfere. Herein a quantitative kinetic model is presented<sup>2</sup> to diagnose these mutually exclusive behaviors, which answers the questions: Where does a given catalytic reaction spatially occur within a MOF particle? And, what fraction of incorporated molecular catalysts within the framework participate in the reaction? The oxygen evolution reaction driven by a chemical oxidant is presented as an example mechanism. Assigning either bulk or surface reactivity is clearly delineated over a wide range of conditions using simple quantitative metrics. Numerical simulations confirm these results. Additionally, the influence of surface reactivity or transport limitations on measured turnover frequencies (TOFs) is discussed. We find that when measured under conditions where surface reactivity persists, apparent TOFs deviate from an intrinsic kinetic value. Importantly, this report shows how to transition from surface to bulk reactivity and identifies which operational parameters to modify to optimize MOF-based molecular catalysis.



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## Flexibility in Functionalized MOF-5 Derivatives

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One of the prototypical and most studied MOFs is MOF-5 or IRMOF-1, which consists of zinc-oxo clusters bridged by bdc (1,4-benzenedicarboxylate) linkers. In contrast to the parent MOF-5, experiments have shown that functionalized derivatives with fu-bdc linkers (fu-bdc: 2,5-alkoxy-functionalized bdc) become flexible, in a sense that in some cases, crystallites can enter a rhombohedrally distorted state, and in other cases, systems even enter an amorphous state, but the crystalline phase can be recovered upon certain stimuli. The type of flexibility depends in a non-linear way on the utilized functionalization. In particular, the series of bdc-type linkers exhibiting aliphatic side-chains 2,5-R<sub>2</sub>-bdc R=O(CH<sub>2</sub>)<sub>n</sub> (CH<sub>3</sub>), n=1 to 7 has been successfully utilized in IRMOF synthesis, and the derived materials were then systematically characterized by an ensemble of techniques. Herein we use our recent MOF-FF parameterization of the fu-bdc linker library, for which a manuscript was submitted within the context of this Faraday Discussion, to perform atomistic forcefield simulations to characterize the framework flexibility for the above mentioned functionalization, in order to aid the experimental findings with an atomistic view on the phase transformations.

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# Electrochemiluminescence in DNA/Ru complex softcrystal device

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Electrochemiluminescence (ECL) is a phenomenon in which light is emitted from the excited state of a redox-active material generated by electrochemical reactions. Among light-emitting device, ECL devices have various advantages in terms of structure and simple fabrication, and they are therefore expected as next generation emitting devices. Concerning to the ECL device, we have reported the improvement of emission response, ECL intensity and stability of the ECL device by employing alternating current (AC)-driven method.<sup>1,2</sup> AC-ECL showed further improvement in ECL properties when TiO<sub>2</sub> nanoparticles,<sup>3</sup> suitable solvent<sup>4</sup> and DNA/Ru(bpy)<sub>3</sub><sup>2+</sup> hybrid films<sup>5</sup> and TTA upconversion<sup>6</sup> were used.

In this paper, we will present applications of softcrystal<sup>7</sup> with DNA to electrochemiluminescent device, because DNA works well as novel optical and electronical materials by hybridizing some functional molecules through some interaction modes such as electrostatic, intercalation and so on. The device exhibit ultra-quick response and unique emission properties. We would like to discuss DNA as an attractive material for next generation electrochemiluminescent system.

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# Crystal Component Linking as a New Controlled Polymerization

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The control of molecular structure in polymer gel is still a challenging problem in the field of polymer chemistry. In this context, we herein introduce new controlled polymerization method for precise synthesis of linear polymers and network polymers by using crystal component crosslinking of porous crystal as the core technology. Metal-organic framework (MOF) was selected as the starting porous crystal. As a result, linear polymers with specific polymerization degrees were obtained, which was dependent on the used MOF crystal structures. Additionally, we obtained polyhedral polymer gels independent on the shapes and sizes, polyhedral hollowed polymer gel, and anisotropically swelling gel.

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# Redox reactions of small organic molecules using ball milling and piezoelectric catalysis

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Over the past decade, photoredox catalysis has harnessed light energy to accelerate bond-forming reactions. The broad success of photoredox catalysis hinges on the susceptibility of the coupling partners to redox activation and ensuing organic transformations with high levels of efficiency and selectivity. There has also been substantial parallel progress in mechanochemical organic synthesis using ball milling. Advantages of mechanochemical organic transformations include the avoidance of potentially harmful organic solvents and external heating, shorter reaction times, and simpler operational handling.

Inspired by the unique profile of photoredox system based on light irradiation and the utility of ball milling in mechanochemistry, we hypothesized that redox activation of small organic molecules could be achieved through a mechanistically distinct approach using mechanical energy. Specifically, we envisioned that the agitation of piezoelectric catalysts via ball milling could generate temporarily highly polarized particles. These particles might act as strong reductants to transfer electrons to small organic molecules, followed by oxidative quenching of a donor, thereby inducing the selective formation of chemical bonds in a manner analogous to photoredox catalysis.

Here we report that agitation of a piezoelectric catalyst, BaTiO<sub>3</sub>, via ball milling reduces aryl diazonium salts.<sup>1</sup> This mechanoredox system can be applied to arylation and borylation reactions under mechanochemical conditions.

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# Cu-MOF Immobilized on Polydimethylsiloxane by Hydrosilylation: Its Characterization and Antibacterial Activities Against Various Bacteria Including MRSA

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To modify the surface of polydimethylsiloxane (PDMS) for therapeutic purposes, flexible antibacterial Cu-MOF (metal-organic frameworks) was immobilized on the PDMS by the hydrosilylation reaction of 1,2-bis(4-bipyridyl) ethylene ligand consisting of the MOF and vinyl-terminated PDMS with H-terminated PDMS at room temperature. The bactericidal activities of the Cu-MOF immobilized PDMS (PDMS@Cu-MOF) and control polymer (PDMS) were tested against three strains of bacteria: *Pseudomonas aeruginosa* (*P. aeruginosa*), *Klebsiella pneumoniae* (*K. pneumoniae*), and *Methicillin-resistant staphylococcus aureus* (MRSA). These results present PDMS@Cu-MOF has more selective antibacterial activities toward *P. aeruginosa* and *K. pneumoniae* at 200 mg×mL<sup>-1</sup> than PDMS. The release test of Cu(II) ion shows PDMS@Cu-MOF to be very stable at PBS buffer. Its physical and thermal properties such as phase transition, swelling ratio, and thermal gravity loss seemed to be approximately the same as those of control polymer without Cu-MOF. Its selective bactericidal activities give the potency of PDMS@Cu-MOF as the new promising candidate in medicinal applications including implant, treatment of skin disease, wound healing, and drug delivery.

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# Isomeric difference in the crystalline-state chemiluminescence properties of 1,2-dioxetanes with a phthalimide chromophore

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Adamantylideneadamantane 1,2-dioxetane (Adox) is one of the stable 1,2-dioxetanes, thermal decomposition of which partially leads to the excited singlet ( $S_1$ ) or triplet ( $T_1$ ) state of 2-adamantanone (AdCO). The  $S_1$  state of AdCO emits 420 nm light weakly.<sup>1)</sup> Adox is a useful chemiluminophore for chemical analyses with light detection. For instance, the chemical analyses of mechanical forces using chemiluminescence (CL) have been developed with Adox derivatives having polymer chains in the field of mechanochemistry.<sup>2)</sup> Similarly, an approach with Adox will be effective to understand chemical reaction behaviors in molecular crystals with “soft crystal” character.<sup>3)</sup> While CL reactions in the crystalline states have been investigated by several groups,<sup>4,5)</sup> establishment of the theoretical background for the crystalline-state reactions is still a challenge. To develop the soft crystal science, we investigated here CL property of an Adox derivative with a phthalimide chromophore<sup>6)</sup> in the crystalline state. The Adox derivative was designed by non-conjugatively linking the Adox moiety to the fluorophore part as both a crystal structure modulator and the emitting moiety by accepting energy from the excited AdCO. In this study, we prepared *syn*- and *anti*-isomers of the Adox derivative and investigated their CL properties in crystals. CL properties observed by heating crystal samples of the isomers at 160 °C showed a contrastive difference in CL intensities, emission maxima and reaction kinetics. The differences in the CL properties are well correlated to the crystal structures, in which each of *syn*- and *anti*-isomers has its own distinctive packing pattern of the Adox and phthalimide moieties. The results clearly indicate emission properties and the reaction kinetics of the crystalline-state CL are dependent on the crystal structures.<sup>7)</sup> To understand the reaction kinetics in detail, we have analyzed the thermal diffusivities in the crystals of the Adox derivatives. Mechanisms of the characteristic CL reaction behaviors in crystals will be discussed.

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# Electrochemically-triggered upconverted luminescence through triplet-triplet energy transfer and subsequent triplet-triplet annihilation upconversion reaction

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Electrochemiluminescence (ECL) is a phenomenon of light emission triggered by electrochemical reactions.<sup>1</sup> However, ECL has not yet been implemented in light-emitting devices due to the weak light emission intensity and short device lifetimes. In particular, in the case of blue ECL, application of a high voltage is necessary because of the large energy gap involved. Thus, side reactions such as solvent decomposition tend to occur when a high voltage is applied, which leads to poor light emission properties. In this study, we aimed to realize blue ECL driven by a low voltage to improve ECL properties. We focused on triplet–triplet energy transfer (TTET) and upconversion based on pair annihilation of two triplet states (triplet–triplet annihilation upconversion: TTA-UC).<sup>2</sup> TTET refers to energy transfer from the triplet state of a donor molecule excited by external stimuli to the triplet state of an acceptor molecule. In TTA-UC, an excited singlet state is produced by a pair annihilation reaction of two triplet states. By using these phenomena, it is possible to develop luminescence of higher energy than the excitation energy, which has attracted the attention of many researchers for the energy utilization efficiency it offers. We investigated electrochemical and optical properties of a Ru(bpy)<sub>3</sub><sup>2+</sup>/9,10-diphenylanthracene (DPA)-containing electrochemical device. By applying an AC voltage to the device that could generate the excited state of Ru(bpy)<sub>3</sub><sup>2+</sup>, blue ECL was generated from S<sub>1</sub> states of DPA molecules by a TTA-UC reaction between T<sub>1</sub> states of DPA molecules generated by TTET from the <sup>3</sup>MLCT state of Ru(bpy)<sub>3</sub><sup>2+</sup>. To the best of our knowledge, such electrochemically triggered upconverted luminescence through TTET and subsequent TTA-UC has not yet been reported. An energy conversion system based on an electrochemical reaction such as the one described could be useful for further development of ECL devices that require a low voltage and offer multicolor luminescence.

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# Separation of Trans-1,3-butadiene from C4 mixture by Metal Organic Framework: A Molecular Dynamics Simulation Study

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Molecular Dynamics simulations have been performed for the separation of butadiene from the components (major) of C4 hydrocarbon mixture using metal organic framework such as ZIF-71. All the simulations were carried out at four different temperatures, 300K, 400K, 500K and 550K and different concentrations of guest molecules. From the values of self-diffusion coefficients (D) at different temperatures, it has been seen that the diffusion follows the order trans-1,3-butadiene > 1-butene > nbutane > i-butene. For all concentrations, it has been found out from the plots (Fig 1) of  $D_{\text{buta}}/D_{\text{other}}$  (where  $D_{\text{buta}}$  refers to self-diffusion coefficient of butadiene and  $D_{\text{other}}$  refers to those of nbutane, 1-butene and i-butene present in the mixture) vs temperature (T) that the separation is better at lower temperature in all the cases. Fig 2 shows the plots of energy distribution between the host atoms of ZIF71 and the guest atoms of all four C4 hydrocarbons at the highest and lowest temperatures under consideration. In all cases, more attractive interaction in lower temperatures also supports the fact stated in Fig 1.

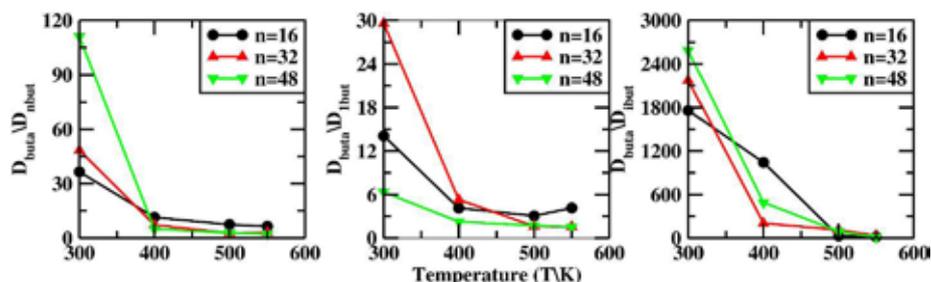


Fig 1: Plot of ratio of self-diffusivity of trans-1,3-butadiene to other components of C4 mixture vs. Temperature for three different concentrations (n=total no. of guest molecules present in the simulation)

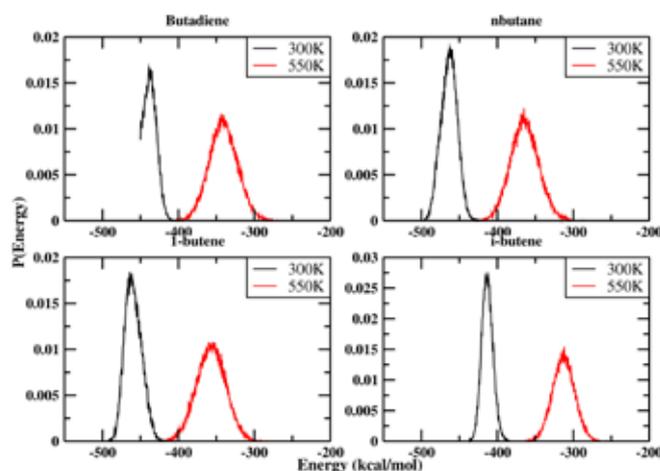


Fig 2: Energy Distribution between hosts atoms of ZIF71 and atoms of components of C4 mixture at lowest (300K) and highest (550K) Temperatures under consideration

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# Oximes and pyridyl alcohols as co-ligands for the synthesis of Metal Organic Frameworks

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Metal organic frameworks (MOFs) are hybrid porous materials, which have attracted the interest of the scientific community the last three decades; such species are promising candidates for a broad variety of applications including gas storage, separation, catalysis, etc. Although MOFs have been extensively studied, there are only a few examples that display interesting magnetic properties, and hence their use as magnetic sensors is yet unexplored.

The choice of the organic ligands and their coordination modes play a crucial role for the formation of a magnetic compound. In this work, we introduce the employment of chelating/bridging 2-pyridyl oximes and pyridyl alcohols, in combination with a polytopic organic linker for the synthesis of MOFs. Such ligands have been used in metal clusters chemistry due to their ability to bridge a large number of metal ions and, often, promote ferromagnetic interactions between the metal centres. [1-3] Although they have led to significant breakthroughs in the areas of single-molecule and single-chain magnetism, they have never been employed in the MOF synthesis. The synthesis of a new family MOFs bearing these ligands will be discussed along with their structural and magnetic characterization. [4, 5]

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# Polymorphism Analysis of Soft Crystal Materials by using Crystal Structure Prediction Technique with Powder X-ray Diffraction Data

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“Soft crystals” that easily transform into another polymorphic phase by macroscopic gentle stimuli at room temperature are expected to become innovative “smart” materials, because they exhibit visually remarkable changes in luminescence and optical properties caused by the polymorphic transition<sup>[1]</sup>. In order to apply them as the “smart” materials by employing their cooperative phenomena, it is important to clarify polymorphism phenomena, mechanism of polymorphic transitions, physical and optical changes related by microscopic and macroscopic structural changes of the soft crystals due to the phase transitions.

On the other hand, we have developed a computational technique for crystal structure prediction (CSP) that predicts crystal structure from the structural formula of a molecule<sup>[2,3]</sup>, and recently reported a new methodology related to the CSP technique with measured powder X-ray diffraction (PXRD) data<sup>[4]</sup>. The latter can computationally find not only the most appropriate crystal structure corresponding to the measured PXRD data, but also detect some polymorphic structures close to the observed structure by searching plausible crystal structures based on assessment of their crystal energies and PXRD patterns. Many of the predictive polymorphs found can be related to each other by atomic rearrangements induced by weak stimuli, and elucidation of such relationships can help to understand the various factors that govern the formation and phase transition phenomena of soft crystals. Moreover, it is thought that this method is effective for an identification of polymorphs where atomic positions are partially disordered due to molecular flexibility and thermal vibrations.

In this presentation, it is demonstrated that this new method is applied to organic molecular materials, and the appropriate crystal structures can be determined by using CSP technique with PXRD data. We also show that this method is widely useful for determining polymorphs and analyzing polymorphic transitions in the flexible organic molecular crystals including “soft crystals”.

This work was supported by JSPS KAKENHI Grant Number JP17H06373.

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# Chiroptical Spectroscopic Studies on Lanthanide Complexes with Valinamide Derivatives in Solution

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Chirality is an important concept for understanding biological issues and can be applied to functional devices in photochemistry. It is also known that the nature of electronic transitions of rare earth ions, such as europium (Eu), terbium (Tb), may be induced and their optical properties affected by coordination systems that can enhance the circularly polarized luminescence (CPL).<sup>[1]</sup>

Here in, we focused on the helical rare earth complex LnL<sup>[2]</sup> which can construct a coordination polymer by incorporating benzene-1,4-dicarboxylate as pillar component<sup>[3,4]</sup>, aimed to clarify the expression and the principle of CPL luminescence for LnL derivatives with an optically isomeric site<sup>[5]</sup>.

EuL<sup>me</sup> and EuL<sup>val</sup> were newly synthesized as chiral lanthanide complexes (Figure). Both complexes showed CPL and their optical anisotropy factor ( $g_{lum}$ ) were estimated at approximately |0.12| and |0.13|, respectively, in acetonitrile. While, circularly dichroism spectra of *S*-/*R*-EuL<sup>val</sup> do not correspond to those of *S*-/*R*-EuL<sup>me</sup>. This means two isostructural chromophores in *S*- or *R*-EuL<sup>me</sup> make a chiral conformation, and their excited states will result in the Davydov splitting as two identical states. Thus, two bipyridine (bpy) moieties in EuL<sup>me</sup> having equivalent electronic state, and take right- and left-handed conformation in solutions. Finally, we found that CPL properties of Eu complexes were not only enhanced by the molecular chirality, but also the number of chromophores or configuration between energy donor and acceptor moieties.

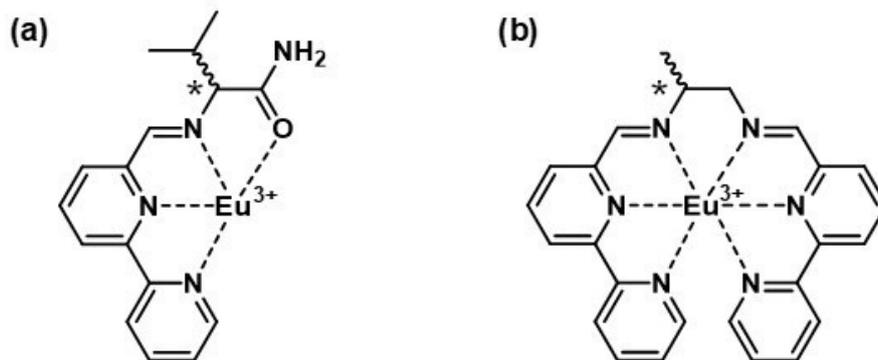


Fig.1 Molecular structure of (a)EuL<sup>val</sup> and (b)EuL<sup>me</sup>.

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# Crystal Structure with Large Pore of C<sub>3</sub>-Symmetry Triaryltriazine Derivatives

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Porous organic materials have garnered a significant interest for applications in gas sorption, energy storage, and others. In general, molecules tend to order in close-packed structure to fill the void space in the solid state. Therefore, there are few examples of molecular crystals in which molecules aggregate without covalent and/or metal–organic bonding and have large pore. In this work, the crystal structures of triaryltriazine derivatives possessing three acridinyl (**1**) or anthryl groups (**2**) were elucidated. As a result, it was found that **2** forms the porous crystals in which molecules are arranged keeping long intermolecular distances.

The both crystals of **1** and **2** were obtained as yellow needles containing the solvent molecules (*o*-xylene and toluene, respectively). The results of X-ray crystallographic analysis revealed that the crystal of **1** has a dense packing structure in which tips of acridinyl groups (N10) are tucked into the bay area of the neighboring molecules. In contrast, the molecules of **2** in the crystal were found to be aligned as tips of anthryl groups (C4–H, C10–H, and C5–H) of three molecules aggregate via CH– $\pi$  interactions. As a result, the intermolecular distances between neighboring molecules of **2** in the crystal are much longer than those of **1**. Interestingly, molecules of **2** in the crystal adopt distorted hexagonal ring structure to form one dimensional (1D) pore that contain solvent toluene molecules. The most noteworthy structural feature of the crystal is a “ $\pi$ -wall” in which the anthracene moieties of **2** lined up along the large 1D pore (13-Å diameter).

Co-crystallization of **2** and C<sub>60</sub> from toluene–MeOH yielded a complex of **2** and C<sub>60</sub> (C<sub>60</sub>@**2**) as black needles. Judging from UV/Vis absorption spectra, the crystal composition molar ratio of **2**/C<sub>60</sub> was determined to be *ca.* 83/17. The results of X-ray crystallographic analysis revealed that molecules of **2** in the C<sub>60</sub>@**2** crystal adopt the alignment manner that is the same as that of molecules in the crystal of **2**. Moreover, it was found out that C<sub>60</sub> molecules are included in the 1D pore of C<sub>60</sub>@**2** as a result of  $\pi$ -orbital interactions between the “ $\pi$ -wall” and C<sub>60</sub>.

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# Nanocomposite MOF/Polymer Hybrids with Improved Processability

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The key limitation of MOFs preventing their system integration is the lack of processability, predominantly owing to their general insolubility and crystalline powdered form<sup>1</sup>. The formation of hybrid composites containing polymers and MOFs represent a novel class of materials with diverse functionality and enhanced processability. However, approaches to fabricate such MOFs are limited by poor dispersion in polymeric matrices, resulting in MOF aggregation, which not only results in pore blocking, but also a reduction of the polymeric structural integrity<sup>2</sup>. Post-synthetic modification of functionalised MOF surfaces could offer a universal approach for the creation of hybrid MOF/polymer core-shell structures, facilitating the uniform distribution of MOFs for their shaping into suitable forms. By combination of synthesis and experimental characterisation, a selection of the proposed MOF/polymer composites were examined to reveal their chemical and thermal stability, porosity, gas uptake, and of course, their processability. Furthermore, a variety of methods were investigated for optimization of polymer coverage on MOF surfaces.

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# Guest-framework cooperation in the methylammonium metal formate perovskites

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The series of “hybrid perovskites” based on the formate linker ion  $\text{HCO}_2^-$ , with general formula  $\mathbf{AB}(\text{HCO}_2)_3$ , are of great interest for their compositional diversity, which rivals that of the inorganic perovskites; the “unconventional” ways in which they can break the aristotype symmetry; and their broad range of order parameters, including both potentially applicable properties such as ferroelectricity and multiferroicity and behaviour of fundamental scientific interest such as higher-order multipolar order.<sup>1</sup> This family of materials contains organic guest cations **A** encapsulated within a cubic framework. Although it is tempting to consider the behaviour of the guests and framework separately, in fact of course they are intimately related. Indeed, there is an intricate balance between the framework’s functions as a *rigid* cage enabling individual guest motion and a *flexible* mediator of that motion, controlling the way in which neighbouring guests interact with one another.

We have previously shown that in the **A** = guanidinium family, the phase behaviour under pressure is dominated by the snug hydrogen-bonded fit of the guanidinium cations into the formate framework, which distorts in response to their collective arrangement.<sup>2</sup> On the other hand, in the **A** = dimethylammonium family, where the guest cations rotate freely at high temperatures, the host-guest hydrogen-bonding patterns actually help to shield neighbouring A cations from each others’ influence.<sup>3</sup>

We now consider the series of methylammonium metal formates,  $\text{CH}_3\text{NH}_3\mathbf{B}(\text{HCO}_2)_3$ , where **B** = Mn, Co, Zn. Two incommensurately modulated phases were recently reported in the **B** = Co material at low temperatures; these structures can be derived from the room-temperature structure by freezing in long-wavelength transverse acoustic modes.<sup>4</sup> However, these are far from the only soft modes in these materials. We have studied the complete soft-mode behaviour by X-ray thermal diffuse scattering and density-functional perturbation theory calculations. We show that there are potential instabilities along many symmetric directions. In particular, a prominent low-frequency chiral mode of  $\Gamma_1^-$  symmetry couples framework shearing to a twisting motion of the guest cations. Thus these materials are in a sense intermediate between the dimethylammonium and guanidinium cases, in that the methylammonium ions act neither as fixed struts nor as free rotors, but instead have substantial freedom of motion in a way that is nonetheless strongly coupled to framework distortions. Our results will be relevant to attempts to engineer both the order-disorder behaviour and the dynamics of framework materials.

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# Zr<sup>4+</sup> MOFs with high efficiency for removal of toxic anion species from aqueous media

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In the last two decades, metal-organic frameworks (MOFs), based on metal ions or clusters connected via extended polytopic ligands, have attracted considerable attention due to their structural diversity, high porosity and potential applications in various fields. MOFs with ion-sorption properties seem very promising for use in wastewater treatment.<sup>1</sup> Zr<sup>4+</sup> MOFs are probably the most promising ones combining a number of important features, such as robustness (stability from extremely acidic to alkaline conditions), high porosity, capability to incorporate various functional groups and ease of synthesis.<sup>2</sup>

Herein, we present new microporous Zr<sup>4+</sup>-terephthalate MOFs with 8-connected frameworks. These materials have shown excellent anion sorption properties, with fast/selective capture of the anions under a variety of conditions and removal capacities > 98% in ≤3 min, even in the presence of tremendous (>200-fold) excess of various competitive anions. The highly efficient anion capture by the MOFs is due to a dual sorption process involving both surface binding (via electrostatic-hydrogen bonding interactions) and intra-framework sorption via replacement of the terminal H<sub>2</sub>O/OH<sup>-</sup> ligands by the inserted anions. The new MOFs were proved to be very effective anion sorbents with exceptional sorption capacities, reusability, rapid sorption kinetics and capability to sorb efficiently these anions in a very wide pH range (1-10), even in the presence of various competitive anions.

## Acknowledgements

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# A switchable iron-based coordination polymer toward reversible acetonitrile electro-optical readout

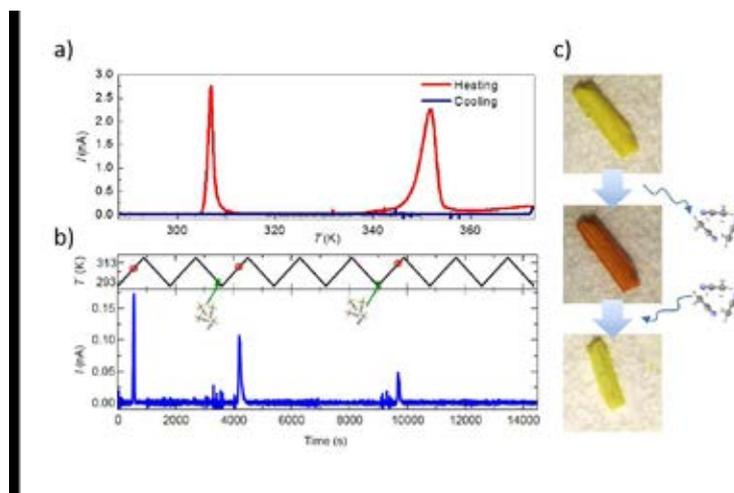
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Increasing emissions of volatile organic compounds (VOCs) and their impact on air quality is now considered of major environmental concern, as some VOCs are identified as toxic or carcinogenic.<sup>[1]</sup> Vapochromic materials, which show dramatic and reversible color changes upon exposure to vapors, have attracted much attention in terms of their potential application as chemical sensors.<sup>[2]</sup> Nowadays, the design and synthesis of coordination polymers (CPs) capable of selectively sensing specific guest molecules is a hot research topic.<sup>[3]</sup> These materials are good candidates for vapochromism since changes in the coordination sphere due to the inclusion of VOCs can lead to a change of color.<sup>[4]</sup> The use of CPs offers solutions to some common problems like sensitivity, selectivity, and reproducibility.<sup>[5]</sup>

Here, a non-porous crystalline 1D Fe(II) coordination polymer acting as a porous acetonitrile host is presented.<sup>[6]</sup> The desorption of interstitial acetonitrile is accompanied by magneto-structural transitions easily detectable in the optical and electronic properties of the material, as well as in the magnetic behavior. The structural switch and therefore its (opto)electronic readout are reversible under exposition of the crystal to acetonitrile vapor.



**Figure 1.** a)  $I$  vs.  $T$ . b) Proof-of-concept sensor of acetonitrile. c) Single crystal at RT (yellow), after heating (orange) and after exposition to acetonitrile (yellow).

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# Efficient capture of toxic oxoanions of Se(VI) and As(V) accompanied with direct crystallographic evidence in a water-stable cationic MOF

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**Abstract:** Remediation of oxo-anions of heavy metals such as selenium and arsenic hold tremendous significance as they have been listed by EPA among highly toxic compounds and priority environmental pollutants. Cationic MOFs, which are suitable receptors for such ions have not been explored for the concomitant capture of such oxo-anions which demands investigation. Herein, we demonstrate successful capture of oxo-anions of Se(VI) and As(V) via a Ni(II) based water stable cationic MOF accompanied with one of highest uptake value observed (~ 100mg/g for  $\text{SeO}_4^{2-}$  and ~ 85mg/g of  $\text{HAsO}_4^{2-}$ ) in the domain of cationic MOFs. This ion-exchange/capture phenomenon was affirmed with direct crystallographic visualization of these extremely toxic anions within the voids of a water-stable cationic MOF. The MOF exhibited selective capture owing to the shape memory effect of  $\text{SO}_4^{2-}$  anions. The extended array of highly aligned  $\text{SO}_4^{2-}$  anions lying along the crystallographic *c*-axis led to facile exchange with incoming toxic anions viz.  $\text{SeO}_4^{2-}$  and  $\text{HAsO}_4^{2-}$ . Moreover, the exchanged crystals were studied using single-crystal X-ray diffraction which revealed interesting insights about the environment of the isolated anions within the framework. The selenate ( $\text{SeO}_4^{2-}$ ) anion was located at the same positions as the ( $\text{SO}_4^{2-}$ ) anion from which we inferred similar interaction site whereas  $\text{HAsO}_4^{2-}$  was present at a variable location due to the larger size. Such crystallographic visualization of the toxic anion within the framework serves as a guide for determining the interaction sites that will contribute directly to the development of materials targeted towards the capture of such toxic anions.

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# Solid state emission and vapochromism of bis-arylethynyl platinum complexes with different diethynylphenanthrolines including TMS and TIPS substituent

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Luminescent studies of phosphorescent square-planar platinum(□) complexes in solid state are attracted to considerable interests because of the high emission intensity of several platinum(□) complexes in solid state. Square-planar platinum(□) complexes with the occupied  $d_z^2$  orbitals are particularly interesting for the supramolecular stacking because they have weak noncovalent  $\pi$ - $\pi$  and/or Pt-Pt interactions in solid state. In particular, platinum(□) organometallic complexes with bipyridine derivatives and various arylethynyl ligands have recently been attracting the attention to their unique photophysical properties such as aggregation-induced emission (AIE) and vapochromism in solid state. We have been reported the synthesis and photophysical properties of platinum(□) organometallic complexes with 3,8-bis-trimethylsilylethynyl-phenanthroline (Pt-TMS) as shown in Fig. 1.<sup>1</sup> Some platinum complexes in this article were revealed the emission in solid state and showed the vapochromism with some volatile organic compounds (VOCs). This is related to the diversity of intermolecular interactions as  $\pi$ - $\pi$  and/or Pt-Pt interactions in solid state.

In present work, we synthesized new platinum complexes with 3,8-triisopropylsilylethynylphenanthroline and several arylethynyl ligands (Pt-TIPS) in Fig. 1. Two types of present platinum complexes were measured by the emission spectroscopy in solution and solid state. The solid state emission showed the difference of the steric effect between two substituents, TMS and TIPS. Vapochromic experiments with several VOCs for two types of present platinum complexes were performed in the dried solid samples. The colors under white light and luminescent color under UV light for several platinum organometallics were revealed to change the intermolecular Pt-Pt interactions in solid state and discussed the vapochromism from <sup>3</sup>MMLCT and/or the mixed transition of <sup>3</sup>MLCT/<sup>3</sup>LLCT. In this symposium, we will propose our idea with the detailed data.

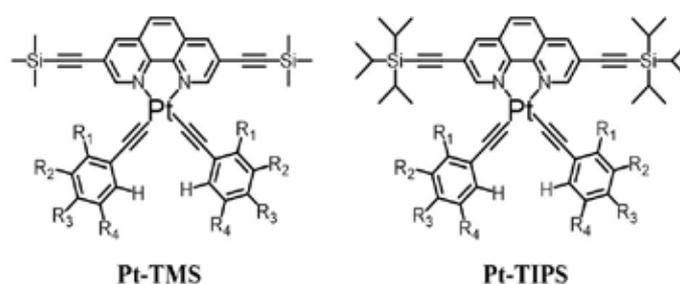


Fig. 1. Molecular structures of Pt-TMS and Pt-TIPS complexes

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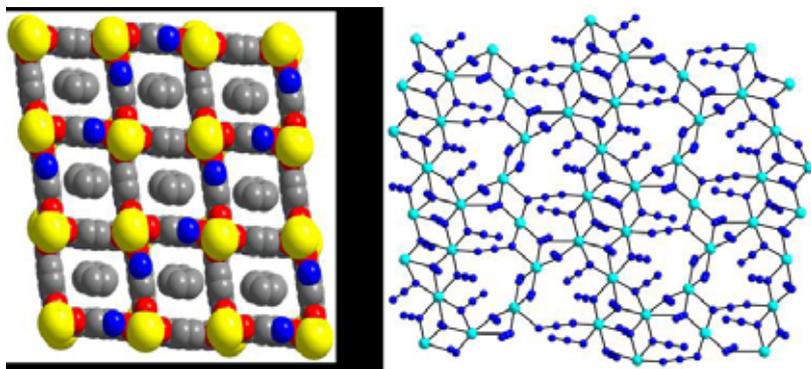
# New Inorganic Framework Materials from the Use of Multifunctional Linkers: Synthesis, Structural and Physicochemical Properties

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Crystal engineering is a cross-disciplinary field of research, which mainly deals with the understanding of the relationship between the structural motifs and properties of molecule-based compounds and materials <sup>[1]</sup>. The choice, and the process of functionalization and modification of organic and inorganic ligands, are exciting toward the preparation of unprecedented metal-organic and metal-inorganic frameworks <sup>[2]</sup>. As a result of the structural diversity and the versatile characteristics of supramolecular coordination chemistry, an impressive number of compounds have been discovered, many of which possessing attractive properties in the areas of catalysis, molecular magnetism, host-guest chemistry, optics, sensing, to name but a few. To this perspective, we present herein our first results from the employment of some multifunctional organic and inorganic linkers in 3d- and 4f-metal chemistry as a means of preparing new inorganic framework materials with primarily interesting structural and magnetic properties. Our synthetic strategy involves both the modification of organic ligands and the exclusive use of pseudohalides as the linkers for the construction of 2-D and 3-D coordination polymers (**Figure 1**).



**Figure 1.** 2-D coordination polymers based on Dy<sup>III</sup>-dicarboxylate (left) and Cu<sup>II</sup>-azido (right) units.

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This research is co-financed by Greece and the European Union (European Social Fund - ESF) through the Operational Programme "Human Resources Development, Education and Lifelong Learning 2014-2020" in the context of the project "New Families of Molecular Ferromagnetic Materials with Implications in Molecular Electronics and Spintronics" (MIS 5047176).

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# Terahertz vibration of ZIF-8 and its response upon gas adsorption

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Intermolecular interactions between ZIF-8 and adsorbed gas molecules, which perform an important role in the adsorption process, can be attributed to non-covalent bonds such as van der Waals forces. The resonance frequency of these bonds falls in the terahertz (THz) frequency band. Skeletal vibration of organic linkers also occurs in this band and seems to be affected by adsorption. Previous studies using DFT calculations suggest that the frequency of open-gate motion exists at the range of 1 to 2 THz.<sup>[1]</sup> Thus, gas adsorption onto ZIF-8 can be observed by monitoring changes in its terahertz transmission spectrum as a function of gas exposure.

First, the terahertz transmission spectra of ZIF-8 after exposure to nitrogen and propane was investigated. Initially, ZIF-8 exhibits adsorption peaks at 2.0, 2.8, 3.9 and 5.3 THz. After exposure to propane or *n*-butane, the peak at 2.0 THz disappears. In contrast, no significant spectral changes were observed after exposure to methane and carbon dioxide.<sup>[2]</sup>

Next, the temporal response of ZIF-8 upon exposure to *n*-butane/nitrogen was observed. The transmittance rapidly increases after the introduction of *n*-butane and slowly decreases during nitrogen exposure. The profile appears to be exponential in nature. The response to propane was similar to that of *n*-butane, while the transitional response to carbon dioxide was much weaker than that of other gases. The species of gases that eliminate the peak at 2.0 THz in the spectrum agree well with the species that can adsorb onto ZIF-8 at room temperature and atmospheric pressure.<sup>[3]</sup>

Differences in the response time constants of these gases will help elucidate the mechanism of gas adsorption onto ZIF-8.<sup>[4]</sup> These results demonstrate the potential of terahertz spectroscopy in applications such as MOF-based gas detectors.

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# Mechanochemical Synthesis of Mixed Metal, Mixed Linker Glass-Forming Metal–Organic Frameworks and their physical properties

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Metal–organic frameworks (MOFs) are hybrid materials which consist of inorganic nodes, or clusters, connected by organic linkers.<sup>1</sup> Recently it has been demonstrated that some MOFs, namely the zeolitic imidazolate framework (ZIF) subclass of MOFs, have a liquid phase and can be melt-quenched to form ZIF glasses. These ZIF glasses are the first new category of glass since the 1970s.<sup>2</sup> The most promising glass forming ZIFs have the cag topology, with imidazole (Im) and benzimidazole (blm) type linkers. ZIF-62 ( $\text{Zn}(\text{Im})_{2-x}(\text{blm})_x$ ) and TIF-4 ( $\text{Zn}(\text{Im})_{2-x}(\text{Clblm})_x$ ) are especially promising due to their relatively wide thermal working range, ability to form transparent glass monoliths.<sup>3</sup>

Unfortunately large scale production of ZIF glasses is limited by the inefficient production of the crystalline ZIFs, which rely on large volumes of solvents, high reaction temperatures and long reaction times.<sup>4</sup> Here we present a catalytic mechanochemical method to synthesise the glass forming multi-linker ZIF-62 and TIF-4 with minimal solvent usage, zero organic linker wastage, at room temperature in 30 minutes. These mechanochemically produced ZIFs can be melt quenched to produce glass ZIFs as per the materials synthesised via solvothermal methods.<sup>5</sup>

ZIF-62 and TIF-4 are Zn based ZIFs, however mixed-metal varieties of these materials can be produced using the catalytic mechanochemical method. By employing a Co salt catalyst/metal source into the reaction, up to 20% inclusion of Co into ZIF-62 can be achieved.<sup>5</sup> By introducing Co into the ZIF-62, one can affect the colour of the resulting glass, as well as the melting point of the crystalline material.

We extend this work to produce ZIF-62 and TIF-4 with varying organic linker content, in order to investigate the relationship between chemical composition, and physical properties of the resulting ZIF glasses. The mechanochemical method allows for direct control over the ratio of organic linkers in the crystalline MOFs produced, which is then maintained in the resulting glasses. This allows relationships to be drawn between the organic content of the ZIF glasses, and physical properties such as: melting point/glass transition temperature, hydrophobicity, refractive index and thermal conductivity.

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# Mechanochemical Synthesis of Mixed Metal, Mixed Linker Glass-Forming Metal–Organic Frameworks

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Current methodologies to produce glass forming metal–organic frameworks (MOFs) rely on non-scalable solvothermal syntheses which have high energy requirements, relatively low yields and large teratogenic solvent usage.<sup>1</sup> Here we use a mechanochemical method to produce the glass-forming MOFs, ZIF-62 and ZIF-UC-5, in 30 minutes at room temperature, using microlitre quantities of solvent and stoichiometric amounts of organic linkers. This method facilitates the accurate synthesis of ZIF-62 structures containing both Co and Zn, allowing the effect of metal-ion dopant upon melting temperature to be studied for the first time. Further to this, we present variable organic linker ratio series of ZIF-62 and of ZIF-UC-5.<sup>2</sup> The specific composition of the materials in the series is made possible by the mechanochemical method. We also present methodology of directly synthesising MOF glasses without the need for high temperature melt-quenching.

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# Magnetic Induction for Controlled Release

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Magnetic induction swing adsorption (MISA) is a method for remotely controlling the release of a stored molecule within an adsorbent. MISA is an example of exploiting the cooperative phenomena of electromagnetism and desorption. Adsorbents such as metal-organic frameworks are capable of storing large amounts of gas, however, a significant portion of that gas can not be released under standard operating conditions. In a similar way to the induction cooking stove, MISA operates upon magnetic elements within the adsorbent to directly heat and consequently release the stored molecules. This method has been demonstrated for the efficient release of carbon dioxide, oxygen and methane.

Magnetic nanoparticles (MNP's) are incorporated within MOF's by either growing MOF crystals around the MNP's or directly mixing pre-synthesized MOF's into a composite. The MNP act as "nano-heaters" within the adsorbent that can be remotely controlled using magnetic induction. The alternating magnetic field is applied through a coil configuration that can be positioned inside or outside the storage vessel. During release of a pressurized gas, cooling occurs which slows and, in some cases, stops the further release of the stored gas. By remotely applying a magnetic field, this cooling effect may be offset by the heating MNP's, and thereby controlling the release of the gas. This same mechanism can also be used to release trapped gas at sub-1 atmosphere which would otherwise remain in the storage vessel under standard pressure swing conditions.

In this work, the configuration and operation of MISA technology is presented to demonstrate the cooperative phenomena of electromagnetism and desorption. Release profiles for carbon dioxide within HKUST-1+MNP composite are presented with and without magnetic induction to highlight the cooperative benefits of induction. New ideas for large-scale operation are also proposed to progress the technology towards commercialisation.

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# Metal-Organic Frameworks - spin crossover complexes hybrid architectures for sensing applications

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Metal–organic frameworks (MOFs) are ideal materials for the modular design of complex assemblies.<sup>[1]</sup> They possess a long-range ordered hybrid structure associated with well-organized porosity. Several MOFs can be used for sensing small molecules, mainly through the modulation of their emissive properties. However, the limited stability of these systems prevents them from being used in real devices.<sup>[2]</sup> An alternative for the development of robust MOFs materials for sensing is to take advantage from spin-crossover (SCO) compounds, capable of switching their spin states upon external stimuli.

Taking into account the ability of MOFs to encapsulate guest molecules, we have inserted SCO complexes inside their porosity. The composite materials retain their crystallinity and a partial porosity compared to the parent MOFs, while the spin state of the inserted cations can be modulated by guest sorption such as water vapors<sup>[3]</sup> or alcohols<sup>[4]</sup>. With Zr(IV)-based mesoporous MOFs as host matrices, cooperative thermal spin transition close to room temperature have been observed. The impact of guest molecules on the complex spin state is currently under investigation. Considering the growing number of mesoporous water stable MOFs and the large diversity of SCO complexes, this paves the way for the design of a new generation of sensing devices based on MOF@spin crossover complexes composites.

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# Electronic signature of the breathing transition in MIL-53(Al) by resonant inelastic x-ray scattering (RIXS)

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The breathing transition in MIL-53(Al) is a key demonstration of the role of dynamics in the behavior of metal-organic frameworks<sup>[1,2]</sup>. Previous experimental and theoretical work have proposed models for the mechanism of guest- and temperature-induced phase transition of this material. In this work, the mechanism of water adsorption and breathing transition in MIL-53(Al) was investigated by resonant inelastic x-ray scattering (RIXS). In particular, oxygen K edge RIXS can probe the electronic states of the carboxylate moiety of the linker and how they are perturbed during the breathing transition. Measurements on MIL-53(Al) both *in vacuum* and *in ambient* conditions were performed using the high-resolution soft x-ray emission spectrometer<sup>[3]</sup> housed in Spring-8 BL07LSU. In ambient conditions (Fig. 1), the RIXS spectra at 532.0 eV excitation (C=O O 1s → π\*) suggests that water adsorption (and guest-induced pore contraction) could perturb the HOMO-3 (π) state<sup>[4]</sup>. In contrast, in vacuum conditions (Fig. 2), the RIXS spectra at 534.4 eV excitation (C=O O 1s → σ\*) shows that pore expansion is accompanied by a shift of density of states from HOMO to HOMO-1<sup>[4]</sup>. Hereafter, the implications of this redistribution of electron density to the current models for the breathing mechanism will be elaborated.

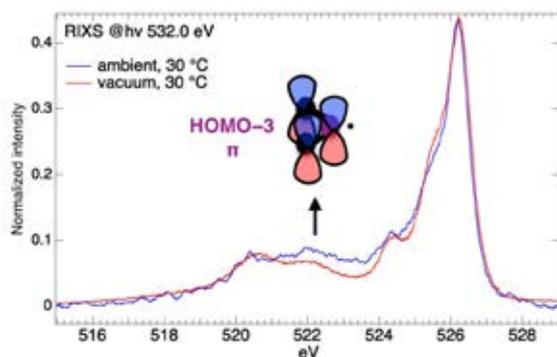


Fig. 1. RIXS spectra at  $h\nu=532.0$  eV excitation of MIL-53(Al) at 30°C in ambient and vacuum conditions.

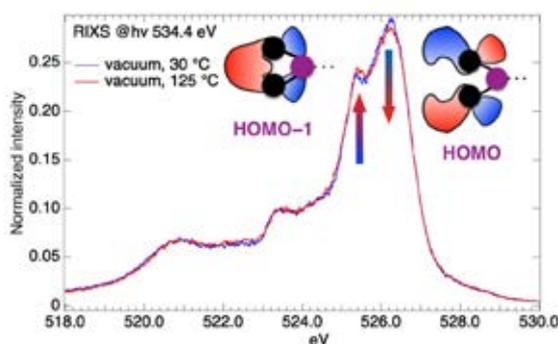


Fig. 2. RIXS spectra at  $h\nu=534.4$  eV excitation of MIL-53(Al) in vacuum at room and high temperature.

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# Exploring magnetic excitations in methylammonium transition metal formates using inelastic neutron scattering

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Dense metal organic frameworks present exciting possibilities for the realization of complex magnets due to the high tailorability and tunability arising from their discrete molecular building-block nature. However, the magnetic properties of such materials are often poorly understood, since little is known regarding the precise magnetic interactions. In order to develop magnetic MOFs for future applications it is vital that this situation is rectified, and therefore we have started a systematic study of the magnetic structure and magnetic excitations in formate perovskites.

Formate perovskites can be prepared with a range of different singly charged organic ions in the interstices, and the metal formate framework is flexible enough that it changes shape substantially depending on the ion involved. Such changes in shape clearly affect these materials' electrical properties, but they also affect the magnetic behaviour by distorting the coordination environment about each metal ion and the geometry of the formate superexchange pathway.

The bulk magnetic properties of the family  $\text{CH}_3\text{NH}_3[\text{M}(\text{HCO}_2)_3]$  have been explored revealing a range of ferrimagnetic transition temperatures between 8 and 34 K<sup>[1]</sup>; with high field measurements indicating that the response is isotropic for  $M=\text{Mn}$  and anisotropic for  $M=\text{Co}$ , as would be expected for  $d^5$  vs  $d^7$  configurations. In addition the Co compound is observed to be multiferroic below 15.9 K, with the suggestion that the multiferroic behaviour is induced by the magnetic order via an inverse DM mechanism<sup>[2]</sup>. However, more recent neutron diffraction measurements have revealed that the paraelectric to antiferroelectric transition is actually concomitant with a structural phase transition at 90 K<sup>[3]</sup>. It is therefore timely to study the microscopic mechanisms driving the cooperative phenomena in these formate perovskites.

Here we will present the results of neutron diffraction and inelastic scattering on perdeuterated powder samples of  $\text{CD}_3\text{ND}_3[\text{Mn}(\text{DCO}_2)_3]$  and  $\text{CD}_3\text{ND}_3[\text{Co}(\text{DCO}_2)_3]$ , and make comparisons with their dimethylammonium analogues<sup>[4]</sup>. The inelastic data is compared with simulations performed using SpinW<sup>[5]</sup> to extract quantitative information about the nature of the magnetic Hamiltonian using Linear Spin Wave Theory.

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# A Photolytic Approach to Hierarchically Porous Metal-Organic Frameworks

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Metal-organic frameworks (MOFs) are novel porous materials which have great potential in various fields such as catalysis and biomedicine. One main goal in this field is to create MOFs with hierarchical pores, which can not only improve mass transfer within frameworks, but also allow for encapsulating large guest molecules. Here we report a facile photolytic strategy to introduce mesopores into microporous MOFs by eliminating photolabile ligands in multivariate MOFs with laser treatment. To prove our concept, we perform photolysis on a multivariate UiO-66 mixed with photolabile ligand, which can be eliminated selectively under laser, and the formation of mesopores are confirmed by N<sub>2</sub> isotherms, IR, NMR and TGA. This strategy features advantages such as accuracy, efficiency and feasibility in multiple MOFs, shedding a light on programmable design of complicated cooperative MOF system.

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# Coordination crosslinking of helical oligoamide nanorods: controlling independent SSA motifs

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Bottom-up nanofabrication using self-assembly principles is a promising direction in the development of novel cooperative framework materials. Organic building blocks offer supreme specificity, selectivity and geometric variability through supramolecular recognition [1], however complexity of achievable structures is limited, at least when using small molecule precursors, by the dynamic nature and competition of common binding motifs. A solution to competitive binding is to use two independent self-assembly motifs for longitudinal (1D) assembly and the controlled crosslinking of the fibrous structures. This is achieved by using a geometrically defined 3-point hydrogen bonding motif for supramolecular self-assembly of small helical oligoamide monomers into one dimensional nanorods [2], and implement metal coordination between the nanorods to create metallo-supramolecular frameworks (MSFs). These MSFs are versatile through the nearly infinite variability of the  $\beta^3$ -oligoamide monomers that form the core nanorods, and the metal used for coordination crosslinking.

In the example presented here,  $\beta^3$ -oligoamide loops flanked  $\alpha$ -histidine payload. Monomeric  $\beta^3$ -oligoamides form a so called 14-helix structure that is already stable at four amino acid oligomer length, irrespective of the chemistry of the side chains. The helices have a diameter of  $\sim 0.4$  nm and when self-assembled head to tail, the resulting nanorods have lengths in the 100  $\mu\text{m}$  range [3]. The self-assembly is not affected by the addition of the  $\alpha$ -histidine units. The addition of divalent  $\text{Cu}^{2+}$  or  $\text{Ni}^{2+}$  ions caused the self-assembly of individual nanorods into higher order structures, as determined by Atomic Force and Scanning Tunneling Microscopies (AFM and STM). Varying the number of histidines varies the resulting MSF morphology. Dynamic behavior was demonstrated when the payload was a single histidine, the resultant MSF forms a one-dimensional array of coordinated sites flanked by four parallel oligoamide nanorods. When the payload was two histidines, the resultant MSF was a well aligned two-dimensional array where the nanorods “zipped up” into a continuous layer. The coordinated MFS can form continuous domains in the range of 100  $\mu\text{m}^2$ .

The peptide backbone is unaffected by metal coordination, as shown by vibrational spectroscopy (FT-IR). Through X-ray photoelectron spectroscopy (XPS) studies it was found that the  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions were reduced to +1 and 0 oxidation states and were coordinated to the histidine and carboxylate moieties.

Our work shows versatile tuneable one- to two-dimensional superstructures based on independent multi-tiered supramolecular self-assembly developed upon metal coordinated oligoamide nanorods.

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# MOFs as hosts to analogues of complex magnetic phases

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Controlling the mesoscopic nature of materials through local interactions can lead to the formation of highly non-topologically trivial structures. The local interactions that lead to the emergence of mesoscopic structures, known as textures, is well understood in magnetic materials. The most studied textures are skyrmions as they have interesting applications in spintronics due to their topological nature and dynamic properties<sup>[1]</sup>. These features are thought to be exclusively a magnetic characteristic; however, they are purely topological in nature and arise due to a specific set of interactions which may not be limited to magnetic materials. As we have an increased understanding of what causes topological properties, we can design/search for specific interactions in non-magnetic materials that may lead to non-magnetic analogues of topologically protected phases.

For skyrmions to exist, three interactions must be present: symmetric exchange, antisymmetric exchange, and a coupling to a magnetic field<sup>[2]</sup>. To explore the possibility of creating analogues of magnetic textures in non-magnetic materials we replace magnetic dipoles with non-magnetic quadrupoles and exchange the magnetic field for a strain field and adapt the interactions accordingly. Here we look at the capability of MOFs to harbor analogous complex magnetic phases such as skyrmions. MOFs are the perfect candidates as there are a plethora of components to play with such as underlying lattice, guest species, and interactions between the framework and the guest.

Through density functional theory calculations, molecular dynamics simulations, and Monte Carlo simulations, we explore the extent to which these interactions may exist in chiral MOF frameworks with quadrupolar guests such as benzene or CO<sub>2</sub> and how varying the relative strengths of the three interaction parameters with temperature affects the behaviour of the non-magnetic textures. Using small angle scattering we have been able to define six distinct phases, giving evidence of quadrupolar skyrmions and interesting textures which are not present in the dipolar analogue. This opens up the field to new ways of creating non-topologically trivial textures that could potentially be less restrictive than chiral magnets.

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## Exploring triplet state functions in metal-organic frameworks

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Photon upconversion (UC), producing shorter-wavelength light (higher energy photons) from longer-wavelength light (lower energy photons), has attracted much attention for many applications such as photovoltaics, photocatalysis, bioimaging, and optogenetics. Among the available UC mechanisms, triplet-triplet annihilation (TTA)-based UC is the subject of intense research because of its potential to upconvert low-intensity and non-coherent incident light. While near-infrared (NIR)-to-visible TTA-UC is particularly important for energy and biology applications, it has been difficult to achieve efficient NIR-to-visible TTA-UC at a weak excitation intensity. To achieve this goal, we combine two strategies. First, we sensitize the triplet state through singlet-to-triplet (S-T) direct transition to avoid energy loss during the common triplet sensitization process through intersystem crossing (ISC). Second, we construct metal-organic frameworks with acceptor-containing ligands to facilitate fast triplet exciton diffusion through regular and dense acceptor arrays. S-T absorption sensitizers are doped in fluorescent MOFs, exhibiting NIR-to-visible TTA-UC from low excitation intensity.

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# Fast and Stable Vapochromic Response Induced Through Nanocrystal Formation of a Luminescent Platinum(II) Complex on Periodic Mesoporous Organosilica

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Vapochromic materials, which show a reversible colour change by the adsorption/desorption of vapour molecules, have attracted considerable attention owing to their implications as the “electronic noses” for the detection of harmful volatile organic compounds (VOCs). Although a number of molecular-based vapochromic materials, especially Pt(II) complexes, were reported to date, the response rate to dilute gaseous molecules is remaining as an issue to be overcome. To accelerate the vapour detection, we have focused on the immobilization of the Pt(II) complex on mesoporous materials, which can rapidly capture gaseous vapour molecules in the pores. In this work, we have succeeded in the development of unique vapochromic system showing rapid vapour-response by using a periodic mesoporous organosilica with bipyridine moieties (BPy-PMO) and a luminescent Pt(II) complex (Figure).<sup>1</sup>



Although this Pt-immobilized BPy-PMO did not exhibit observable luminescence at room temperature, an intense red luminescence appeared after the exposure to the methanol vapour, and disappeared on exposure to the pyridine vapour and heating. Interestingly, the vapochromic response was drastically accelerated in the second vapochromic cycle and cycles thereafter. Scanning and transmission electron microscopies (SEM/TEM), absorption and emission, and nuclear magnetic resonance (NMR) spectroscopies, mass spectrometry, and powder X-ray diffraction (PXRD) indicated that methanol vapour induced Si-C cleavage and thus liberated [Pt(ppy)(bpy)]Cl (ppy = 2-phenylpyridinate, bpy=2,2'-bipyridine) from the BPy-PMO framework. Furthermore, the self-assembling properties of the Pt(II) complex resulted in the formation of highly luminescent micro/nanocrystals that were homogeneously dispersed on the porous support. The details of this finding will be discussed in detail.

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# Dynamical observation of ammonia confined in defective UiO-67 type metal-organic frameworks

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Understanding the structural responses of metal-organic frameworks (MOFs) upon the inclusion of guest molecules has gained increasing attention in several applications, such as gas storage, energy storage, drug delivery, and molecular sensing. Herein, high-resolution neutron diffractions along with Rietveld refinement and density functional theory calculations have been used to elucidate the structural responses of Zr-based MOFs upon the adsorption of ammonia (NH<sub>3</sub>) at a molecular level. UiO-67 and UiO-bpydc containing biphenyl dicarboxylate and bipyridine dicarboxylate linkers, respectively, were selected due to their high thermal and chemical stability. The results establish the influence of functional linkers and missing linker defects of these MOFs on their NH<sub>3</sub> responsive behaviors. Despite of their structural similarities, the alteration of stepped NH<sub>3</sub> adsorption profiles takes place when the phenyl groups are replaced by the pyridine ones. This unusual adsorption transition has proved to result from cooperative hydrogen-bond networks between the bipyridine scaffold and the adsorbed NH<sub>3</sub>. The concept of an adaptable pore environment leads to the stepped NH<sub>3</sub> adsorption at different relative pressures. Temperature-dependent neutron diffraction also reveals the ammonia-induced structural transformation of the organic linkers. We demonstrate that the structural responses of the linkers on UiO-type MOFs can play a significant role in the type of gas uptake, which otherwise is believed to be rigid and non-interactive. Ongoing efforts are focused on using neutron scattering and molecular modeling to establish the dynamic behaviors of this system and support the hydrogen-bond network model.

## References

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