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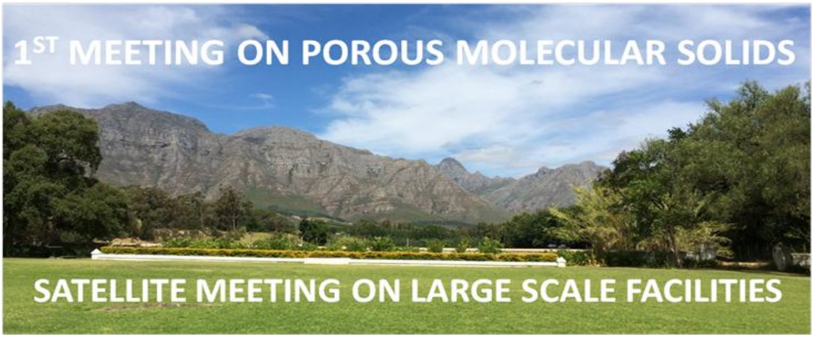

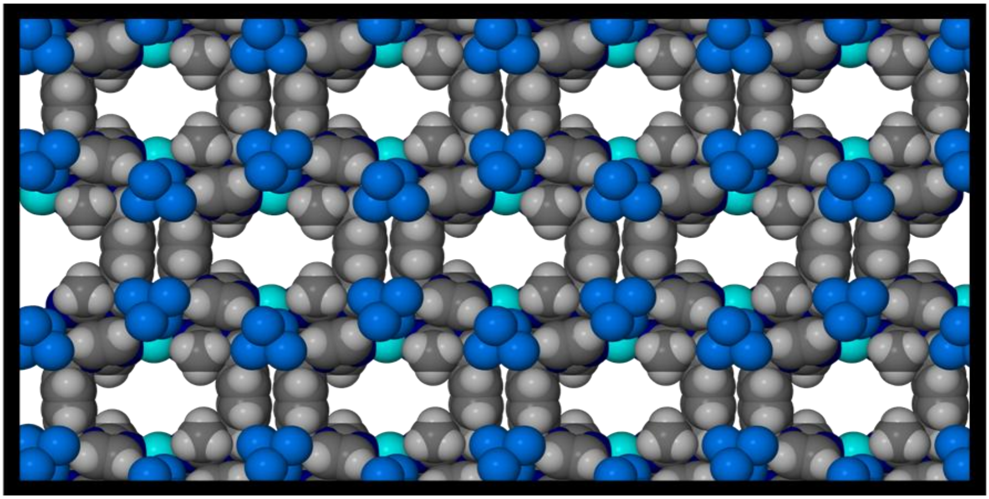

Switching of Degree of Interpenetration and its Effects on Porosity in Metal-Organic Frameworks

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Solid–solid phase transformations resulting from guest insertion/removal into/from inclusion compounds are important for the utility of porous crystalline systems such as metal–organic frameworks (MOFs)[1]. Some of the most important attributes of a MOF include its rigidity, free volume and surface area. Typically, a MOF would be prepared (usually under solvothermal conditions) and then 'activated' by removal of the solvent molecules. In ideal cases the material would retain its framework connectivity without collapse or distortion of the network – MOFs with metal cluster nodes (i.e. secondary building units) are generally thought to be more robust to the activation process. There are various reports in literature where researchers have lamented the apparent loss of porosity upon activation. We investigated some of these systems and discovered that these MOFs undergo change in degree of interpenetration upon desolvation, thus resulting in a more dense/less porous framework[2,3]. This contribution also probes the limits to which a single-crystal material can undergo structural rearrangement while still maintaining the macroscopic integrity of the crystal a discrete entity.

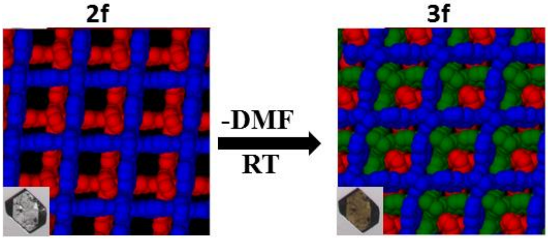

Figure 1. Change of interpenetration from twofold to threefold upon activation in an MOF

References

1. a) H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276. b) S. Horike, S. Shimomura, S. Kitagawa, *Nat. Chem.* **2009**, *1*, 695.
2. H. Aggarwal, P. M. Bhatt, C. X. Bezuidenhout, L. J. Barbour, *J. Am. Chem. Soc.* **2014**, *136*, 3776.
3. H. Aggarwal, P. Lama, L. J. Barbour, *Chem. Commun.* **2014**, *50*, 14543.

Noble gas inclusion compounds of an organic molecular host 4-phenoxyphenol

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Dianin’s compound has been known for its unique inclusion behaviour which is likened to that of zeolites in solid state supramolecular chemistry.[1] 4-phenoxyphenol, an analogue od Dianin’s compound, has been found to show remarkable inclusion behaviour towards carbon dioxide.[2] consequently, we have investigated the inclusion behaviour of 4-phenoxyphenol towards all noble gases with the exception of radon. Crystals were grown by sublimation and slow cooling in a gas rich medium at 3 bar pressure. The crystals obtained were elucidated by means of single crystal-ray diffraction analysis and hot-stage mass spectrophotometry.

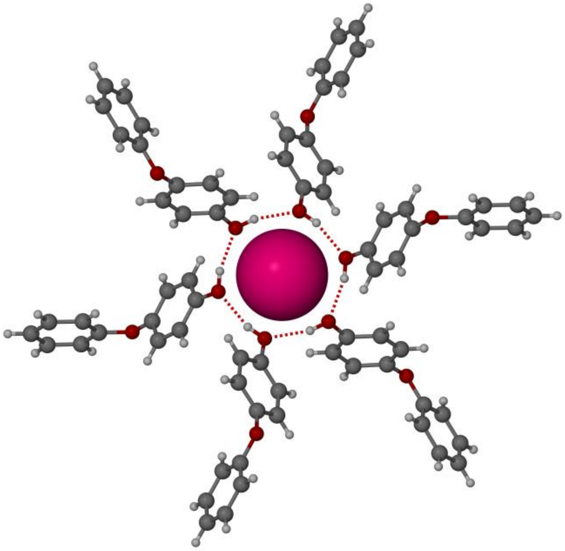

Figure 1: Position of Ar gas within the cavity of the host along a-b plane.

References

1.R. M. Barrer, V. H. Shanson J. Chem. Soc., Chem. Commun. (1976), 333.
2.T. Jacobs, V. J. Smith, L. H. Thomas and L. J. Barbour, Chem. Commun. (2014), 50, 85-87.

Pleochroism as a probe to monitor the solvent exchange process in a 1-D metal-organic framework with 1-D solvent accessible channels.

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Interest in metal-organic frameworks (MOF)has increased significantly owing to their wide range of applications such as catalysis, separation, sorption, sensing, etc. In the work of Lu et.al. they demonstrate the use of an organic chromophore (3,6-di(pyridin-4-yl)-1,2,4,5-tetrazine - dptz) to produce a porous MOF with solvatochroic properties.[1] Materials such as this is the basis for small molecule chemical sensing. The layering of Cu(Acetate)2 in methanol and dptz in chloroform, with a 1:1 methanol:chloroform buffer, at 50℃ to afford dark-purple block-shaped crystals of [Cu2(acetate)2(dptz)•2CHCl3] (**1a**). Microscopy under normal and polarized light of **1a** revealed the pleochroic properties of this solvate.

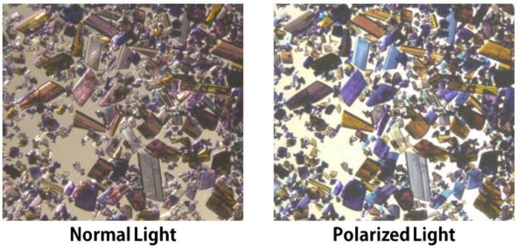

Figure 1. Pictures of 1a crystals under normal and polarized light.

Solvent exchange with pure acetonitrile (ACN) and nitromethane (NM) induces structural changes and yields the ACN and NM solvates **1b** and **1c** respectively. Crystal structures determined from single-crystal X-ray diffraction data shows all three frameworks in the triclinic spacegroup P-1. The structural changes in 1b and 1c are sufficient to significantly shift the colours observed under polarized light. This provided a useful probe to monitor the solvent exchange process using polarized light microscopy.

References

1.Zhen-Zhong Lu , Rui Zhang , Yi-Zhi Li , Zi-Jian Guo , and He-Gen Zheng *, J. Am. Chem. Soc., **2011**, *133* (12), pp 4172–4174

The SNBL at the ESRF and *in-situ* experiments on porous materials

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X-ray diffraction, X-ray absorption spectroscopy and Raman scattering are commonly used for studies of crystal and electronic structure of materials. At the Swiss-Norwegian Beamlines (SNBL) at the European Synchrotron (ESRF) it is possible to perform these different X-ray measurements non-X-ray based techniques in a quasi-simultaneous way, so that real-time dynamic processes can be followed.

In particular, *in-situ* gas adsorption experiments are particularly suited thanks to the gas mixing and gas flow control system developed in the past years. Additionally, non-X-ray based techniques like Raman, galvanometry and/or residual gas analysis (RGA) can be performed in parallel to enhance the information output even further.

In this presentation, I will show how this multi-technique and *in-situ* approach has been successfully employed in the investigation a large number of large porous materials (MOFs and zeolites), on the basis of a selection of users experiments.

Using Metal-Organic frameworks to investigate the properties of ferrihaem

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Ferriprotoporphyrin IX [Fe(III)PPIX] or ferrihaem, together with its ferrous counterpart, is a ubiquitous and important prosthetic moiety.[1] It is an important drug target in many pathologies and its role in malaria has been well established. Although the crystal structures of some ferrihaem-antimalarial complexes have been isolated and solved by single crystal diffraction, the crystal structures of both ferrihaem and its complex with chloroquine (an archetypical antimalarial) remain elusive.[2] Fujita *et al.* have developed a protocol using metal organic frameworks (MOFs) as 'crystalline sponges' or 'molecular flasks'.[3] These compounds have a complex molecular structure; most importantly they have a large void space in the centre of the crystal which allows guest molecules to be included into the crystal framework. Using this idea, a similar MOF has been designed using the ligand 4,4′ ,4″ -s-triazine-2,4,6-triyl-tribenzoic acid (TATB) to selectively encapsulate both free ferrihaem and ferrihaem in the presence of chloroquine.

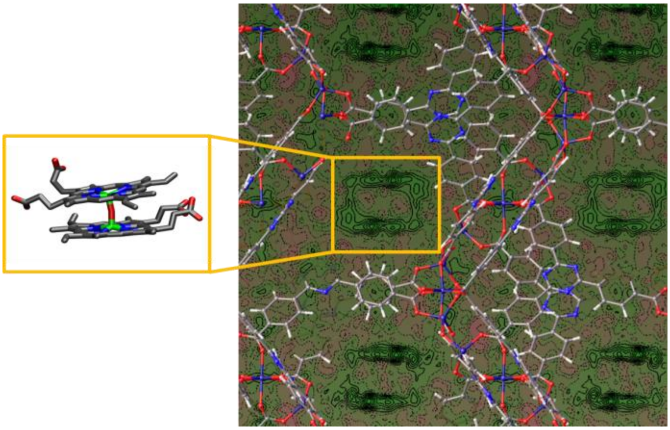

Figure 1. Fourier difference map of ZnTATB framework viewed along 100 plane. The difference map indicates the presence of the μ-oxo dimer form of haematin.

References

1.K. A. de Villers, H. M. Marques and T. J. Egan, *J. Inorg. Biochem.*, 2008, **102**, 1660-1667
2.K. A. de Villiers, J. Gildenhuys and T. le Roux, *ACS Chem. Biol.*, 2012, **7**, 666-677
3.Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai, Y. Hitora, K. Takada, S. Matsunaga, K. Rissanen and M. Fujita, *Nature*, 2013, **495**, 461

A Flexible MOF Showing Thermotropic Phase Transition under Simultaneous Gas Pressure

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In recent years, porous metal-organic frameworks (MOF) have attracted immense interest due to of their potential applications as gas sorption, sensors, size-selective separation, heterogeneous catalysis and etc.

Most of the well-known porous materials are having solvent occupied infinite channels in at least one particular direction. Other than these, there are alternative type of materials exist which are recognized as ‘seemingly non-porous’ materials.[1] In these cases, there are no contemporary infinite channels. Instead, the solvent molecules exist in in the isolated pockets. Surprisingly, compounds undergo guest removal or exchange without disrupting their structure much. Though the particular landscape of the guest transmission is still not well known yet this phenomenon appears to comprise of cooperative dynamic process within the host thus creating transient openings to facilitate the guest transport.

As part of our current works with seemingly non-porous hosts, we have re-examined recently reported seemingly non-porous MOF, $[Cd(HBTC)BPA]_n\cdot nDMF$ (**1**) ($HBTC^{2-}$ = mono-porotonated 1,3,5-benzene tricarboxylate, BPA = 1,2-bis(4-pyridyl)ethane, DMF= *N*,*N′*-dimethyl formamide) (Scheme 1) by Oliver and co-workers.[2]

The variable temperature x-ray powder diffraction patterns of the appohost upon gas pressure show phase transition behaviour. The variable temperature single-crystal x-ray diffraction studies reveals that this phase transitions are associated with the movements in the ligand units. In this case the phase transition is occurs only upon coincident effect of temperature and pressure. Also, the transition temperature depends only upon nature of the gas.

References

1. L. J. Barbour, *Chem. Commun.*, 2006, 1163–1168.
2. A. Husain, M. Ellwart, S. A. Bourne, L. Öhrström, and C. L. Oliver, *Cryst. Growth Des.* 2013, **13**, 1526 –1534.

Large scale facilities used in a PhD research project: an integrated approach for novel science

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Calcium-aluminium-rich inclusions (CAIs) are the oldest dated materials in the Solar System[1], and the CAI mineral hibonite ($CaAl_{12}O_{19}$) is modelled to be the second mineral to condense from a solar composition gas[2]. As hibonite is structurally able to contain both Ti^{3+} and Ti^{4+}, it has been proposed as a single-mineral oxybarometer[3].

To determine if Ti^{3+}/Ti^{4+} ratios in hibonites varied during crystal growth, *in situ* measurement with micro- to nanometre scale spatial resolution is required. Such quantification is not yet possible using conventional and/or non-destructive laboratory techniques, but Ti^{3+}/Ti^{4+} may be determined using synchrotron-based spectroscopic techniques such as X-ray absorption near edge structure (XANES) spectroscopy. Indeed, Ti K-edge XANES spectra are influenced by Ti oxidation state, coordination and site geometry[4,5,6]. Hibonite has five sites onto which Ti may substitute[7], so it is crucial that matrix-matched standards that are fully characterized with respect to site substitution and geometry be used when determining Ti^{3+}/Ti^{4+} by Ti K-edge XANES spectroscopy.

Rietveld refinement of neutron powder diffraction data, collected from a suite of synthetic Ti^{3+},Ti^{4+}-bearing hibonites, shows that Ti^{3+} occupies the M4 octahedral site, whereas Ti^{4+} splits between the M2 trigonal bipyramidal site and the M4 octahedral site in a near-constant ratio[7]. A spectral parameter that varied as a function of Ti^{3+}/Ti^{4+}, but not site geometry, was selected to define a Ti calibration curve[6] that may be used to determine Ti^{3+}/Ti^{4+} in meteoritic hibonite[8]. In addition, Ti L-edge X-ray absorption spectroscopy images and spectra were collected using X-ray photoemission electron microscopy (XPEEM). Nanometre-scale zoning in Ti content was observed in hibonites that had variable Ti^{3+}/Ti^{4+} ratios[5,9].

References

1. J.N. Connelly, M. Bizzarro, A.N. Krot, Å. Nordlund, D. Wielandt, M.A. Ivanova Science (2012), 338, 651-655.
2. K. Lodders Astrophys. J (2003), 591, 1220-1247.
3. J.R. Beckett, D. Live, F.-D. Tsay, L. Grossman, E. Stolper Geochim. Cosmochim. Acta (1988), 52, 1479-1495.
4. G.A. Waychunas Am. Min. (1987), 72, 89-101.
5. P.M. Doyle PhD thesis, Imperial College London, (2012), p. 270.
6. P.M. Doyle, A.J. Berry, P.F. Schofield, J.F.W. Mosselmans (under review).
7. P.M. Doyle, P.F. Schofield, A.J. Berry, A.M. Walker, K.S Knight. Am. Min. (2014), 99, 1369-1382.
8. P.M. Doyle, S.S. Rout, A. Bischoff (almost submitted).
9. P.M. Doyle, P.F. Schofield, A.D. Smith, A.T. Young, A. Scholl, A.J. Berry (in prep).

Single-crystal guest exchange and phase transformations in a porous metallocycle

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One of the target architectures for porous crystals investigated by our group is the “doughnut-shaped” metallocycle. The “doughnut” shape of the metallocycles prevents them from packing efficiently and results in the formation of crevices, cavities or channels in the packing arrangement. Naturally, owing to close-packing requirements the occurrence of empty space in the crystal structure is energetically unfavourable and therefore the available “space” is usually occupied by solvent molecules. Ideally, the porous phase can be obtained by removing the solvent molecules from the channels without disrupting the host framework. In this regard we have conducted a further investigation of the porous metallocycle previously reported by Barbour et al.[1] Single crystals of a previously reported porous metallocycle $[Ag_2L_2](BF_4)_2 \bullet 2CH_3CN$ (1) were grown from acetonitrile and immersed in different organic solvents. The crystals thus treated were subjected to single-crystal X-ray diffraction analysis, which revealed that the acetonitrile guest molecules had been replaced by the solvent that the compound was exposed to, yielding five different solvates: $[Ag_2L_2](BF_4)_2 \bullet 2(CH_3)_2CO$ (2), $[Ag_2L_2](BF_4)_2 \bullet 2CHCl_3$ (3), $[Ag_2L_2](BF_4)_2 \bullet C_6H_6$ (4), $[Ag_2L_2](BF_4)_2 \bullet C_6H_4F_2$ (5), $[Ag_2L_2](BF_4)_2 \bullet C_7H_8$ (6). Thermogravimetric analysis supports these findings. [2]

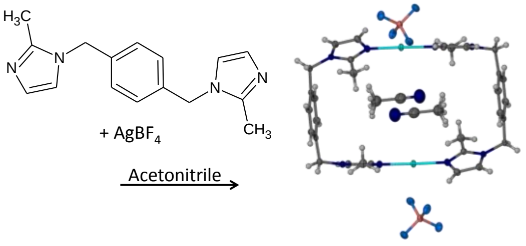

Figure 1. Formation of $[Ag_2L_2](BF_4)_2 \bullet 2CH_3CN$ (1) where L = 1,4-bis(2-methylimidazol-1-ylmethyl)benzene.

References

1.L. Dobrzańska, G. O. Lloyd, H. G. Raubenheimer, L. J. Barbour *J. Am. Chem. Soc.* (2005), 127, 13134.
2.M. du Plessis, V. J. Smith, L. J. Barbour *CrystEngComm.* (2014), 16, 4126.

Accessing porous phases of a metal-organic framework by solvent exchange

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A great diversity of porous metal-organic frameworks (MOFs) are known and chemists are familiar with their ability to absorb gases.[1] However, in many potentially porous MOFs, when the guest solvent is expelled the framework collapses[2] or undergoes a change in degree of interpenetration to minimise the resultant available free volume.[3] The metal organic framework $Zn_2(bpdc)_2bpy$ (bpdc = biphenyl-4,4′-dicarboxylic acid, bpy = 4,4′-bipyridine) has previously been shown to have limited permeability to nitrogen and carbon dioxide at low temperatures.[4] We have activated this compound directly (i.e. without exchanging the occluded reaction solvent) and via solvent exchange. By single-crystal X-ray diffraction we determined that, for $Zn_2(bpdc)_2bpy$, the identity of the guest solvent at the start of activation affects the available free volume of the resultant activated phase. When activated directly, the final phase has limited porosity (10% calculated free volume for a 1.2 Å probe). By contrast, when activated after exchange with diethyl ether or ethyl acetate the resultant structures exhibit obvious guest-free pores and possess 23% and 26% calculated free volume respectively.

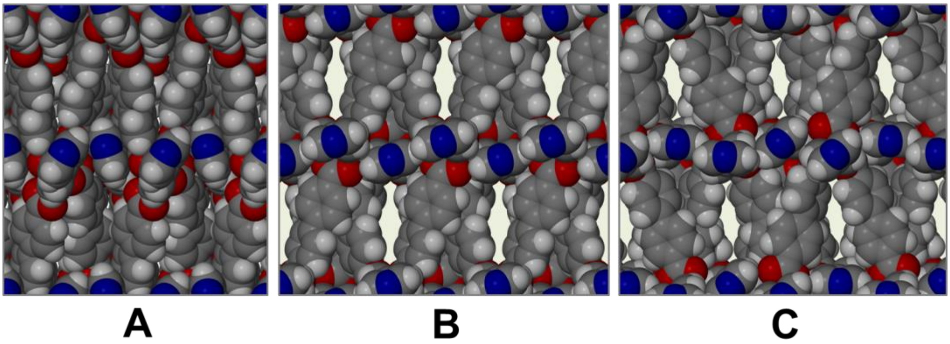

Figure 1. Space-filled packing diagrams for the phases obtained by activating $Zn_2(bpdc)_2bpy$ directly (A) and after replacing the guest solvent with diethyl ether (B) and ethyl acetate (C).

References

1. H. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi, Nature (1999), 402, 276; J.L.C. Rowsell, O.M. Yaghi, Micropor. Mesopor. Mat. (2004), 73, 3.
2. A. Schneemann, V. Bon, I. Schwedler, I. Senkovska, S. Kaskel, R.A. Fischer, Chem. Soc. Rev. (2014), 43, 6062.
3. H.A. Aggarwal, P.M. Bhatt , C.X. Bezuidenhout , and L.J. Barbour, J. Am. Chem. Soc. (2014), 136, 3776.
4. P.V. Dau, M. Kim, S.J. Garibay, F.H.L. Münch, C.E. Moore, S.M. Cohen, Inorg. Chem. (2012) 51, 5671.

On-demand acetonitrile activated porous material: a cyclopeptoid single crystal-to-single crystal transformation

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Researchers in many areas have been studying natural and synthetic macrocycles for their versatile functions. Among them, cyclopeptoids show biostability and potential diversity, which make them ideal building blocks for supramolecular architectures with novel chemical properties and defined biological activities.

Peptoids and peptides differ by the position of the side chain, that is no longer bound to the α-carbon but to the nitrogen atom. Due to the lack of the amide proton, the formation of NH···OC hydrogen bonds is prevented and weaker interactions such as CH···OC and CH-pi play a key role. Inter-annular CH···OC hydrogen bonds provide either face to face or side by side arrangement of macrocycles mimicking β-sheet secondary structure in proteins.[1]

Different sized cyclopeptoids have been synthesized and characterized from Salerno's group[2] and many biological activities have been demonstrated, such as transport across a phospholipid membrane[3] and antifungal activity and no toxicity toward red blood cells.[4]

Herein is reported an example of conformational flexibility, where the choice of the side chains affects the solid state dynamic behaviour upon solvent uptake and release, making the cyclopeptoid an on-demand acetonitrile activated porous material

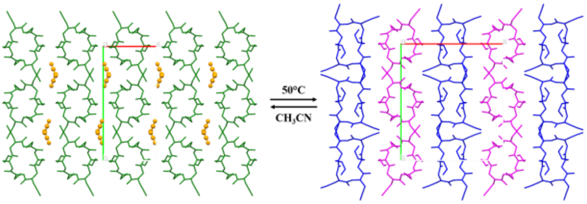

Figure 1. Single crystal-to-single crystal transformation for the cyclopeptoid *cyclo-(Nme-Npa)$_2$* upon loss and re-uptake of acetonitrile [Nme = N-(methoxyethyl)glycine, Npa = N-(propargyl)glycine]

References

1. C.Tedesco, L. Erra, I. Izzo, F. De Riccardis CrystEngComm (2014), 16, 3667.
2. a) N. Maulucci, I. Izzo, G. Bifulco, A. Aliberti, C. De Cola, D. Comegna, C. Gaeta, A. Napolitano, C.Pizza, C. Tedesco, D. Flot, F. De Riccardis Chem. Comm. (2008), 3927; b) I. Izzo, G. Iannello, C. De Cola, B. Nardone, L. Erra, G. Vaughan, C. Tedesco, F. De Riccardis Org. Lett. (2013), 15, 598.
3. C. De Cola, S. Licen, D. Comegna, E. Cafaro, G. Bifulco, I. Izzo, P. Tecilla, F. De Riccardis Org. Biomol. Chem. (2009), 7, 2851.
4. D. Comegna, M. Benincasa, R. Gennaro, I. Izzo, F. De Riccardis Bioorg. Med. Chem. (2010), 18, 2010.

Tuning MOF sequestration and storage

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Petrochemical and commodity chemical industries have been simultaneously powering and destroying many forms of modern living for the last 250 years. Examples of this include the combustion oxidation of hydrogen, methane and light hydrocarbons as a source of energy, which sustains various aspects of terrestrial life but a by-product of which is the formation of anthropogenic CO_2, a key factor in ozone depletion. Traditional separation methods such as condensation and distillation no longer present viable options due to their high-energy-high-cost refinement and unfriendly environment practices. MOFs have certain unique features not seen in traditional porous materials, which include channels that can be rationally tuned, functional sites that can be readily immobilised and high thermal stability. As a result, recent years have seen the rapid development of MOFs due to their potential applications in gas storage, separation and catalysis.[1-7]

This work describes two isostructural MOFs composed of the same components but differing in metal centre. The minor change of metal plays a surprising role in the selectivity capabilities of each MOF. Furthermore, due to the pleochroic nature of the cobalt MOF, visibly tuneable solid-solutions were formed (enabling potential sequestration regulation) along with the growth of an epitaxial crystal.

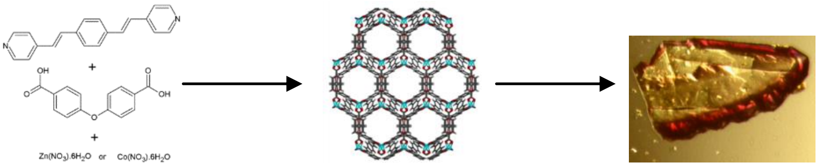

Figure 1. Synthesis conditions and extended packing of the two isostructural MOFs as well as an epitaxial crystal of the two forms.

References

1. R. B. Getman, Y. -S. Bae, C. E. Wilmer, R. Q. Snurr, *Chem. Rev.* (2012), 112, 703.
2. K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. -H. Bae, J. R. Long, *Chem. Rev.* (2012), 112, 724.
3. S. Horike, Y. Inubushi, T. Hori, T. Fukushima, S. Kitagawa, *Chem. Sci.* (2012), 3,116.
4. H. -C. Zhou, J. R. Long, O. M. Yaghi, *Chem. Rev.*(2012), 112, 673.
5. H. -S, Lu, L. Bai, W. -W. Xiong, P. Li, J. Ding, G. Zhang, T. Wu, Y. Zhao, J. Lee, Y. Yang, B. Geng, Q. Zhang, *Inorg. Chem.* (2014), 53, 8529.
6. J. Gao, K. Ye, L. Yang, W. -W. Xiong, L. Ye, Y. Wang, Q. Zhang, *Inorg. Chem.*(2014), 53, 691.
7. J. Gao, M. He, Z. Y. Lee, W. Cao, W. -W. Xiong, Y. Li, R. Ganguly, T. Wu, Q. Zhang, *Dalton Trans.*(2013), 42, 11367.

Investigation of the potential porosity of a 1,2,3,5-dithiadiazolyl radical

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Work done by Clarke *et al.*[1] showed the formation of a channel-containing material based on a partially fluorinated 1,2,3,5 dithiadiazolyl radical. Subliming the radical under a partial pressure of various gases results in crystals containing channels in which the guest molecules reside. Subliming the radical under vacuum results in a close-packed structure, with structural similarities to the clathrate.

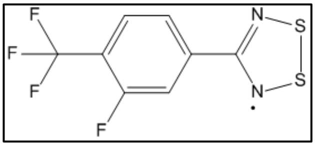

Figure 1. The aromatic 1,2,3,5-dithiadiazolyl radical in question.

Having successfully and reproducibly obtained crystals of both the nitrogen-containing inclusion compound and the close packed form of this organic radical, further characterisation along with exchange experiments have been carried out. The possibility of interconversion between the close-packed and channel-containing forms will also be investigated.

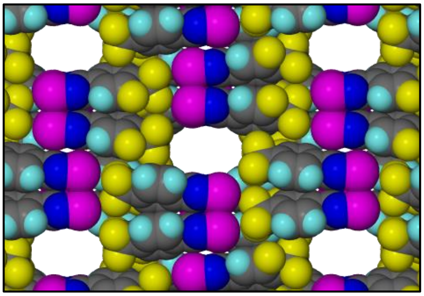

Figure 2. Packing diagram of the 1,2,3,5-dithiadiazolyl radical, showing the presence of channels.

References

1. C. S. Clarke, D. A. Haynes, J. M. Rawson and A. D. Bond, *Chem. Commun.*, 2003, 2774-2775.

Cyclic hexapeptoids: synthesis and structural features

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Peptoids, or oligomers of *N*-substituted glycines, represent a promising class of biocompatible compounds recapitulating the functions and capabilities of natural polypeptides while retaining in vivo metabolic stability and remarkable structural diversity.

The cyclization of linear oligomers represents a useful strategy to induce conformational rigidity to obtain scaffolds which provide ample chemical diversity, structural ordering; and controlled flexibility.

At the University of Salerno several cyclic hexa-*N*-substituted glycines were prepared and characterized [1,2]. It has been demonstrated that cyclic peptoids promote the transport across a phospholipid membrane, probably via a carrier mechanism [3] and for this reason they may represent new motifs on which to base artificial ionophoric antibiotics. The biological assays indicated in some cases antifungal activity and no toxicity toward red blood cells [4].

For their high affinity to metal cations they have been tested also as phase transfer catalysts (with performances comparable to crown ethers) [5] and as powerful ligands for the gadolinium ion [6].

The most efficient synthetic strategies to obtain cyclic *N*-substituted hexaglycines will be described, with particular emphasis on the submonomeric approach and the template effects of metal ions.

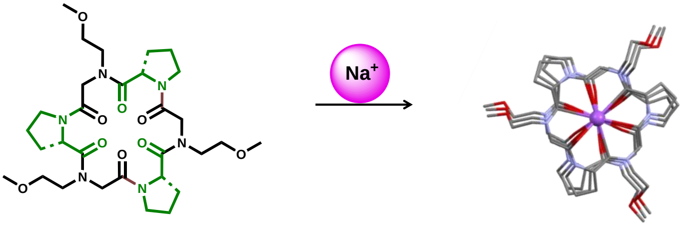

Figure 1. Sodium cation recognition by a prolinated cyclohexapeptoid.

References

1.N. Maulucci, I. Izzo, G. Bifulco, A. Aliberti, C. De Cola, D. Comegna, C. Gaeta, A. Napolitano, C. Pizza, C. Tedesco, D. Flot, F. De Riccardis ChemComm., (2008) 3927.
2.I. Izzo, G. Ianniello, C. De Cola, B. Nardone, L. Erra, G. Vaughan, C. Tedesco, F. De Riccardis Org. Lett., (2013) 15, 598.
3.C. De Cola, S. Licen, D. Comegna, E. Cafaro, G. Bifulco, I. Izzo, P. Tecilla, F. De Riccardis Org. Biomol. Chem., (2009), 7, 2851.
4.D. Comegna, M. Benincasa, R. Gennaro, I. Izzo, F. De Riccardis Bioorg. Med. Chem., (2010), 18, 2010.
5.G. Della Sala, B. Nardone, F. De Riccardis, I. Izzo Org. Biomol. Chem., (2013), 11, 726; R. Schettini, B.Nardone, F. De riccardis, I. Izzo Eur. J. Org. Chem. (2014), 7793.
6. F. De Riccardis, C. De Cola, G. Fiorillo, A. Meli, S. Aime, E. Gianolio, I. Izzo Org. Biomol. Chem., (2014) 12, 424.

A Study Of The Crystal Packing Of Proline-rich Cyclopeptoids

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The design of new supramolecular architectures is an area of intense research that involves different subjects such as material science, catalysis, crystal engineering. The focus of chemists is toward the development of macrocyclic systems with potential application in nanotechnology sciences. A new class of promising macrocyclic compound is represented by cyclic α-peptoids. Peptoids differs from peptides because the side chain is attached to the backbone amide nitrogen instead of the α-carbon. Cyclic peptoids are attractive building blocks due to their simple synthesis and great variability in functional groups. The understanding of the solid state assembly of cyclic α-peptoids is fundamental to direct the design of new materials with specific properties in terms of catalysis, biochemistry, drug discovery. The inclusion of proline along the peptoid backbone could afford conformational rigidity, moreover the presence of a stereogenic centre in the proline residues generates chirality, which is another important feature for the design of new materials. An example of solid state assembly of prolinated cyclopeptoids has been recently reported by us [1] its crystal packing features a triple decker in which there are three cyclopeptoid rings, four Na + and one molecule of acetonitrile (figura 1). A survey of analogous prolinated macrocycles has been performed and their Hirshfeld surfaces [2] have been calculated. Their crystal packing will be discussed and compared by means of Hirshfeld fingerprint analysis, considering in particular the effect of the ring size.

References

1. I. Izzo, G. Ianniello, C. De Cola, B. Nardone, L. Erra, G. Vaughan, C. Tedesco, F. De Riccardis Org. Lett. (2013), 15, 598.
2. J. J. McKinnon, D. Jayatilaka and Mark A. Spackman, Chem. Comm. (2007), 3814

Controlling interpenetration by solvent size on porous material

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Interpenetration in metal–organic frameworks (MOFs) is an intriguing phenomenon with significant impacts on the porous material such as diminishing porosity and reduced the space availability on porous material. So, prevention of interpenetration in porous material is extremely important.[1] Hence, here we report two new porous material of [(ZnSiF) (1,2-dibenzylidenehydrazine)($CHCl_3$ and MeOH)] and [(ZnSiF) (1,2-dibenzylidenehydrazine)($CHCl_3$ and DMAC)] that grown upon slow diffusion as yellow crystalline materials .Single crystal X-ray analyses reveal an example of 2D noninterpenetrating network and 2D interpenetrating with different pore size and solvent on it, The different conformation by pore size and solvent size might be the main factor resulting in these non-interpenetrated/interpenetrated porous material.

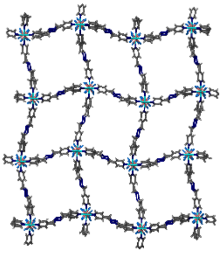

Figure 1. Noninterpenetrated

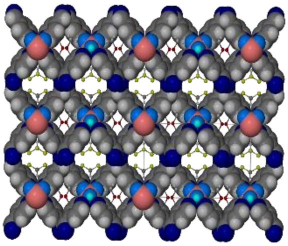

Figure 2. Interpenetrated

References

1.H. Xiang, L. Xiao-Peng, Yu-Yang Tian, L. Ming-Xing, S. Zhu, F Xinga E. Russell Morrisb. CrystEngComm. (2013), 15, 9442.

Organic Macrocycles as Building Blocks for Porous Materials

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The development of self-assembled solid-state supramolecular architectures with nanosized pores or cavities is an intensively active research area, aiming at the preparation of new materials with potential applications in nanotechnology such as molecular sieves, sensors, and gas-storage devices. Organic solids could represent a competing alternative to zeolites, clays, metal-organic frameworks, mesoporous metal oxides. They feature not only the required porosity but also high selectivity, which can be achieved both by tailoring channel dimensions to guest molecules, and also by providing specific interactions with organic functional groups. Moreover, dynamic structural transformations based on flexible porous frameworks are always possible leading to functional materials with the fabrication of switches or actuators at a supramolecular level.

Two types of macrocycles will be considered, namely calixarenes and cyclopeptoids. Both represent a class of very versatile compounds, which can be easily modified to achieve the desired building blocks. While cyclopeptoids constitute a class of relatively new compounds, whose properties are still unexplored, [1-3] calixarenes have been successfully employed to obtain porous nanostructured materials.[4-8] Examples of the solid state assembly of both class of compounds will be reported to show their extreme versatility as building blocks for designing new materials.

References

1. N. Maulucci, I. Izzo, G. Bifulco, A. Aliberti, C. De Cola, D. Comegna, C. Gaeta, A. Napolitano, C. Pizza, C. Tedesco, D. Flot, F. De Riccardis ChemComm. (2008), 3927.
2. I. Izzo, G. Ianniello, C. De Cola, B. Nardone, L. Erra, G. Vaughan, C. Tedesco, F. De Riccardis Org. Lett. (2013), 15, 598.
3. C. Tedesco, L. Erra, I. Izzo, F. De Riccardis CrystEngComm (2014), 16, 3667.
4. C. Tedesco, I. Immediata, L. Gregoli, L. Vitagliano, A. Immirzi, P. Neri CrystEngComm (2005), 7, 449.
5. P. K. Thallapally, B. P. McGrail, J. L. Atwood, C. Gaeta, C. Tedesco, P. Neri Chem. Mater. (2007), 19, 3355-3357.
6. C. Tedesco, L. Erra, M. Brunelli, V. Cipolletti, C. Gaeta, A. N. Fitch, J. L. Atwood, P. Neri Chem. Eur. J. (2010), 42, 2371.
7. L. Erra, C. Tedesco, V. R. Cipolletti, L. Annunziata, C. Gaeta, M. Brunelli, A. N. Fitch, C. Knöfel, P.L. Llewellyn, J. L. Atwood, P. Neri Phys. Chem. Chem. Phys. (2012), 14, 311.
8. C. Tedesco, L. Erra, I. Immediata, C. Gaeta, M. Brunelli, M. Merlini, C. Meneghini, P. Pattison, P. Neri, Cryst. Growth Des. (2010), 10, 1527.
9. 8. L. Erra, C. Tedesco, I. Immediata, L. Gregoli, C. Gaeta, M. Merlini, C. Meneghini, M. Brunelli, A. N. Fitch, P. Neri, Langmuir 2012, 28, 8511-8517.

Elucidating the mechanism responsible for anisotropic thermal expansion in a Metal-Organic Framework

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Anomalous thermal expansion of a three-dimensional metal-organic framework (compound **1**) is examined through theoretical calculations. The methanol solvate ($[Zn(\mathbf{L})(OH)]_n \cdot nCH_3OH$, $\mathbf{1_{MeOH}}$, **L** = 4,4′-bis(2-methylimidazol-1-ylmethyl)-1,1′-biphenyl)) was obtained following the procedure developed by Grobler *et. al* and subsequently desolvated in a single-crystal to single-crystal transformation to yield the apohost form, $\mathbf{1_{apo}}$.[1] Variable temperature single crystal X-ray diffraction (SCD) analysis on the same crystal of $\mathbf{1_{apo}}$ under static vacuum revealed colossal positive thermal expansion along the *c* axis ($\alpha_c = 123$ MK^{-1}) and biaxial negative thermal expansion along the *a* and *b* axes ($\alpha = -21$ MK^{-1}). Inspection of the 100, 190, 280 and 370 K SCD structures pointed towards a concerted change in the labile coordination sphere of the zinc centre so as to elongate the coordination spiral in the *c* direction (O(H)-Zn-O(H) angles enlarge), while the largely unaltered ligands (Zn···**L**···Zn distance constant) are pulled closer together in the *ab* plane.

In this study a mechanistic model that reproduces the convergent expansion of the material's coordination spiral is developed and evaluated at the DFT level of theory. The linear increase in energy calculated for the extension of a model consisting of six zinc centres and truncated ligands compares favourably to results obtained from a periodic DFT evaluation of the SCD structures.

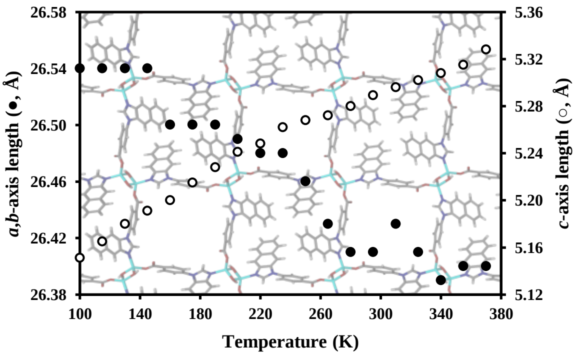

Figure 1. Graph of unit cell lengths determined by single crystal X-ray diffraction on the same crystal of $\mathbf{1_{apo}}$ ($[Zn(\mathbf{L})(OH)]_n$) under static vacuum showing variation with temperature.[1]

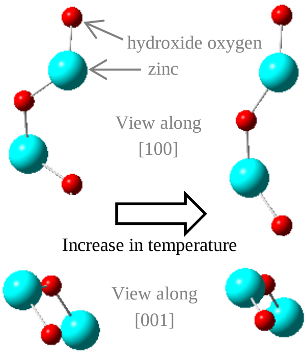

Figure 2. Schematic representation of the convergent expansion mechanism of the coordination spiral of **1**.

References

1. I. Grobler, V.J. Smith, P.M. Bhatt, S.A. Herbert, L.J. Barbour *J. Am. Chem. Soc.* (2013), 135, 6411.

Development of novel supramolecular framework materials based on organic salts

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Framework materials such as metal-organic frameworks (MOFs)[1], covalent organic frameworks (COFs)[2] and nanoporous molecular materials[3] have been extensively studied for their function as hosts with potential application in separation and drug delivery. The aim of this project is to use purely organic molecules to design and synthesise ionic organic framework materials based on carboxylate salts, with the intention of engineering interesting properties, such as porosity, into these materials.

A hydrogen-bonded organic framework, 3,4-lutidinium pamoate hemihydrate, with THF-filled channels in the solid state, illustrated in Figure 1, was serendipitously discovered.[4] It is a porous framework that exchanges for a wide variety of guests, with many of these exchanges occurring in a single-crystal to single-crystal fashion. The selectivity of this framework was investigated through competition experiments and the results of these experiments will be reported. The kinetics of guest exchange were studied and it was possible to identify a kinetic model that best describes the process.

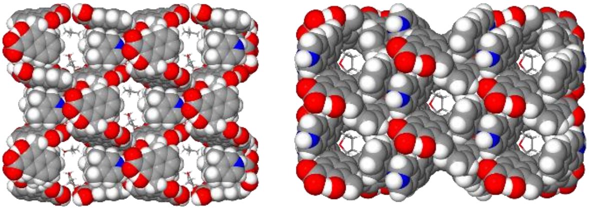

Figure 1. The porous framework with THF-filled channels is shown on the left and the framework-type material with THF-filled cavities is shown on the right

A second novel framework-type material, 4-phenylpyridinium pamoate, was identified, as well as five isostructural frameworks containing different guest molecules. This framework contains guest molecules in constricted cavities in the solid state (Figure 1). Though not porous, it is thermally quite stable and also highly selective. The results of competition experiments conducted with this framework-type material will be reported.

References

1. X.-D. Zheng, M. Zhang, L. Jiang and T.-B. Lu, Dalton Trans. (2012), 41, 1786.
2. H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortés, A. P. Côté, R. E. Taylor, M. O'Keeffe and O. M. Yaghi, Science (2007), 316, 268.
3. J. R. Holst, A. Trewin and A. I. Cooper, Nat Chem (2010), 2, 915.
4. H. Wahl, D.A. Haynes, T. le Roex, Chem. Commun.(2012), 48, 1775.

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