

[1] Neutze et al., *Nature* **2000**, *406*, 752-757. [2] D.K. Saldin et al., *J. Phys.: Condens. Matter* **2009**, *21*, 134014. [3] D.K. Saldin et al., *Phys. Rev. B* **2010** *81*, 174105. [4] D.K. Saldin et al. *Phys. Rev. Lett.* **2011**, *106*, 115501. [5] e.g. M. Schmidt et al., In: *Methods in Molecular Biology*, **2005**, Vol. 305, *Protein-Ligand Interactions: Methods and Applications* (G.U. Nienhaus ed.), Humana Press, Totowa, NJ, p. 115 ff.

Keywords: biomacromolecules, X-ray free electron laser

MS.37.5

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Imaging biological molecules using X-FELs

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Tremendously boosted by ever improving synchrotron X-ray sources, X-ray diffraction has been a central tool in structural biology. X-ray free-electron lasers (FELs) provide up to 9 orders of magnitude brighter and much shorter X-ray pulses that may yield diffraction patterns of biological samples before significant radiation damage has occurred (“diffraction before destruction”) [1]. We present results from diffraction experiments with biological samples, both crystalline [2] and single-particle, performed using FEL sources. Analysis of the data shows the potential of FELs for structural biology

[1] R. Neutze, R. Wouts, D. van der Spoel, E. Weckert, J. Hajdu, *Nature* **2011**, *406*, 752-757. [2] H.N. Chapman, P. Fromme, A. Barty, et al. *Nature* **2011**, *470*, 73-77.

Keywords: free electron lasers, nanocrystals, protein crystallography

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Flexible pyrene-derived frameworks for sensing and separation

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Open frameworks prepared using the well established principles of coordination chemistry are significantly more flexible than their wholly oxide counterparts, leading to novel guest-responsive adsorption behaviors. [1] Such framework flexibility can be pre-determined through the use of deliberately flexible ligands such as dipeptides [2], or can arise from seemingly quite rigid organic linking groups. [3]

The tetracarboxylate ligand 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene (TBAPy) is based on a rigid planar pyrene core, but has sufficient rotational freedom about the benzoate substituents to permit framework dynamics upon metal-binding. This dynamic behavior has been studied using a combined approach of diffraction, solid-state NMR and molecular dynamics simulations.

In this contribution I will present two materials prepared from d¹⁰ metal ions where the structural changes resulting from these benzoate rotations influence the physical properties of the material. Firstly, [In₂(OH)₂(TBAPy)] is a microporous 3-dimensional framework displaying linker-centered emission with a ms lifetime. [4] The emission response is highly dependent on the chemical nature and loading level of guest molecules, and in particular how these affect the framework structure through induced structural changes or specific framework-guest interactions.

Reaction of TBAPy with Zn(II) yields a layered framework of composition [Zn₂(TBAPy)(H₂O)₂] which is linked via the common paddlewheel motif. Large structural changes occur on desolvation, which are consistent with benzoate rotations as evidenced by NMR. Further investigation of the desolvated structure using molecular dynamics simulation reveals a novel rearrangement of the paddlewheel building units transforming the structure into a 3-dimensional porous network that displays modest selectivity for xylene isomers.

[1] S. Horike, S. Shimomura, S. Kitagawa *Nature Chem.* **2009**, *1*, 695-704. [2] J. Rabone et al *Science* **2010**, *329*, 1053-1057. [3] C. Serre et al *Science* **2007**, *315*, 1828-1831. [4] K. Stylianou et al *J. Am. Chem. Soc.* **2010**, *132*, 4119-4130

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Unusual porous functions of stimuli responsive porous coordination polymers

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The discovery of a new nanoporous compound that has unique porous properties is scientifically and technologically topical. In particular, the creation of a porous compound that possesses a switchable pore surface and channel structure is currently a major challenge in material science. This has not yet been realized with currently available materials. The recent advent of porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) as new functional crystalline microporous compounds, has attracted the attention of scientists because of the great practicality of regular nano-sized spaces prepared by simply mixing their organic and inorganic molecular components which result in their finding unusual porous functions such as in storage, catalysis and highly enantio-, size- and shape-selective adsorption. [1]

Here we report new flexible PCPs that show large structural transformation in response to the adsorption of specific guest molecules,

resulting in high selectivity for guest inclusion or multi-step adsorption behaviors.[2-4] Dynamic effects can arise either locally from flexible ligands and/or flexibility of the coordination geometry of the metal ions, or from the global cooperative movement of the framework on a periodic scale. The mechanism of the dynamics of flexible PCPs was investigated by a coincident adsorption/X-ray powder diffraction measurement system.

In addition, we will report a new photo-responsive PCP composed of azide modules as dormant precursors. The pore surface of PCP can be activated by UV irradiation and the resulting reactive species were regularly arranged in the framework, which was observed not only by spectroscopic measurements but also crystallographic analysis using synchrotron X-ray diffraction data. The highly reactive species can react or interact with guest molecules. According to the result of adsorption measurement under photoirradiation, we found that the adsorption activity for oxygen was significantly improved by photoirradiation.[5]

[1] R. Matsuda, T. Tsujino, H. Sato, Y. Kubota, K. Morishige, M. Takata, S. Kitagawa, *Chem. Sci.* **2010**, *1*, 315-321. [2] S. Shimomura, M. Higuchi, R. Matsuda, K. Yoneda, Y. Hijikata, Y. Kubota, Y. Mita, J. Kim, M. Takata, S. Kitagawa, *Nature Chem.* **2010**, *2*, 633-637. [3] S. Bureekaew, H. Sato, R. Matsuda, Y. Kubota, R. Hirose, J. Kim, K. Kato, M. Takata, S. Kitagawa, *Angew. Chem., Int. Ed.* **2010**, *49*, 7660-7664. [4] J. Seo, R. Matsuda, H. Sakamoto, C. Bonneau, S. Kitagawa, *J. Am. Chem. Soc.* **2009**, *131*, 12792-12800. [5] H. Sato, R. Matsuda, K. Sugimoto, M. Takata, S. Kitagawa, *Nature Mater.* **2010**, *9*, 661-666.

Keywords: coordination, microporous, adsorption

MS.38.3

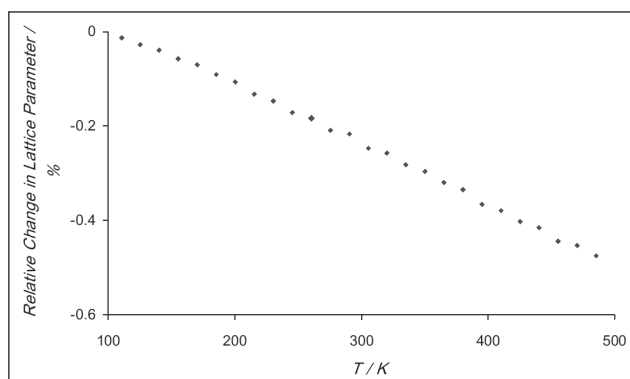
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Negative thermal expansion in porous framework materials

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The recent interest in metal-organic frameworks (MOFs) has stemmed from their wide range of potential applications, from gas storage devices to drug delivery systems [1]. Here we focus on a selection of MOFs that display the unusual property of negative thermal expansion (NTE; i.e., contraction upon warming). NTE materials have potential applications in composite materials that show zero thermal expansion over wide temperature ranges, thus being suitable for high precision instruments that are affected by thermal expansion. Through establishing mechanisms for NTE and investigating how systematic structure changes affect the size of the NTE, materials may be tailored to meet specific needs.

In this study members of the IRMOF series of compounds were investigated. These materials share a common tetranuclear metal cluster, $Zn_4O(\text{carboxylate})_6$, bridged by varying dicarboxylate ligands. Synchrotron powder X-ray diffraction (S-PXRD) reveals the materials show linear thermal expansion from 500 – 100K, with all except one investigated here exhibiting NTE. Through comparison of the coefficients of thermal expansion (CTEs) the impact on the NTE of the variations in structure has been observed. The use of single crystal X-ray diffraction (SCXRD) to compare bond lengths at varying temperatures has also provided valuable insight into the mechanisms responsible for NTE in these multi-hinged structures.



[1] R.J. Kuppler, D.J. Timmons, Q.-R. Fang, J.-R. Li, T. A. Makal, M.D. Young, D. Yuan, D. Zhao, W. Zhuang, H.-C. Zhou, *Coordination Chemistry Reviews* **2009**, *253*, 3042.

Keywords: framework, NTE, porosity

MS.38.4

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Tuning of the structural flexibility and chemical properties of the MIL53-Al and MIL47-V

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The Porous Coordination Polymers (PCPs) or Metal-Organic Frameworks (MOFs) are a unique class of hybrid solid-state materials with bright future due to their permanent porosity and high thermal stability. The use of these materials ranges from gas storage, separation and catalysis, to a number of diverse potential applications, including optoelectronics, sensors, smart membranes etc. To incorporate the new functions into the 1-D channel PCPs we performed detailed study of the broad series of inclusion compounds into $[\text{Al}(\text{OH})(\text{bdc})]_n$ (MIL53-Al) and $[\text{V}(\text{O})(\text{bdc})]_n$ (MIL47-V) [1], [2], [3]. $[\text{Al}(\text{OH})(\text{bdc})]_n$ shows a well-pronounced breathing effect on the contrary to $[\text{V}(\text{O})(\text{bdc})]_n$, which demonstrates neither breathing effect but has well documented catalytical and electrochemical activities. Nevertheless, both phases have the same framework topology, which makes possible to prepare mixed Al/V frameworks in a broad concentration range.

Here, we present our results obtained in the course of preparation and investigation of the mixed metal $[\{\text{Al}(\text{OH})\}_x/\{\text{V}(\text{O})\}_{1-x}(\text{bdc})]_n$ and $[\{\text{Al}(\text{OH})\}_x/\{\text{V}(\text{O})\}_{1-x}(\text{ndc})]_n$ ($0 < x < 1$, bdc = benzeneterephthalate, ndc = naphthaleneterephthalate) phases which show new structural and chemical features. Crystal structures, flexibility and inclusion phenomenon were investigated in details using PXRD, spectroscopic and electrochemical techniques. Structural characteristics (cell parameters and volume) show linear dependence on the composition in the whole range. On the other hand, structural flexibility and stability show behavior characteristic for $[\text{V}(\text{O})(\text{bdc})]_n$. Inclusion compounds Cobaltocene@ $[\{\text{Al}(\text{OH})\}_x/\{\text{V}(\text{O})\}_{1-x}(\text{bdc})]_n$ and benzene@ $[\{\text{Al}(\text{OH})\}_x/\{\text{V}(\text{O})\}_{1-x}(\text{bdc})]_n$ were synthesized to characterize chemical properties and flexibility of the mixed-metal phases. Crystal structures of the inclusion compounds were also solved using PXRD technique. Guests molecules are localized in the middle of the 1-D channel and their positions show flexibility of the framework induced by the framework reduction and charge transfer between cobaltocene and vanadium centers of the backbone. The phases obtained proposed as electrochemically, magnetic and catalytically active porous materials with CO_2 vs. N_2 selectivity.

[1] M. Meilikhov, K. Yusenko, R.A. Fischer, *Dalton Trans.*, **2009**, 600. [2]