

MS.73.2*Acta Cryst.* (2008). A64, C125**In-situ reactivity and selective chiral sorption in metal-organic frameworks**Matthew J Rosseinsky

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The precisely defined interior cavities of porous metal-organic frameworks with a high degree of chemical diversity are attractive for selective sorption. We describe a family of amino-acid based open frameworks (1) which display chirally selective sorption that is highly specific to the functional group disposition within the sorbed molecules. The nature of the interaction between the framework and sorbate is revealed by computational approaches used in protein-ligand docking. The cavities within metal-organic framework materials are also attractive hosts for the observation of chemical reactions with atomic-scale resolution by crystallography, permitting the observation of co-operative involvement of the surrounding solid in accommodating the changes at the reacting centre. (2)

[1] R. Vaidhyanathan et al, *Angew. Chem. Int. Ed. Engl.* 45, 6495 (2006); J. Rebilly et al *Chem. Eur. J.* in press 2008; M. Ingleson *Chem Comm* 2007, 2008

[2] D. Bradshaw et al. *Science* 315, 977 - 980, 2007.

Keywords: porous materials, reactions, amino-acid coordination compounds

MS.73.3*Acta Cryst.* (2008). A64, C125**Porosity in flexible metal-organic systems**Len J Barbour

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Over the past decade the study of porous crystalline solids has become highly topical, especially with regard to potentially important applications such as gas storage, separation and sensing. Well-known systems include zeolites and metal-organic frameworks and, to a lesser extent, organic molecular crystals. However, discrete metal complexes have received little attention as components of porous materials. One of the basic tenets of the solid state is that molecules tend to pack closely, thus affording minimal free space at the molecular scale. We are attempting to overcome this tendency by designing simple complexes that cannot pack efficiently without including solvent molecules. Indeed, we are specifically interested in forming solvent-templated complexes that do not collapse upon subsequent solvent removal. We have recently discovered several systems that behave in this manner; some of these structures can be considered to be porous in the conventional sense, but we have also noted that conventional porosity is not a prerequisite for mass transport in the solid state. These systems have now been studied using a variety of complementary techniques, including X-ray diffraction, isothermal gas sorption and molecular modeling. Non-conventional use of these techniques has enabled us to gain a deep understanding of the relationship between structure and gas sorption dynamics.

Keywords: porous materials, self assembly, crystal engineering

MS.73.4*Acta Cryst.* (2008). A64, C125**The synthesis and structure of multifunctional metal-organic frameworks**Guangshan Zhu, Fuxing Sun, Qianrong Fang, Shilun Qiu

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Metal-organic frameworks (MOFs) have received widespread attention recent years, due to the fact that they are porous with high surface areas, have tunable pores sizes and topologies.^{1,2} MOFs always exhibit amazing magnetic and optoelectronic properties at the same time as multifunctional materials. The research interests in our group are focused on the synthesis of MOFs with intriguing topologies and multifunctional properties, including: (1) MOFs with excellent hydrogen and methane storage properties. We have already synthesized a new MOF JUC-48, with the largest reported one-dimensional (1D) hexagonal nanotube-like channels of $2.4 \times 2.8 \text{ nm}^2$ and rare *etb* topology, which exhibits hydrogen uptakes of about 2.8 wt% at 40 bar and 77K, 1.1wt% at 100 bar and room temperature.³ (2) MOFs with large metal carboxylate clusters. The metal carboxylate clusters could expand the inorganic nodes to obtain large pores, and introduce similar physical properties to those nanosized metal oxide materials. We have successfully synthesized an open framework JUC-35, which contains the largest known undecanuclear clusters and shows optoelectronic properties.⁴ (3) Rare earth MOFs. Rare earth metals are attracting much attention to construct MOFs for their special physical characteristics. About this issue, we have synthesized a lanthanide-organic framework with 1D rhombic channels of $2.5 \times 1.7 \text{ nm}^2$.⁵

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Keywords: metal-organic framework, multifunction, structure

MS.73.5*Acta Cryst.* (2008). A64, C125-126**Elucidating negative thermal expansion in metal-organic frameworks**Nina Lock¹, Yue Wu², Mogens Christensen³, Bo B Iversen¹, Cameron J Kepert²

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The majority of solids expand upon heating, a property known as positive thermal expansion (PTE). Considerable excitement has arisen over the past decade with the discovery of negative thermal expansion (NTE) in a number of relatively simple oxide- and cyanide-based materials [1]. The combination of NTE and PTE materials has potential applications in the preparation of zero thermal expansion materials, which are sought for a multitude of engineering purposes. NTE was recently discovered for some