

Oral Contributions

[MS33-05] The Effect of Solvent and Pressure on the Post-Synthetic Modification of a Metal-Organic Framework Scott C. McKellar^a, Alexander J. Graham^a, M. Infas H. Mohideen^b, Russell E. Morris^b and Stephen A. Moggach^a

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Porous metal-organic frameworks (MOFs) have an array of potential applications including gas storage, separation processes and catalysis. As such, hundreds of MOF-themed research papers are now published annually[1], with many reporting synthetic approaches to making more sophisticated, novel frameworks. Recently, this has led to strong interest in the concept of post-synthetic modification (PSM).[2] This has proven to be a very elegant technique in which to modify MOFs after they have been synthesised, since it offers the potential to tune the pore size, topology and functionality while conserving the integrity of the structure, and is an attractive route for covalent modification that is unachievable by established synthetic routes. To date, two main approaches have been used for PSM of MOFs. In the first method, the organic linker is covalently modified by introducing new functional groups. The second method involves first exposing a free site on the metal, usually by removing a ligand. Here we have investigated the PSM behaviour of the porous MOF, STAM-1 (St Andrews MOF-1).[3] We report four new phases of the material, including the first ever example of a pressure-induced PSM. STAM-1 is comprised of copper 'paddle-wheels' linked by monomethyl-esterified benzene-1,3,5-tricarboxylic acid ligands, with water molecules axially coordinated on the CuII ions. The ester and water groups yield a framework containing both hydrophobic and hydrophilic channels, respectively. Here we show how single-

step PSM is possible via ligand exchange at the axial metal coordination site with a number of organic solvents, resulting in significant changes in the pore size and functionality. Specifically, hydrophilic channels in native STAM-1 can be converted into discrete hydrophobic pores. A range of organic solvents have also been used as hydrostatic media for high-pressure single-crystal X-ray diffraction experiments. This has allowed us to induce ligand exchange using pressure and investigate the effect of ligand exchange on the stability and compressibility of the framework, demonstrating that post-synthetic ligand exchange is very sensitive to both the molecular size and functionality of the solvent. This work is, to the best of our knowledge, the most extensive study conducted on the importance of hydrostatic media selection for the investigation of porous materials under pressure. We also demonstrate the ability to force hydrophilic molecules into hydrophobic pores using high pressures, and present the first example of a pressure-induced chemical decomposition of a porous material.

[1] Champness, N. R. (2011) *Dalton Trans.* 2011, **40**, 10311-10315

[2] Wang, Z & Cohen, S. M. (2009). *Chem. Soc. Rev.* **38**, 1315-132.

[3] Mohideen, M. I. H et. al.(2011). *Nature Chem.* **3**, 304-310.

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