Many of today’s Metal-Organic Frameworks (MOFs) are based on commercially available linkers or derivatives thereof. However, there are huge possibilities for new discoveries made available through synthesis of novel linkers developed through collaboration between organic and materials chemists. Here we present the synthesis and structures of new MOFs based on the until now unexplored linker 4,4’-dimethoxy-3,3’-biphenyldicarboxylic acid (H₂L). The linker is prepared via a 3-step synthesis from commercially available precursors by a synthesis path based on literature procedures [1]. The new MOFs are synthesised from the linker H₂L and various divalent metal sources by solvothermal synthesis and show differing topologies which are dependent on the geometry of the Secondary Building Unit (SBU). The title linker H₂L is an isomer of another recently developed linker which has also yielded several new MOFs reported in the literature [2,3].

Keywords: coordination polymers; structural relationships; powder and single crystal diffraction


**MS26-P9** New MOFs based on the unexplored linker 4,4’-dimethoxy-3,3’-biphenyldicarboxylic acid. Fredrik Lundvall, David S. Wragg, Pascal D. C. Dietzel, Helmer Fjellvåg. Department of Chemistry/Centre for Materials Science and Nanotechnology, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway. EAStCHEM School of Chemistry and Centre for Science at Extreme Conditions, The University of Edinburgh, Edinburgh, UK. E-mail: fredrik.lundvall@kjemi.uio.no

Metal-organic frameworks (MOFs) are porous materials containing a very active area of research due to their potential applications in gas adsorption and storage, liquid separation, catalysis and drug delivery. The framework properties are directly related to the pore size and topology. Post-synthetic modification of MOFs [1] offers the potential to tune the pore size, topology and functionality of a crystalline framework while conserving the integrity of the structure. Such an approach is achievable using a variety of methods [1] and is an attractive route for covalent modification that is unachievable by established synthetic routes. Exposure of MOFs to high pressures has recently been used to non-covalently modify the pore size, shape and/or guest content. [2,3] Presented here is the first example of post-synthetic dative modification of a MOF using high-pressure crystallography.

STAM-1 (St Andrews MOF-1) [4] is a MOF comprised of copper ‘paddle-wheels’ linked by monomethyl-esterified benzene-1,3,5-tricarboxylic acid ligands. It is a porous framework with water molecules axially coordinated on the Cu²⁺ ions. The ester groups and coordinated water yield an axial Cu²⁺ site dependent on the molecular size and functionality of the hydrophobic and hydrophilic channels, respectively. Here we demonstrate that specific organic solvents can exchange with the coordinated water upon application of pressure, as observed with high-pressure single-crystal X-ray diffraction. The exchange reaction is not possible under ambient pressure conditions, but the solvent-exchanged STAM-1 sample is stable upon decompression and recovery at ambient pressure. This post-synthetic modification of the MOF crystal structure alters the selectivity of the hydrophilic pore, in effect creating a second hydrophobic pore. Successful solvent exchange at the axial Cu²⁺ site is dependent on the molecular size and functionality of the hydrostatic medium. STAM-1 also exhibits interesting compression characteristics, namely hydration of the hydrophobic pores followed by a pressure-induced decomposition.


Keywords: high-pressure crystallography, metal-organic framework, post-synthetic modification