

# Keynote Lectures

## [KN15] Building responsive metal-organic frameworks: modifying properties by structure

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Dynamic materials, capable of responding to their environment, require flexibility which may be achieved using weak interactions such as hydrogen bonding [1] or through the use of suitable metals and ligands in coordination compounds [2]. In recent years, our laboratory has prepared a series of metal-organic framework and network materials using a variety of pyridine and carboxylic acid derivatives with transition metals and lanthanides. Compounds are characterised by single crystal and powder x-ray diffraction. Their thermal stability and decomposition behaviour are studied using Differential Scanning Calorimetry, Thermogravimetry and Hot Stage Microscopy. Guest-exchange reactions in channel compounds are followed by means of powder x-ray diffraction and thermogravimetry as well as purpose-built sorption apparatus. One focus of our work is the preparation of MOFs which are porous and thermally stable. This is challenging as crystallization is sensitive to slight changes in conditions such as concentration or solvent system [3]. MOFs of  $Zn^{II}$  with 1,3,5-benzenetricarboxylic acid ( $H_3BTC$ ) and 1,4-benzenedicarboxylic acid ( $H_2BDC$ ) proved to be robust and porous. The anionic frameworks  $[Zn_6(m-OH)_2(BTC)_4(DMF)_{2.5}(H_2O)_2]$  and  $[Zn_2(HBTC)(BTC)(H_2O)_3]$  have the capacity to dehydrate and rehydrate through flexing of the organic bridging ligands. The latter compound can heal structural damage caused during these processes. [4,5] Solvatochromism is the ability of a chemical species to change colour on exposure to or inclusion of different solvents. It arises as a result of a change in the energy gap between ground and excited states, which in turn is caused

by interactions between chromophore and solvent molecules. Solvatochromism has been observed in supramolecular systems as a result of changes in hydrogen-bonding interactions [6], and in transition metal complexes, usually as a result of changes in the coordination centre which leads to changes in the visible d-d energy transitions [7]. The latter is often accompanied by large changes in the structure of the complex [8]. As metal organic frameworks (MOFs) frequently contain solvent-accessible voids or channels, they are ideally suited for use as solvatochromic sensors. Using the versatile ligands, 3-(pyridin-4-yl)benzoic acid (34pba) and 4-(pyridin-4-yl)benzoic acid (44pba), we have prepared a series of metal-organic networks, which contain channels to accommodate guest molecules. Drying of the  $Co^{II}$  MOFs yields crystalline material which, on exposure to various solvents, triggers reversible chromotropic transformations [9]. Kinetic studies of the sorption and desorption processes give insight into the structural transformations which are characterized by spectroscopic and diffraction methods. These effects are fully reversible, a desirable property for a potential sensor material.

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