Guest disorder as a way to achieve multistep spin crossover in metal–organic frameworks

H. J. Windsor* and C. J. Kepert

*School of Chemistry, The University of Sydney, New South Wales 2006, Australia hunter.windsor@sydney.edu.au

Keywords: spin crossover, disorder, supramolecular chemistry

Designing new materials is challenging from both a crystal engineering and functional properties perspective. The principles of crystal engineering which enable the a priori design of new crystal structures can equally be applied to metal–organic frameworks (MOFs) which, due to their modular construction, are excellent candidates for producing crystalline architectures that exist over a wide topological space. Thus, these principles can be exploited to achieve MOF topologies that are predisposed towards exhibiting desired properties.

We have been interested in MOFs that exhibit spin crossover (SCO), which is an electronic switching phenomenon associated with the thermally-induced intraionic shift between the paramagnetic high spin and diamagnetic low spin states of iron(II). The SCO response in these systems can thus be tuned by incorporation of supramolecular interactions that lead to cooperative or anti-cooperative communication pathways between the iron(II) nodes. Through this switching modality, the physicochemical differences between the iron(II) high spin and low spin states can be exploited to achieve sensing and data storage applications [1].

Incorporating guest molecules within a porous host lattice offers another way to modulate the resulting SCO behaviours. Accordingly, we synthesised and characterised the 3D Hofmann-like MOF [Fe\(_{11}\)(dpbtz)(Au\(_1\)(CN)\(_2\))\(_2\)]·0.5chrysene (1) (dpbtz = 4,7-di(pyridy1)-2,1,3-benzothiadiazole) by an array of structural and physical techniques. Encapsulation of the polycyclic aromatic hydrocarbon (PAH) chrysene within 1 results in a host–guest arrangement where the host lattice itself is periodic yet the arrangement of chrysene guest molecules is aperiodic. Framework 1 displays an unusual example of two-step SCO which we ascribe to a guest disorder effect in the chrysenes causing local site inequivalencies of the iron(II) nodes in the host lattice [2]. The principle of exploiting aperiodic moieties in an underlying periodic lattice is known to occur for example in DNA when comparing the structure of the double helix to the base-pair sequence itself. Such structures offer higher density information storage capacities due to the absence of a domain-size constraint that limits the amount of information that is accessible within each crystalline domain. Extending these ideas into the realm of materials chemistry is a challenging yet rewarding task for producing complex materials, one that we hope has been advanced by our work.

Figure 1. A chrysene-loaded spin crossover material exhibits a two-step thermally-activated spin transition driven by guest-induced local symmetry breaking.