

MOF, built by the reaction of dicarboxylate bridging ligands with a first-row transition-metal ion, and have incorporated a metal complex fragment into the bridging 'pillars'. The complex becomes part of the framework structure itself, rather than trapped as a guest, and undergoes *in situ* photoinduced rearrangements without altering the material's crystallinity (Fig. 1).

They prepared two different materials by using two types of metal fragment. In one of the materials prepared, the bridging ligand used to build the framework is the Re(I) unit $fac\text{-}[\text{Re}(\text{CO})_3\text{LCl}]^{2-}$ (where L is 2,2'-bipyridine'-5,5'-dicarboxylate). These Re(I) units are combined with Mn(II) fragments in a 1:1 ratio to afford a three-dimensional MOF based on Mn(II)-carboxylate chains that are crosslinked by $\{\text{Re}(\text{CO})_3(\text{diimine})\text{Cl}\}$ units. The rhenium-based ligand was chosen partly because the $fac\text{-}\{\text{Re}(\text{diimine})(\text{CO})_3\text{Cl}\}$ moiety is photoactive in its own right, undergoing a facial to meridional rearrangement of the three CO ligands under prolonged UV irradiation (such that two CO ligands rearrange to lie opposite one another). In addition, it is also a photosensitizer, having a metal-to-ligand charge-transfer (MLCT) excited state that can react with nearby species by photoinduced electron transfer or energy transfer⁹. The resulting MOF displays channels lined with the Re(I) units, making this an interesting example of a MOF that contains photochemical sensitizers in a regular, ordered array surrounding cavities where substrates could bind.

A second, structurally analogous material was built, using the same ligand L (2,2'-bipyridine'-5,5'-dicarboxylate) but with Mn(I) instead of Re(I), giving a MOF that contains $fac\text{-}\{\text{Mn}(\text{diimine})(\text{CO})_3\text{Cl}\}$ units interconnecting Mn(II)-carboxylate chains. Although not a photochemical sensitizer in the same way as its Re(I) analogue, the $fac\text{-}\{\text{Mn}(\text{diimine})(\text{CO})_3\text{Cl}\}$ unit is also capable of undergoing isomerization to the meridional tricarbonyl isomer under UV excitation.

Champness, George and co-workers demonstrated the photochemical reactivity of the two $\{\text{M}(\text{diimine})(\text{CO})_3\}$ units by UV excitation of single crystals, which resulted in fast conversion of the $fac\text{-}$ to the $mer\text{-}\{\text{M}(\text{diimine})(\text{CO})_3\}$ unit in both cases. This was revealed by changes in the infrared spectra, and changes in the electron density distribution obtained from single-crystal X-ray diffraction studies. The degree of conversion was about 10% for the rhenium fragment and 25% for the manganese one. The crystalline host lattice of the MOF has thereby provided an environment in which photochemical isomerization reactions can take place. This constitutes a unique example of photochemically triggered post-synthetic modification of a MOF — something that is normally achieved only by chemical means¹⁰ — because the chromophores concerned are part of the MOF superstructure. These observations pave the way for many intriguing possibilities, such as use of MOFs as hosts to stabilize short-lived photochemically generated species, and the development of photochemical reactors in which the excited

states of units such as $\{\text{Re}(\text{diimine})(\text{CO})_3\text{Cl}\}$ built into the MOF framework can induce transformations of guest species that have diffused into the cavities.

Ultimately an important goal in the general field of supramolecular chemistry is to make an artificial catalyst that can harvest light and use it to effect a useful transformation (or a series of transformations). An artificial system that uses light to catalyse the conversion of CO₂ into fuel, as in the photosynthetic reaction centre of plants and bacteria, may be a long way off but represents one of the most important challenges that modern chemistry faces, and Champness, George and co-workers have taken one more step towards that goal. □

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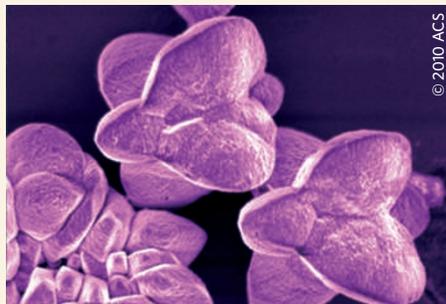
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IONIC SELF-ASSEMBLY

Porphyrins pair up

Porphyrins — macrocycles that can accommodate a metal ion in their centre through coordination to four nitrogen atoms — easily assemble into a variety of supramolecular architectures. In a collaboration between several institutions in the USA and Portugal, a team of researchers led by John Shelnutz at Sandia National Laboratories have now observed the ionic co-assembly of sulfonate and pyridinium porphyrins into binary dendritic architectures that resemble four-leaf clovers (pictured; *J. Am. Chem. Soc.* **132**, 8194–8201; 2010).

The metal atoms that occupy the central cavity of porphyrins confer on them particular electronic properties: a macrocycle hosting a zinc(II) atom is the electron donor, whereas one hosting



a tin(IV) atom is the electron acceptor. Despite this, the morphology of the self-assembled architectures was found to be largely independent of the metals. Rather, it depends on the temperature and the ionic strength of the reaction solution — both factors that modify the diffusion rates of

the porphyrins, and thus the rate of the self-assembly process.

Four binary anionic-cationic combinations (Sn/Zn, Zn/Sn, Sn/Sn and Zn/Zn) all formed closely related structures. X-ray powder diffraction measurements revealed that they also adopted similar crystalline packing, regardless of which metal occupied the central position of which porphyrin. This shows that the ionic interactions between the porphyrins, rather than those arising from the metals, mainly drive the self-assembly process.

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