

## METAL–ORGANIC FRAMEWORKS

## A tale of two entanglements

Entanglement of interpenetrating metal–organic frameworks has been considered a drawback to porosity. However, the pore size of these structures can be controlled through framework dynamics to achieve selectivity and increased binding of ions and gases.

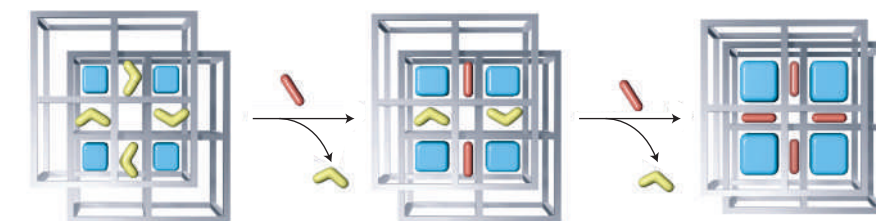
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**M**etal–organic frameworks (MOFs) are extended porous structures composed of transition metal ions (or clusters) that are linked by organic bridges. They are prepared as crystalline solids by solution reactions of metal ion salts with organic linkers. A wide variety of metal ions and organic reagents have been used leading to over 2,000 MOF structures with compositional and architectural diversity unparalleled by any other class of materials. Among these are the original MOFs with very open structures and ultrahigh porosity that recently have been shown to be important for gas (hydrogen, methane and carbon dioxide) storage and separation, among many other applications<sup>1</sup>. However, from its very beginning, the chemistry of MOFs had a real limitation, or so it seemed: when long organic links are used in building certain nets, especially those of primitive cubic topology, the resulting frameworks are entangled over the entire crystal structure<sup>2</sup>. In other words, two or more independent frameworks are found completely interpenetrated to fill what otherwise would have been large pores. Often, this precludes binding of guests. This is nature's way of filling up space; an aspect that many considered a drawback to porosity. Recently, a number of studies showed that interpenetration is not quite so bad as once thought, especially with respect to increasing hydrogen volumetric density uptake in MOFs. Indeed even highly entangled MOFs can be designed to be highly porous<sup>3</sup>.

The latest benefits of MOF entanglements are reported on page 142 of this issue<sup>4</sup> by T. Maji, and co-authors, who elegantly show that interpenetrating MOF structures can expel gases and shift with respect to each other to change their pore dimension and provide highly selective and increased binding of ions and gases. To build the MOF structure,



**Figure 1** Shifting networks. A schematic of two infinite entangled (interpenetrated) MOF networks having water (blue) and dicyanamide (yellow bent rods) as guests. When the latter is exchanged with a linear ion such as  $\text{N}_3^-$  (red rods), the two networks shift towards each other to make more space for water molecules and consequently uptake 25% more carbon dioxide than the original crystal.

the researchers combined Ni(II) ions with two kind of linkers: a long slightly flexible bpe (1,2-bis(4-pyridyl)ethane) and a short, more rigid, but bent  $\text{N}(\text{CN})_2$  (dicyanamide). The links serve as 'struts' in the resulting extended MOF structure, which is based on a primitive cubic topology, and can be viewed as Ni–bpe square layers that are linked together along the perpendicular plane by dicyanamides to form a three-dimensional (3D) porous structure. This arrangement encompasses a large volume into which another identical framework is entangled throughout the infinite lattice of the crystal to yield smaller pores in rectangular and hexagonal shapes. As a third framework would not fit in the remaining space, these pores are found instead to be occupied by excess dicyanamide anions and water molecules, respectively.

The material behaves in some remarkable ways previously thought to be unlikely for solids with 3D structures. The researchers found that when the water guests in the hexagonal pores are evacuated, the remaining space has high affinity for carbon dioxide molecules. Even though the openings of the pores are large enough to permit diffusion of oxygen and nitrogen gas, these are completely excluded. Yet carbon dioxide molecules, with a similar size, can enter. Maji *et al.* propose that the strong interaction of oxygen and nitrogen with the pore walls clogs the entrance and prevents any gas molecule from entering.

However, in the case of carbon dioxide the strong dipole-induced dipole interaction between the carbon dioxide and the bpe links overcomes this impediment. This means that the MOF entanglement selects guests not just based on their size and shape but also according to their 'electronic fit' within the internal structure of the pore complex. The pores of these MOFs are highly polarized environments that can have an impact on the course of adsorption, as illustrated here for carbon dioxide versus oxygen and nitrogen.

Another unusual feature of the MOF of Maji *et al.* is the possibility of changing the pore size by selective guest exchange, as shown schematically in Fig. 1. The researchers found that on exchanging bent dicyanamide guests with linear  $\text{N}_3^-$  ions, the two frameworks shifted to enlarge the hexagonal pores as a result of contraction of the rectangular pores. The expansion is beautifully confirmed by a 25% increase in carbon dioxide uptake in the  $\text{N}_3^-$ -exchanged material relative to the original material.

On a fundamental level, this research clearly shows that MOF structures can be built to be rigid, but that when entangled can provide pathways to fluxional and adaptable behaviour for highly selective binding of guest molecules<sup>5</sup>. One may even say that endless entanglements of this kind provide a way for the 'designer' to impart complexity on solid-state structures commonly believed to be incapable of

'pumping' and 'flexing' dynamics. We should have expected this from MOF structures especially as they are constructed from well-defined molecular units that are in themselves capable of dynamic behaviour, which they should largely maintain even when held together in a crystal structure.

Could the ideas illustrated by these two entangled frameworks be the basis for designing crystals capable of responding to a stimulus (light, pressure or pH) by shifting their components to release a drug molecule or trap a harmful contaminant? I believe this will be achieved in due course, as the tale of such entanglements is as endless as they are.

#### References

1. Li, H., Eddaoudi, M., O'Keeffe, M. & Yaghi, O. M. *Nature* **402**, 276–279 (1999).
2. Batten, S. R. & Robson, R. *Angew. Chem. Int. Edn* **37**, 1460–1494 (1998).
3. Reineke, T. M. *et al. J. Am. Chem. Soc.* **122**, 4843–4844 (2000).
4. Maji, T., Matsuda, R. & Kitagawa, S. *Nature Mater.* **6**, 142–148 (2007).
5. Kitagawa, S., Kitaura, R. & Noro, S. *Angew. Chem. Int. Edn* **43**, 2334–2375 (2004).

## RESPONSIVE MATERIALS

# Soft answers for hard problems

Soft matter has the remarkable ability to respond to stimuli in a variety of ways. Not only does this enable its application to existing scientific problems, but it also allows previously unimagined technological directions to be explored.

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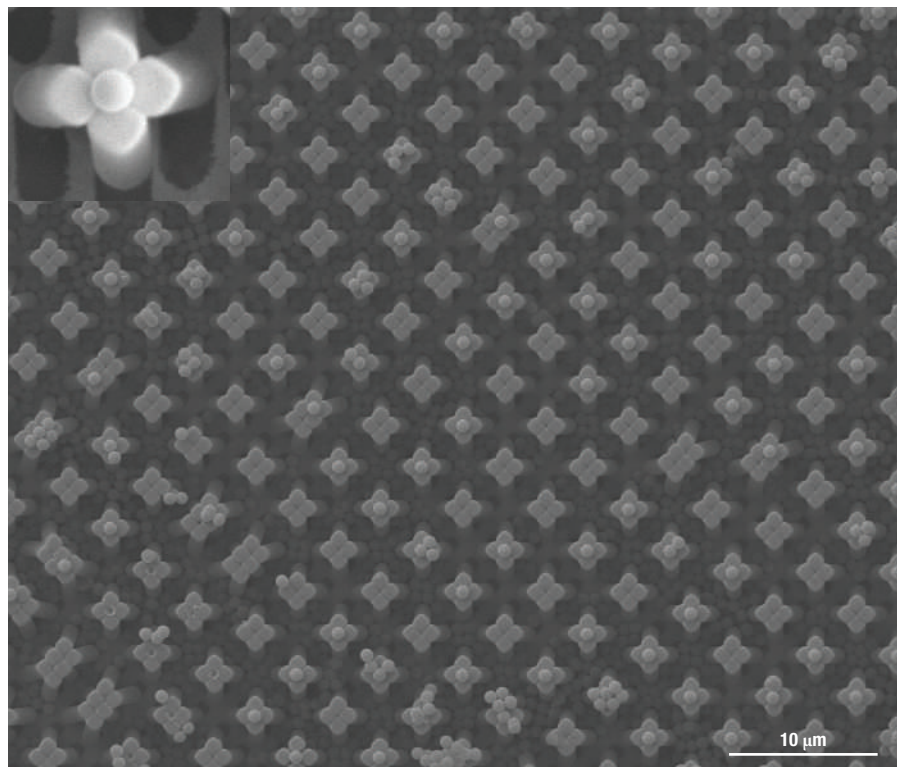
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It is becoming increasingly clear that novel approaches to applications such as biomimetic sensing and actuation demand the synthesis and manipulation of 'soft' materials, with their unique capacity to respond to external stimuli. Indeed, research on soft materials has recently increased dramatically, and is attracting equal attention from chemists, physicists and engineers. Hundreds of researchers convened at a symposium\* devoted to the topic as part of the 2006 Fall Meeting of the Materials Research Society in Boston, Massachusetts, USA, to explore new functionalities of responsive soft materials, highlighting the timeliness of this area and revealing surprising versatility among materials formerly dismissed as 'weak'. Indeed, ordinarily disparate fields ranging from robotics to hydrogels and from peptides to nanofabrication were brought together by the common feature of responsiveness. Sessions focused on artificial muscles, controlled release of drugs, dynamic surfaces, photonic and phonic materials, and assembly of soft material structures.

In the area of stimuli-driven actuation — artificial muscles — Tim Swager (MIT, USA) presented exciting molecular-level

approaches, where rigid polymer molecules contained 'hinges' in the form of multiple-ring aromatic moieties that change conformation on electrical reduction or oxidation. These conformational changes are amplified mechanically to measurable strains, although it was pointed out that significant effort is still needed to scale-up the

phenomena to yield functioning actuators. In contrast, Ray Baughman (UT, Dallas) explained the inner workings of his group's recently reported chemical actuation system (Ebron, V. H. *et al. Science* **311**, 1580–1583; 2006), which combines exothermic chemical reactions with heat-driven two-way shape-memory alloys (SMAs). In an inspirational



**Figure 1** Selective assembly of particles on the top of polymer superlattices, where the surface of individual micropillars was coated with thermoresponsive polymer brushes. Trapped microspheres can be seen on some groups of pillars, and one is shown magnified in the inset.

\*Symposium A: *Responsive Soft Matter — Chemistry and Physics for Assemblages, Films, and Forms* Materials Research Society Fall Meeting, Boston, Massachusetts, USA, 27 November to 1 December 2006.