

molecule–tip bonds can stretch without breaking, the system shows a weak change in conductance on modulation of the tip–substrate distance. In contrast, conduction in a non-bonded system is dominated by tunnelling through the solvent, which shows a much stronger dependence on the tip–substrate distance.

Measuring the current response while modulating the tip–substrate distance with the STM tip enabled the researchers to determine unambiguously whether the molecule was bridged between the two contacts, and to study the current–voltage characteristics of the molecular device. They observed a rectifying behaviour, and showed that the ‘high current’ direction corresponded to the current flowing from the dipyrimidinyl to the diphenyl moieties. In good agreement with theoretical calculations, Tao and co-workers suggested that this is due to the localization of the

orbitals at one end of the molecule under an applied bias.

When the non-symmetric molecule was bound to only one electrode, however, the current–voltage characteristics measured were found to be symmetrical. This clearly shows that the molecule–contact coupling also has a significant effect on the current flow through the device, in addition to the non-symmetry of the molecule itself. In fact, breaking the coupling symmetry of the contacts is another possible route to a rectifying behaviour, and can induce rectification even with a symmetric molecule. This is illustrated in Fig. 1b,c; in the case shown, the coupling of the molecule is much stronger with one of the contacts — here, the density of molecular states between the contact Fermi levels is much higher in Fig. 1c, leading to a higher current in this bias direction.

Since the thought experiment of Aviram and Ratner, molecular electronic structures

have proved to be well suited for the study of energy coupling at the nanoscale, and have contributed to our fundamental understanding of charge flow. An efficient electronic technology based on molecular components may not yet be possible, but 35 years of molecular electronics have provided important insights about both molecules and the ultimate limits of charge-based electronics. □

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METAL-ORGANIC FRAMEWORKS

Entering the recognition domain

The host–guest properties of metal–organic frameworks have usually relied on molecular separation by the pore aperture or non-specific binding with the pore walls. Incorporating supramolecular recognition units into the frameworks has now enabled the docking of a specific guest.

Kimoon Kim

Molecular recognition arises from specific interactions between two or more molecules through non-covalent bonds. It is crucial in biological processes, as illustrated by various ligand–receptor systems such as enzyme–substrate or antigen–antibody, often described as a ‘lock-and-key’ fit¹. Inspired by nature, chemists have developed synthetic receptors to entrap specific guest molecules with high affinity and selectivity based on their size, shape and

fit to the recognition site. Metal–organic frameworks (MOFs) — crystalline materials built with inorganic joints (metal ions or clusters) and organic struts (ligands that associate with two or more inorganic joints) — have attracted increasing attention for their porous structures². In *Science*, Qiaowei Li, Wenyu Zhang and co-workers from the University of California, Los Angeles, and Northwestern University report how they have now combined these two approaches

to prepare a new type of MOF with built-in synthetic receptors to capture specific organic species by molecular recognition³.

MOFs have stable structures with accessible pores and large surface areas, so they show great promise as molecular sieves and sponges for small organic molecules or gases. To date, most MOFs have used two architectural ‘domains’ — the aperture of pores representing the sorting domain and their internal surface, the coverage

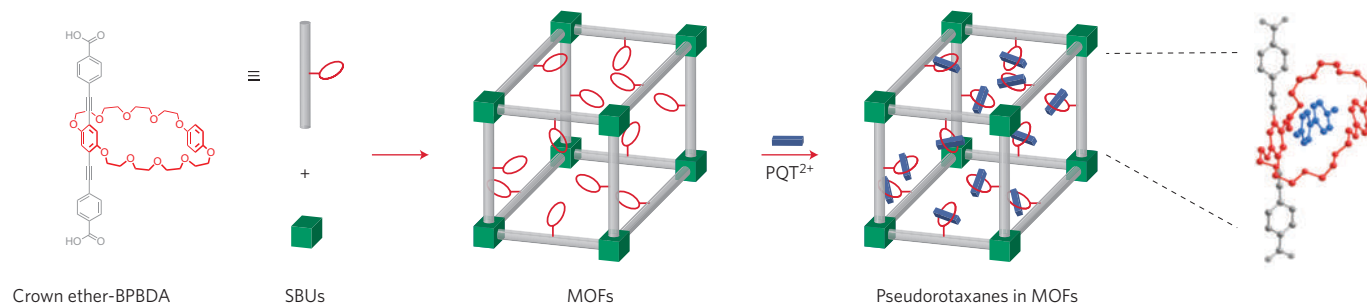


Figure 1 | Illustration of the way molecular recognition sites are incorporated into MOFs. MOFs are built from octahedral zinc oxo-clusters [Zn₄(O)(CO₂)₆] as secondary building units (SBUs; green building blocks) and organic struts (BPBDA; grey rods), each comprising a built-in recognition sites (crown ether; red rings) for the inclusion of paraquat dications (PQT²⁺; blue rods), as shown in the structure on the far right.

domain. The aperture enables the separation of guests according to their size and shape, whereas the internal surface provides space to accommodate them⁴. However, the binding of guest molecules on the pore walls is usually non-specific and weak, which only allows the frameworks to serve as passive platforms for the adsorption of gases and molecules. In their approach, Li, Zhang and co-workers have now introduced molecular-recognition sites as a third domain in MOFs, to manoeuvre and dock incoming guests in a highly selective manner, controlled by stereochemistry and electronic interactions (Fig. 1).

The researchers designed a MOF based on the topology of MOF-5 — a rigid, three-dimensional framework formed by linking octahedral zinc oxo-clusters $[\text{Zn}_4(\text{O})(\text{CO}_2)_6]$ with linear benzene dicarboxylic acid ligands as a strut⁵. They had previously found that using a longer strut (1,4-bis(phenylethynyl)benzene dicarboxylic acid; BPBDA) led, under the same reaction conditions, to the formation of a framework (MOF-1000) with the same topology as that of MOF-5. As often happens with highly porous MOFs, MOF-1000 consists of four interpenetrated frameworks — where the pores of one network are occupied by three other identical, independent structures — so that its void space is significantly reduced. However, despite this blockage, obtaining the same topology encouraged the researchers to use the same synthetic procedure to introduce recognition sites within the frameworks.

Long phenylethynyl ligands were modified to bear macrocyclic polyether rings — 34- and 36-membered crown ethers that have been extensively used as receptors for electron-deficient molecules. When these ligands were used as organic struts under the same reaction conditions, the new frameworks MOF-1001 and MOF-1002, respectively, were obtained. Despite the large unit-cell parameters, it was possible to determine the structures of the two MOFs by single-crystal X-ray diffraction.

As expected, they showed the same cubic framework topology as MOF-1000,

with $\text{Zn}_4(\text{O})(\text{CO}_2)_6$ clusters as octahedral joints linked by linear ligands. Moreover, the macrocyclic receptors were integrated precisely and periodically inside the resulting robust frameworks. In these new frameworks, the built-in macrocyclic units not only offer recognition sites for guest molecules, but they also prevent the interpenetration of frameworks, thus allowing high volumes of open space for incoming substrates in the pores. Molecular-modelling calculations suggest that more than 85% of the unit-cell volume of MOF-1001 is available for the inclusion of guest molecules.

The researchers then investigated the molecular recognition properties of MOF-1001, using the built-in macrocycles as docking sites. The macrocycles are known to bind paraquat dications (1,1'-dimethyl-4,4'-bipyridinium; PQT^{2+}), a herbicide⁶. The crystals of MOF-1001 immediately turned red on soaking in a saturated solution of PQT^{2+} in acetone, which indicated the formation of charge-transfer complexes between the electron-deficient cations PQT^{2+} and the electron-rich crown ether units. This process may also be viewed as the formation of pseudorotaxanes in which the macrocycles (rings) comprise the PQT^{2+} cations (axles). The reappearance of the original light-yellow colour on rinsing the crystals with acetone showed that the uptake of PQT^{2+} is reversible, and X-ray powder diffraction analysis confirmed that the crystallinity of the framework remained intact during the process.

A combination of NMR spectroscopy and single-crystal X-ray diffraction studies provided unequivocal evidence of the host-guest interaction between the crown ether unit and PQT^{2+} , and revealed that each built-in crown ether unit in MOF-1001 encircled one electron-deficient PQT^{2+} through π - π stacking and C-H...O hydrogen-bond interactions. In a control experiment, negligible uptake of PQT^{2+} of a MOF with a similar structure but devoid of polyether struts confirmed that the built-in macrocycles are crucial for the substrate docking, and that the uptake of PQT^{2+} occurs through stereo-electronic host-guest

interactions rather than non-specific diffusion and adsorption processes.

The field of MOFs has developed rapidly over the past decade. With emerging properties and functions, MOFs have already shown great promise in many applications that had not been envisaged with other porous materials, such as in enantioselective catalysis and biological applications, including drug delivery⁷. As beautifully demonstrated by Li, Zhang and co-workers in this work, a new level of complexity has now been incorporated into MOFs through the introduction of recognition sites built-in pores. This type of MOF with active recognition domains have great potential in many applications ranging from the detection and capture of toxic chemicals to the storage and controlled release of drugs. The synthetic manipulation of built-in hosts within MOFs may allow them to be used in catalysis.

During the past decade, molecular machines and switches based on rotaxanes and pseudorotaxanes have been extensively studied⁸. Building these into MOFs may thus offer interesting functions for applications in molecular electronics, such as memory and switches. With new features of MOFs, many avenues of research still remain to be explored. This new concept sends signals to the scientific community that MOFs can function not just passively, but as smart materials, adapting and responding to their environment or external inputs. □

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