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# Rectifying current behaviours

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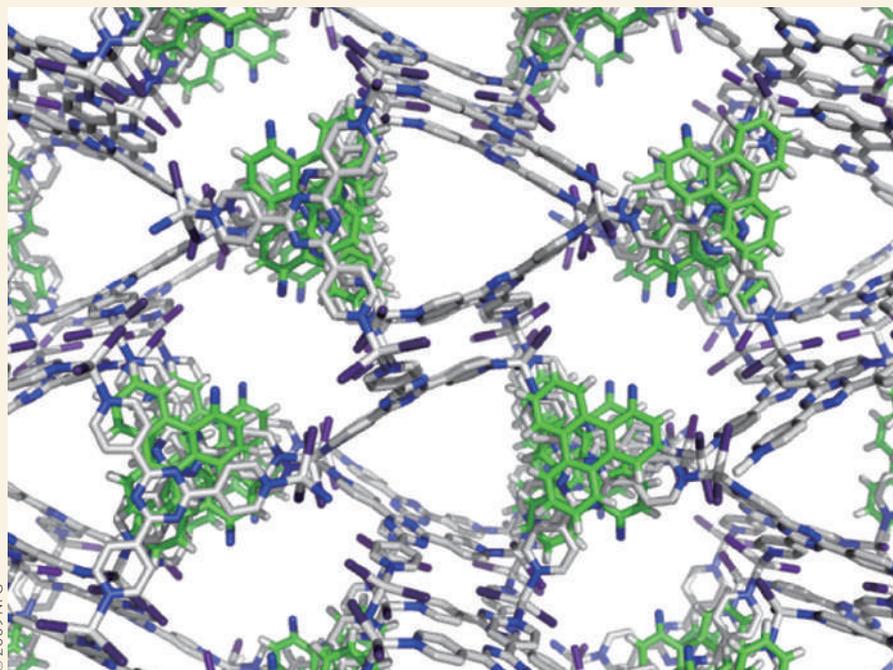
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## X-RAY CRYSTALLOGRAPHY

## Transient trapped



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By their very nature, determining the structure of transient intermediates is difficult, and usually requires the use of a variety of spectroscopic techniques at low temperature. X-ray crystallography is

the gold standard for structural analysis, but the requirements for obtaining a crystal structure and for observing a highly reactive intermediate would usually be regarded as mutually exclusive.

Now, Makoto Fujita and co-workers from the University of Tokyo and the Japan Science and Technology Agency have shown that conducting an imine formation inside the pores of a coordination polymer can stabilize the transient hemiaminal intermediate sufficiently to allow an X-ray crystal structure to be obtained (pictured; *Nature* **461**, 633–635; 2009). The porous coordination polymer is formed from a flat, aromatic trivalent ligand — trispyridyltriazine (light grey and blue) — which coordinates to zinc. The network formed is an ideal host for a large flat aromatic amine — aminotriphenylene (green) — so that the amino group is presented in the open pores.

When a single crystal is mounted on the diffractometer and then exposed to acetaldehyde, the amine reacts with the aldehyde inside the pores. Cooling the crystal to 90 K is sufficient to 'pause' the reaction so that an X-ray crystal structure of the intermediate can be obtained. This approach could offer a general method to acquire snapshots of chemical reactions that cannot be monitored by other means.

STEPHEN DAVEY

## MOLECULAR ELECTRONICS

## Rectifying current behaviours

Inorganic semiconductors have long been used to construct rectifying diodes, but making them out of single molecules has remained a challenge. Now, two separate studies have induced rectification behaviour within molecular systems through different approaches.

David Janes

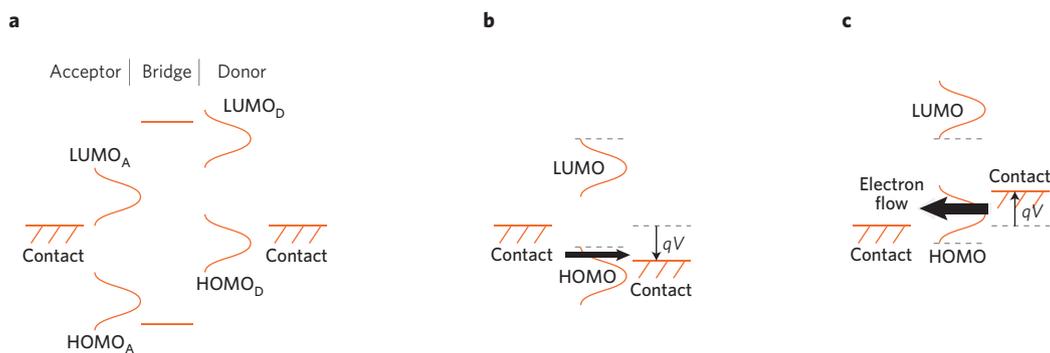
**R**ectifiers, which allow an electrical current to flow in one bias direction but not in the other, are widely used for a variety of devices. But although efficient rectification in bulk semiconductor materials has been well known and well understood for many years, observations of comparable behaviour in molecular systems is much more recent. Several articles have now reported investigations of such molecular rectifying diodes, and two studies in particular illustrate the significant role

of both the molecular structure and the metallic contacts to the molecule.

On page 635 of this issue, Nongjian Tao and co-workers report how they have combined experiment and theory to prepare a non-symmetric molecule, containing dipyrimidinyl and diphenyl moieties, that shows rectification behaviour<sup>1</sup>. In a different approach described in *Proceedings of the National Academies of Science*, Jinlong Yang, Jianguo Hou and co-workers have induced rectification and switching behaviours in a melamine molecule adsorbed on a

copper surface, using the tip of a scanning tunnelling microscope<sup>2</sup>.

The concept of a single-molecule rectifier was first introduced in 1974 by Aviram and Ratner<sup>3</sup>. They proposed a molecule, attached to two conductive electrodes, which consisted of a  $\pi$ -donor and a  $\pi$ -acceptor moiety separated by a  $\sigma$ -bonded bridge. They predicted that the molecular orbital energies would not be symmetric owing to the donor–acceptor structure (Fig. 1a), and that the presence of the bridge would prevent any 'spill over' of the orbitals



**Figure 1** | Energy-band diagrams for metal/molecule/metal systems, illustrating two different approaches used for rectification. **a**, Aviram-Ratner configuration, in which the molecule consists of a  $\pi$ -donor and a  $\pi$ -acceptor moiety separated by a  $\sigma$ -bonded bridge. Rectification is caused by different alignments of the donor and acceptor levels in the two bias directions. **b,c**, Positive (**b**) and negative (**c**) bias conditions for a device with non-symmetric contacts (the dashed lines indicate the zero-bias case). In the case illustrated, the coupling to the right contact is much stronger. Under an applied bias, the Fermi levels of that contact therefore have a stronger influence on the energy of the molecular levels, shifted by the energy  $qV$  (where  $V$  is the applied voltage and  $q$  the electronic charge). As the two bias directions yield different densities of molecular states in the energy range between the two contact Fermi levels, the resulting currents will be different. Note that the dominant current flow is through the HOMO level in both bias directions.

between the two moieties. This would in turn lead to an enhanced current flow in one bias direction, and non-symmetric current-voltage characteristics would be observed.

Such molecular devices remained 'thought experiments' for almost 25 years, until the first experimental reports of the resistance of a molecule between metallic contacts and a 'unimolecular' rectifier<sup>4,5</sup>. Since then, significant progress in that field has required the development of new tools, including approaches for immobilizing molecules on conductive surfaces, realizing well-controlled contacts, and characterizing the resulting structures.

A molecular device, that is, a single molecule between two metallic contacts, can best be viewed as a nanoscale system with different properties from those of the isolated molecule or contacts. The properties of the isolated molecule or molecular crystals, such as the energies of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively), represent a useful starting point for designing a device. On binding to the metallic contacts, the energy of these orbitals are broadened and shifted. Under an applied bias, the molecule is far from its equilibrium conditions, which can potentially result in significant electronic and/or structural reconfigurations — for example, contact-induced redox events can modify the local charges, which may explain many observed memory effects<sup>6</sup>.

In contrast to inorganic semiconductors and organic thin-film devices, which can be understood using bulk electrostatic models and bulk materials parameters such as carrier mobility and doping, molecular electronic devices require an understanding

of conduction at the nanoscale. Charge transport through such a system can be quantitatively described in terms of the Landauer formalism, in which an electron moves, often ballistically, from a filled electron state in one contact to an empty state in the other contact. Although this process is broadly referred to as tunnelling, Landauer-based approaches<sup>7</sup> provide a means to incorporate the specific number and density of electronic states associated with the molecule; model its dependence on the bias applied; and understand effects such as rectification. The probability of an electron traversing the device at a given energy is proportional to the density of states in the molecule's energy levels, and the strength of the coupling between the molecule and the contacts. The two articles described here provide illustrative examples of how rectification can be achieved by altering these aspects of the system.

One approach to inducing rectification is by controlling the non-symmetry of the molecule, essentially extending the original Aviram and Ratner approach (Fig. 1a). However, as Tao and co-workers point out, non-symmetry in the molecule does not necessarily imply non-symmetry in the current-voltage relationship. Rectification requires a molecular structure in which the molecular energy levels within various sections of the molecule are affected differently by a bias, resulting in a higher current density in one direction.

In the study by Yang, Hou and co-workers, the conducting properties of a molecule are modified using surface chemistry and probed using a scanning tunnelling microscope (STM). They first adsorbed a melamine molecule on a copper

surface. On application of high-voltage pulses through the STM tip, the researchers observed that the molecule acted as a rectifier. They suggested that this was due to a current-induced tautomerization process by the displacement of a hydrogen atom in the head group of the molecule. In addition, the melamine molecule also showed conductance-switching properties. This is believed to be caused by a bond-rotation process that enables the new tautomer to adopt two configurations. Essentially, in these processes the head group can be systematically altered in a controlled manner while the groups bonded to the substrate remain unchanged.

In their approach, Tao and co-workers prepared a non-symmetric molecule consisting of two phenyl and two pyrimidinyl rings. They then assembled the molecules on a gold electrode, using selective protection and deposition techniques to control their orientation. Different protecting groups (trimethylsilylethyl and cyanoethyl) were employed at each end of the molecule: this allowed the cyanoethyl group to be removed first so that the molecules self-assembled in a monolayer with the diphenyl end on the gold surface.

Tao and co-workers then used a special probing technique to discriminate between chemisorbed and physisorbed contacts. The gold substrate on which the molecules were deposited was used as one of the contacts and an STM tip was used as the other, which allowed fine control of the tip-to-substrate distance. When the tip and the molecule are chemically bonded, the conduction between the tip and the substrate occurs through the bridged molecule. As the Au-Au and

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.

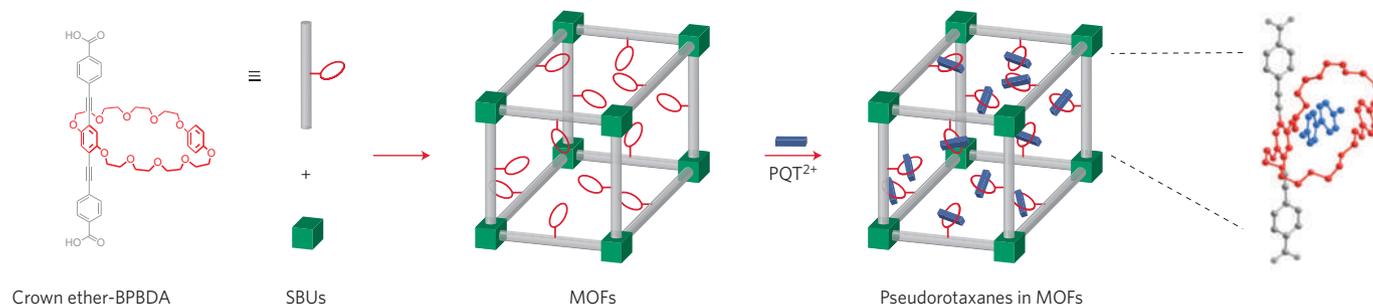
Kimoon Kim

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’ fit<sup>1</sup>. 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 structures<sup>2</sup>. 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 recognition<sup>3</sup>.

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 [ $Zn_4(O)(CO_2)_6$ ] 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 (PQT<sup>2+</sup>; blue rods), as shown in the structure on the far right.