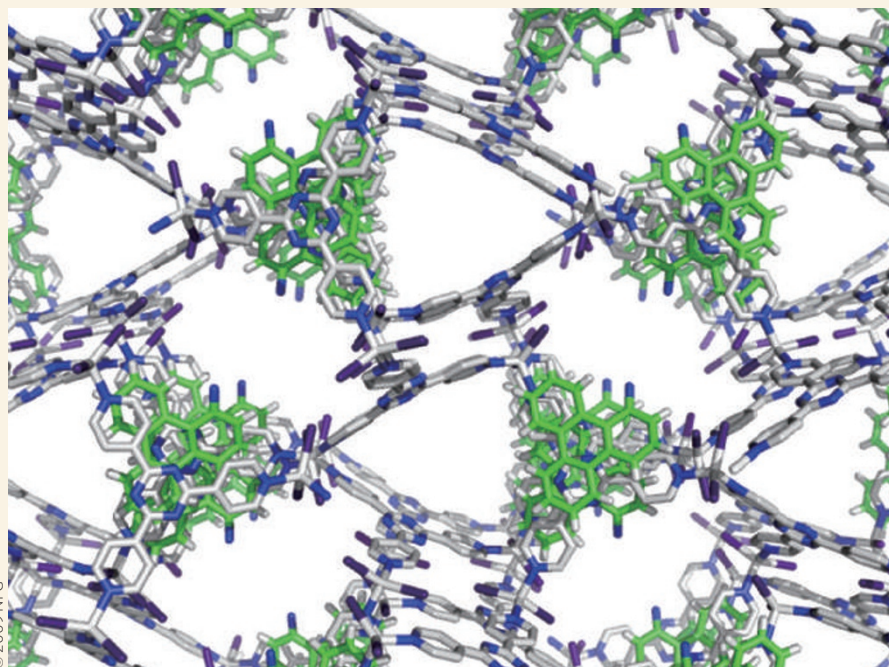


## X-RAY CRYSTALLOGRAPHY

## 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