PLANETARY SCIENCE

Polar roller

In July 2005, the Cassini space probe observed immense plumes of water vapour (pictured) spouting from an anomalously warm region near the southern pole of the saturnian moon Enceladus. That spectacular observation confirmed a long-held belief that Enceladus is the source of the icy grains that make up its home — the outer lane, or 'E ring', of Saturn's ring system.

But why are these plumes where they are? In this issue, Francis Nimmo and Robert T. Pappalardo

(*Nature* 441, 614–616; 2006) show that the spout's polar location could, theoretically, be explained by the formation of a diapir, an upwelling region of low-density material, in Enceladus' interior. Simple gravitational considerations require that the moon swings round so that this less weighty, tectonically active region is aligned with the moon's axis of rotation — and so ends up at the pole.

There are caveats. The authors show that if the diapir is within

Enceladus' subsurface ice shell, then the moon's outermost layer, or lithosphere, must be relatively rigid. Otherwise, the upwelling material would simply bulge out from the surface. That region would then tend to migrate not towards the poles, but towards the moon's equator.

A diapir within Enceladus' silicate core, on the other hand, would cause a poleward reorientation. But it would preclude the existence of a global subsurface ocean: such an ocean would decouple the core gravitationally from the ice shell, preventing reorientation.

Nimmo and Pappalardo's low-

density diapir should be detectable through its effect on the moon's gravity field. Further analysis of data returned by radio instruments aboard Cassini should provide a conclusive test for its existence.

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activated carbons do not permit such structurally well-characterized arrangements: their larger pore sizes mean that the guest molecule always has some freedom to move, resulting in highly disordered arrays that must be modelled statistically.

Compared with conventional hosts, coordination polymers also possess unusual flexibility and their physical and chemical properties can be tuned by adding specific functional groups at the surface. Their molecules and ions can also be designed in minute detail. Complex frameworks can thus be built up, in which clusters, wires, ladders and other exotic molecular conformations can be contained. Molecules confined to these pore networks experience an unusually high, internally generated pressure⁶, giving rise to condensed assemblies whose properties differ from those of the bulk solid or those of assembled forms in an ambient environment.

Takamizawa *et al.*³ investigated oxygen trimers included along a channel constructed from a linear chain of a coordination polymer over a wide range of temperatures, from room temperature down to 10 K. They observed an evolution from a 'softer', more flexible assembly of oxygen trimers at higher temperatures to a rigid, three-dimensional ordered assembly at the lowest temperatures. Analysis of the geometry of the trimers showed that the internal distance between the trimer elements increased steadily with temperature, but that the distance between trimers first decreased to a minimum at around 90 K, and then increased once again. This indicated the presence of an intermediate, unstable phase at minimum trimer separation that could — according to measurements of magnetic correlations between the trimers involved — be treated as a quasi-one-dimensional chain of oxygen molecules.

Interestingly, the authors also show that this intermediate trimer structure changes its form under the influence of a magnetic field. Porous crystalline coordination polymers are often much more dynamic than is generally believed, and numerous studies have shown

that they possess a structural flexibility that can lead to physical changes when an external stimulus — in most cases the chemical stimulus of a guest molecule — is applied⁷. In Takamizawa and colleagues' case³, it seems that the host framework itself flips back and forth between states, allowing the oxygen trimer to change its form in response to the applied magnetic field. This demonstration follows the magnetically induced rearrangement of an included oxygen dimer last year⁸.

These results could lead to new methods for the remote control of molecular structures. Whereas molecular devices that respond to light have been readily synthesized, similar systems that respond to magnetic fields have not, as the energy contained in magnetic interactions is generally too small to drive structural transformations. Magnetically induced phase transitions in an assembly of included guest paramagnetic molecules offer a way round this

obstacle, as even a small stimulus could give rise to larger-scale structural change in both guest and host. In particular, guest molecular clusters could provide new quantum spin states that are strongly coupled to those of the polymer structure surrounding them.

Because Takamizawa and colleagues' polymer framework is so flexible, it can easily accommodate guest compounds that are not just paramagnetic, and thus responsive to magnetic fields, but also dipolar, and therefore sensitive to electric fields. These molecules range from heterodiatom molecules such as carbon monoxide (which is dipolar) and nitrogen oxide (paramagnetic and dipolar) to larger polyatomic molecules such as sulphur dioxide (dipolar) (Fig. 1). With so many guests to choose from, it is inevitable that new topics of discussion will arise concerning ultramicroscopy⁹. What is emerging is a new science of 'coordination space' that studies the role of nanospaces in determining the chemical and physical functions of guest and host frameworks.

Small gas molecules such as O₂, CO, NO and SO₂ have, in their separate ways, important roles in gas separation and storage, catalysis and pollution control. An in-depth understanding of field-responsive properties of the hybridized gas assemblies offered by Takamizawa and colleagues could pave the way to new applications in environmental, energy and life sciences.

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Figure 1 | Versatility of Takamizawa and colleagues' porous coordination polymer³. Coordination polymers provide nanometre-sized vessels to accommodate paramagnetic and/or dipolar molecules in low-dimensional arrays. Their flexible framework means that the host polymers can change their form to better suit their guests, allowing molecular configurations of gas molecules to be created — and subsequently readily released — without the need for extreme temperatures or pressures.

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