Molecule transforms metal–organic framework to become conducting

Although they have been around for just over a decade, metal–organic frameworks (MOFs) are already considered to be promising materials for gas storage, gas separation, drug delivery, and other conventional applications for porous materials. Many MOFs are inexpensive to synthesize, can be deposited under mild conditions, and are heat-tolerant and chemically stable. Alec Talin of Sandia National Laboratories at Livermore and the National Institute of Standards and Technology, Andrea Centrone of NIST and the University of Maryland, and their colleagues have taken these materials one step farther. By introducing a guest molecule within its pores, a well-studied MOF known as HKUST-1 becomes electrically conductive, opening an entirely new array of possible applications.

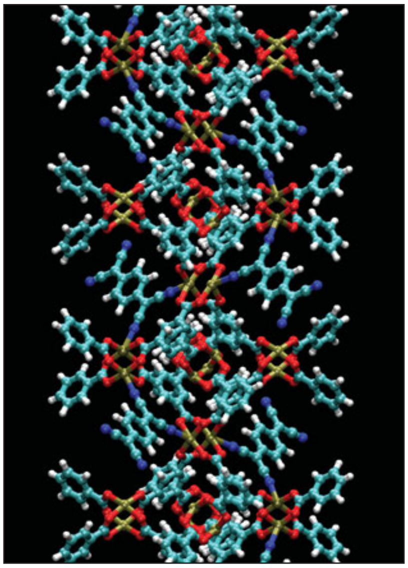
MOFs, as the name implies, are comprised of metal cations bonded to rigid organic "linkers," creating a stable nanoporous structure. With record-setting surface areas (as high as 7000 square meters per gram), they are ideal for applications such as CO_2 sequestration and catalysis. While efforts to develop MOFs for these applications made major strides over the past decade, electrically conducting frameworks were much more illusory. "What motivated us were the possible applications," said Talin, lead author of the study published in the January 3, 2014 issue of *Science* (DOI:10.1126/science.1246738; p. 66). He cites a host of promising avenues, such as novel electronic devices, photovoltaics, supercapacitors, and electrocatalysis.

But creating an electronically conductive MOF was not a simple matter. Until this innovation, virtually all known MOFs were electrically insulating, due to the primarily ionic nature of the metal-linker bonds. Rather than trying to change the framework itself, the research team took this different approach of introducing a guest molecule into the pores.

The molecule they chose, tetracyanoquinodimethane, or TCNQ, is also an insulating material. However, it has been known that in combination with other organic molecules or metal ions such as copper, TCNQ forms electron-conducting charge-transfer complexes. The researchers started with a well-known copper-containing MOF known as HKUST-1.

They soaked a thin film of HKUST-1 grown on patterned electrodes in a solution of TCNQ, causing the TCNQ molecules to infiltrate the pores. The result was startling: the MOF film became $>10^6$ times more conductive than the film without TCNQ. "The framework is insulating, the guest molecule is insulating," said Talin, "but when they come together, they make a conducting material."

Moreover, the effect is tunable. By altering the exposure time to TCNQ, the magnitude of the conductivity could be controlled. TCNQ is the first step, said Talin; there are many other types of guest molecules that create other electronic behaviors leading to a wide range of applications.



The molecule tetracyanoquinodimethane (TCNQ) was added to a metal–organic framework (MOF). The chain of TCNQ molecules creates an electrically conducting path through the MOF structure. The turquoise spheres represent carbon atoms, white are hydrogen, blue are nitrogen, red are oxygen, and bronze are copper. Courtesy of Sandia National Laboratories.

From here, Talin plans to investigate what happens when these MOF devices are scaled to much smaller dimensions, approaching those of molecular electronic devices that require a high level of adaptable control. Energy-storage and energy-conversion applications are also a top priority.

Meg Marquardt

Energy Focus

Inexpensive organic flow battery is metal-free

The mismatch between the availability of intermittent wind or sunshine and the variability of demand is a major obstacle to getting a large fraction of electricity from renewable sources. A growing number of engineers have focused their attention on flow battery technology, which reversibly converts chemical energy directly to electricity. Until now, flow batteries have relied on chemicals that are expensive or difficult to maintain, driving up the energy-storage costs. Now, a team of scientists and engineers from Harvard University has developed a metal-free flow battery that relies on the electrochemistry of naturally abundant, inexpensive, small organic (carbon-based) molecules called quinones, which are similar to molecules that store energy in plants and animals.

The active components of electrolytes in most flow batteries have been metals. Vanadium is used in the most commercially advanced flow battery technology now in development, but its cost sets a high floor on the cost per kilowatt-hour at any scale. Other flow batteries contain precious metal electrocatalysts such as the platinum.

As reported in the January 9 issue of *Nature* (DOI:10.1038/nature12909; p. 195), the flow battery developed by the Harvard team already performs as well as vanadium flow batteries, with chemicals that are significantly less

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