

CHEMISTRY

Framework Materials Grab CO₂ And Researchers' Attention

Porous solids have become a rich playground for chemists, who can tailor the materials' makeup for use in gas storage, filtering, and catalysis

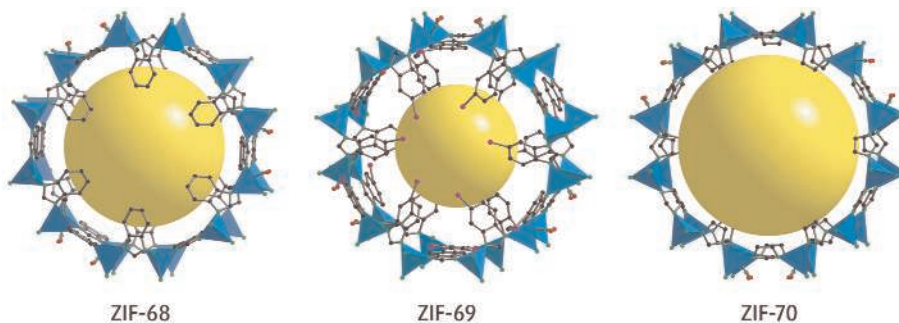
In most synthetic chemistry projects, researchers struggle to stitch molecules together one bond at a time. Not so in the lab of Omar Yaghi, a chemist at the University of California (UC), Los Angeles. Yaghi and his colleagues work to find just the right set of conditions so that entire networks of materials fabricate themselves when given the go-ahead.

In the late 1990s, Yaghi first worked out the formula for creating a family of highly porous, yet stable, crystalline materials known as metal organic frameworks. MOFs have a Tinkertoy-like construction with metals that serve as the hubs and connecting struts made from organic compounds. By tweaking his recipe, Yaghi and others have since made thousands of such porous crystals. That's made MOFs and related compounds one of the hottest playgrounds in chemistry, and Yaghi their greatest inventor. "His work is terrific," says Thomas Mallouk, a chemist at Pennsylvania State University in State College. "He does beautiful fundamental science that is knocking on the door of important applications."

On page 939, Yaghi and colleagues report a new robotic high-throughput scheme for creating MOF relatives known as zeolitic imidazolate frameworks (ZIFs). And Mallouk and others say that the work is again an important blend of fundamental research and a critical application: materials that might help coal-fired power plants filter out carbon dioxide from their smokestacks. Mallouk calls the new work "very clever" because Yaghi and his colleagues have designed their hubs and linkers to mimic the construction of zeolites, a family of natural porous compounds widely used as catalysts and filters in industry. But because ZIFs are stable at high temperatures and are easier to tailor by adding desired chemical functional groups, they may prove even more useful in the long run.

Attempts to gain control over open-framework materials have a long and frustrating history. The frameworks are synthesized in solution and can take on a wide variety of structures depending on the hubs and linkers used. For decades, however, researchers

found that their frameworks almost always collapsed when they removed the solvent. Equally troubling, they found it nearly impossible to make large pores, as multiple networks would form simultaneously and interpenetrate one another. Yaghi and colleagues solved both of these problems in the late 1990s. They increased the strength of their frameworks by selecting starting materials that preferentially assembled into a network of rigid prisms and cages. They also worked out designs that keep separate frameworks from interpenetrating. It's been off to the races ever since.



Carbon traps. Cagelike zeolitic imidazolate frameworks and their kin excel at straining carbon dioxide out of a mixture of gases, a knack that could lead to CO₂ scrubbers for power-plant smokestacks.

One key race is to create a MOF that can store hydrogen for use in future fuel-cell cars. High-pressure gas tanks do the job fairly well. But pressurizing gases is a big energy drain and can create a hazard if the gas tank is punctured in a crash. By filling part of the tank with a MOF's cagelike network built with hydrogen-absorbent metal hubs and organic struts, however, it is possible—at least in theory—to store more of the gas at a lower pressure. Slightly raising the temperature or releasing the pressure then liberates the gas. Yaghi's group and Jeffrey Long's group at UC Berkeley both recently created MOFs that can hold up to 7.5% of their weight in hydrogen, better than a benchmark for hydrogen storage set by the U.S. Department of Energy. Unfortunately, they only do so at 77 kelvin (−196°C), making them impractical for real-world use.

In July 2007, researchers led by William Goddard III of the California Institute of

Technology in Pasadena reported in the *Journal of the American Chemical Society* that adding lithium to a MOF should make it possible to store 6% of its weight in hydrogen at room temperature. Long says many groups are working on it, but "it's not trivial." Lithium, he points out, tends to hold strongly to solvent molecules after synthesis, and removing the solvent requires so much energy that it typically blows apart the framework.

Other MOF applications are pushing ahead as well. Several of the new ZIFs appear to have a strong preference for binding CO₂. Yaghi suspects that carbon-rich benzene rings in their struts act as valves that let CO₂ molecules pass in and out of the pores. Once inside, the CO₂'s carbon atoms, which have a partial positive charge, readily bind to nitrogen atoms in the framework, which carry a partial negative charge. Yaghi says ZIFs could be used to capture CO₂ in power-plant smokestacks. Once full, the ZIFs can be removed, and the ensuing pres-

sure drop would release the CO₂ from the pores, allowing the ZIFs to be reused. MOFs are also being looked at as filters for a variety of hydrocarbons.

Other teams are beginning to explore using the porous solids as scaffolds for catalysts. By tuning the materials to allow certain gases inside easily while excluding others, researchers can control which compounds in a mixture gain access to a catalytic metal atom inside. Because the materials are solids, they can easily be recovered and reused after running a reaction, unlike many highly active catalysts that must be separated from a solution. With all the possible ways to construct MOFs and their many applications, today dozens of groups around the world are streaming into the field. "Interest in these materials has been increasing extremely rapidly," says Long. "The trajectory is still going way upward."

—ROBERT F. SERVICE