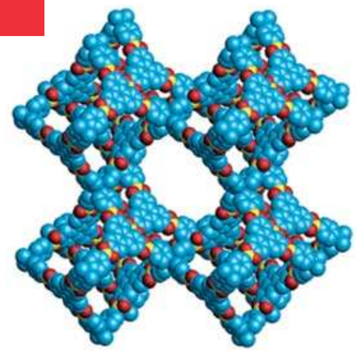
MATERIALS

Covalent organic frameworks debuted and multiplied quickly

The variety of porous, metal-free crystals and their applications has grown, but no signs yet of commercialization

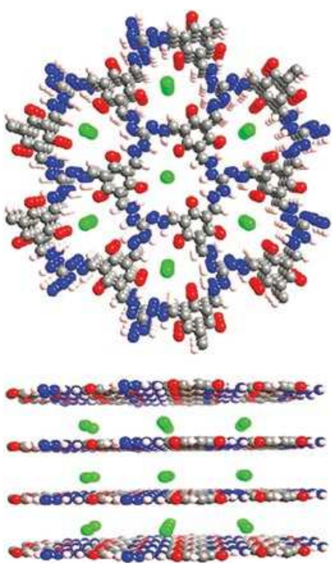


First reported in 2007, COF-108 is built from tetrahedral and planar triangular building blocks joined by C_2O_2B rings. Boron is yellow, carbon is blue, and oxygen is red.

In a 1993 essay in *Scientific American*, chemistry Nobel laureate Roald Hoffmann of Cornell University reflected on the ability of chemists to systematically construct highly complex molecules. "Organic chemists are masterful at exercising control in zero dimensions," he noted, referring to the creation of single, small molecules. Polymer chemists, he said, extend that control to one dimension by building molecular chains. "But in two or three dimensions, it's a synthetic wasteland," Hoffmann wrote, suggesting that chemists of the time were not yet skilled at making organic structures that extended "infinitely" in space.

That situation started to change in 2005 when Omar M. Yaghi and his colleagues synthesized two-dimensional, porous, crystalline networks composed entirely of light elements, such as carbon, boron, and oxygen, held together by strong covalent bonds. In 2007, Yaghi, now at the University of California, Berkeley, and coworkers made the first 3-D versions of these materials, dubbed covalent organic frameworks, or COFs (*Science* 2007, DOI: 10.1126/science.1139915). The COFs exhibited intriguing properties, including very low density, exceptionally high surface area, and high thermal stability—all features that suggested these materials may be useful for storing and separating gases.

Weak stacking interactions cause this COF to form robust 2-D sheets, not 3-D crystals. Hydrogen is white, carbon is gray, nitrogen is blue, oxygen is red, and chlorine is green.



By the time 3-D COFs came on the scene, Yaghi and other researchers had already spent more than a decade synthesizing a related and now better-known class of porous, crystalline materials called metal-organic frameworks, or MOFs. Unlike COFs, MOFs contain metal ions or clusters of metal ions connected by organic linkers. COFs, on the other hand, are constructed entirely from covalently bonded organic building blocks and so have none of the coordination bonding characteristics of metal complexes.

As a rule of thumb, the all-organic nature of COFs renders them more stable than MOFs against degradation by water, acids, and bases. According to William R. Dichtel, a COF specialist at Northwestern University, the fully organic quality of COFs also means researchers can draw from the rich assortment of tools in the organic chemistry toolbox to precisely tailor the size and shape of COF pores and carefully position a wide range of functional groups inside the pores. The ability to fine-tune the structure and composition of COFs enables scientists to customize the crystals to suit intended applications.

In the decade since COFs made their debut, dozens of research groups have climbed aboard the porous framework train and have published hundreds of papers detailing a wide variety of COFs and COF applications. However, none of the researchers C&EN contacted for this story is aware of plans to commercialize these materials.

"It's just too early," Dichtel says. "We haven't come up with a killer application that the market will pay for." Dichtel points out that MOF commercialization began just recently, and those materials had a roughly 15-year head start over COFs.

Nonetheless, COF development marches onward. In addition to using the materials to store and separate gases such as carbon dioxide, methane, and hydrogen, researchers have shown that these materials can serve as water-purification membranes to remove organic pollutants, salts, and metal ions. COFs have been used as charge conductors and as energy storage materials for batteries and capacitors. The porous compounds have also been used as catalysts to facilitate condensation reactions in organic synthesis and electrochemical reduction of CO_2 to CO, which is important for industrial production of hydrocarbons. And the materials have even been used to make membranes with antimicrobial properties.

Taking COFs in a different direction, Yaghi and coworkers reported last year that the materials can be used as "molecular threads" to form interwoven structures with reversible elasticity. The woven materials, which bend and stretch without breaking bonds, eventually may lead to new types of flexible thin films and electronic devices (*Science* 2016, DOI: 10.1126/science.aad4011).

"We're always interested in applications," Yaghi says. "But as chemists, first and foremost, we think about new kinds of molecules, bonds, and reactions." As chemists continue to fine-tune the properties of COFs, applications will surely follow, he adds.—MITCH JACOBY

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