POROUS CRYSTALLINE ORGANIC FRAMEWORKS

DESIGNED SYNTHESES lead to covalent 3-D materials with potential uses in gas storage and separation

RON DAGANI, C&EN WASHINGTON

THE RECIPE is exceedingly simple: Add one or two organic building blocks to a solvent mixture, heat at 85 °C inside a sealed tube for several days, and—voilà—you have created a new class of crystalline materials with remarkable properties.

The new materials are three-dimensional covalent organic frameworks (COFs)—that is, porous networks constructed entirely of strong covalent bonds between light elements such as carbon, boron, and oxygen. They are stable to temperatures above 450 °C, and their surface areas (as high as 4,210 m^2/g) are among the highest known for any materials. Most strikingly, these materials have extremely low densities. In fact, one member of this family, designated COF-108, boasts a density of just 0.17 g/cm^3—the lowest-density crystal known. A diamond, by comparison, has a density of 3.5 g/cm^3.

"We believe these porous materials are going to have a large impact on gas separation and storage technology," says Adrien P. Côté, a senior member of the research team led by chemistry professor Omar M. Yaghi of the University of California, Los Angeles, that reported the first 3-D COFs in April (*Science* **2007**, *316*, 268).

Yaghi's group and other labs previously reported crystalline metal-organic frameworks that "exhibit impressive levels of gas uptake," according to a *Science* commentary by chemist Peter M. Budd of the University of Manchester, in England. Yaghi's COFs, though, are purely organic, and as Budd explains, "materials based only on light elements are advantageous in applications where mass must be kept to a minimum, such as for storing hydrogen aboard vehicles."

COFs might also be useful for capturing and storing carbon dioxide from power plant smokestacks before it reaches the atmosphere.

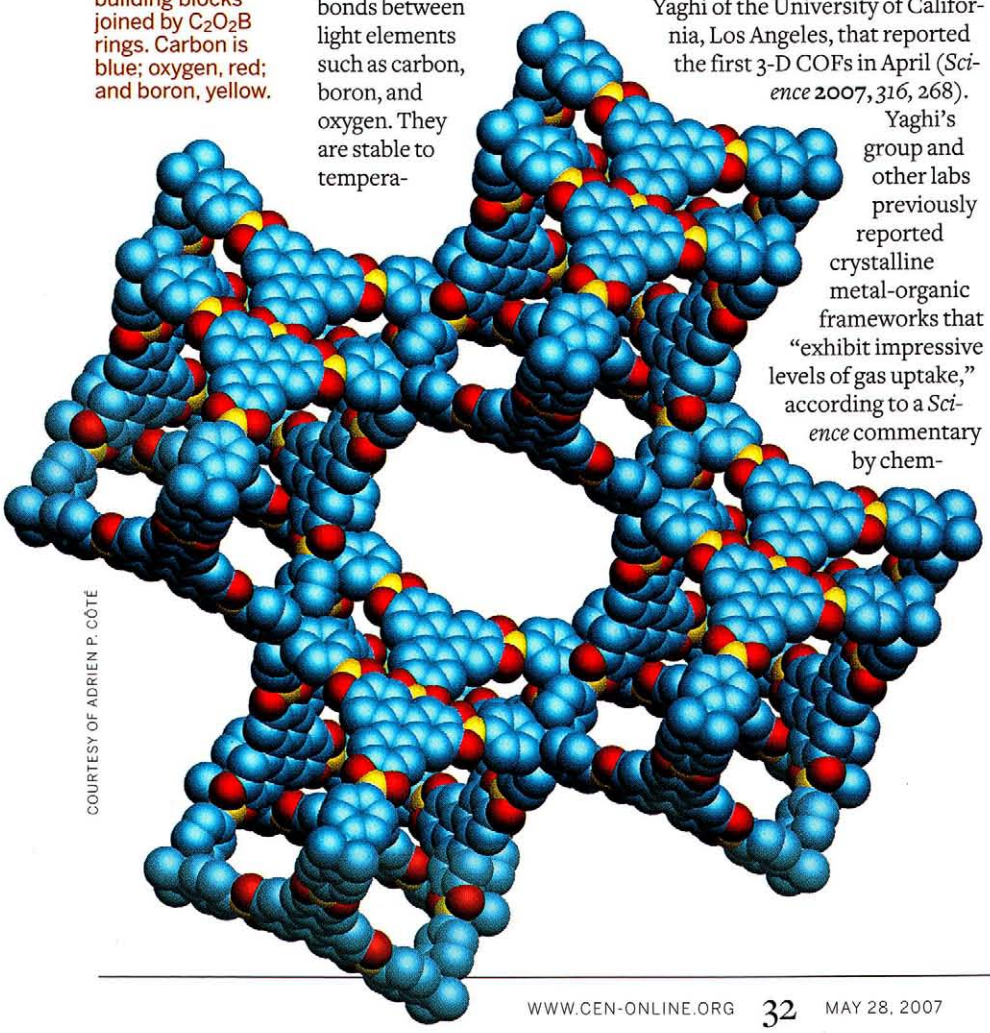
Budd points out another important distinction of the 3-D COFs: "Chemists have found ways to prepare a wide variety of porous materials, but it has proved difficult to form organic polymer networks with perfectly controlled pore dimensions—until now."

The pore dimensions in COFs are perfectly controlled because the architecture of the frameworks is precisely designed. For the first time, Yaghi says, chemists can "draw a blueprint of a solid-state extended structure, go to the lab, and assemble the material." This approach is called reticular chemistry, which means the linking of rigid molecular building blocks into predetermined structures held together by strong bonds.

Yaghi's *Science* paper describes the construction of four 3-D organic frameworks using three molecular building blocks, two of which are tetrahedral molecules and one of which is a planar triangular molecule. The tetrahedral building blocks are four-armed structures where each arm is tipped with a boronic acid [$B(OH)_2$] group. Three of these building blocks condense, with loss of three H_2O molecules, to form a B_3O_3 ring that serves as the triangular core of what might be called a tri-tetrahedron unit.

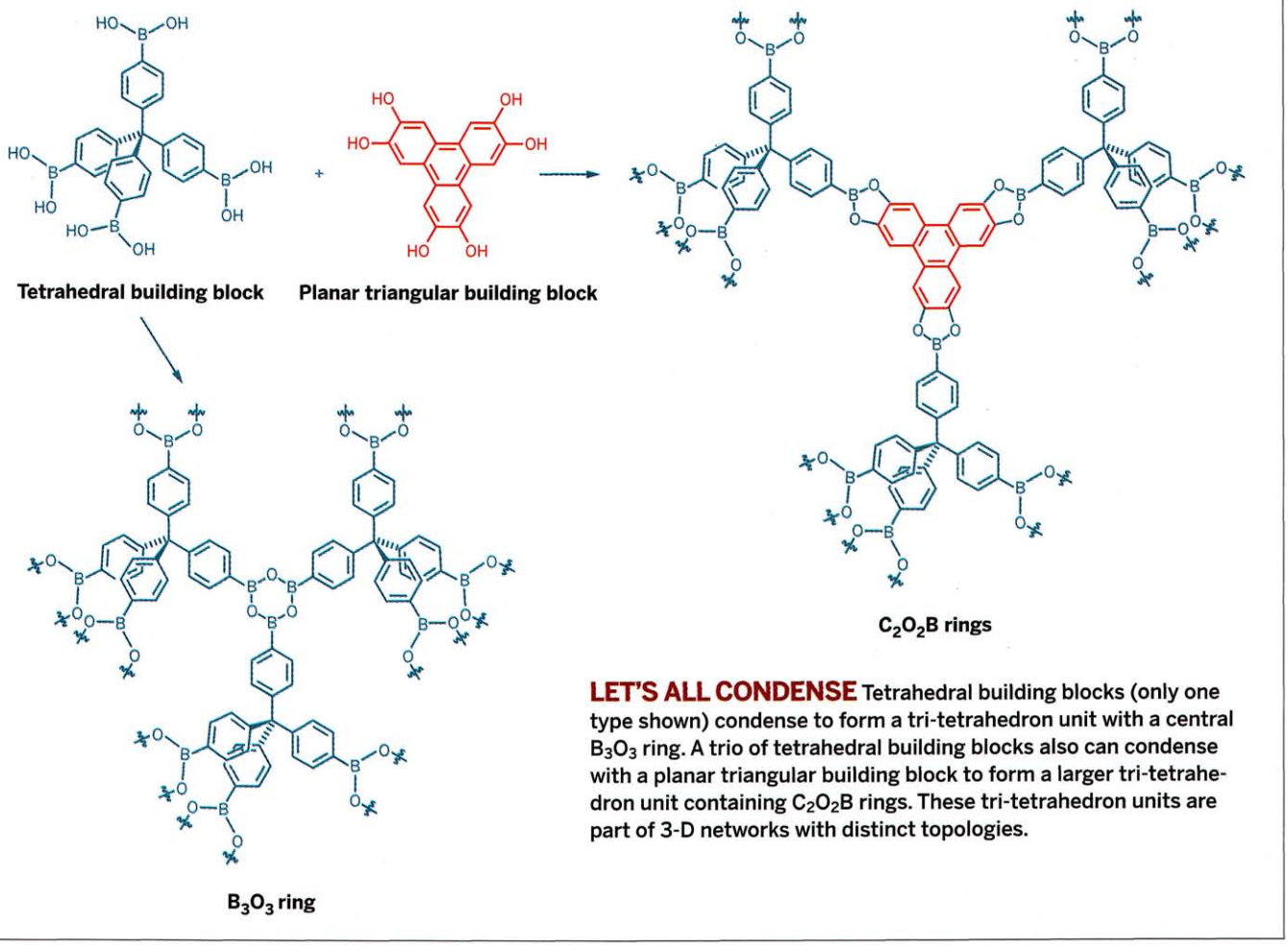
A similar, but larger, tri-tetrahedron unit can be formed in a different reaction by condensing three tetrahedral building blocks with the hydroxyl groups on the periphery of a single planar triangular building block to form C_2O_2B rings, with loss of water.

The boronic acid groups on these two types of tri-tetrahedron units undergo further condensation reactions with available building blocks to yield extensive organic networks of two distinct topologies. The topologies differ with respect to how the tetrahedral and triangular building blocks are oriented relative to each other and in the distribution and size of the pores.



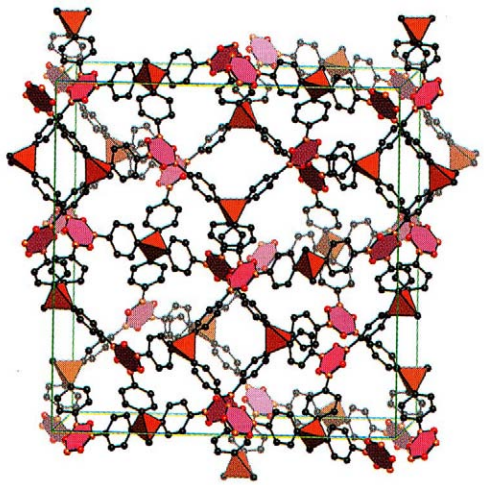
PORES GALORE The highly porous organic framework known as COF-108 is built from tetrahedral and planar triangular building blocks joined by C_2O_2B rings. Carbon is blue; oxygen, red; and boron, yellow.

COURTESY OF ADRIEN P. CÔTÉ



LET'S ALL CONDENSE Tetrahedral building blocks (only one type shown) condense to form a tri-tetrahedron unit with a central B_3O_3 ring. A trio of tetrahedral building blocks also can condense with a planar triangular building block to form a larger tri-tetrahedron unit containing C_2O_2B rings. These tri-tetrahedron units are part of 3-D networks with distinct topologies.

© SCIENCE 2007



CRYSTAL NET This covalent organic framework is constructed of tetrahedral building blocks linked via B_3O_3 rings. Tetrahedral carbon atoms are represented by tetrahedra. Other carbon atoms are black; oxygen, red; and boron, yellow.

"COFs are tantamount to crystals of cross-linked polymers," Côté says. Most chemists had assumed that COFs could not be made as crystalline materials because the polymerization reaction would have to be reversible, so that it occurs under thermodynamic control. Yaghi, Côté, and coworkers succeeded because they relied on boronic acids, which can undergo reversible condensation reactions.

The trick, Côté explains, is to use a solvent mixture that doesn't fully dissolve the starting materials and to use a sealed tube as the reaction vessel so that by-product water cannot escape. These conditions promote both the reversibility of the condensation reactions and slow crystallization, which leads to better quality crystals.

The first crystalline COFs were two-dimensional materials reported by Côté, Yaghi, and their colleagues less than two years ago (*Science* **2005**, *310*, 1166). Extending this approach to 3-D frameworks was not trivial because any given combination of building blocks could give rise to an enormous variety of products, Budd notes.

The UCLA researchers drew on their experience with porous frameworks "to select the most realistic targets and used a computer model to help predict the structures that were likely to form," Budd writes. "This helped them to design the synthesis and identify the products.

"The results," Budd continues, "open a new chapter in the story of porous organic materials." He expects that COFs will provide "a rich and fruitful area of research." On the basis of results coming out of their laboratory and the potential they envision, Yaghi and Côté couldn't agree more. ■