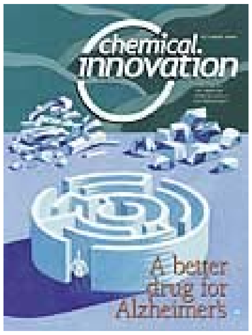

October 2000
Vol. 30, No. 10, 3–4.

Leading the Way

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Omar M. Yaghi

A molecular world full of holes

The importance of porous materials to the world's chemical industry is reflected by their nearly U.S. $350 billion sector of the global economy. Zeolites (aluminosilicates) and porous carbon have extended channel structures that are able to recognize and separate incoming molecules by size and shape. Indeed, these two classes of materials represent the majority of porous compounds currently used in catalysis, air and liquid separation, and detergents. New technologies based on porous materials (including environmental cleanup, sensors, nanoelectronics, biomolecule separations, and regio- and stereoselective heterogeneous catalysts) require periodic networks that have

- large pores to allow the separation of large molecules such as complex pharmaceuticals and high-boiling petroleum fractions and
- pores that can be functionalized and tailored to perform highly selective chemical transformations.

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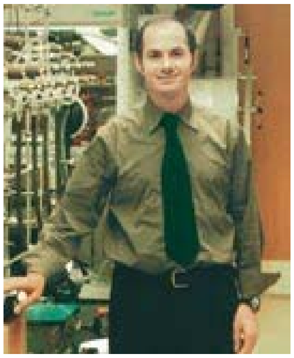

To accomplish these goals, my research group has been developing the fundamentals of a new field known as modular chemistry. This field deals with phenomena at the interface of inorganic, organic, and solid-state chemistry, namely, the design of extended structures and solid materials from molecular building blocks. My research programs have focused on linking together simple, inexpensive, and versatile organic molecules, metal complexes, and clusters into extended porous networks for use in highly selective catalysis, separations, sensing, and molecular encapsulation.

The first metal–organic frameworks (MOFs) were constructed by copolymerizing mono- and divalent metal ions with nitrogen-containing organic linkers (Figure 1). These frameworks were found to be structurally unstable. Removal or exchange of guests resulted in their collapse to more condensed and nonporous solids. To realize the full potential of MOFs, it was essential to design a synthetic pathway leading to rigid frameworks that would support permanent porosity. A new strategy based on bidentate linkers, in particular carboxylates (Figure 2), proved to be the preferred route to functional MOFs. My research group and I believe that the tendency of carboxylate linkers to form M–C–O clusters represents a key factor in the construction of rigid secondary building units (SBUs). These SBUs function to lock into position the carboxylates and the benzene links in the extended structure and ultimately yield a robust molecular architecture.

Now, by the judicious choice of building blocks, it is possible to assemble a particular network in a beaker at room temperature to give the product in high yield. The following example illustrates the effectiveness of this strategy in achieving tailored and highly porous materials.

We take a conceptually very simple cubic framework and use a cluster of tetrahedra, ZnO_4 in this case, as a building unit. Several such units are linked by long, rigid terephthalic acid (1,4-benzenedicarboxylic acid) molecules to make the very open framework (Figure 3). As prepared, the cavities of the structure are filled with solvent molecules; however, these can be removed without disrupting the framework, and a remarkably empty structure results. We believe, in fact, that this is the most porous material ever made—more than 80% of the structure is empty space. This is the first such structure to be prepared free of solvent molecules. Of the crystalline materials that are stable at room temperature and pressure, only elemental lithium (the lightest metal) has a lower density. The secret of success lies in using clusters of atoms as the nodes of the network and rigid planar rods of atoms (the terephthalate anions) as the linking units to provide a rigid framework consisting only of strong bonds (C–C, C–O, and Zn–O) (*1*).

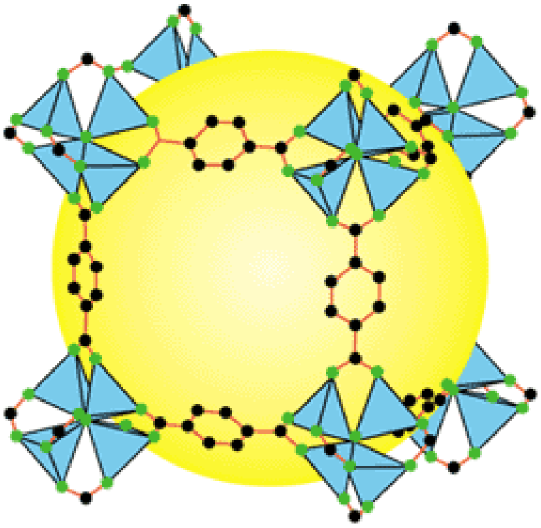

Figure 3. A very open cubic framework is made from clusters of ZnO_4 tetrahedra linked by tere phthalic acid molecules. Solvent molecules can be removed from the cavities without disrupting the framework. The result is a structure having >80% empty space.

It is obvious from the foregoing discussion that variation in the size of the SBU and the length of the linker should yield a limitless array of porous materials with unusual compositions and pore sizes, shapes, and functions (*2*). Furthermore, SBUs have allowed the preparation of porous MOFs with open metal sites (coordinately unsaturated metal centers) that are desirable for air separation and catalysis applications. Functionalizing the benzene rings has resulted in gated and decorated pores.

Our research has illustrated that the process of transforming discrete molecules to extended solids is essential to translating molecular geometry into extended structures and, more significantly, to converting molecular reactivity into physical properties.

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