

mechanistic and therapeutic insights as these “fat” keys open more locks.

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CHEMISTRY

Putting Order into Polymer Networks

Peter M. Budd

Microporous materials contain pores or channels with diameters of less than 2 nm—only a little bigger than many molecules. These pores or channels may be used as filters that allow some species through but not others, as containers to isolate or store specific molecules, or as tiny chemical reactors. 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. On page 268 of this issue, Yaghi and co-workers report the generation of highly porous, organic, three-dimensional crystalline covalent networks (see the figure) (1).

Inorganic microporous materials, such as zeolites, usually have well-defined network

structures made up of silicon and aluminum atoms linked via oxygen atoms. Windows and cages within the zeolite framework allow small molecules to access high internal surface areas. Some types of zeolite are found naturally, but many more have been synthesized in the laboratory. In recent years, many researchers have tried to create organic analogs of zeolites. Organic components, although inevitably limited in the temperatures they can withstand, allow much greater control over the chemical nature of the accessible surface. For example, groups may be incorporated that recognize specific molecules or catalyze particular reactions. Furthermore, materials based only on light elements are advantageous in applications where mass must be kept to a minimum, such as for storing hydrogen onboard vehicles.

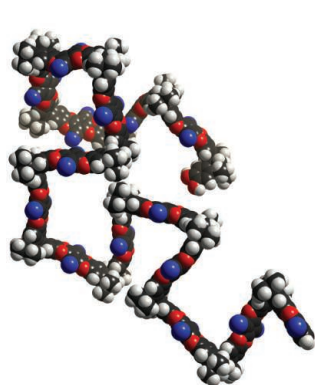
There is some truth in the saying that nature abhors a vacuum. Thermodynamics works against the formation of tiny spaces and the

Organic, three-dimensional microporous structures have been synthesized. Such “organic zeolites” are light and chemically versatile, offering a range of possible applications.

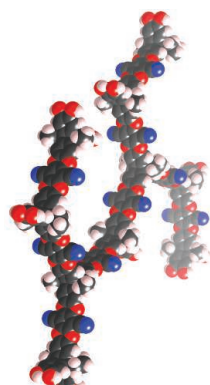
surfaces that surround them. Zeolites are usually metastable structures and, given appropriate conditions, they will transform to more stable, denser phases. During the preparation of porous materials, the spaces are filled with solvent or other small molecules. All too often, a promising-looking structure disintegrates when the molecules propping up the pores are removed. Many new “porous” materials have been reported, but the porosity is often not permanent in the sense of the material remaining intact on evacuation of the pores.

An important step toward organic zeolites was achieved with the development of materials in which rigid organic components are linked by noncovalent interactions, such as metal-ligand or hydrogen bonds. In particular, crystalline metal-organic frameworks have been produced that exhibit impressive levels of gas uptake (2, 3).

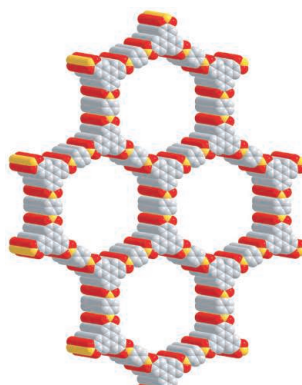
Crystallinity is not necessary for microporosity. Indeed, amorphous porous materi-



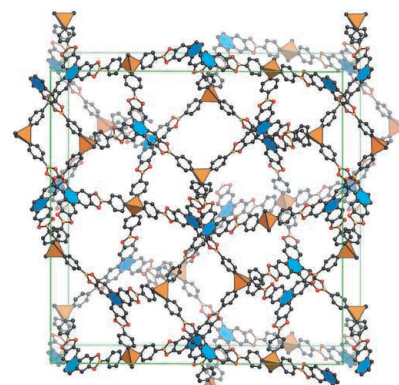
Membrane-forming microporous polymer



Network-forming microporous polymer



Two-dimensional covalent organic framework



Three-dimensional covalent organic framework

From disorder to three-dimensional order. Porous polymers can display different degrees of order. From left to right, this figure shows a soluble, membrane-forming microporous polymer (6), a network-forming microporous polymer that exhibits high gas uptake (8), a two-dimensional covalent organic framework (9), and one of the three-dimensional covalent organic frameworks described by Yaghi and co-workers in this issue.

als, such as activated carbons, are widely used in industry. In recent years, microporous organic polymers have been created that are chemically well defined, even though they are disordered and therefore possess a distribution of pore sizes.

One approach to microporous polymers involves tying polymer chains together with a large number of rigid bridges, to give “hyper-cross-linked” polymers (4, 5). Another approach starts with the design of the polymer backbone. By connecting rigid ladder-like components with units that force the backbone to twist or turn, it is possible to construct polymers that cannot pack together and fill space efficiently in the solid state. A variety of these “polymers of intrinsic microporosity” (PIMs) have been developed (6–8) (see the figure). Some are soluble and can be processed into useful forms such as membranes, whereas others are three-dimensional networks. They are commonly prepared by making use of a reaction that joins two aromatic rings together with a pair of oxygen bridges. This approach has the potential to

generate polymers that are ordered in two or three dimensions, but in practice, amorphous materials are generally obtained.

Current theories suggest that to form a crystalline polymer network, the polymerization reaction must be reversible, so that it occurs under thermodynamic control. Yaghi’s group set out to generate ordered polymer networks by making use of reversible condensation reactions of boronic acids. Using this approach, they first produced two-dimensional covalent organic frameworks that incorporate carbon-boron-oxygen linkages (see the figure) (9). A similar, but slightly easier, route to a two-dimensional covalent organic framework was taken by Lavigne and co-workers (10). But extending this concept to three-dimensional covalent organic frameworks is not trivial, because any given combination of building blocks could potentially give rise to an enormous variety of products. In their latest work (1), Yaghi’s group drew on their experience of porous frameworks to select the most realistic targets and used a computer model to help predict the structures

that were likely to form. This helped them to design the synthesis and identify the products.

The results open a new chapter in the story of porous organic materials. It is likely that routes will now be found to a host of novel crystalline covalent networks. Their high porosity and controllable pore size, coupled with the versatility of organic synthesis, promises that this will be a rich and fruitful area of research.

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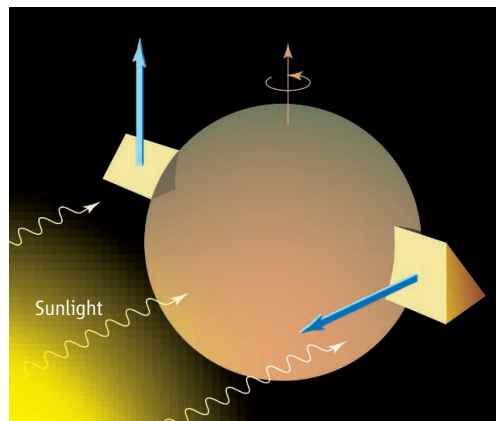
PLANETARY SCIENCE

As Tiny Worlds Turn

David P. Rubincam and Stephen J. Paddack

Sunlight changes the rotation rate of an asteroid? The idea seems absurd, but on page 272 Lowry *et al.* (1) and on page 274 Taylor *et al.* (2) report observations that indicate sunlight is doing just that to the small asteroid 2000 PH5, and Kaasalainen *et al.* indicate the same is happening on 1862 Apollo (3). The mechanism is the Yarkovsky-O’Keefe-Radzievskii-Paddack effect, mercifully shortened to YORP. With YORP now on a solid foundation, we may be able to understand a number of strange observations involving small spinning asteroids and asteroid binary systems.

The saga of sunlight changing into spin began with Ivan Yarkovsky, a Polish engineer who realized more than a century ago that the infrared radiation escaping a body warmed by sunlight carries off momentum as well as heat (4). Point this heat in the right direction, and it will function like a rocket motor: Each infrared photon escaping the object carries away momentum, thanks to the relationship $p = E/c$, where p is the photon’s momentum, E is its



Spinning in the Sun. Sunlight speeds up rotation due to reflection off the vertical and slanted faces of the wedges (blue arrows). Infrared radiation emitted by the faces also causes speed-up. If the body spins in the opposite sense, then YORP will slow it down.

energy, and c is the speed of light. By the principle of action-reaction, the object emitting the photon gets a kick in the opposite direction. (Yarkovsky knew nothing of photons and based his reasoning on the outmoded ether concept, but his idea survives the translation to modern physics.) Yarkovsky thrust is tiny, but space is

so empty there is no friction to stop it. Moreover, because the Sun is always shining, the Yarkovsky effect goes on century after century with an inexhaustible supply of photonic fuel, profoundly altering the orbits of meter-sized meteoroids (5).

V. V. Radzievskii applied the photon thrust idea to rotation by imagining each face of a cubical meteoroid painted white on one half and black on the other; sunlight reflected by the white part pushes that area more than the black half, causing a torque, which changes the rotation rate (6). His mechanism is weak because the black half, although it reflects little, makes up much of the difference by emitting infrared photons. Moreover, most small solar system objects have fairly uniform albedoes (that is, the fraction of light reflected) across their surfaces.

Building on this work, John A. O’Keefe and one of us (S.J.P.) at NASA realized that shape was a much more effective means of altering a body’s spin rate than albedo and set about measuring spin changes in the laboratory. The idea was that light reflecting off of various angled surfaces on the object could