Chemists probe new crystalline vistas

Unload a box of hollow rods and connectors shaped like an X twisted at the waist. Start building. Before long, you'll have a structure resembling diamond's tetrahedral lattice or the hexagonal structural motif of lonsdaleite, another all-carbon mineral. Using molecules as the rods and copper atoms as the linkers, two Australian chemists have begun to develop what they hope will become a set of chemical Tinkertoys for making novel materials with "unprecedented and possibly useful properties."

Compared with the tight crystal lattice of diamond or sodium chloride, regular molecular frameworks made with rod-like units host spacious interconnected cavities. By controlling the size of the rods, and thereby the size of the cavities within the framework, the scientists hope to tailor-make materials that can isolate specific components of chemical mixtures. The high proportion of empty space in these new structures also suggests possibilities for inventing extremely light solid materials, the researchers propose. Mostly, though, they say they don't know what to expect.

"I see the most important possibilities in the area of catalysis," remarks chemist Richard Robson of the University of Melbourne in Parkville, Victoria. He and crystallographer Bernard F. Hoskins hope to design frameworks into which only specific reactant molecules can enter and then leave after being transformed into specific products at internal catalytic sites.

In the July 19 Journal of the American Chemical Society, the scientists describe "the first example of a deliberately designed and constructed infinite framework consisting of tetrahedral centers linked together by rod-like units." In an experiment Robson calls "simple in the extreme," they built the molecular network by replacing each of four roughly spherical acetonitrile groups (a carbon atom bonded to three hydrogen atoms and one carbon-nitrogen couple), loosely hooked to a common copper atom, with a more complex chemical made of four rod-like molecular segments, each capable of bonding to a copper atom.

The liquid-phase reaction produces colorless, diamond-like crystals. "If you keep the crystals under the liquid they grow out of, they retain their sharp edges, nice shiny faces and internal clarity," Robson says. "If you take the crystals out and dry them, they become milky and opaque because they lose some of their [structural] regularities."

Using X-ray crystallography to probe the crystal's architecture, Hoskins found the framework resembles an extra-airy diamond-like lattice. The framework molecules constitute roughly one-third of the crystal's volume. Solvent and ions fill the rest of the space, apparently as a liquid that seems able to flow between the solid framework's polyhedral cavities.

The researchers assess their work as a proof-of-concept effort showing the feasibility of designing and building new "infinite" crystalline frameworks by linking rod-like segments in three dimensions. Researchers elsewhere have focused on different tactics to achieve somewhat similar results. At the University of Minnesota at Minneapolis, for instance, chemist Margaret C. Etter uses weak intermolecular bonds called hydrogen bonds to coax two kinds of chemicals into novel solid materials by forcing them to crystallize together. *—I. Amato*

Estrogen effects assessed

A large study of the relationship between estrogen supplements and breast cancer in postmenopausal women adds lots of new numbers to the existing mountain of conflicting data. The study of 23,244 Swedish women suggests estrogen pills may increase a woman's risk of breast cancer significantly—or not at all—depending on the number of years she takes them, the type of estrogen used and whether the estrogen is taken with another hormone, progestin.

Estrogen therapy cuts the risk of cardiovascular disease in postmenopausal women and helps prevent osteoporosis. But after more than a dozen studies, its effects on the incidence of breast cancer remain uncertain. In the new report, researchers led by Leif Bergkvist at the University Hospital in Uppsala, Sweden, calculate a 10 percent added risk of breast cancer overall among postmenopausal women who take estrogen for an average of 5.7 years. The added risk exceeds 70 percent after nine years of use.

In contrast to previous U.S. studies, however, the Swedish numbers show no clear evidence of increased breast cancer risk among women who use conjugated estrogen — the kind most commonly prescribed in the United States. The Swedish researchers say they don't know if they would have recognized a small risk increase among these women, because only 20 percent of their group took conjugated estrogen and the doses were lower than those taken by most U.S. women. Estradiol, another estrogen form, carried the highest risk, they say in the Aug. 3 New England Journal of Medicine.

Progestin, increasingly prescribed with estrogen because of its ability to counter estrogen's links with endometrial cancer, did nothing to lessen the women's risk of breast cancer and may even have increased it slightly. The researchers say their report highlights the need for further studies to solve estrogen's complex risk-benefit equation. □

A novel fossil seed roils botany theory

Seeds surfaced less than 100 million years after land plants evolved from their water-borne ancestors. These nutritional nuggets — the reproductive units of the world's most highly evolved plants — arose from spore-producing predecessors that lacked sophisticated structures for collecting pollen. Because all early fossil seeds found so far look almost identical in structure, most plant biologists assume that a single group of spore-spreading plants, or pteridophytes, led to nonflowering seed-bearing plants, the gymnosperms, says paleobotanist Lawrence C. Matten of Southern Illinois University in Carbondale.

But two European paleobotanists recently put a kink in this theory. Sifting through sediments in southern France, they found an intact fossilized seed that looks like no other from the early Carboniferous—the period about 350 million years ago during which plants apparently acquired the seed-bearing habit. Whereas other fossil seeds feature a funnel designed to trap wind-carried pollen grains, this one sports a stub where the funnel should be, reports Jean L. Galtier of Université des Sciences et Techniques in Montpellier, France.

The newly found fossil might represent the first evidence of an intermediate stage between pteridophytes and early seed plants. Alternatively, it may have served a primitive gymnosperm that later gave rise to a subgroup of today's gymnosperms, Galtier says. The latter interpretation, implying that gymnosperms evolved from more than one ancestral group, could cause scientists to reevaluate the "monophyletic" theory for gymnosperm origins, Matten says.

Since the seed lacks a specialized wind-pollination piece and contains some loose, air-filled tissue characteristic of water plants, the plant from which it sprang may have lived in an aquatic or marshy habitat, suggest Galtier and Nicholas P. Rowe in the July 20 Nature. The primitive plant's seed was probably adapted to receive pollen from water instead of wind, Galtier says.

Although the fossil might reflect a prepollination stage in the plant's development, this explanation is unlikely because "the well-preserved tissue at the seed apex is clearly mature," writes Bill Chaloner at London University's Royal Holloway and Bedford New College in Egham, England, in an article accompanying the report.

Over the past decade, Galtier has found numerous fossilized plant fragments at the same site, all of which he believes stem from the same species. But only last year did he stumble across the singular seed. *—I. Wickelgren*