

Chemistry With A Thousand Faces

Like a species that has moved into open niches, evolved, and diversified, chemistry can no longer be seen as a discrete scientific field. Its methods, concepts, and practitioners are penetrating virtually every nook and cranny of science and technology. That message came through clearly 2 weeks ago in New York City at the Fourth Chemical Congress of North America—a week-long conference organized by the American Chemical Society, the Chemical Institute of Canada, and the Chemical Society of Mexico and attended by some 10,000 scientists, engineers, and entrepreneurs. In roughly 4200 papers, participants explored such topics as borrowing from nature to improve industrial processes and electronic devices, and controlling the molecular architecture of clays and polymers.

New Ways to Play With Clay

Throwing pots may never be the same again. People have been molding clay into intricate and useful forms since the dawn of technology, and now chemists are beginning to shape this most workable of materials on the molecular level. Take the so-called super-gallery pillared clays that Thomas J. Pinnavaia of Michigan State University in East Lansing has been developing with his students.

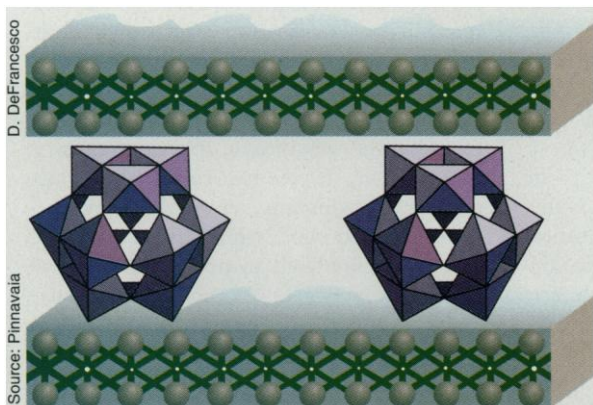
At the Chemical Congress, Pinnavaia and his colleagues described their strategies for controlling the shape and size of the open spaces, or galleries, between the flat crystal layers that make up clay minerals. The resulting materials, Pinnavaia says, might serve as catalysts that “squeeze more energy out of a barrel of oil” and detoxify polluted waters as the oil or toxin molecules slip between the clay layers and are broken down. He also

which consist mainly of aluminosilicates with varying proportions of hydrogen and oxygen—for any other molecules to slip in between. Clay chemists are trying to wedge the layers apart by inserting guest ions between the host stacks, a process called intercalation. But individual ions generally don’t open up the clay structure far enough for the purposes Pinnavaia has in mind.

So he and others are developing ways to turn the galleries into “supergalleries”—ones in which the gallery heights are at least twice the thickness of the layers—by inserting “molecular pillars,” built of repeated ensembles of metal, oxygen, and hydrogen atoms. “The trick here is to space the pillars laterally in the gallery without stuffing it full” and defeating the purpose of the gallery, Pinnavaia says. One tactic his group has been exploring—so far with only limited success—is coating the pillars with a film of organosilane compounds, which keeps the pillars separated until a heat treatment secures them while burning away the film. Another tactic is to build pillars from clusters of negative ions— $\text{SiW}_{12}\text{O}_{40}$, for example. The mutual electrostatic repulsion between such charged pillars keeps them separated.

Pinnavaia has already begun toying with some of his creations, testing their catalytic ability and filling the galleries with certain epoxy polymers to make composites. In such composites, the polymers withstand temperatures of more than 400°C, or up to 200 degrees higher than the plain epoxy polymers,

he finds. Pinnavaia thinks such clay composites might one day serve as tough coatings for aircraft surfaces heated by air friction. Not bad for a material traditionally relegated to bricks and pottery.



Pillared clay. Metal oxide-based polyhedral pillars prevent adjacent layers of clay from collapsing into a closed structure.

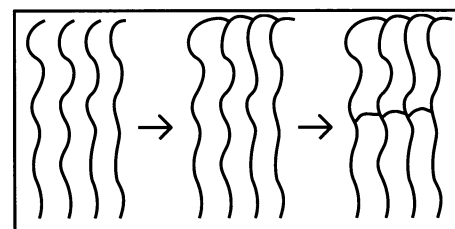
envisions filling the spaces between the layers with polymers to make composites with otherwise unattainable properties.

In unmodified clays there’s too little headroom between adjacent mineral layers—

Turning Polymer Spaghetti Into Lasagna

On the molecular level, most polymers in today’s technoscape resemble a jumble of tangled spaghetti strands, each a single long molecule made up of many identical chemical building blocks. Materials scientist Samuel I. Stupp and his colleagues at the University of Illinois at Urbana-Champaign are bringing some order to the picture by packing, aligning, and stitching together the strands to form layered molecular structures that look more like stacks of lasagna than jumbled spaghetti.

Because of the rigorous alignment of the molecules in these “two-dimensional polymers,” Stupp says, the individual compo-



Double stitch. Monomers link at their ends and then in their middles to form two-dimensional sheets.

nents can cooperate to yield characteristics that would never emerge from a spaghetti of the same molecules. Among the products he envisions: filtering membranes that allow only specific molecules to slip through and optical materials that change the frequency of light passing through them.

To make two-dimensional polymers, the Illinois scientists first synthesize the molecules as a liquid crystal—a polymer solution in which the molecules align like logs floating on water. Because the molecules have a consistent “handedness,” like a vast set of left- or right-handed gloves, adjacent molecules tend to nest together in exactly the same orientation. Next, bonds form between the ends of aligned chains, cross-linking them into comb-like intermediate molecular structures. Finally, more rigid polymer sheets emerge when a second chemical stitch forms between adjacent molecular prongs.

Thanks to this regimentation, the properties of individual molecular building blocks add up in startling ways, says Stupp. Each one, for example, has a tiny electric field. When the fields are precisely arranged en masse in the two-dimensional polymer, they affect the propagation of the electromagnetic waves in light. Stupp has found that, after further processing, his two-dimensional polymers can convert invisible infrared light into red light—a property that

might make them valuable for future computing and communication technologies relying on light rather than electrons.

The molecular regimentation may also result in curious—and valuable—mechanical properties, Stupp notes. Theories of polymer behavior predict that sheet-like polymer structures like these should suddenly crumple or flatten out in response to, say, changes in their chemical environment. Stupp suggests that the polymers might serve as “molecular wrapping paper” that could shuttle a drug to a specific location in the body and deliver it there by uncrumpling, or capture pollution particles to ease the cleanup of troubled waters.

Coopting Nature's Own Nano-electronics

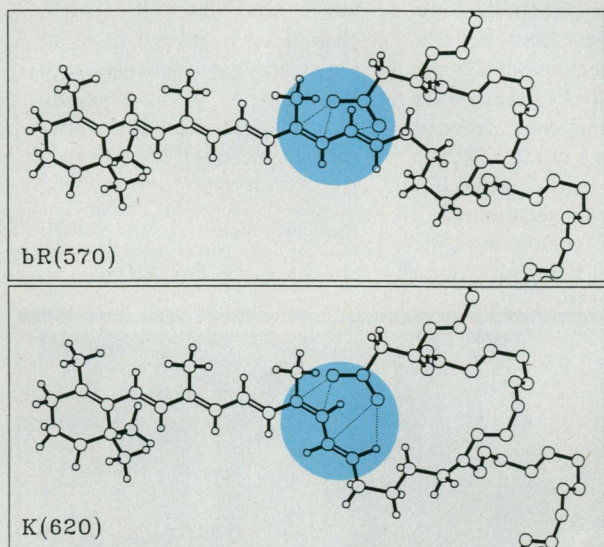
Investigators in the field of molecular electronics, which seeks to harness single molecules as switches, transducers, and the like, are finding that nature has done much of their work for them. When molecular electronics researchers gathered for a 4-day symposium at the Chemical Congress, much of their discussion centered on ways to put biological molecules to work in simple electronic and optical devices—a first step, the workers hope, toward smaller and faster computers, denser memories, and higher-capacity communications systems.

Bacteriorhodopsin, a membrane-bound protein that harvests light energy to fuel the metabolic activity of certain photosynthetic bacteria, was one of the featured biomolecules. Robert R. Birge, director of the Center for Molecular Electronics at Syracuse University and bacteriorhodopsin's most vocal champion, reported that he and his colleagues had embedded the molecules, whose purple color changes to yellow on exposure to certain wavelengths of light, within cubes of plastic to create a data-storage medium. By using criss-crossed laser beams, Birge and his colleagues hope to read and record densely packed data—encoded in the color of the rhodopsin molecules—in specific micro-regions in the cube. A 1-inch cube theoretically could host several billion bits of data, enough to store entire libraries, Birge said.

Elias Greenbaum of Oak Ridge National Laboratory described his efforts to harness another piece of nature's molecular machin-

ery: the photosynthetic reaction center, a complex of molecules that enables green plants to capture sunlight for making food in the form of carbon compounds. The reaction center actually performs only the first phase of the process, turning photons of light into a flow of energetic electrons. And that ability is just what interests Greenbaum. “The photosynthetic reaction center is a nanometer-scale optoelectronic device with picosecond [trillionth of a second] switching times,” he said.

By turning optical signals into electronic ones, transducers based on the reaction center might play a role in future computers or communications systems, Greenbaum speculates. For now, he's studying ways of putting the molecular complex to work to capture solar energy. His tack is to precipitate tiny islands of platinum metal onto thylakoid membranes, the membranes that house the reaction centers in the chloroplasts of living plants. These contacts enable Greenbaum to hijack the energetic electrons produced when light strikes the reaction centers to generate hydrogen molecules. Ultimately, he envi-



Molecular switch. Light-sensitive part of bacteriorhodopsin changes shape as it absorbs light.

sions myriad platinum-wired reaction centers working in parallel in what he calls “photobioelectrochemical cells,” producing fuels such as hydrogen or other chemicals. He already has made experimental versions that stoke his optimism.

Molecular electronics may be commonplace in nature, but even the enthusiasts agree it will be a while before, say, desktop computers start sporting bacteriorhodopsin memories. “Our state of the art is rather primitive,” conceded Ari Aviram of the IBM Thomas J. Watson Research Center in Yorktown Heights, New York, a longtime advocate of molecular electronics. Still, company representatives from Digital Electron-

ics Corp. and Biological Components Corp. were nosing around the session, alert to hints of commercial promise.

Bacterial Indigo Gives the Blues to Industrial Chemists

When we buy a pair of jeans, we don't generally summon visions of 19th-century indigo plantations—much less of the band of turn-of-the-century German chemists who essentially consigned such plantations to the past. But the fact is that until the day those little-remembered chemists learned how to synthesize indigo molecules on an industrial scale, the only source for the blue dyestuff, used in denim and other cotton clothing, had been natural indigo. With that success, the chemists sealed the fate of entire plantations and helped to usher in the era of industrial chemistry, which was to put out of business biological sources of dyes, flavorings, and many other key chemicals.

Judging from one of the presentations at the Chemical Congress, biology may soon be making a comeback. By genetically modifying bacteria, genetic engineers may succeed in snatching preeminence in indigo-making away from industrial chemists and giving it back to biology, according to Timothy C. Dodge of Genencor International in Rochester, New York. “This [indigo] could become one of the first chemically synthesized products to be replaced by a biotechnology process,” Dodge said.

The nasty ingredients that go into the nearly century-old chemical process of making indigo—sodium cyanide and formaldehyde, to name two of them—provide a major incentive for coming up with an alternative, Dodge noted. An early hint that bacteria might offer a kinder, gentler route to indigo came in 1983 from other researchers who were studying a gene that enables the bacterium *Pseudomonas putida* to break down hydrocarbons. When they inserted the gene—which codes for the enzyme naphthalene dioxygenase—into the common bacterium *Escherichia coli* to probe its activity, they serendipitously discovered that the genetically engineered bugs could turn the amino acid tryptophan into indigo.

Dodge and his colleagues at Genencor are now trying to pin down the conditions (such as temperature, acidity, and tryptophan supply) under which the bugs churn out indigo most efficiently without also producing bio-cidal chemicals, thereby committing biochemical suicide. If the process works, the blue-blood bugs should have their work cut out for as long as people like their old blue-jeans. ■ IVAN AMATO