Where Chemists React: ACS Meeting in Atlanta

Chemistry showed its startling diversity last week in Atlanta, where more than 9000 scientists were gathered at the national meeting of the American Chemical Society to discourse on topics ranging from acid rain to those soccer ball-shaped molecular celebrities known as buckyballs to new light-manipulating polymers to new biosensors for detecting everything from bacteria to glucose. Much excitement was focused on the nanoscale, a realm inhabited by structures bigger than ordinary molecules but smaller than solids.

Tinkertoys Grow Up

Chemist Josef Michl dreams of playing with a construction set small enough for virus-sized children. He's well on the way to having the right pieces. As he puts it: "I have engaged my research group in an attempt to develop a 'tinkertoy' set of rods and connectors on a molecular scale." What's more, he and his associates already have begun putting some of these pieces together.

Subsequent generations of the tinkertoy parts, he says, could be chemically customized to, say, absorb or emit specific wavelengths of light, or to generate tiny electric or magnetic fields, or to get more rigid in the presence of certain chemicals. They could then be assembled to make "designer solids." "We want to control a solid's properties, molecular layer by molecular layer," he says.

At the moment, this scenario remains on the fiction rack. But it has been inching closer to reality since 23 December 1987. It was on that day that a former graduate student, Piotr Kaszynski, came into Michl's office at the University of Texas at Austin to discuss an unexpected turn that his research had taken. The flywheel-shaped hydrocarbon molecules—aptly called propellanes—he was studying had apparently linked together along their hubs into knobby rod-like structures. "Here is an approach to molecular tinkertoys," Michl remembers realizing. (His young son's fanatic attachment to LEGO construction blocks may also have helped midwife this insight, he notes.)

Building on Kaszynski's discovery, Michl and his collaborators went on to string together different numbers of propellanes into straight, rigid molecular rods, which they call "staffanes." "We have a set of rods we are reasonably happy with," Michl says.

Rods are no use in a construction set unless you can connect them, and so Michl and Mohamed A. Ibrahim have moved onto phase II of the molecular tinkertoy project. "Now we're working on spools," he told scientists at a meeting of the American Chemical Society. Each of the molecular spools they have devised has a pair of rhodium metal atoms at its hub, bonded to each other and more loosely to 10 appendages made of acetonitrile (an organic compound), which serve as temporary plugs for the spool's attachment points. The entire complex carries four positive charges, which help to glue the rods to the spool.

Although the spools aren't ready for any heavy-duty construction, Michl says he has already started building them into some simple structures. In one set of experiments, he and Ibrahim capped one end of each rod with a negatively charged carboxylate group and the other with a bulky "protective group" that can be removed for later reactions. When the chemists mixed these modified rods with the spools, four rods displaced acetonitrile groups from each spool, bonding to the attachment points with help from their own negatively charged carboxylates. "This produces a planar cross," Michl says. This simple structure should be easy to weave into larger and larger networks by simply removing the protective groups from the points of the cross, exposing the reactive rod ends.

"One aim is to produce a square grid, whose nodes are spools and with staffanes on the sides," Michl explained. Such constructions might serve as "fine molecular sieves like a fish net," useful, perhaps, for such jobs as separating gases. Such payoffs are years away at best. "We are nowhere near any practical situations," Michl admits. But meanwhile he expects to have a grand old time playing with his growing set of molecular tinkertoys.

Arrested Growth

What do you get as countless minuscule molecules first start assembling into a solid? Just a small chunk of solid, you might think. But you would be wrong. The route from molecules to bona fide solids passes through territory that is practically unexplored, populated by molecular assemblages with tantalizing properties. Michael Steigerwald of AT&T Bell Laboratories has fallen prey to the spell of this borderland, and he has been exploring the odd ways of some of its inhabitants.

"The new materials I am talking about are actually intermediates in this molecule-to-solids progression," he told his audience at the ACS meeting. The trick to making them, he explained, is finding some way to put the brakes on this assembly process, before it yields a full-fledged solid.

In one series of experiments, Steigerwald and his collaborators did so by trapping a growing material in nanoscale cages. The researchers mixed cadmium- and selenium-bearing molecules in a soapy solution teeming with reverse micelles, tiny spheres he describes as "inside-out soap bubbles" because the layer of hydrocarbons that lines ordinary soap bubbles lies on the exterior surface of the reverse micelles. Cadmium and selenium-based molecules entered the spheres and began reacting to form the semiconducting compound cadmium selenide. But the spheres stymied the growth of the bulk material; trapped inside, the cadmium selenide was limited to forming clusters of up to several thousand atoms, measuring tens of angstroms in diameter.

This truncated growth process was accompanied by a brilliant display of colors, which point to one of the unusual properties of the clusters. "An amazing reaction happens, and it's still amazing to me, having done it many, many times," Steigerwald says. The solution takes on striking yellows or reds, the exact color depending on the size of the particles. Because the color of a material is generally an expression of its electronic structure, it appears that the size of these "nanoparticles" determines their electronic properties.

Steigerwald says that he and his colleagues can readily control the size (and hence the color) of the nanoparticles by changing the concentration of the reactants or the composition of the reverse micelles. The group has even succeeded in freeing the nanoparticles from their micelle prisons by bonding a stable organic coating to the particles, making them easier to extract from the soapy solution. This step yields colorful powders, which Steigerwald brought to his talk in small vials.

The colors aren't indelible, though; they can be altered by shining a laser of a specific wavelength on the nanoparticles, temporarily distorting their electronic structure. This effect, Steigerwald suggests, could enable nanoparticles to serve in laser-driven optical switches. But before Steigerwald looks for ways to put his nanoparticles to work, he's going to spend a lot more time getting acquainted with them. ■ IVAN AMATO