New iron-filled, light-blocking fullerenes

Those rounded all-carbon molecules called fullerenes have rolled a little closer to exiting the laboratory door, nudged by two reports that these chemical superstars harbor potentially useful properties. In India, chemists inserted an iron atom into a buckyball, the soccerball-shaped, 60-carbon fullerene, then made measurable quantities of the caged iron. In the United States, scientists demonstrated light-limiting properties of fullerene materials.

Like eyeglasses that darken in sunlight to shield the eyes, fullerenes block bright light. But unlike the lenses, whose molecules rearrange in less than a second in the presence of bright light, fullerenes act much faster and via a much different mechanism.

"It's a purely electronic rearrangement on the order of nanoseconds," says Lee W. Tutt, a chemist at Hughes Research Laboratories in Malibu, Calif. This lightning-fast response means that fullerene materials may one day guard sensors — or perhaps eyes — against damage by lasers. Such protection becomes more necessary as lasers proliferate in a variety of applications, Tutt notes.

Most materials do not handle light this way. Like old-fashioned sunglasses, they allow a constant percentage of light energy to pass through them. Thus, if a light is bright enough, enough gets through to do damage. But fullerenes and a few other substances show nonlinear optical (NLO) properties. Thus, Tutt says, when light intensity gets high enough, NLO materials change their light-transmitting properties, becoming ever more opaque as intensity increases. Thus, NLO materials transmit a maximum amount, rather than simply a percentage, of incoming light.

Tutt and Alan Kost, also at Hughes, tested the light-limiting properties of the buckyball and its 70-carbon cousin in separate solutions. They subjected each to 8-nanosecond-long pulses from a green laser and sampled the laser's energy entering and exiting the solution.

The buckyball solution, which at lower light levels transmits 80 percent of the energy, becomes more opaque when the laser's energy exceeds 240 millijoules per square centimeter (cm^{-2}). It keeps transmitted light to 80 percent of the 240 level even when its energy reaches 3 joules per cm^{-2}, they report in the March 19 NATURE.

The Hughes researchers also assessed other light-limiting materials. "If they're really comparing apples to apples, then they show that C_{60} is superior to other materials that have been studied in the past," comments Zakya H. Kafafi, a chemist at the Naval Research Laboratory in Washington, D.C. She and her colleagues have studied NLO properties of fullerenes using a different color light.

Tutt and Kost think fullerenes limit light because of the way their electrons react to light energy. The laser causes the electrons to jump to a slightly higher energy state; while excited, the electrons are much more likely to absorb energy and thus temporarily exhibit a greater ability to block even intense light.

However, the Navy lab's work indicates that the laser energy alters optical properties by heating the fullerenes. Thus thermal, not electronic, effects may lead to optical limiting, Kafafi notes.

Instead of using fullerenes to limit light, T. Pradeep and colleagues at the Indian Institute of Science in Bangalore have used them as cages. By trapping atoms inside fullerenes, scientists hope to create fullerenes with useful electronic or magnetic properties.

The Indian chemists added an iron compound to the reaction chamber in which they vaporize graphite to make fullerenes. From the soot, they extracted 60-, 58- and 56-carbon fullerenes containing single iron atoms, they report in the March 11 JOURNAL OF THE AMERICAN CHEMICAL SOCIETY.

"If this bears out, this will be the first report of a C_{60} cage with a metal atom that has been isolated," notes Richard E. Smalley, a chemist at Rice University in Houston. Like others, Smalley has trapped atoms inside fullerenes but has been unable to purify enough of the resulting material to study it in detail. Pradeep's group made enough iron-fortified fullerenes to contrast their character with that of fullerenes with iron attached to the outside of the carbon cages. Their results indicate the iron inside binds tightly to the carbon atoms and retains its electrons. *– E. Pennisi*

Slowing chemical reactions in tight spaces

No action comes more naturally to a chemist than swirling the contents of a test tube to hasten a chemical reaction. But the chemistry that takes place when reacting chemicals must thread long, narrow tubes or wander through a maze of tiny pores doesn't necessarily follow the same familiar rules as the chemistry in spacious, well-stirred vessels.

Raoul Kopelman and his co-workers at the University of Michigan in Ann Arbor have now demonstrated experimentally that under certain conditions, two reacting chemicals confined to a thin tube spontaneously tend to segregate themselves rather than mix. Because molecules of the two substances rarely get close enough for a reaction to occur, the rate at which the reactants combine to form a product decreases as the reaction proceeds. In contrast, conventional theory, which assumes mixing, predicts that this reaction rate should actually increase.

Kopelman and his colleagues first came across the phenomenon of reactant segregation in their computer simulations of reactions on confined surfaces, which severely restrict molecular movement. Because a collision between two different molecules leads to the immediate formation of a product, any mixing naturally gets rid of both reactants. But because molecules diffuse extremely slowly, replacement molecules take a long time to arrive in the depleted areas. The combination of these two factors produces a curious patchwork of depleted zones and concentrations of one or the other reactant.

Any molecules straying to a boundary get "killed" before they can penetrate each other's territories, Kopelman says. It's the survival of the most isolated.

"This doesn't come out of any of our [conventional] physical or chemical formulations because they always assume that everything is nicely stirred up," he adds. "But when you treat it as a Darwinian-like principle, it's obvious."

To demonstrate the same effect in the laboratory, the Michigan researchers devised an experiment in which two substances of contrasting colors diffuse from opposite ends toward the middle of a narrow, horizontal, gel-filled tube. A vertical boundary forms between the two reactants where they meet and combine to create a new chemical substance.

Classical theory predicts that the reaction rate in this situation should increase steadily as the two substances gradually interpenetrate and mix. Instead, the Michigan group found that the reaction front actually develops into a distinct region where the concentrations of both reactants sink very low. In effect, this visible gap keeps the reactants segregated, and in the absence of mixing, the reaction rate eventually falls nearly to zero.

"Here you can see it with your own eyes," Kopelman says. "This is the first experimental evidence that different molecular reactants segregate themselves into like groups when confined to small spaces."

These findings may prove important in the study of a variety of chemical processes. "Once you establish a certain principle, you can use it to explain and interpret a lot of other situations," Kopelman says. "If the conditions are right, it should also happen in less controlled situations — inside a biological cell or on a catalytic surface."

Kopelman described this research at an American Physical Society meeting held last week in Indianapolis.

– I. Peterson