MEETING AMERICAN CHEMICAL SOCIETY

Science Invades the Magic Kingdom

ORLANDO, FLORIDA—With nine major theme parks dominating the landscape here, fantasy reigns supreme. But nearly 14,000 chemists, materials scientists, and physicists tore themselves away from wild roller coaster rides long enough to present some 6500 papers. Among the highlights: a color-switching molecular motor, a novel scheme for improving hybrid organic-inorganic solar cells, and a safer way to make an antismog fuel additive that's more environmentally friendly than the most widely used additive, MTBE.

Nano-motor's Rainbow Connection

Nanotechnology's forte—manipulating matter at near the atomic scale—is also its biggest weakness. Several research groups, for example, have built tiny rotary motors that spin in circles. But getting those motors to do work that makes a difference in our macrosized world has been hard. At the ACS meeting, Ben Feringa, a chemist at the University of Gröningen in the Netherlands, reported progress that puts the nano-to-macro transition in a new light.

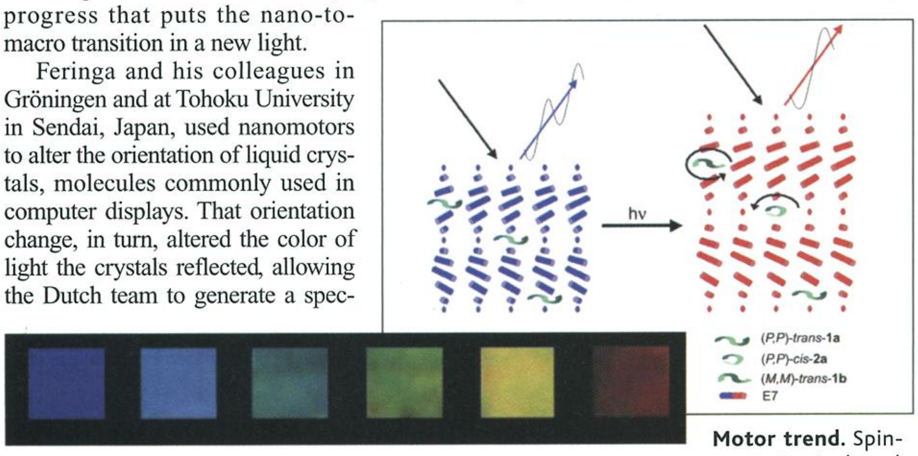
Feringa and his colleagues in Gröningen and at Tohoku University in Sendai, Japan, used nanomotors to alter the orientation of liquid crystals, molecules commonly used in computer displays. That orientation change, in turn, altered the color of light the crystals reflected, allowing the Dutch team to generate a spectrum of different colors from a display without the need for the electronic circuitry that currently drives such devices.

The results—also published in the online edition of the *Proceedings of the National Academy of Sciences*—are unlikely to lead to quick commercial applications, Feringa cautions. Nevertheless, the work is impressive, says George Whitesides, a chemist and nanotechnology expert at Harvard University in Cambridge, Massachusetts. "It's a terrific example of trying to couple molecular-scale stuff to something real," he says.

Feringa says that's exactly what he was hoping to accomplish. Three years ago his group reported making one of the first examples of a light-driven molecular motor. These compounds harbor two separate three-ring groups that rotate relative to one another. A full 360° spin occurs in four separate steps. First, the top half of the molecule absorbs a photon, causing it to turn 90° and adopt an energetically unstable orientation. The molecule stabilizes itself by making another quarter-turn, a reaction that occurs spontaneously because it is energetically favorable. Those two steps are then repeated, causing the molecule to spin in one direction.

The early molecular spinners were less than ideal. Among other drawbacks, the reactions that drove the spin worked only at high temperatures. Now the researchers have tweaked the structure of their motors to allow them to work at room temperature and to spin much more quickly than previous versions, making them potentially more powerful. They have also added the new-model motors to a thin film of rod-shaped molecules, called cholesteric liquid crystals. These molecules tend to stack like pencils lying flat one atop the other. Each layer is slightly offset from the one beneath it, so that collectively they twist upward like a spiral staircase.

Researchers have long known that the spacing between the molecules in a liquid crystal can change the color of light it reflects—tightly packed liquid crystals reflecting short wavelengths such as blue, widely spaced molecules reflecting longer wavelengths such as red. Feringa's team found that shining light on their motor-spiked liquid crystals caused the motors to turn, increasing the pitch of the liquid crystals and forcing them to move apart slightly (see diagram). The resulting color change wasn't instant. It took 10 seconds of illumination for the crystals to turn from violet to blue, and nearly a minute and a half to cross the entire visible spectrum. The speed of the color change is likely to underwhelm displaymakers looking for ways to scrap energy-hogging electronic components used by current setups. But Feringa says his efforts are just getting started. "This is the first demonstration that a molecular motor can be used to control the movement of many molecules and have a macrosized effect," he says. And that could give nanotechnology a whole new strength.



Motor trend. Spinning molecules (green) twist liquid crystals into changing color.

Stellar Way to Catch More Rays

Star-shaped plastics may just help the sunshine go a bit farther. Although most plastics are made from chainlike molecules, in recent years researchers have come up with a bevy of techniques for coaxing polymers to grow into tiny balls called dendrimers. Groups are looking at using dendrimers as everything from drug carriers to catalysts. At the ACS meeting, chemist Jean Fréchet of the University of California, Berkeley, reported that dendrimers may also help solar cells squeeze more electricity out of sunlight.

Fréchet's group has been working to improve a type of solar cell that uses an organic dye to collect the energy in sunlight and generate an electrical current. The researchers created dendrimers packed with light-harvesting compounds and added them to the solar cells. The dendrimers acted as antennae to capture more light, greatly enhancing the cells' light absorption.

"It's a promising approach" to improving conventional solar cells, says Mary Ann Fox, a chemist and the chancellor of North Carolina State University in Raleigh, whose group is pursuing similar research. Dendrimers currently are prohibitively expensive for high-volume applications, Fréchet notes. But if they yield promising light-absorbing compounds, researchers may be able to mimic the effect with cheaper conventional polymers.

Most commercial solar cells today use only inorganic semiconductors, such as silicon and the alloy cadmium telluride, to convert sunlight into a steady stream of electrons that can serve as a power source. But in 1991, Michael Grätzel of the Swiss Federal Institute of Technology in Lausanne devised a novel hybrid solar cell made from both organic and inorganic components.

CREDITS: VAN DELDEN *ET AL.*, *PNAS*

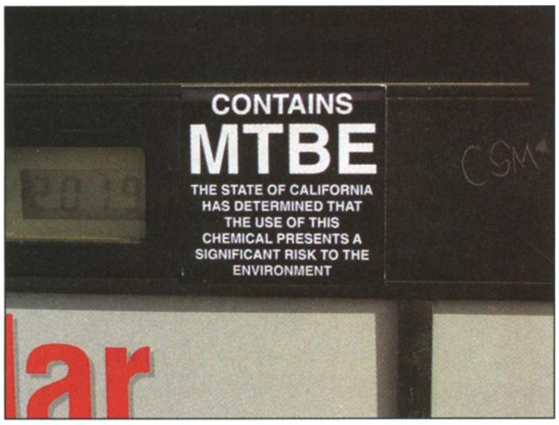
The device uses a rhodamine-based dye to absorb sunlight, which excites electrons in the dye and gives them enough energy to hop around. The mobile electrons quickly jump to a network of neighboring inorganic particles of titanium dioxide, which ferries them to an electrode that is connected to an external circuit, allowing them to power lights, toasters, or other electrical equipment. Grätzel cells, as they have come to be known, are cheap to make. But most such cells convert only about 6% of the energy in incoming sunlight to usable electrons, far below what many pure inorganic solar cells can accomplish. Hence Fréchet's interest in using dendrimers to increase that efficiency.

Unlike chainlike polymers, dendrimers have a branching structure that gives them a large surface area, perfect for attaching light-harvesting groups. Fréchet's group created dendrimers shrouded with coumarin 2 dyes, which readily absorb ultraviolet light, then added them to the mix of light-absorbing organics in a Grätzel cell and turned on a test lamp. "We get a huge enhancement" in the absorbed light, Fréchet says—enough to boost the electrical efficiency of the device by a couple percent.

Fréchet is quick to note that the current tests were done with ultraviolet lamps in the lab. But the Berkeley group is getting ready to repeat the tests with dendrimers designed to capture natural light. If all goes well, a few polymeric stars may hold the future to harnessing the power of the sun.

Cleaning Air While Sparing Water

Kermit the Frog was right: It's not easy being green. The United States Clean Air Act requires that smog-ridden municipalities such as Los Angeles add oxygen-rich compounds to gasoline to help it burn more cleanly and thereby reduce smog-forming exhaust. However, cries for banning the most widely used additive, methyl tertiary-butyl ether (MTBE), are growing. MTBE readily dissolves in water and has fouled groundwater supplies around the country. A possible MTBE replacement, called dimethyl carbonate (DMC), does an even better job at helping gasoline burn cleanly. But the most prevalent scheme for making it carries its own environmental baggage, and alternatives are more costly.



Greener gasoline? A benign alternative to a double-edged fuel additive may soon be easier to come by.

CREDIT: SARAH PHELAN

At the ACS meeting, however, researchers led by chemist Yiling Tian at Tianjin University in China reported a potentially greener and cheaper approach to making DMC. The key is a new catalyst that turns carbon dioxide and cheap, nonhazardous starting materials into DMC. "It's a very interesting result," says Michele Aresta, a chemist at the University of Bari, Italy. He cautions, however, that because proprietary concerns kept Tian silent about details of the new catalyst, the process's commercial prospects are hard to assess.

Even though DMC is nontoxic and therefore a potentially benign fuel additive, it has been anything but benign to make. Most producers start with a poisonous gas called phosgene, which requires expensive equipment to keep it contained. To make matters worse, generating DMC from phosgene produces chlorinated byproducts that can damage wastewater streams, says Chang-jun Liu, a chemist at Tianjin University, who is not affiliated with Tian's project.

Cleaner schemes do exist. One, which uses a catalyst to carry out a reaction between methanol, carbon dioxide, and ethylene oxide, has already been commercialized. But the reaction is still too expensive to be useful for making DMC in high volumes, Tian says.

Seeking a cheaper, more effective alternative, Tian and colleagues devised a catalyst containing two different metals that makes DMC from methanol, dimethyl ether—a cheap methanol derivative—and a pressurized form of CO_2 called supercritical CO_2. What is more, Tian says the reaction works under mild conditions and turns out DMC in high yield. That combination, Liu says, should make the process easy to scale up to generate DMC in the high volumes needed to bring the price down.

The new process could have other environmental benefits as well, Tian contends. Not only are the starting materials and byproducts nontoxic, but the process could be designed to tap CO_2 present in oil fields, instead of releasing it to the atmosphere, and thereby help prevent the buildup of greenhouse gases. According to Tian, the Chinese energy giant Sino Petroleum, which funds part of his work, is considering scaling up the new process. If it succeeds, petroleum companies may have an easier time hewing to Kermit's hue.

–ROBERT F. SERVICE

Snapshots From the Meeting

Electronic nose for liquids. Researchers around the globe are perfecting strategies for making polymer-based sensors that detect an array of different gases and produce an electrical signal. At the meeting, physicist Ananth Dodabalapur and colleagues at Lucent Technologies' Bell Labs in Murray Hill, New Jersey, reported the first conducting polymer transistors that work in liquids to detect a wide variety of compounds. Look for these to be integrated with microfluidic devices to automatically detect compounds coming from handheld medical diagnostic equipment.

Circular polyethylene. Virtually all common plastics are made from hydrocarbon groups linked together in long chains, like boxcars in a train. In a few exotic varieties, however, researchers have linked the ends of these polymer chains together to form large circles. At the meeting, chemist Robert Grubbs of the California Institute of Technology in Pasadena reported that his group has created a catalyst that turns one of the most common linear polymers, polyethylene—the stuff of grocery bags—into polymer circles. Watch for studies that show whether the new circular polyethylene has unique properties that push the ubiquitous polymer into new markets.

More on drug pollution. The U.S. Geological Survey came out with a widely publicized study last month showing that a handful of prescription and over-the-counter drugs could be detected in U.S. waterways, raising concerns that they pose a new threat to fish and other aquatic life. Padma Venkatraman and colleagues at Johns Hopkins University in Baltimore reported here that the problem could be much more widespread. To guide future studies, they tracked sales and prescription data for the 200 most popular prescription drugs and fingered numerous antimicrobials, anticonvulsants, antidepressants, and anticancer compounds that could further endanger aquatic life. Results from ongoing field studies by the group will better define the true magnitude of the threat.

–R.F.S.