Chemistry Community Swarms Into Windy City

Two times each year, legions of chemists gather in North America for a massive meeting to discuss the state of the art in their science. The second of this year's get-togethers occurred 2 weeks ago, when the 206th national meeting of the American Chemical Society (ACS) drew about 13,000 chemists, scientists, and onlookers to Chicago. Researchers shared 4800 or so papers and posters on everything from making waste plastic into fuel oil to the chemical basis for the stench of ginkgo fruit to modeling the first instants of photosynthesis.

Harvesting Light With Molecular Leaves

Within each of the thousands of sun-drinking leaves that make up a tree's canopy are arrays of light-absorbing molecules. These arrays, each made up of hundreds of chlorophyll molecules, capture solar energy and shunt it to photosynthetic reaction centers; the chemical energy produced there drives the plant's biochemical machinery.

Scientists know much more about the second part of this process—the energy producing steps—than they do about the initial steps, the capture of light by the chlorophyll arrays. Chemist Jonathan Lindsey and coworkers at Carnegie-Mellon University told an ACS session that they aim to fill this knowledge gap with a novel set of synthetic light-absorbing molecules. The molecules can be used as "Lego building blocks" to construct models of a plant's chlorophyll assemblages. (The scientists also reported on their plans 2 weeks earlier in the *Journal of the American Chemical Society*.)

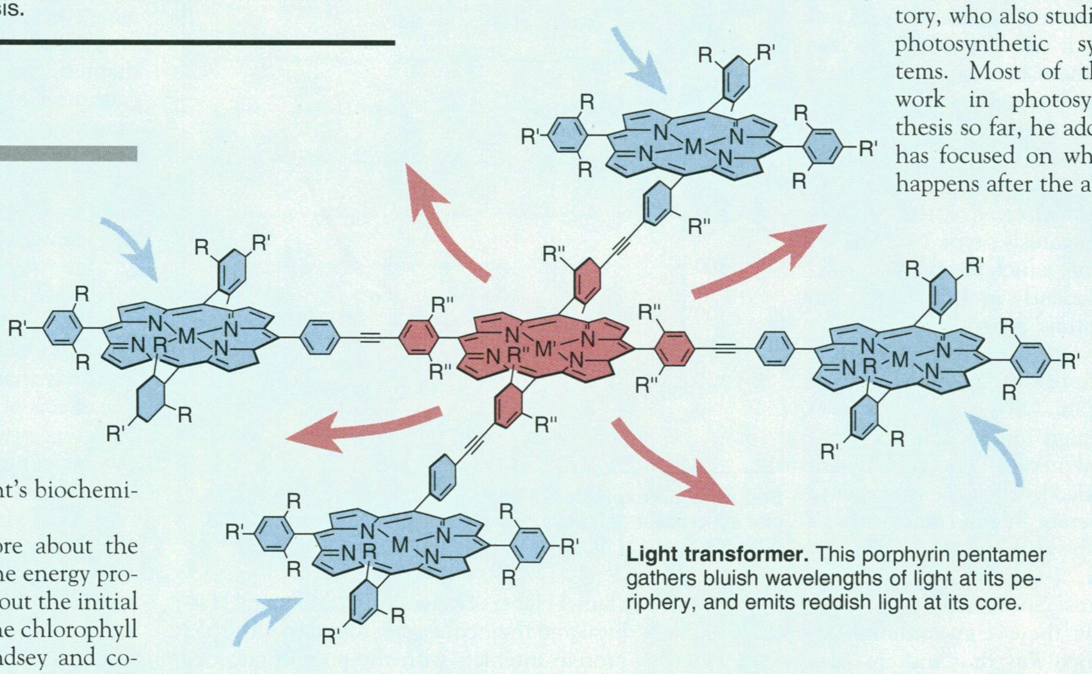
The reason for the gap in knowledge is that chlorophyll arrays are extremely complex and nobody has been able to figure out their structure or precisely how their configuration relates to their light-capturing function. So researchers have turned instead to porphyrin molecules, which are closely related in structure to chlorophyll and, like chlorophyll molecules, they capture light. But porphyrin molecules have an important advantage: They can be more easily modified chemically, giving chemists a chance to link them together in various configurations. The goal, Lindsey says, is to hook tens or hundreds together to help piece together information about the natural arrangement of chlorophyll molecules.

Lindsey and his team built porphyrin pentamers, each made of one central porphyrin molecule flanked on each of its four sides by another porphyrin molecule. Researchers elsewhere have done similar work, but their structures have two problems: They are not architecturally rigid nor are they soluble. Ridigity is key, Lindsey says, because it is more difficult to determine the structure of floppy molecules, and in chemistry knowledge of structure is paramount. And to study the structures as individuals, the pentamers need to be in solution.

The Carnegie-Mellon creations meet both criteria. The researchers conferred rigidity by connecting the four outer porphyrins to the core using stiff triple-bond linkages. And to ensure solubility, they modified the porphyrin molecules with carbohydrate appendages that point above and below the plane of the molecules. In that form, the pentamers cannot stack like plates, forming an insoluble agglomeration.

With those problems solved, the chemists turned to the mission of their molecules: catching light and moving it along. The outer quartet of porphyrins, they found, absorbs light of specific wavelengths and rapidly transfers the light energy to the core porphyrin, which vents the energy input by fluorescing. Lindsey and his colleagues, postdoctoral associate Sreedharan Prathapan and graduate student Thomas Johnson, are heartened by the results so far, but Lindsey says they really are just out of the starting gate. "Now the question is whether this building block approach will work with 10 [or more] times as many chromophores [porphyrin] molecules," Lindsey says.

The technique already has won plaudits from other researchers. "This provides a mechanism for designing well-characterized antennae arrays," says chemist Michael Wasielewski of Argonne National Laboratory, who also studies photosynthetic systems. Most of the work in photosynthesis so far, he adds, has focused on what happens after the antennae have done their job. But researchers using these porphyrin-based models will be able to analyze the process by which pigment molecules like chlorophylls can absorb light and then pass it along their molecular anatomies in a form that later can be tapped to drive chemical reactions.



Light transformer. This porphyrin pentamer gathers bluish wavelengths of light at its periphery, and emits reddish light at its core.

SOURCE: LINDSEY *ET AL.* ILLUSTRATION: K. SUTLIFF

And answering questions about photosynthesis may not be the end to the usefulness of the porphyrin-based system. If the approach proves to be as versatile as Lindsey hopes, the Carnegie-Mellon chemist speculates that well-designed porphyrin constructions could go beyond models of natural photosynthesis and enter the realm of technology, serving as molecular information processing devices in which information is carried by photons absorbing and emitting from molecules rather than electrons skitting through microelectronic chips.

Gas Your Car With Coal and Plastic Bottles

When most people view the country's abundant supplies of used tires, discarded plastic, rotting paper, and agricultural waste, it looks like little more than an eyesore and a disposal problem. Energy researchers at the ACS meeting, however, look at the same landscape and see a vast, untapped oil field.

In a symposium on converting waste into fuel, researchers proposed a method for taking this waste and turning it into black gold, which can be used to produce gasoline and other fuels. And they're not just talking about a little black gold, either. If all of these waste and biomass sources were converted to oil, it could replace the 10 million barrels of imported petroleum used each day in the United States, noted Gerald Huffman, a chemist at the University of Kentucky, where he directs the Consortium for Fossil Fuel Liquefaction Science (CFFLS).

The technology behind this proposed environmental alchemy was developed for the consortium's previous work on liquefying coal. The idea, whose origins go back to the early part of the century, is to use coal instead of petroleum for making liquid fuels such as gasoline, says chemist Irving Wender, a consortium member at the University of Pittsburgh. The coal conversion process, which is currently too expensive to compete in the energy marketplace with crude oil, takes place in a stainless steel reactor heated to roughly 400 degrees Celsius. Coal is dissolved in a hydrogen-rich solvent and then fed into the reactor along with a catalyst—in this case, an iron-based catalyst. In the reactor the materials are surrounded by an atmosphere of pressurized hydrogen. The result is oil, a liquid mixture of hydrocarbons, at an efficiency of 50%-60%.

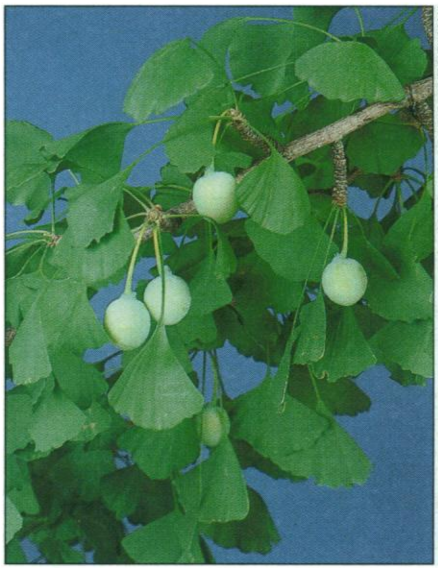
The CFFLS researchers thought they might do better with plastic waste and solve a pressing national waste disposal problem in the bargain. Since most plastic and rubber starts out as petroleum, and other wastes including biomass have plenty of carbon and hydrogen—the building blocks of petroleum—why, they asked themselves, couldn't these waste materials be turned into oil?

Preliminary experiments show that the prospects look good. When mixed with plastic or rubber waste, for example, the efficiency of coal liquefaction goes up between 5% and 15%, Wender says. Researchers are not sure what is responsible for the boost in efficiency, but they speculate that the higher hydrogen content of the plastic or the rubber's carbon black—a sooty filler and binding material in tires that might be serving as a liquefaction catalyst—could be partly responsible for the improvement.

The estimated cost of the coal/waste-to-oil conversion is about $35 per barrel, which is not cheap enough to compete in the energy marketplace, where a barrel of crude oil goes for about $20 per barrel. But replacing the coal entirely with wastes like plastic and rubber could yield a price that is closer to market reality.

CFFLS researchers have found that liquefaction can turn major sources of plastic waste, such as beverage containers (which are usually made out of polyethylene terephthalate), into high-grade oil at efficiencies of about 90%; the same figure applies to rubber liquefaction. Part of the efficiency boost stems from the greater hydrogen content of these wastes compared to coal. According to rough economic estimates by consortium researchers, the process now costs about $28 per barrel. And there's a bonus: Unlike petroleum, plastic-derived oil contains no sulfur or nitrogen, which can lead to acid rain when burned. "It is better in quality than oil imported from the Middle East," Huffman contends.

It's also easy to refine because it is not as rich in the larger and harder-to-refine hydrocarbon molecules found in petroleum. "I am amazed how easy it is to make gasoline from it," Wender adds. Still, he thinks that coliquefaction of waste and coal is the most likely scenario if and when the process becomes economically competitive. "You won't always be able to rely on enough waste to be shipped or trucked into your plant," but coal will always be available, he says. The two sources together, therefore, would sum into a steady feedstock.


RUNK/SCHOENBERGER/GRANT HEILMAN

The nose knows. And chemists now know what's behind the vile odor of the ginkgo tree.

Of course all of that depends on whether some combination of politics, science, and technology development render the process economically competitive with petroleum, says Harold H. Schobert, chairman of the Fuels Science Program at Pennsylvania State University, where he and other researchers study coal liquefaction for fuel and other applications. Still, Schobert ranks coal liquefaction developments over the past 15 years, including the process developed by the CFFLS researchers, as "heroic." In the 1970s, he notes, analysts predicted that coal liquefaction would become economical when petroleum went to $80 a barrel. "Now the number is more $32-$34 per barrel," he says, and that would put the CFFLS colifquefaction into the ballpark.

However, Schobert notes that liquefaction of coal still has problems. One serious drawback is that it yields fuels that are higher in aromatic hydrocarbons than petroleum, a result that places the process at odds with 1990 amendments to the Clean Air Act that call for lower aromatic content in fuels. And consumers will likely have trouble accepting a fuel that solves one environmental problem by adding to another.

Sniffing Out the Origins of Ginkgo-Stink

Everybody who knows ginkgo trees also knows that ginkgo berries give off a, well, unusual odor. Not everybody is deterred by the smell of ginkgo flesh, however. Some Chinese aficionados of ginkgo berries for example, covet the nut inside as a delicacy. And at least one chemist was intrigued enough to want to know just why the berries smell so bad.

Last fall, Sara McGarty, an information specialist at General Foods USA's Technical Center in Tarrytown, New York, trekked to the fruiting *Ginkgo biloba* trees at the New York Botanical Garden to harvest a few juicy specimens for Thomas H. Parliment, a flavor chemist at General Foods who normally focuses on keeping bad smells out of food and who became interested in the origin of the unmistakable ginkgo odor.

Parliment shared his findings at the ACS meeting. After pureeing the ginkgo flesh in water, steam distilling the slurry, and extracting the organic compounds in the distillate, he injected samples into a gas chromatograph to separate and identify the volatile compounds, which are the ones that carry aroma. He also sent the separated compounds through a mass spectrometer to help in the chemical IDs. The results: Ginkgo's stink derives mainly from the presence of butanoic and hexanoic acid, though the fruit also contains traces of octanoic acid and methyl hexanoate.

"These are the same lower [small] fatty acids found in rancid butter or romano cheese," Parliment says. "The unique thing, though, is that the levels of these chemicals are so high." Butanoic acid, for example, is noticeable to the human nose at a level of about 1 milligram per quart of water. Ripe ginkgo flesh has 300 times that level. The nuts, luckily, seem free of the foul smelling compounds.

Parliment, although he says he wouldn't turn up his nose at further ginkgo aroma investigation, has no present plans to pursue this research further.

–Ivan Amato