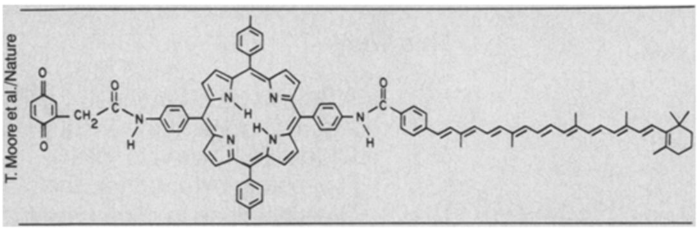
SCIENCE NEWS of the week

A Step Toward Synthesizing Photosynthesis


T. Moore et al./Nature

Electron transfer in this recently fabricated molecule mimics the first steps of photosynthesis.

If only green plants and algae would spill the beans about photosynthesis, then we humans could copy nature's magical process to convert sunlight into forms of energy useful for our needs. After 200 years of study, with many of the intricacies of photosynthesis yet to be worked out, chemists have come to understand the basic steps well enough to attempt to mimic them with artificial models. So far scientists have been successful in devising molecules that efficiently harvest sunlight and then transform that radiant energy into electrochemical potential energy by transferring an electron from one end of the molecule to the other (SN: 8/2/80, p. 68).

The problem has been in keeping the molecule polarized long enough so that the charged parts could then chemically react with other molecules. (In natural photosynthesis this is the first step in a long chain of reactions that lead to the production of glucose). For most fabricated molecules the charges recombine after a few hundred picoseconds. Now, a group of chemists at Arizona State University in Tempe have designed a stable molecule that has a charge separation lifetime nearly 10,000 times longer. By exploring the factors that produce this unusual lifetime, chemists hope to uncover some of the details of natural photosynthesis. Practical solar cells based on these principles, however, are still a long time in coming, say the researchers.

The molecular system that Devens Gust, Thomas A. Moore and co-workers synthesized over the last two years is made from three parts: a porphyrin (P) molecule, built like chlorophyll in natural systems, to absorb light; a quinone (Q) molecule that accepts an electron from the excited porphyrin; and a carotenoid (C) that becomes positively charged by donating an electron to the porphryin. Hydrocarbons link the C and Q molecules to opposite sides of the porphyrin. As reported in the Feb.16 issue of NATURE, flash spectroscopy revealed that the final charge-separated state C^+PQ^- can live up to 3 microseconds.

The Arizona group, in aiming for the long lifetime, based the architecture of their molecule on several considerations. First, chlorophyll and quinones are known to inhabit chloroplasts, the subcellular photosynthesis factories in plants. Second, while scientists are unsure of the complete composition and inner workings of the chloroplast, they suspect that the conversion of solar energy is accomplished when an electron leapfrogs through a series of molecules. Most of the previously synthesized molecules have consisted of two parts, allowing an electron to jump only once. The new triad molecule, says Michael Wasielewski, a chemist at Argonne (Ill.) National Labs, is an important demonstration that two electron steps can lead to a longer lifetime.

Another advantage of the triad molecule over a double one is that the separated charges have farther to travel before they can recombine. Gust thinks that this increased distance is partially responsible for the extra stability of the tripartite molecule.

The construction of a triad system does not, however, guarantee a longer lifetime. Recently, for example, a group of Japanese researchers made a molecule from a porphyrin and two quinones that had a relatively short lifetime. So what makes the CPQ molecule from Arizona so different? Chemists don't really know, but they have some ideas where to look for answers. Gust's group has started a slew of experiments pinching and probing the components, linkages and structure of the molecule. As a step toward constructing an artificial photosynthesis system, they also plan to try to initiate chemical reactions with other molecules. According to Gust, the main purpose is to learn more about the chemical and physical requirements for maintaining charge separation, as one of many steps in photosynthesis. The molecule, he says, "is not designed to be put up on somebody's roof and start running their air conditioner. It's fundamental knowledge we're after." —*S. Weisburd*

Agent Orange study finds adverse effects

Aerial spraying of herbicides over Vietnam by the U.S. military was carried out for nine years, beginning in 1962. Code-named Ranch Hand, this defoliation program rained an estimated 19 million gallons of herbicides—all of them contaminated with dioxin—over some 10 to 20 percent of Vietnam. A just-released $11 million Air Force study — comparing all 1,269 Ranch Hand participants with 19,000 military-cargo flight-crew members and support personnel who served in Southeast Asia during the same period—shows subtle and unanticipated problems among the Ranch Handers and their offspring. What has analysts baffled is why the observed effects are different from those previously identified in human populations exposed to dioxin.

Ranch Hand participants — pilots, crew members and support personnel — received substantial exposure to herbicides and dioxin on almost a daily occupational basis. In fact, the study estimates that the average participant "received, at a minimum, 1,000 times more exposure to Herbicide Orange [of six defoliants, the most frequently used] than would an average unclothed man, standing in an open field directly beneath a spraying aircraft."

That's what makes conspicuous by their absence any findings among Ranch Handers of chloracne (chemical-induced skin eruptions), porphyria cutanea tarda (liver defect causing blotchy, easily bruised skin), or soft-tissue sarcomas: All have been reported among humans exposed to high levels of dioxin. What the study did find was a reported rate of neonatal and infant deaths four-fold higher among children of Ranch Handers. It also found a four-fold increase in minor birth defects (primarily birth marks) and a slightly higher number of physical handicaps reported among Ranch Handers' offspring. These associations are being ruled tentative, though, until they can be confirmed by medical records.

Though the differences are too small to be statistically significant, the report points to a 30 percent higher skin-cancer rate for Ranch Handers and a doubling in their genito-urinary and otopharyngeal cancer rates. More perplexing are the subtler effects: The rate of uptake for one measured hormone, T_3, showed Ranch Handers might have more of a tendency to develop an underactive thyroid. Their glucose-tolerance-test results signaled a possibly greater disposition for developing diabetes. Ranch Handers also had a greater preponderance of enlarged livers and reported more miscellaneous liver disorders. These and other findings will be followed up when the Air Force repeats this study—using the same participants—five times over the next 18 years. —***J. Raloff***