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Small-Molecule Photosynthesis

Attempts To Mimic A Plant's Light-Harvesting And Water-Splitting Megamachinery

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By some estimates, humanity's demand for energy will increase by 50% in 2030 from what it is today. Faced with this impending colossal demand, many researchers are pointing to the sun as a necessary source of energy. The challenge remains to harness that energy in a cost-effective, environmentally friendly way.

Plants have been doing just that for about 2.5 billion years by means of photosynthesis, by which light energy is used to split water, subsequently producing oxygen gas and building sugar fuels. Many researchers have looked to this ancient process for inspiration.

In fact, all solar energy research can be considered a form of so-called artificial or synthetic photosynthesis. The precise definition of photosynthesis is, after all, making something—electricity or fuel—by using light. Artificial photosynthesis can include everything from silicon-based photovoltaics to nanostructured materials that house light-driven water-oxidation and fuel-building catalysts.

Meanwhile, a subset of researchers is taking a more biomimetic approach, aiming to emulate with small molecules what plants do with a megaprotein complex. In particular, they are trying to build scaled-down versions of the plant's photosystem II (PSII), a 20-protein machine that "captures sunlight using pigments and funnels the excitation energy into its reaction centers," explains [Leif Hammarström](#), a photochemist at Uppsala University, in Sweden.

The overall efficiency of photosynthesis for making sugar fuels is low—only about 2–3%—because plants' primary goal is to live and reproduce, not store fuel. But the first steps performed by PSII are much more energy efficient, about 30%. So researchers want to "take the basic chemistry and the basic physics of the photosynthetic reaction center" and build a molecular version in the lab, says [Devens Gust](#), a photochemist at Arizona State University. In effect, they want to produce a molecular photovoltaic that, like PSII, produces a current of electrons that could be used to split water and thus drive the production of a fuel such as hydrogen gas.

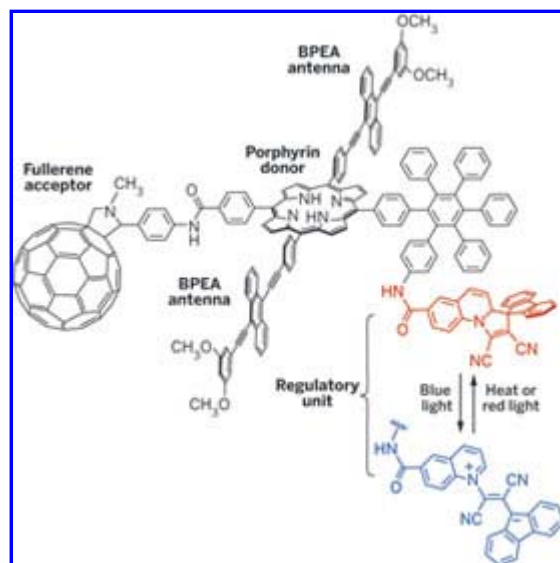
The idea of directly mimicking photosynthesis to serve the world's energy needs is not new. It was first proposed in a 1912 conference address by an Italian photochemist named Giacomo Ciamician. Ciamician "had a vision of artificial photosynthesis removing our need for using coal as energy," Gust says. "But the idea didn't move forward for a long time because people didn't know how natural photosynthesis worked at a molecular level."

In the late 1970s and '80s, biophysical techniques such as electron paramagnetic resonance and protein X-ray crystallography were beginning to provide clues about the molecular makeup and function of PSII. Concurrently, researchers began building simple systems made of porphyrin donors, which are more stable relatives of chlorophyll, the primary light-harvesting pigment in PSII. To the porphyrin, they attached an electron-accepting quinone, Gust says. "Then they shined light on that and got a very high yield of light-induced charge separation," that is, a light-excited electron and the leftover hole.

"But the problem was that the charge-separated state that was made had a short lifetime. The electron just jumped back to the oxidized porphyrin, and it recombined and made heat before you could do something useful with the electrons and holes. You made chemical energy, but it was lost on the picosecond timescale," Gust says.

Nowadays, "we separate the negative charge and the positive hole by a longer distance, to slow down the recombination step. That distance gives you a long enough lifetime that you can start to think about doing some chemistry with the charge separation," he says. Gust and his longtime collaborators Ana Moore and Thomas Moore, both at Arizona State University, have designed a variety of artificial photosynthetic systems, including some with light-gathering anthracene-based antennas attached to an electron-donating porphyrin and an electron-accepting fullerene.

Last year, the team made an additional step forward by adding a self-regulating molecular component that can help the molecule avoid photodamage in harsh light, much in the same way plants do. In particular, the team attached a control moiety that can photoisomerize between a dihydroindolizine and a betaine. In normal light the dihydroindolizine doesn't alter electron transfer, whereas in bright light the betaine can pull the excitation energy out of the antenna system to block electron transfer. This addition mimics a process in natural photosynthesis by which pigments called zeaxanthins pull excitation energy out of the PSII when the machine is being driven too hard by excessive sunlight. The next steps are to attach a water-splitting catalyst to the molecular photovoltaic and to get the system to work efficiently. But neither of these goals has been achieved



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Damage Control A regulatory unit interconverts between a dihydroindolizine (red) and a betaine (blue) in response to changes in light or heat, controlling the light-induced charge transfer between the porphyrin donor and the fullerene acceptor. The dihydroindolizine form has no effect on the porphyrin photochemistry, whereas the betaine form quenches the porphyrin excited state.

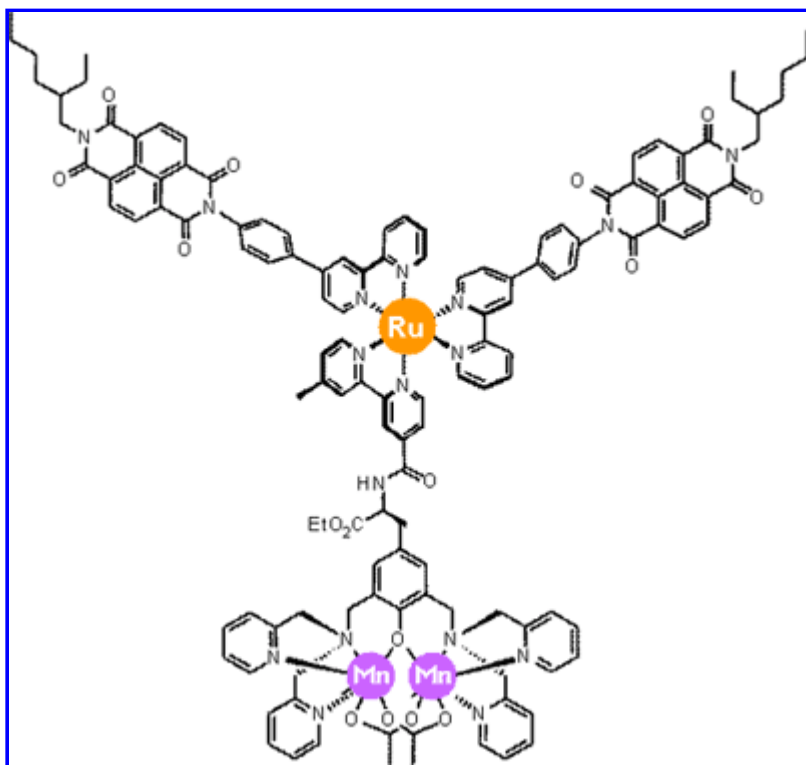
Although some researchers in this field focus on staying organic—just like the natural system—by employing light-harvesting molecules such as porphyrins or bacteriochlorins, others take an inorganic approach. For example, [Thomas Meyer](#), a chemist at the University of North Carolina, Chapel Hill, says he prefers to borrow the strategy of photosynthesis, but not its organic scaffolding, because inorganic materials are more robust in withstanding radiation damage. His team developed a bipyridine and ruthenium-based donor-acceptor system. "Light pops an electron from the ruthenium donor to the bipyridine acceptor" in a so-called metal-ligand charge transfer, he says. Meyer's strategy is then to attach a ruthenium-based water-oxidation catalyst. The idea is to use the electronic current from the light-harvesting apparatus to power the water-oxidation catalyst, but they still haven't been able to get the system to split water with incident light.

Then there are researchers, such as Hammarström, who straddle the inorganic and organic worlds. Hammarström is trying to integrate the light-harvesting apparatus and the water-oxidation catalyst by using a ruthenium-based system that harvests light and drives the oxidation of a dimanganese unit. Hammarström hopes that if the manganese is oxidized four times, the system might be able to split water, but so far the team has achieved only three oxidations.

Currently, all of the researchers who are working with small-molecule mimics of photosynthesis are still trying to use the light they harvest to split water. The next stage of their plan would be to incorporate catalysts that could take the electrons and protons produced during water-splitting and use them to build a fuel, but this milestone remains far afield.

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Courtesy of Leif Hammarström

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Two-For-One This synthetic photosynthesis strategy aims to combine the light-harvesting apparatus with a water-oxidation catalyst. The ruthenium component harvests light and drives the oxidation of the dimanganese unit, which is still being developed as a water-splitting catalyst.