MIMICKING NATURAL PHOTOSYNTHESIS

Systems that imitate aspects of natural photosynthetic energy conversion offer a number of potential payoffs

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Each hour, Earth's surface receives an amount of energy from the sun that approximately equals the amount of fossil fuels consumed globally in one year. The prospect of developing artificial chemical systems to harness this virtually infinite source of energy has excited scientists throughout this century.

Photosynthesis, the process that nature developed several billion years ago to trap solar energy and store it in the fuels that are essential for life on Earth, is, in essence, simple. Sunlight supplies the energy to reduce carbon dioxide to carbohydrates (the fuels) and to oxidize water to the oxygen needed to burn those fuels. Oxidation of the fuels generates the energy needed to sustain life.

Nature's system for carrying out this photoinduced redox process is highly complicated, however. Arrays of molecules, typically chlorophylls, harvest the photons, or quanta of energy, that make up sunlight. The energy is then transferred to reaction centers consisting of several molecular components where a series of electron-transfer reactions occurs.

The result is a separation of electrical charge and therefore a redox potential. The reduction potential leads to the conversion of CO₂ to carbohydrates through a complex series of reactions. At the same time, the oxidation potential pulls electrons off water, generating protons and oxygen molecules. Both reduction and oxidation processes require the assistance of enzymes—and some sophisticated chemistry.

"The plants are unsurpassed masters of—or marvelous workshops for—photochemical synthesis of the fundamental substances, building up from carbon dioxide with the help of solar energy," said Italian photochemist Giacomo Ciamician, chemistry professor at the University of Bologna, at the 8th International Congress in New York City in September 1912.

"Is fossil solar energy the only one that may be used in modern life and civilization?" he asked prophetically. "The fundamental problem from the technical point of view is how to fix the solar energy through suitable photochemical reactions."

Research into this fundamental problem has attracted intense interest over recent decades. "In the 1970s, there was huge interest in artificial photosynthesis because of the oil crisis," points out James R. Durrant, advanced research fellow at the Center for Photomolecular Sciences, Imperial College, London. "A lot of research started up then. In the 1990s, the field has been revitalized because of concern over CO₂ emissions."

And some geologists now believe that the world will begin to run short of oil in the next 10 to 20 years [Science, 281, 1128 (1998)].

Harry B. Gray, chemistry professor at California Institute of Technology, points to another reason why we should stop burning oil, gas, and coal. "We have to stop burning hydrocarbons as soon as possible because they're wonderful raw materials," he stresses [Eng. Sci., (3) 28 (1997)]. "We desperately need them to make dyes and drugs and tee shirts and chairs and automobiles—it's crazy to burn them. So sometime in the next century you'll see a massive conversion of this fossil-fuel-burning world of ours into a world that burns clean fuel."

The need to reduce dependence on fossil fuels and to develop technologies to produce clean fuels such as hydrogen is one of the major forces driving artificial photosynthesis research.

"The main targets of research are to identify systems that achieve efficient harvesting and conversion of sunlight to chemical or electrical energy using the fundamental concepts that nature developed 3.5 billion years ago in photosynthesis," says Michael Gratzel, professor of physical chemistry at the Swiss Federal Institute of Technology in Lausanne (EPFL).

Definitions of the term "artificial photosynthesis" vary. According to Arthur J. Nozik, senior research fellow and leader of...
Light-powered molecular machines

"Our research on solar energy conversion has led to an interesting spin-off," says Vincenzo Balzani, chemistry professor at the University of Bologna, Italy. "We have shown that light can be used to induce the mechanical movement of molecules."

The photochemistry includes photolytic reactions, may eventually lead to new applications, such as sunlight and photoinduced electron-transfer processes that are required for an artificial system for photosynthetic water splitting, can be used to generate movements in the molecular components of cleverly designed supramolecular systems," says Balzani.

The team points out that molecular-level machines, like macroscopic ones, require energy to work and signals to communicate with the operator. "Light can provide an answer to this dual requirement since mechanical movement can be induced by a photochemical reaction and its occurrence can be followed by absorption or emission spectroscopy," the researchers state.

Balzani, J. Fraser Stoddart, a professor of organic chemistry at the University of California, Los Angeles; and their co-workers incorporated a metal-based photosensitizer into a cyclophane host ligand to obtain a light sensitive host complex.

When excited by light in the presence of a sacrificial electron donor such as sodium oxalate, the photosensitizer reduces the host ligand. Reduction weakens the noncovalent bonding between host and guest and the guest departs. When oxygen is allowed to enter the system, the guest reenters the host. The guest and host are effectively a piston and cylinder driven by a photosensitizer acting as a light-fueled motor.

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the chemical sciences team at the National Renewable Energy Laboratory (NREL) in Golden, Colo., the term generally refers to man-made structures and systems that allow solar photochemistry to produce fuels and useful chemicals from simple substrates such as water, CO₂, and nitrogen. The photochemistry includes photolytic water splitting to make hydrogen; photoreduction of CO₂ to methane, other hydrocarbons, and alcohols; and photoreduction of N₂ to reduced nitrogen usable by green plants.

"The photoactive species in these man-made systems can be semiconductors for photoelectrochemical energy conversion or molecules for photochemical energy conversion," Nozik says. "Biological materials like blue-green algae and photosynthetic bacteria can also be manipulated for photobiological energy conversion. Combinations of these systems are also feasible.

"The obvious attraction for solar photochemical and photoelectrochemical conversion is that fuels, chemicals, and electricity may be produced with minimal environmental pollution and with closed renewable energy cycles that provide for an unlimited energy resource," he adds.

Some experts, although recognizing the importance of various approaches to solar energy conversion, prefer to restrict the use of the term "artificial photosynthesis" to molecular-based biomimetic systems, excluding photoelectrochemical methods of converting solar energy. Devens Gust, a chemistry professor at Arizona State University, Tempe, says, "When I talk about artificial photosynthesis, I mean the design, synthesis, and study of molecular or supramolecular systems that mimic the important aspects of natural photosynthetic energy conversion.

"Ultimately, electricity generation may not be the best way to use solar energy," Gust continues. "The use of sunlight to generate fuels such as hydrogen or methane could avoid the storage problem one has with electricity. Artificial photosynthesis, which may be coupled to chemical reactions, may eventually lead to such technology."

Gust points to other potential spin-offs of artificial photosynthetic research. "These include molecules-scale photonic and optoelectronic devices and sensors and photomedical applications," he says. "There are also a huge number of energy requiring enzymatic reactions, all of which could, in principle, be powered by artificial photoconversion."

Chemist Marye Anne Fox, chancellor of North Carolina State University, Raleigh, points out that research on artificial photosynthesis can lead to deeper insight into natural photosynthesis, many aspects of which are still veiled in mystery.

"The main scientific question that drives artificial photosynthesis," she says, "is why nature employs such exquisite structural order to control the direction and efficiency of a very simple electron transfer and why the light-collection devices have such extraordinary order and symmetry. If these structural parameters can be understood, we would be in an excellent position to synthesize more robust arrays that duplicate and improve on the materials used by nature to control these optical events."

"The ramifications would be significant for solar energy conversion, for optoelectronic devices, and for materials science," she continues. "Understanding these ef-
fects, of course, addresses some of the most fundamental of all questions in traditional physical organic chemistry."

**Mimicking the reaction center**

"Artificial photosynthetic systems for the generation of fuels should most likely include four basic features," says Vincenzo Balzani, chemistry professor of the University of Bologna, Italy. "These are antennae for light harvesting, a reaction center for charge separation, catalysts, and a membrane to provide physical separation of the products."

According to Gust, most research on artificial photosynthesis has been directed toward mimicry of the natural reaction center. This center, he says, functions as a molecular-scale solar photovoltaic device. "The job of the reaction center is to convert light energy into chemical energy that can be transported, stored, and ultimately used to power the various energy-requiring chemical reactions necessary for maintenance, growth, and reproduction of the organism," he explains.

Green plants employ chlorophyll, a magnesium-containing porphyrin, as the chromophore to harvest light. The trapped light energy is used to promote electrons into high-energy excited states. However, electrons in these states tend to decay back to their ground states within nanoseconds, wasting the harvested energy as heat. Chromophores in green plants prevent this from happening by donating the excited electrons to acceptor molecules at a rate faster than the rate of decay. The acceptors are chlorophyll derivatives or quinone molecules. The resulting separation of negative and positive charges at the reaction center preserves some of the photon energy as chemical potential energy.

The electronic coupling between donor and acceptor is controlled by a protein matrix that contains these two components, Gust points out. The protein also provides the medium within which the electron transfer occurs.

"An artificial reaction center thus requires at the minimum some kind of chromophore that can absorb light and act as an electron donor, an electron acceptor moiety, and an organizational principle that controls the electronic interaction between the donor and the acceptor and thus the rate and yield of the photoinduced electron-transfer reaction," he says.

Takuzo Aida, chemistry professor at the University of Tokyo, notes that achieving a long-lived charge separation is the key to realizing artificial photosynthesis. One way to do this, he says, is to spatially separate the donor from the acceptor. His group has designed and synthesized dendrimers—highly branched macromolecules—that achieve this separation [J. Am. Chem. Soc., 118, 3978 (1996)].

"We utilized a negatively charged spherical aryl ether dendrimer containing a zinc porphyrin at its center," he tells C&EN. "In water, mixing of this dendrimer with a positively charged acceptor results in a spatially separated donor-acceptor system where the acceptor molecules are trapped on the exterior surface of the dendrimer."

Upon excitation of the zinc porphyrin core of the dendrimer with visible light, Aida explains, long-range photoinduced transfer of electrons to the acceptor molecules occurs. This gives a charge-separated system that is long-lived because it's unlikely that electrons will transfer back through the dendrimer architecture to the zinc porphyrin.

Gust and coworkers Thomas A. Moore and Ana L. Moore, professors of biochemistry and chemistry, respectively, at Arizona State, have built artificial reaction centers that are "supermolecules" composed of organic chromophores and electron donors and acceptors structurally related to those found in natural systems. Whereas nature uses a protein matrix to link these functional moieties, the Arizona team uses covalent bonds to link the components.

The first such systems, developed in the 1970s, were "dyad" molecules consisting of synthetic porphyrins covalently linked to quinone moieties. Following
absorption of light, the porphyrin molecule (P) transfers an electron to a quinone molecule (Q) resulting in a charge-separated state consisting of a cationic radical P\(^+\) and an anionic radical Q\(^-\). However, the lifetime of P\(^+\)-Q\(^-\) is very short because of the so-called back-reaction. The electron rapidly returns to the porphyrin molecule, losing energy as heat, and the ground state of the molecule is restored.

In the 1980s, Gust, the Moores, and their coworkers showed that the back-reaction could be slowed down substantially with a "triad" molecule composed of a tetraarylporphyrin covalently linked to both a carotenoid (C) and a quinone. The slowing results from the formation of the charge-separated state C\(^+\)-P-Q\(^-\) in which the two radical ions are separated by a neutral porphyrin.

"Making a photoexcitable molecule that is flanked on two sides by an electron donor and an electron acceptor is a popular motif in artificial photosynthesis research," comments Thomas E. Mallouk, a chemistry professor at Pennsylvania State University, University Park. "Such arrangements are mimetic of the 'guts' of the photosynthetic reaction center, which moves electrons across a membrane in response to photoexcitation."

Gust points out that the greater distance and reduced electronic interaction between the charged moieties slow down charge recombination, generating a long-lived, charge-separated state, the energy of which can potentially be harvested for useful purposes.

"In many triad molecules, the lifetime of the charge separation is increased by a factor of about 10,000 relative to that in dyad systems," he says. "This strategy, in which the electron is moved from the excited donor to the ultimate acceptor by a series of short-range, fast, and efficient electron-transfer steps, permits the design and preparation of artificial reaction centers that rival the natural ones in terms of quantum yield, energy stored, and charge-separation lifetime."

Using this strategy, the Arizona researchers have produced a variety of multicomponent artificial reaction centers, including molecular pentads, which have high quantum yields and very long charge-separation lifetimes. Last year, for example, the team reported the use of a fullerene as an electron acceptor. The carotenoporphyrin-fullerene triad undergoes photoinduced electron transfer to yield the long-lived, charge-separated state C\(^+\)-P-C\(_{60}\)\(^-\) [J. Am. Chem. Soc., 119, 1400 (1997)].

The group also has used artificial triad reaction centers to power light-driven proton pumps [Nature, 385, 239 (1997)]. In natural photosynthesis systems, protons are pumped across membranes by a proton motive force that is generated by the charge-separated states.

"Our system is based upon artificial liposomes, which are balloonlike structures a few hundred nanometers in diameter," explains Gust. "There is water inside and outside the 'skin' of the liposome, which is made of a phospholipid bilayer membrane similar to a cell membrane."

The lipid bilayers of these self-assembled systems contain C-P-Q triad molecules and lipid-soluble quinones. When the system is activated by light, protons are transported from outside the liposome to the inside.

"This builds up a proton gradient, or proton motive force," says Gust. "We have thus mimicked the photosynthetic proton pump."

In biological systems, the photosynthetic proton pump is used to drive the synthesis of adenosine triphosphate (ATP) from adenosine diphosphate and inorganic phosphate. The process is catalyzed by the enzyme ATP synthase. ATP is the biological energy currency involved in the synthesis of carbohydrates and many other important biomolecules.

Earlier this year, the Arizona team reported the use of their liposome system for the light-driven synthesis of ATP [Nature, 392, 479 (1998)]. Working in collaboration with French researcher Jean-Louis Rigaud at Institut Curie, Paris, the team incorporated ATP synthase into the liposomes.

"We have been able to incorporate the ATP synthase enzyme from spinach into liposomes containing the proton pump," Gust explains. "When illuminated, the pro-

### System photosynthesizes adenosine triphosphate

A hybrid bioorganic system developed at Arizona State University photosynthesizes adenosine triphosphate (ATP). The system consists of a hydrophobic lipid bilayer containing an artificial reaction center and the enzyme ATP synthase. The reaction center, which consists of a carotenoid-porphyrin-quinone triad (C-P-Q), absorbs light and forms the long-lived, charge-separated state C\(^+\)-P-Q\(^-\). The quinone radical ion reduces a shuttle quinone (Q\(_{sh}\)), which then picks up a proton from the aqueous solution outside the liposomal membrane. Protonated Q\(_{sh}\) diffuses across the bilayer to the carotenoid radical ion where it is oxidized and releases a proton to the aqueous solution inside the membrane. As the concentration of protons becomes greater inside the membrane, a proton motive force is established. The enzyme uses the proton motive force to synthesize ATP from adenosine diphosphate (ADP) and inorganic phosphate (P\(_i\)). The system stores light energy as chemical potential energy in ATP. The sequence of events is functionally analogous to the solar-energy harvesting system of photosynthetic bacteria.

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ton pump transports hydrogen ions into the interior of the liposome. They then flow out again through the ATP synthase, making ATP when all the necessary ingredients are present."

These proton-pumping systems, which produce biological energy in the form of ATP or of proton motive force, are miniature solar power packs, Gust suggests. "In principle, these can be used to power various enzymatic systems in order to study biological pathways or perhaps make high-value biological materials," he says. "Alternatively, they might be used to power synthetic or natural machines. For example, the flagellar motors of bacteria are driven by proton motive force."

According to Imperial College's Durrant, the development of these systems is an impressive scientific achievement. "Gust and his coworkers have mimicked natural photosynthesis with a simple system that is remarkably efficient in converting solar energy into ATP," he comments.

"However, it is unlikely that these systems will prove to be commercially viable for large-scale solar energy conversion because of their limited stability," he says. Durrant points out that the half-life of photosynthesis systems in green plants is typically 30 minutes.

In the future, the design of artificial photosynthesis devices for solar energy conversion is likely to rely on the use of solid-state components, he suggests.

**Light harvesting**

The University of Bologna's Balzani, working with research groups at the Universities of Messina and Pisa in Italy, is attempting to develop an artificial system for photochemical water splitting that combines three functions: light harvesting, charge separation, and multielectron transfer catalysis.

"A light-harvesting antenna is an organized multicomponent system in which several chromophoric molecular species absorb incident light and channel the excitation energy to a common acceptor component," Balzani points out.

Synthetic porphyrin arrays are obvious candidates for the design of artificial antenna systems because porphyrins are the main chromophores of natural photosynthesis, notes Balzani. Other candidates include cytochromes functionalized with chromophores and various types of chromophore-labeled organic dendrimers.

"We are trying to develop wedge-like dendrimers that are capable of directing the collected solar energy toward an edge," he explains. "We will then try to link such an edge to an artificial reaction center, consisting of a charge-separation triad, and a manganese complex."

Manganese, he points out, is part of the catalytic center of the watersplitting enzyme used in natural photosynthesis. The center is a cluster of manganese and oxygen atoms that serves as a charge accumulator. It uses the positive charge from the photoinduced charge-separation process to extract electrons from water with the result that water is oxidized to oxygen and hydrogen ions in a four-electron process.

The cluster passes through several oxidation states during this multielectron redox process. The detailed structure of the cluster and mechanism of the process are not known. Nor has it been possible to synthesize a model for the cluster to date.

"The lack of knowledge of the intimate mechanism of the catalytic process that leads to oxygen production in natural photosynthesis has hindered the design of multielectron redox catalysts for artificial photosynthesis," Balzani says.

The dendrimers that the Italian group is developing are designed to act as artificial antennae for light harvesting in the same way that arrays of chlorophyll molecules act as natural antennae in green plants.

The Italian researchers designed redox-active dendrimers based on transition-metal complexes [Acc. Chem. Res., 31, 26 (1998)]. The dendrimers typically consist of arrays of ruthenium(II) or osmium(II) polypyridine-type complexes. Their strategy allows a step-by-step control of the dendrimer growth process so that building blocks containing different metals or ligands can be introduced at each step.

"Our dendrimers absorb strongly in the visible region and therefore they are really able to collect sunlight," Balzani says, "whereas other reported antenna systems absorb only in the UV and are therefore useless as far as solar energy conversion is concerned."

Other groups are also pursuing light-harvesting arrays. For example, Robert R. Birge, David F. Bocian, Dewey Holten, and Jonathan S. Lindsey (chemistry professors at Syracuse University; the University of California, Riverside; Washington University, St. Louis; and North Carolina State University, Raleigh, respectively), and their coworkers have designed and synthesized light-harvesting arrays that comprise a central porphyrin and one, two, or eight boron-dipyrrin (BDPY) accessory pigments [J. Am. Chem. Soc., 120, 10001 (1998)].

Bocian comments: "I think the BDPY-porphyrin array with eight BDPY units clustered around the porphyrin is a marvelous example of synthetic design that affords extremely close packing of light-harvesting elements around a central energy trap. From a functional aspect, the array also supports controlled, highly efficient en-

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**Borondipyrin units cluster around porphyrin in light-harvesting array**

[Diagram of boron-dipyrrin units cluster around porphyrin in light-harvesting array]
energy transfer. In particular, the energy flows between the light-harvesting pigments and the trap without deleterious side reactions such as inter-BDPPY quenching.

The authors suggest that BDPY-porphyrin arrays are "excellent candidates for inclusion in light-harvesting model systems and as input elements of prototypical molecular photonic devices—for example, molecular-scale information-processing devices—and molecular-based sensors."

Meanwhile, the University of Tokyo's Aida and coworker Dong-Lin Jiang have developed a strategy for harvesting low-energy photons to carry out chemical transformations. "The energy of infrared light is so low that in general it cannot induce any chemical transformation," explains Aida. "However, with dendrimers as light-harvesting antennae, many infrared photons are trapped and the excitation energy is channeled to the interior reaction center to cause a chemical transformation."

Jiang and Aida prepared highly branched dendrimers from aryl ethers containing a photoisomerizable azobenzene core [Nature, 388, 454 (1997)]. Following infrared excitation of the aromatic units, the absorbed energy channels to the core where it isomerizes the azobenzene. The dendrimer matrix prevents de-excitation.

"This is the first example of utilization of infrared photons for chemical transformation," Aida says. "The discovery will hopefully open up a new technology that utilizes low-energy photons."

Carbon dioxide reduction

Etsuko Fujita, a chemist at Brookhaven National Laboratory, Upton, N.Y., points out that the use of solar energy to reduce CO₂ to CO, formic acid, or methanol might also help solve the problems of fossil fuel depletion and global warming.

"Both water splitting and conversion of carbon dioxide to useful chemicals and fuels pose many scientific challenges owing to their great stability and chemical inertness," she says. "Because of their stability, energy is needed to effect the desired transformations, and because of their inertness, catalysts are required that are capable of binding, activating, and transforming water or carbon dioxide to desired products by multielectron processes."

Much of the work on catalysts for photochemical splitting of water and CO₂ reduction has focused on transition-metal catalysts, she points out.

For example, her group has used techniques such as X-ray absorption near edge structure (XANES) spectroscopy and the analysis of extended X-ray absorption fine structure (EXAFS) spectroscopy to study the photochemical and electrochemical reduction of CO₂ using tetrazamacrocyclic complexes of cobalt and nickel as catalysts. Her work shows that such complexes can promote electron transfer to CO₂ bound to the complexes and thereby facilitate CO₂ reduction [J. Am. Chem. Soc., 119, 4549 (1997)].

"We have shown that a cobalt(II) complex with a tetrazamacrocyclic diene ligand serves as a catalyst for photochemical and electrochemical CO₂ reduction to form mainly carbon monoxide," she says. "Similar complexes with cobalt(II) form two kinds of CO₂ adducts. Our results provide the first unambiguous evidence that active metal catalysts such as the cobalt(t) macrocyclic complex can transfer two electrons to bound CO₂ and thereby facilitate its reduction."

The photocatalytic system used by Fujita and her coworkers for the reduction of CO₂ to CO contains not only the cobalt macrocycle as the catalyst, but also p-terphenyl as a photosensitizer and triethylamine as an electron donor.

"Our projects are aimed at developing a basic understanding of photochemical and electrochemical CO₂ reduction systems," she explains.

Their systems won't ever be used for the commercialization of CO₂ reduction, she points out, because the stability of the systems is limited, their catalytic activities are too low, and they require a sacrificial agent. This agent, triethylamine, is oxidized when CO₂ is reduced.

"The overall costs are too high for commercialization," she says. "However, the insight obtained from our systems will provide the knowledge for the future design of practical systems. We believe the next challenging step would be to couple the reduction of CO₂ with oxidation of water or methane in order to eliminate the sacrificial agent."

In another project, Fujita has collaborated with a group of chemists at Howard University, Washington, D.C., and the National Institute of Standards & Technology (NIST), Gaithersburg, Md., to investigate the use of cobalt-containing porphyrins for the catalyzed reduction of CO₂ [J. Phys. Chem. A., 102, 2870 (1998)]. Last year, the group, which is led by NIST research chemist Pedi Neta, reported similar studies using iron-containing porphyrins [J. Phys. Chem. A., 101, 248 (1997)].

"The aim of this work is to examine the use of synthetic metalloporphyrins to convert light energy into chemical energy and store it by reducing CO₂ to carbon monoxide and formic acid, which could then serve as chemical feedstock for other processes," explains Neta. "We have shown that iron and cobalt porphyrins catalyze the photoreduction of CO₂. Such porphyrins have been shown before to catalyze the electrochemical reduction of CO₂."
To achieve CO₂ photoreduction, the group first photochemically reduced the metal (M) in the metalloporphyrin (MP) from M(II) to M(0). “M(0)P reacts rapidly with CO₂ and reduces it to CO and formic acid,” explains Neta. “In the process, M(0)P is oxidized back to M(II)P, which recycles. The CO₂ reduction process is therefore catalytic.

“We have been able to achieve a high percentage conversion of CO₂ into CO and formic acid, but the system still requires improvements in the light efficiency and the long-term survival of the porphyrins,” Neta says.

Itamar Willner, chemistry professor at Hebrew University of Jerusalem, in Israel, has investigated the use of naturally occurring enzymes in artificial photosynthetic systems for photocatalytic transformations such as CO₂ fixation and the photoreduction of nitrate to ammonia.

“In the concept we call ‘photoenzymes,’ we take a native protein, exclude its active center, and implant a well-defined donor-acceptor pair via synthetic and reconstitution methodologies,” he explains.

As an example, Willner cites research with Hebrew University of Jerusalem graduate students Eran Zahavy and Vered Heleg-Shabtai in which two proteins—a myoglobin and a hemoglobin—are reconstituted with a cobalt(II) porphyrin and an eosin photosensitizer [J. Am. Chem. Soc., 118, 1249 (1996)]. The group has shown that the reconstituted proteins exhibit enzymelike behavior. Both are photocatalytically active in hydrogenation processes—for example, in the photohydrogenation of acetylene to ethylene.

The photoreduced cobalt(II) species of the reconstituted proteins, which is generated when the cobalt(II) species accepts an electron, revealed pronounced stabilities against back-electron transfer to the eosin, according to Zahavy and Willner. They attribute this to the spatial separation of the redox species by the rigid protein assemblies.

“The system is thus a model for the photosynthetic reaction center, and it also performs a photocatalytic transformation,” Willner says.

“I feel that the combination of synthetic catalysts together with biomimetic approaches, such as reconstituted photoenzymes or de novo proteins where photosensitizer, acceptor, and catalyst are implanted, will find serious interest in the future,” he adds.

One example of such research is the design and chemical synthesis of two de novo metalloproteins for light-induced electron transfer [Proc. Natl. Acad. Sci. USA, 95, 11526 (1998)]. The work was carried out by a group of researchers at Albert-Ludwigs-University of Freiburg, Germany, led by biology professor Wolfgang Haehnel. The team synthesized proteins in high purity by assembling peptide modules on a template. Heme and a ruthenium complex were incorporated into the proteins as cofactors.

“The strategy to assemble synthetic proteins with variations in single peptide elements in a modular way offers the possibility to create families of proteins with specifically tuned functions,” the team states. “It shows the chemical synthesis of a nanomodule with high yield by controlled assembly of peptides and cofactor building blocks and represents a step toward artificial photoenzymes.”

Dye-sensitized solar cells

“Most green plants operate with biological photosynthesis efficiencies of a few percent, but there are a few, such as eucalyptus, that reach as high as 5%,” says NREL’s Nozik. “Artificial systems have much higher thermodynamic upper-limit efficiencies ranging from 30 to 60%, depending on the details of the systems. The most efficient systems to date are based on semiconductors.”

Imperial College’s Durrant notes that commercial solid-state photovoltaic cells employ silicon as the semiconductor to harvest light and convert the energy into electricity with a typical solar-to-electrical energy conversion efficiency of around 15%. “It is possible to achieve over 20% efficiency, but such solar cells are extremely expensive,” he says. “The ones used to power calculators employ much cheaper amorphous silicon and are of the order of 5 to 6% efficiency.”

Nozik points out that more than 30% efficiency has been achieved with a solid-state p-n photovoltaic cell—that is, a cell with a junction between positive (p) and negative (n) semiconductors. This was achieved at very high light intensity at NREL using a semiconductor solar cell with a p-n gallium indium phosphide junction on top of a p-n gallium arsenide junction, he notes.

EPFL professor of physical chemistry Grätzel explains that in conventional p-n junction silicon solar cells the same semiconductor material must simultaneously perform several tasks, for example, light absorption, charge separation, and charge transfer. “This renders the system difficult and expensive to produce,” he says.

A photovoltaic cell with 15% photon-to-electric-current conversion efficiency can be coupled to a conventional electrolytic cell to split water into hydrogen and oxygen, yielding an overall photovoltaic conversion efficiency of about 10%. The manufacture of hydrogen using such coupled systems is not commercially viable, however, because the photovoltaic cells are too expensive. Hydrogen can be manufactured more cheaply from coal or natural gas.

Penn State’s Mallouk points out that “hydrogen iodide is an easier nut to crack than water.” He and coworkers at Penn State and Tulane University, New Orleans, have developed photocatalytic systems that use photosensitized layered metal-oxide semiconductors for the visible light photocatalysis of hydrogen iodide.

“Our assembly of organized lamellar systems makes hydrogen photochemically using iodide as a nonsacrificial electron donor,” he says.

Mallouk’s lamellar semiconductor consists of layers of KₓNbₓOᵧ, containing internal clusters of platinum, which serve to catalyze the production of gaseous hydrogen and aqueous triiodide from aqueous hydrogen iodide. The sensitizer is a ruthenium bipyridyl complex, which is adsorbed onto the surface of the semiconductor.

The photon-to-electron conversion efficiency of the system is low, however. Mallouk’s group has shown that this is caused by the transfer of electrons in the conduction band of the semiconductor back to the aqueous solution. Last year, the team demonstrated that back-electron transfer reactions could be slowed down...
by modifying the surface with an anionic polyelectrolyte layer \( [ J. \text{ Phys. Chem. B, 101, 2508 (1997)} ] \). This improved the quantum efficiency of the system by a factor of 10 and the initial rate of hydrogen evolution by a factor of up to five.

Earlier this year, NREL chemists John A. Turner and Oscar Khaselev reported the integration of a gallium arsenide photovoltaic cell with a gallium indium phosphide photoelectrochemical cell to produce hydrogen from water at a record 12.4% efficiency (C&EN, April 20, page 11). However, the complexity and potential cost of the system are likely to be a disadvantage.

Photoelectrochemical cells that employ inexpensive semiconducting materials, such as titanium dioxide, offer a promising alternative. Photoelectrochemical cells are electrolytic cells with photoactive semiconducting electrodes. Harvested photons excite electrons in the semiconductor, causing a separation of charge and the generation of the electricity required for electrolysis.

In 1972, Japanese researchers Akira Fujiwara of Kanagawa University, in Yokohama, and Kenichi Honda of the University of Tokyo reported the use of a titanium dioxide electrode in a photoelectrochemical cell to split water into hydrogen and oxygen.

"The problem with this cell is that titanium dioxide absorbs light poorly," explains Durrant. "The solar energy conversion efficiency is therefore very low."

Grätzel and his colleagues at EPFL have improved the efficiency considerably by developing a cell that uses nanocrystalline titanium dioxide sensitized with a dye, typically a ruthenium bipyridyl complex, to harvest the light. The nanocrystalline material is mesoporous and therefore has a very high surface area. When coated with a thin film of dye, the material is able to harvest more than 90% of the incident photons.

"The attractive and unique feature of a dye-sensitized photovoltaic system is that the color of the cell can be selected by choosing an appropriate sensitizer," Grätzel says.

The incident photons excite electrons in the dye that are then injected into the conduction band of the titanium dioxide. Loss of electrons leaves positive holes in the dye that are carried away by a triiodide-iodide redox electrolyte.

"The dye mimics chlorophyll in plants," says Grätzel. "The electron injection into the oxide particle is analogous to charge separation in the photosynthetic membrane. And instead of the stacking of the thylakoid vesicles in the green leaf, our cell uses the mesoporous film structure, which accomplishes efficient harvesting of sunlight using a molecular absorber in a similar way to plants."

Grätzel points out that up to 11% overall solar-to-electrical energy-conversion efficiency has been achieved with these cells.

"These dye-sensitized solar cells are remarkably stable, making practical applications feasible," he tells C&EN. "A record-breaking 14,000-hour-long light-soaking test without performance decline has been achieved recently, showing that the device is inherently stable and can attain the 20-year longevity required for practical applications."

"Commercial development of these cells is well on its way," he continues. "The technology has been licensed to eight industrial corporations in Europe, Japan, and Australia. The cells are being targeted to supply electric power to stand-alone consumer electronic devices such as electronic displays and mobile communications."

Grätzel anticipates further improvements with these cells. "After years of effort, during which over 700 sensitizers were synthesized and tested, we have finally found a black dye that harvests all the visible and part of the near-infrared light up to 900 nm," he says. "This opens up the possibility of increasing substantially the conversion efficiency of the system."

Durrant points out that one of the key factors controlling the efficiency of energy conversion in these semiconductor devices, and also in natural and artificial photosynthesis systems in general, is the rate of charge separation and of charge recombination.

"In the case of solid-liquid interfaces in, for example, dye-sensitized solar cells, it has been very unclear what controls charge recombination," he says.

Durrant and colleagues at Imperial College have been investigating the kinetics of charge recombination in dye-sensitized nanocrystalline titanium dioxide films \( [ J. \text{ Phys. Chem. B, 102, 1745 (1998)} ] \).

"We have shown that the rate of charge recombination is to a large extent controlled by the number of electrons in
the conduction band of the titanium dioxide," he explains. "This is critical for photovoltaic production because a solar cell works by putting electrons into the semiconductor. We show that as you put more and more electrons in, the recombination gets faster and faster, and this potentially limits its function."

In research being carried out jointly with University of Geneva chemistry professor Jan Augustynski and University of Bern chemistry professor Gion Calzaferri, Grätzel and his group are developing a tandem cell that incorporates a dye-sensitized solar cell and directly cleaves water with light. The overall efficiency of the cell currently is about 4%.

The tandem cell consists of two photo-systems in series. One cell has a nanocrystalline tungsten trioxide electrode that absorbs light in the blue part of the solar spectrum. When excited by light, this electrode oxidizes water to oxygen and hydrogen ions. The electrons removed by the oxidation process are fed to the second cell. This is a dye-sensitized titanium dioxide cell with an iodide electrolyte. The cell absorbs the green and red parts of the spectrum to generate a photovoltage. The voltage ensures that electrons flow back to the other cell to generate hydrogen gas from the hydrogen ions.

"One of the advantages of our device is that it accomplishes water splitting directly without the need to use a water electrolyzer," Grätzel explains. "The project is still in a research stage, the main goal being to improve the efficiency of hydrogen evolution from around 4% at present to 10%.

The use of liquid electrolytes in the dye-sensitized solar cells originally developed by Grätzel is a disadvantage, according to Wim C. Sinke and Martijn M. Wienk, members of the Solar Energy Group of the Netherlands Energy Research Foundation, in Petten [Nature, 395, 544 (1998)]. They point out that use of a liquid electrolyte can limit device stability because the liquid may evaporate when the cell is imperfectly sealed. And more generally, interdiffusion and reaction of water or oxygen molecules may worsen cell performance. "The liquid electrolyte also makes the manufacture of multicell modules difficult because cells must be connected electrically yet separated chemically, preferably on a single substrate," they state.

Replacement of the liquid electrolyte with a solid conducting material can over-
come these problems. Grützel and co-workers at EPFL; Hoechst Research & Technology Deutschland, Frankfurt, Germany; and Max Planck Institute for Polymer Research, Mainz, Germany, reported earlier this month that they have achieved this by using an amorphous organic hole-transporting material [Nature, 395, 583 (1998); C&EN, Oct. 12, page 36].

The material, which consists of four triarylamine components linked by a tetrahedral carbon atom, removes positively charged holes in the dye. These holes are generated when electrons in the dye are excited by light and transferred to the titanium dioxide semiconductor.

The cell converts photons to electric current with 33% efficiency, or quantum yield. This is high for an organic solid device, although much lower than the maximum 90% efficiency achieved with the cells that use liquid electrolytes. With an electric load, however, the energy-conversion efficiency of the solid-state organic solar cell drops to 0.74%, possibly because of losses arising from charge recombination.

"The efficiencies achieved by Grützel are much higher than those for previously reported dye-sensitized solid-state devices," comments Durrant. "It is therefore an important scientific advance. The design combines all the low-cost advantages of the original Grützel design without the problems of a liquid electrolyte."

The development of solid-state dye-sensitized solar cells is still in its infancy, comments Sinke and Wienk. "The promise of very low production costs and reasonable to high efficiencies warrants intensive work in this area."

But as they point out, it may be many years before the resulting solar modules cover our roofs.

Two groups master vancomycin nucleus

In five back-to-back communications, two groups of chemists have reported independent total syntheses of the aglycon of vancomycin, one of the few antibiotics active against certain drug-resistant bacteria [Angew. Chem. Int. Ed., 37, 2700, 2704, 2708, 2714, 2717 (1998)]. The aglycon lacks the disaccharide substituent that is attached to the natural product itself, but contains the complex heart of the molecule, including three macrocyclic rings and five unusual amino acids.

These accomplishments—by the research groups of organic chemistry professor David A. Evans at Harvard University and of organic chemistry professor K. C. Nicolaou of Scripps Research Institute, La Jolla, Calif., and the University of California, San Diego—pave the way to synthetic variations on the component building blocks in search of analogous antibiotics with greater activity against recently encountered vancomycin-resistant infections. But the efforts also represent an upping of the ante in natural-product synthesis as chemists come to grips with ever more subtle stereochemical problems.

In the past, chemists have assembled molecules with ever-increasing numbers of asymmetric carbon atoms, all with correct configurations. With vancomycin, chemists have taken on the challenge of atropisomerism—chirality arising from restricted rotation about certain single bonds, resulting in two senses of helicity. One example is the chirality of biphenyls whose rotation is hindered by ortho substituents.

Indeed, in vancomycin, one of the macrocyclic rings contains a bond between two phenyl groups that is constrained as a single atropisomer because of hindered rotation. Vancomycin also contains two chiral biaryl ether macrocycles; chlorine substituents on their β-hydroxytyrosine components hinder rotation of the aryl rings, constraining these macrocycles in single atropisomeric forms. Thus the synthesis of vancomycin depends not only on getting the configurations right at nine asymmetric carbons, but also on closing one 12-membered and two 16-membered rings such that five previously rotatable single bonds are locked correctly in place.

Evans' group succeeded in making the natural atropisomer of vancomycin aglycon by inducing the correct atropisomerism at each step. This control of atropisomerism is not a first in natural products synthesis, but it is the most complex effort to date. Evans' collaborators were graduate students Jeffrey L. Katz, B. Wesley Trotter, and James C. Barrow and postdoctoral fellows Christopher J. Dinsmore, Timothy I. Richardson, Paul S. Watson, and Michael R. Wood.

Nicolau's group has also reported making the natural atropisomer of vancomycin aglycon. But the California researchers achieve that goal by separating out the nonnatural atropisomeric intermediates along the way. Nicolaou's coworkers were graduate students Christopher N. C. Boddy, Robert Hughes, and Hui Li and postdoctoral fellows Toshikazu Bando, Nareshkumar F. Jain, Alexandros E. Koumbis, Swaminathan Nataraajan, Joshi M. Ramanjulu, Michael E. Solomon, and Masaru Takayanagi.

In one atropisomeric sense, the difference between the Harvard and Scripps approaches is a series of asymmetric syntheses versus sequential separations of diastereomers. The approach to the 12-membered ring serves as an example of the differences between the two approaches. The Scripps workers coupled a substituted iodoaryl glycine with a substituted benzeneboronic acid to assemble the biaryl unit directly, followed by separation of atropomers. Then they inserted the unit with the correct atropisomeric conformation into the 12-membered ring.

By contrast, the Harvard group strung together all the components of the 12-membered ring except for the aryl-aryl bond. The Evans group found that the atropisomeric sense of the biaryl bond formation depended on the configuration of the α-stereocenter of a single amino acid.

Tantalizingly, the "right" atropisomerism could be reached only by using the "wrong" α-stereocenter. The correct atropisomer could be obtained in the presence of the natural α-stereocenter by initially forming the "wrong" atropisomer, then isomerizing it (by heating the compound in methanol) to the desired biaryl macrocycle.

Stephen Stinson