Bioinspired energy conversion*

Rodrigo E. Palacios[1], Stephanie L. Gould[1], Christian Herrero[1],
Michael Hambourger[1], Alicia Brune[1], Gerdenis Kodis[1],
Paul A. Liddell[1], John Kennis[2], Alisdair N. Macpherson[3],
Devens Gust[1,‡], Thomas A. Moore[1,‡], and Ana L. Moore[1,‡]

[1]*The Center for the Study of Early Events in Photosynthesis, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287, USA;* [2]*Department of Biophysics, Division of Physics and Astronomy, Faculty of Sciences, Vrije Universiteit, 1081 HV Amsterdam, The Netherlands;* [3]*Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK*

Abstract: Artificial photosynthetic antenna systems have been synthesized based on carotenoid polyenes and polymer-polyenes covalently attached to tetrapyrroles. Absorption of light in the blue/green region of the spectra excites the polyenes to their S_2 state, and ultra-fast singlet energy transfer to the tetrapyrroles occurs when the chromophores are in partial conjugation. The additional participation of other excited states of the polyene in the energy-transfer process is a requirement for perfect antenna function. Analogs of photosynthetic reaction centers consisting of tetrapyrrole chromophores covalently linked to electron acceptors and donors have been prepared. Excitation of these constructs results in a cascade of energy transfer/electron transfer which, in selected cases, forms a final charge-separated state characterized by a giant dipole moment (>150 D), a quantum yield approaching unity, a significant fraction of the photon energy stored as chemical potential, and a lifetime sufficient for reaction with secondary electron donors and acceptors. A new antenna-reaction center complex is described in which a carotenoid moiety is located in partial conjugation with the tetrapyrrole π-system allowing fast energy transfer (<100 fs) between the chromophores. In this assembly, the energy transduction process can be initiated by light absorbed by the polyene.

Keywords: bioinspired; energy conversion; photosynthesis; carotenoid polyenes; antenna systems.

INTRODUCTION

Energy security is an issue facing humanity that is no less significant than war, famine, disease, the plight of refugees, and the guarantee of human rights across the lands. Indeed, providing energy security is a necessary step that societies must take to resolve conflicts. Nature's photosynthetic process provides paradigms for sustainable global energy production and efficient energy transformations, which are conditions that underpin energy security. The combination of mechanistic and structural informa-

tion available for energy-transducing biological structures serves to guide organic, inorganic, and materials chemists in their efforts to abstract and mimic the active elements of nature's energy-processing constructs and press them into human-directed service. Toward these ends, in our laboratory we have designed a number of artificial photosynthetic constructs and assembled them into energy-converting systems [1].

LIGHT HARVESTING

Effective absorption of light by chromophores in photosynthetic membranes is achieved by complex arrays of tetrapyrrole macrocycles, carotenoids, and other pigments. In many biomimetic systems, the conversion of excitation energy to electrical or chemical energy by electron- or proton-transfer reactions must occur at a phase boundary. This can limit the useful absorption of light to a monolayer of chromophores at or near the surfaces of membranes or of semiconductors. Therefore, in these constructs there is a fundamental problem due to the limited light capture cross-section of dye molecules. One successful strategy has been the use of high-surface-area materials consisting of nanocrystalline wide band-gap semiconducting oxide particles with a mesoporous architecture over which a monolayer of dye is deposited [2,3]. Other approaches include the use of covalently linked arrays of porphyrins and other chromophores as well as self-assembled constructs to form compact structures with high-absorption cross-sections which could be positioned at an interface for charge separation [4–7]. An example of a porphyrin array linked to a free-base porphyrin-fullerene artificial reaction center is illustrated by **1** [8,9].

1
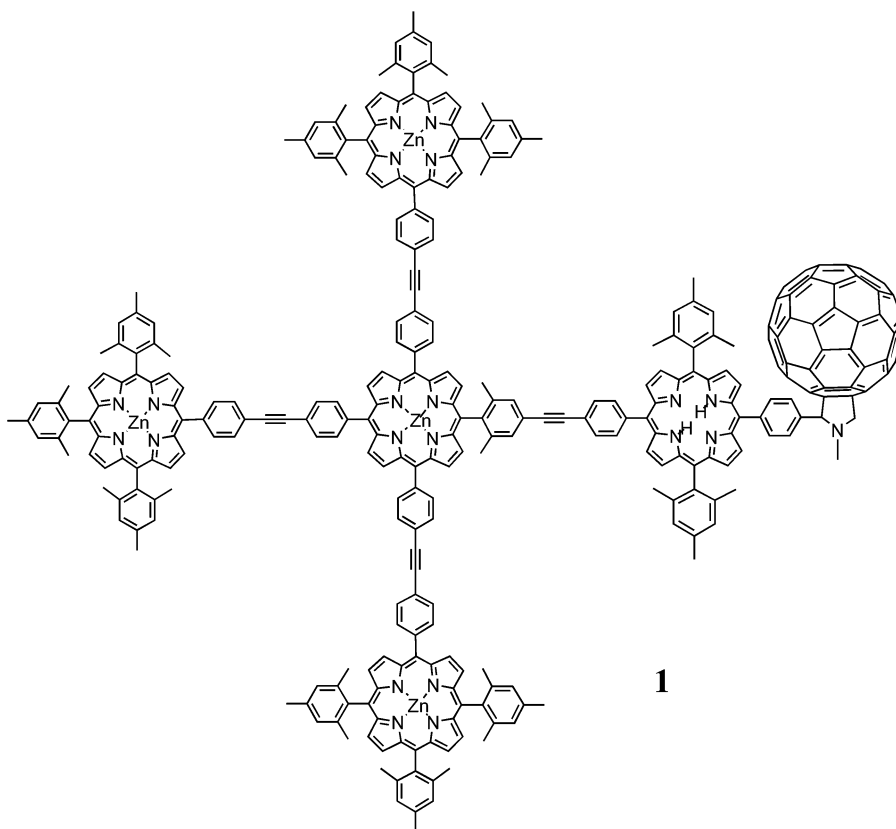
Time-resolved absorption and emission studies revealed that excitation of a peripheral zinc porphyrin in **1** is followed by singlet–singlet energy transfer among the four porphyrins of the antenna array, with final trap of the excitation by the free-base porphyrin, which acts as an energy sink. The excited state of the free-base porphyrin decays by electron transfer to the fullerene with a time constant of 25 ps and generates the $(P_{zn})_4–P^{\bullet+}–C_{60}^{\bullet-}$ state with a quantum yield of 0.98, based on light absorbed by the antenna zinc porphyrins. Thermodynamically favorable migration of the positive charge into the zinc porphyrin array transforms the initial state into a long-lived $(P_{zn})_4^{\bullet+}–P–C_{60}^{\bullet-}$ charge-separated state with a quantum yield of ~0.90 and lifetime of 25 µs in benzonitrile. In this process, the light-gathering power of the system is increased tremendously at many wavelengths, as four zinc porphyrin moieties feed excitation energy to the reaction center. However, by inspection of the absorption spectrum of **1** shown in Fig. 1, it is evident that there is little absorption of light in the vicinity of 500 nm, the region of maximum solar irradiance, by the array of antenna porphyrins. In order to ameliorate this deficiency, typical of porphyrin-based antennas, we have designed artificial antennas with carotenoid pigments to "fill in" absorption in regions where tetrapyrrole absorption is low.
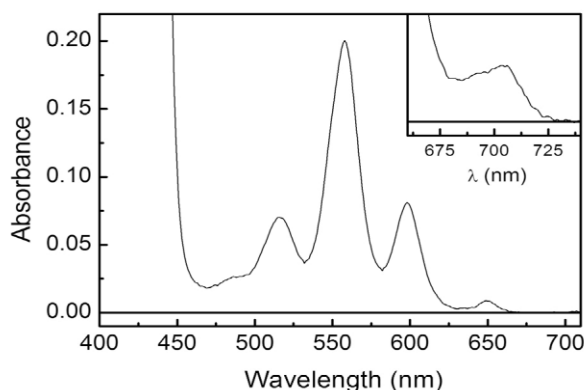

Fig. 1 Absorption spectra of **1** in 2-methyltetrahydrofuran. The inset is an expansion of the fullerene long-wavelength absorption region.

Carotenoid polyenes are found in essentially all the chlorophyll-binding antennas of photosynthetic organisms where, among other vital photoprotective functions, they absorb light in the blue/green region of the spectrum, and efficiently transfer energy to chlorophylls, which are located in van der Waals contact with them. Carotenoid antenna function is perplexing in that although antenna function requires singlet–singlet energy transfer among chromophores, carotenoids in solution do not undergo singlet energy transfer to other chromophores. Artificial antennas containing a carotenoid moiety must have covalent bonds between the carotenoid and the cyclic tetrapyrrole in order to display efficient carotenoid-to-tetrapyrrole singlet energy transfer. This is due to the extremely short lifetime of the carotenoid excited states, which requires relatively strong electronic coupling for rapid energy transfer. An example of a covalently bonded system that does show energy transfer is **2**, in which a carotenoid is covalently attached to a purpurin through an amide linkage, which leads to partial conjugation between the chromophores [10].

Ultrafast fluorescence upconversion measurements on the carotenopurpurin dyad **2** and an unlinked model carotenoid demonstrate that the fluorescent (optically allowed) S_2 excited state of the carotenoid model compound has a lifetime of 150 fs, while the corresponding excited state of the carotenoid in **2** is quenched to 40 fs. This quenching is assigned to energy transfer from the S_2 state of the carotenoid to the purpurin with 73 % efficiency, which is in accord with the quantum yield obtained by steady-state fluorescence excitation measurements. The lifetime of the optically forbidden S_1 state of the carotenoid (7.8 ps), which is populated by internal conversion from the S_2 state, is the same in

2
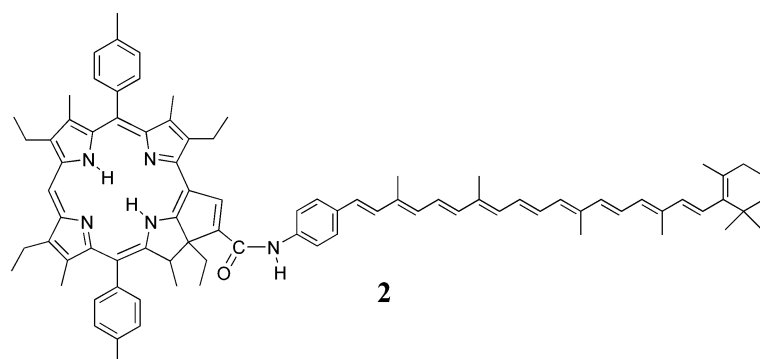
both the carotenoid model and dyad **2**. Thus, in this case, it is unequivocal that the S_2 state of the carotenoid moiety is the sole donor state in the observed singlet energy-transfer process. The efficiency is limited by the extremely short lifetime of this state, the spectral overlap term, and the requirement for even stronger electronic coupling than provided by the amide linkage.

In a different architecture, light-harvesting constructs were synthesized by covalently linking two carotenoids to the central silicon atom of a phthalocyanine (Pc) (see triads **3** and **4**) [11,12]. Triad **3** binds two carotenoids having nine conjugated carbon–carbon double bonds, whereas triad **4** binds two carotenoids having ten carbon–carbon double bonds in conjugation. Fluorescence excitation experiments indicated that in triad **3** dissolved in *n*-hexane, the carotenoid-to-Pc singlet energy-transfer efficiency is ca. 92 %, whereas in triad **4** it is 30 %. This is a striking difference in the antenna function of the carotenoids resulting from addition of a carbon–carbon double bond. In order to identify the basis

3

4
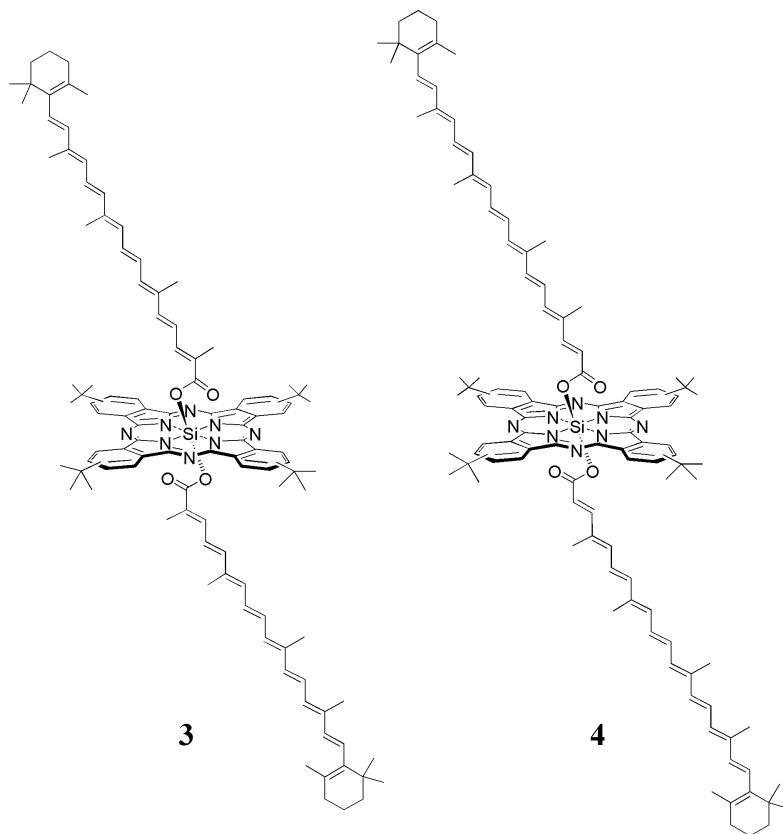
for this behavior, time-resolved absorption studies were performed. Results from ultrafast laser spectroscopy indicate that upon population of the optically allowed S_2 state of the carotenoid, the optically forbidden states including S_1, vibronically excited S_1, and a recently described S*, are rapidly generated in both triads **3** and **4**. In triad **3**, all of these states contribute singlet energy to Pc. As was the case in **2**, in triad **4** singlet energy transfer to Pc occurs primarily from the S_2 state with little energy transfer to Pc via the S_1 state, and there is no evidence for energy transfer via S*. Moreover, in triad **4** we find a multiphased quenching of the Pc singlet excited state on the picosecond and nanosecond time scales, indicating a back energy transfer and/or electron transfer from the excited singlet state of Pc to the carotenoid moiety.

Triad **3** is a remarkable example of an artificial antenna with nearly complete light harvesting through the participation of all the known excited states of the carotenoid. Upon completion of the light-harvesting function, the carotenoids in triad **3** efficiently carry out their photoprotective function by accepting energy from the triplet state of Pc that is formed by normal intersystem crossing; the triplet–triplet energy transfer takes place at a rate much faster than the Pc singlet state decay rate of $(5.6 \text{ ns})^{-1}$ and is, therefore, not measured directly by flash spectroscopy.

Conjugated-polyene-polymers are, in principle, attractive building blocks for the construction of artificial antennas. A living polymerization of dipropargyl malonate using Schrock's procedure [13,14] was terminated with 4-formyltetraphenylporphyrin, resulting in a polymer-polyene-porphyrin antenna system **5**. The crude reaction mixture exhibits extended absorption that covers the entire visible spectrum, making it a nearly ideal antenna for sunlight. It was expected that conformational disorder would limit the effective conjugation length of the polymer, providing a distribution of shorter effective conjugation lengths necessary for energy transfer to the tetrapyrrole. However, only limited energy transfer from the polyene-polymer to the porphyrin was detected by fluorescence excitation measurements in fractions enriched in polyene moieties containing pentamers and hexamers (11 and 13 carbon double bonds, respectively). Triplet–triplet energy transfer from the porphyrin to the polymeric-polyene was detected by flash-photolysis experiments which indicated the transient formation of polyene triplet(s) having a maximum at ~620 nm and a lifetime of 6 μs (in argon-purged solutions). The lifetime was quenched to ~200 ns by the addition of oxygen.


5
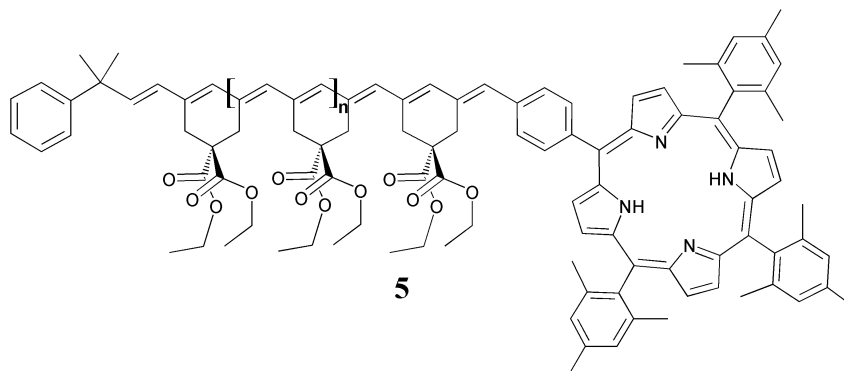
ARTIFICIAL REACTION CENTERS

A number of analogs of photosynthetic reaction centers consisting of tetrapyrrole chromophores covalently linked to electron acceptors and donors have been designed and synthesized. An example is triad **6** [1,15]. Excitation of these artificial reaction centers results in a cascade of energy transfer/electron transfer processes which, in selected cases, form a final charge-separated state characterized by a giant dipole moment (>150 D), a quantum yield approaching unity, a significant fraction of the photon energy stored as chemical potential, and a lifetime sufficient for reaction with secondary electron donors

6
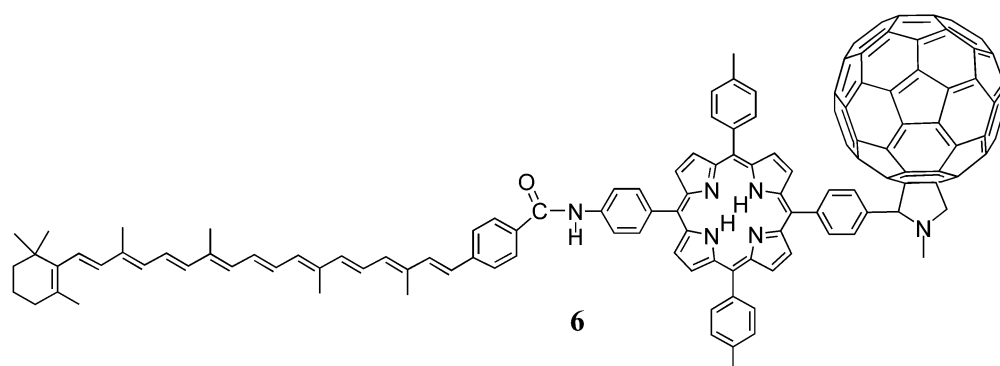
and acceptors. Reaction with secondary electron/hole transfer species may occur in solution, in membranes, or through interactions with conductive surfaces [16,17].

In artificial reaction centers such as **6**, light harvesting is carried out mainly by the porphyrin moiety. The carotenoid moiety does not act as an effective antenna, but rather as secondary electron donor, resulting in the formation of a final charge-separated state with the hole delocalized in the polyene chain.

A new antenna reaction center, structure **7**, in which a carotenoid moiety has been located in partial conjugation with the tetrapyrrole π-system, allowing fast energy transfer (<100 fs) between the chromophores has recently been synthesized. In this assembly, the energy transduction process can be initiated by light absorbed by the polyene. As expected, because of the structural similarity with antenna model **2**, singlet energy transfer from the carotenoid to the tetrapyrrole is ~70 % efficient [10]. Once the excitation arrives at the tetrapyrrole (purpurin), fast electron transfer to C_{60} is observed in 10 ps to form C–Pur$^{\bullet+}$–$C_{60}^{\bullet-}$, followed by a slower charge shift reaction involving the carotenoid moiety in 30 ps to form the final charge-separated state C$^{\bullet+}$–Pur–$C_{60}^{\bullet-}$, which recombines to a triplet state localized on the carotenoid in 1600 ps.

7
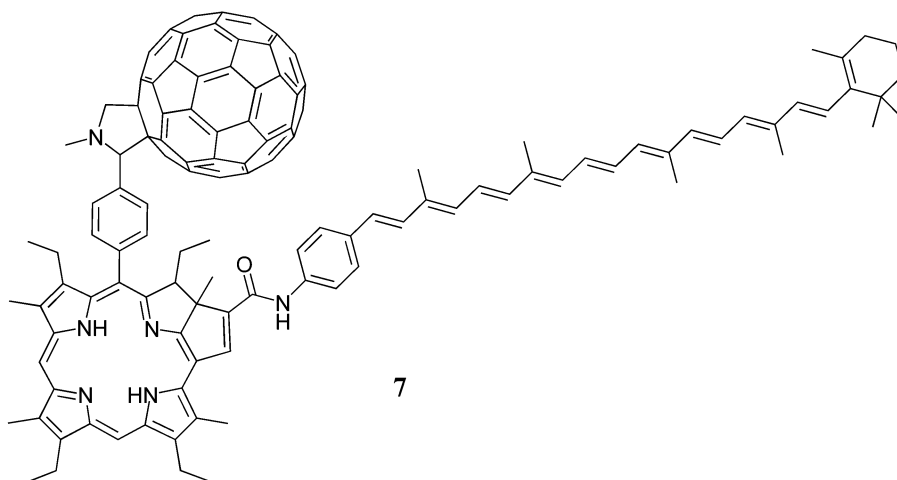
The results obtained with this antenna-reaction center system point to several areas for optimization. For example, the rate of recombination of the initial charge-separated state C–Pur$^{\bullet+}$–$C_{60}^{\bullet-}$ is extremely fast (70 ps), resulting in a relatively low yield of the final charge-separated state (~50 %). The fast rate of recombination can be traced to the excessive driving force for photoinduced electron trans-

fer (0.56 eV), which locates the initial charge-separated state (C–Pur$^{\bullet+}$–C$_{60}$$^{\bullet-}$) lower in energy than optimal to take advantage of the Marcus inverted region effect to slow recombination. Tuning the redox potential of the purpurin moiety by introducing electron-withdrawing groups and thereby increasing the energy of C–Pur$^{\bullet+}$–C$_{60}$$^{\bullet-}$ should slow recombination. Of course, a balance must be found that preserves sufficient driving force for photoinduced electron transfer to ensure a good quantum yield. Also, the relatively short-lived final charge-separated state could be traced to, among other factors, the proximity of the C$_{60}$ to the carotenoid in compound **7**. Different architectures with the carotenoid moiety located at the 15-meso position of the macrocycle (opposite to the C$_{60}$ moiety) are being considered.

FUTURE DEVELOPMENTS

A photoelectrochemical biofuel cell

We are developing a hybrid cell that consists of a dye-sensitized nanoparticulate semiconductor photoanode working in combination with an enzyme-catalyzed biofuel cell. The anodic half-cell can be coupled to various cathodic half-cell reactions through an ion-permeable membrane in a two-compartment electrochemical cell. The photoanode consists of a Grätzel-type nanoparticulate TiO$_2$ electrode coated with a porphyrin sensitizer [18]. Upon visible light excitation of the porphyrin (**P**), electrons are injected from the S$_1$ state of the porphyrin into the TiO$_2$ conduction band. Glucose or other reduced carbon compounds in the anode aqueous solution are oxidized by the appropriate NAD-linked dehydrogenase enzyme reducing NAD$^+$ to NADH. NADH is in turn oxidized by the porphyrin radical cation, regenerating **P** for subsequent rounds of photoexcitation. Key to the operation of the cell is the coupling of the anode photoreactions to the oxidation of biological fuels by the NADH/NAD$^+$ coenzyme and NAD-linked dehydrogenase enzyme and the facile and cyclical electron donation to the oxidized sensitizer P$^{\bullet+}$ by NADH, generating NAD$^+$, which is not reduced by charge recombination reactions at the photoanode.

When the photanode is coupled to a Hg/Hg$_2$SO$_4$ cathode (for evaluation purposes), theoretical values for open-circuit voltage (1.25 V) are produced with fill factors of ~0.6. These hybrid cells are nonregenerative systems; the reduced carbon compounds are the source of electrons and the photosensitizer/NADH/enzyme constitute a catalytic cycle. Thus, the electrons produced by the photoanode are available to carry out useful reductions in the cathode compartment.
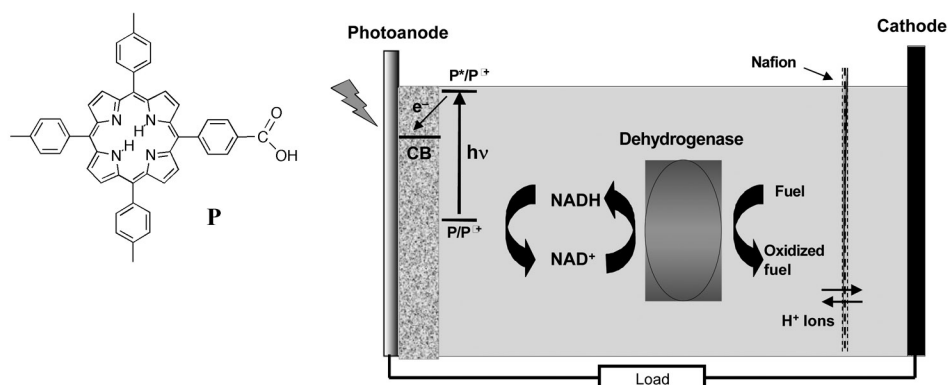

Fig. 2 Schematic diagram of a hybrid photoelectrochemical biofuel cell.

ACKNOWLEDGMENTS

REFERENCES

1. D. Gust, T. A. Moore, A. L. Moore. *Acc. Chem. Res.* **34**, 40–48 (2001).
2. B. O'Regan and M. Grätzel. *Nature* **335**, 737–739 (1991).
3. A. Hagfeldt and M. Grätzel. *Acc. Chem. Res.* **33**, 269–277 (2000).
4. X. B. Peng, N. Aratani, A. Takagi, T. Matsumoto, T. Kawai, I. W. Hwang, T. K. Ahn, D. Kim, A. Osuka. *J. Am. Chem. Soc.* **126**, 4468–4469 (2004).
5. N. Aratani, H. S. Cho, T. K. Ahn, S. Cho, D. Kim, H. Sumi, A. Osuka. *J. Am. Chem. Soc.* **125**, 9668–9681 (2003).
6. K. Muthukumaran, R. S. Loewe, C. Kirmaier, E. Hindin, J. K. Schwartz, I. V. Sazanovich, J. R. Diers, D. F. Bocian, D. Holten, J. S. Lindsey. *J. Phys. Chem. B* **107**, 3431–3442 (2003).
7. K. Y. Tomizaki, L. H. Yu, L. Y. Wei, D. F. Bocian, J. S. Lindsey. *J. Org. Chem.* **68**, 8199–8207 (2003).
8. G. Kodis, P. A. Liddell, L. de la Garza, P. C. Clausen, J. S. Lindsey, A. L. Moore, T. A. Moore, D. Gust. *J. Phys. Chem. A* **106**, 2036–2048 (2002).
9. D. Kuciauskas, P. A. Liddell, S. Lin, T. E. Johnson, S. J. Weghorn, J. S. Lindsey, A. L. Moore, T. A. Moore, D. Gust. *J. Am. Chem. Soc.* **121**, 8604–8614 (1999).
10. A. N. Macpherson, P. A. Liddell, D. Kuciauskas, D. Tatman, T. Gillbro, D. Gust, T. A. Moore, A. L. Moore. *J. Phys. Chem. B* **106**, 9424–9433 (2002).
11. G. Kodis, C. Herrero, R. Palacios, E. Marino-Ochoa, S. Gould, L. de la Garza, R. van Grondelle, D. Gust, T. A. Moore, A. L. Moore, J. T. M. Kennis. *J. Phys. Chem. B* **108**, 414–425 (2004).
12. E. Marino-Ochoa, R. Palacios, G. Kodis, A. N. Macpherson, T. Gillbro, D. Gust, T. A. Moore, A. L. Moore. *Photochem. Photobiol.* **76**, 116–121 (2002).
13. P. Wood, I. D. W. Samuel, R. Schrock, R. L. Christensen. *J. Chem. Phys.* **115**, 10955–10963 (2001).
14. H. H. Fox, M. O. Wolf, R. Odell, B. L. Lin, R. R. Schrock, M. S. Wrighton. *J. Am. Chem. Soc.* **116**, 2827–2843 (1994).
15. J. L. Bahr, D. Kuciauskas, P. A. Liddell, A. L. Moore, T. A. Moore, D. Gust. *Photochem. Photobiol.* **72**, 598–611 (2000).
16. G. SteinbergYfrach, P. A. Liddell, S. C. Hung, A. L. Moore, D. Gust, T. A. Moore. *Nature* **385**, 239–241 (1997).
17. I. M. Bennett, H. M. V. Farfano, F. Bogani, A. Primak, P. A. Liddell, L. Otero, L. Sereno, J. J. Silber, A. L. Moore, T. A. Moore, D. Gust. *Nature* **420**, 398–401 (2002).
18. L. de la Garza, G. Jeong, P. A. Liddell, T. Sotomura, T. A. Moore, A. L. Moore, D. Gust. *J. Phys. Chem. B* **107**, 10252–10260 (2003).