

# Final Technical Report

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**Project Title:** Supramolecular Structures for Photochemical Energy Conversion  
**Reporting Period:** 01/15/2000 – 06/14/2003  
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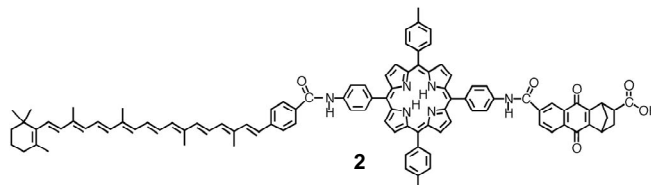
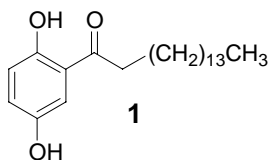
This final technical report covers results for the last three-year competitive renewal period of the above award. Technical details for earlier funding periods may be found in the previously-submitted Continuation Progress Reports for those periods.

The overall goal of this research project was to mimic the energy transduction processes by which photosynthetic organisms harvest sunlight and convert it to forms of energy that are more easily used and stored. The results of such research may lead to new technologies for solar energy harvesting based on the natural photosynthetic process. They may also enrich our understanding and control of photosynthesis in living organisms, and lead to methods for enhancing natural biomass production, carbon dioxide removal, and oxygen generation.

Progress has been made toward these goals in several complementary research areas. This is summarized briefly below, and reported in more detail in the publications listed in section F.

## A. Transmembrane ion transport

**1. Light-powered  $\text{Ca}^{++}$  pump.** In previous work, we have demonstrated that it is possible to synthesize artificial photosynthetic reaction centers and insert them vectorially into the lipid bilayers of liposomes. In the presence of a suitable membrane-soluble shuttle molecule, these reaction centers can power the light-driven transport of protons into the liposome via a redox loop mechanism. Recently, we have applied this same approach to the transport of  $\text{Ca}^{++}$  into liposomes. Transport of calcium ions across membranes and against a thermodynamic gradient is a form of biological energy conversion that is essential to myriad processes, including muscle contraction, the citric acid cycle, glycogen metabolism, release of neurotransmitters, vision, biological signal transduction and immune response. Synthetic systems that transport metal ions across lipid or liquid membranes are well known. Typically, a carrier molecule located in a symmetric membrane binds the ion from aqueous solution on one side and releases it on the other. The thermodynamic driving force is provided by an ion concentration difference between the two aqueous solutions, or coupling to such a gradient in an auxiliary species. Our approach is different. Active transport is driven not by concentration differences between the two aqueous phases, but rather by light-induced electron transfer in a photoactive artificial reaction center asymmetrically disposed across a lipid bilayer. The system comprises a synthetic, light-driven transmembrane  $\text{Ca}^{++}$  pump based on redox-sensitive, lipophilic  $\text{Ca}^{++}$  binding shuttle molecule **1** and powered by intramembrane carotenoid-porphyrin-quinone artificial



photosynthetic reaction center **2**. It uses light energy to transport calcium ions across the bilayer of a liposome to develop both a calcium ion concentration gradient and a membrane potential.

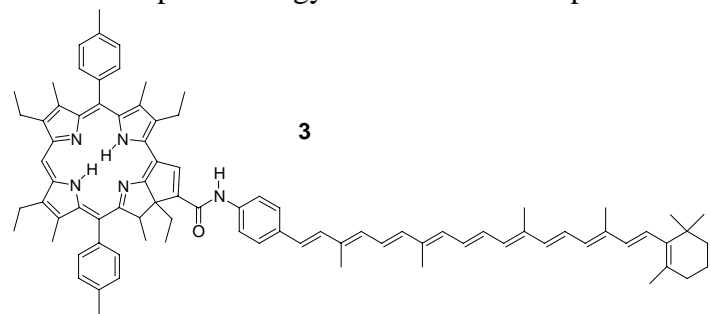
Although the quantum yield is relatively low ( $\sim 1\%$ ), the  $\text{Ca}^{++}$  electrochemical potential developed is significant. These results are described in a paper published in *Nature*.<sup>1</sup>

**2. Light-powered proton pumping.** As alluded to above, we have previously found that triad **2**, when inserted into liposomal bilayers and paired with a suitable quinone shuttle molecule, can use light energy to power the transport of hydrogen ions into the liposome interior, building up a proton motive force. Insertion of the enzyme ATP synthase into the bilayer allows us to use the proton motive force to drive ATP production. This is a novel and exciting finding that can only be fully understood by a detailed investigation of the various interfacial reactions occurring across the membrane. We have made some progress in understanding this process during the current grant period,<sup>18, 11, 12, 16</sup> but much remains to be learned.

### B. Mimicking carotenoid photosynthetic antenna function

One of the major functions of carotenoid polyenes in photosynthesis is light gathering. Essentially all photosynthetic species incorporate carotenoids into their antenna systems, and in some organisms, the vast majority of the sunlight is captured by carotenoids. Paradoxically, carotenoids appear to be very poor choices as antenna pigments. Their first excited singlet states cannot be populated by direct excitation, are short lived ( $\sim 10$  ps), and are essentially non-fluorescent. On the other hand, the  $S_2$  states have large extinction coefficients, but are extremely short lived ( $\sim 200$  fs). These properties make the transfer of singlet energy to antenna or reaction center chlorophylls problematic. In spite of this, natural carotenoid antenna systems function rather well, with quantum yields of energy transfer to chlorophyll in the range of 50% to nearly 100%. How is this achieved?

For many years, we have been investigating the transfer of singlet excitation energy from carotenoids to tetrapyrrole pigments in model systems. Recent advances in laser technology now allow us to probe energy transfer on the subpicosecond time scale.<sup>17</sup> For example, model



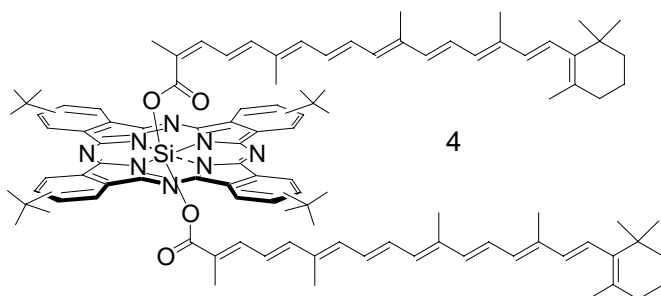
photosynthetic antenna system **3**, consisting of a carotenoid moiety covalently linked to a purpurin (a porphyrin derivative with absorption at long wavelengths), was recently prepared and studied.<sup>5</sup> Ultrafast fluorescence upconversion measurements of carotenopurpurin dyad **3** and an unlinked reference carotenoid

demonstrate that the fluorescent  $S_2$  excited state of the carotenoid model has a lifetime of  $150 \pm 3$  fs, while the corresponding excited state of the carotenoid in the carotenopurpurin dyad is quenched to  $40 \pm 3$  fs.

This quenching is assigned to energy transfer from the carotenoid  $S_2$  state to the purpurin with a  $73 \pm 6\%$  efficiency, which is in accord with the  $67 \pm 4\%$  quantum yield obtained by steady state fluorescence excitation measurements. Concomitant with the decay of the carotenoid  $S_2$  excited state, a single exponential rise of the excited  $S_1$  state of the purpurin moiety was observed at 699 nm with a time constant of 64 fs. However, the decay of the fluorescence anisotropy was faster at this wavelength (40 fs) and isotropic rise times as short as 44 fs were determined at other emission wavelengths. The lifetime of the  $S_1$  state of the carotenoid (7.8 ps) was the same in both the carotenoid model and the dyad. Taken together, these results unequivocally demonstrate that the  $S_2$  state of the carotenoid moiety is the sole donor state in the

singlet-singlet energy transfer process. Thus, although the  $S_2$  state is very short lived, the dyad possesses sufficient electronic coupling between the moieties to ensure relatively efficient energy transfer.

In another study, carotenoid pigments have been linked as axial ligands to the central silicon atom of a phthalocyanine derivative forming molecular triad **4**.<sup>8</sup> Laser flash studies on the

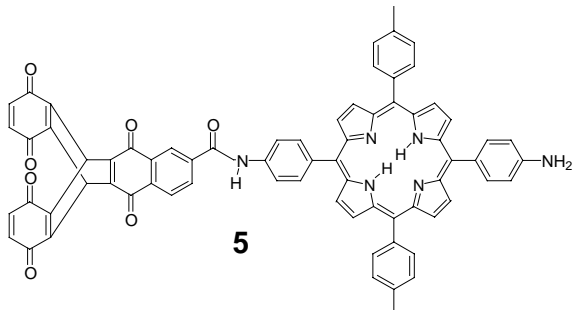


fs and ps time scales show that both the carotenoid  $S_1$  and  $S_2$  levels act as donor states, resulting in highly efficient (>95%) singlet energy transfer from the carotenoids to the phthalocyanine. The short-lived (quenched to 53 fs) carotenoid  $S_2$  state directly transfers excitation to the phthalocyanine with 35% efficiency, and energy transfer from the longer-lived

(quenched to 2.6 ps)  $S_1$  excited state occurs with an efficiency of 58%, based on light absorbed via  $S_2$ . Triplet energy transfer in the opposite direction was also observed. In polar solvents electron transfer from a carotenoid to the phthalocyanine excited singlet state is efficient and charge recombination yields the ground state of **4**.

### C. New approaches to artificial photosynthetic reaction centers

Much of the research in this project has been directed toward the development of new approaches to artificial photosynthetic reaction centers. These have been based on the electron transfer principles used in natural reaction centers, but explore new ways to apply these

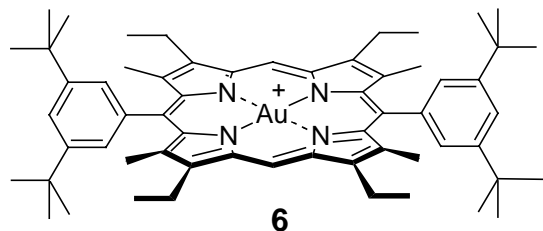


principles. During the last grant period, we synthesized molecular tetrad **5**, which consists of a porphyrin (P) covalently linked to a naphthoquinone (NQ) that in turn bears two benzoquinone moieties (BQ), and investigated its photochemistry using time-resolved spectroscopic techniques.<sup>2,3</sup> Excitation of the porphyrin chromophore of the P-NQ-BQ<sub>2</sub> tetrad in benzonitrile solution is followed by photoinduced electron transfer with a rate constant of  $8.3 \times 10^{10}$

$s^{-1}$  to produce an initial  $P^{\bullet+}$ -NQ $^{\bullet-}$ -BQ<sub>2</sub> state with a quantum yield of unity. A charge shift reaction gives a final  $P^{\bullet+}$ -NQ-(BQ $^{\bullet-}$ BQ) charge-separated state, which decays to the ground state with a rate constant of  $1.9 \times 10^{10} s^{-1}$ . The tetrad features both sequential multistep electron transfer pathways, which lead to a long-lived charge-separated state, and parallel multistep electron transfer pathways, which increase the yield of the long-lived state. No evidence was found for significant involvement of direct electron transfer from the porphyrin first excited singlet state to a benzoquinone. This is in distinction to results reported in the literature by other workers for a P-Q-Q triad that also featured a triptycene linkage joining quinone moieties. It appears that the conclusions reached in the earlier work were based in part on a mistaken interpretation of transient absorption data.<sup>2</sup>

In future experiments, we intend to use porphyrins as electron acceptors in artificial photosynthetic reaction centers. Gold porphyrins are often used as electron-accepting chromophores in artificial photosynthetic constructs due to their high reduction potentials. Due

to the heavy-atom effect, the gold porphyrin first excited singlet state undergoes rapid intersystem crossing to form the triplet. The lowest triplet state can undergo reduction by electron donation from a nearby porphyrin or other moiety. In addition, it can be involved in triplet-triplet energy transfer interactions with other chromophores. In contrast, little has been

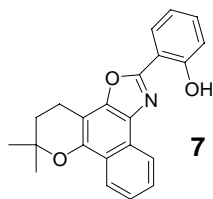


known about the short-lived singlet excited state.

We have therefore used ultrafast time resolved absorption spectroscopy to investigate the singlet excited state of Au(III) 5,15-bis(3,5-di-*t*-butylphenyl)-2,8,12,18,-tetraethyl-3,7,13,17-tetramethylporphyrin (**6**) in ethanol solution.<sup>4</sup> The excited singlet state is found to form with the laser pulse, and to decay with a time constant of 240 fs to

give the triplet state. The triplet returns to the ground state with a lifetime of 400 ps. The lifetime of the singlet state is comparable to time constants for energy and photoinduced electron transfer in some model and natural photosynthetic systems. Thus, it would be kinetically competent to take part in such processes in suitably-designed supermolecular systems.

One strategy under investigation for increasing the yield of high energy charge-separated states from photoinduced electron transfer in artificial reaction centers is to couple the electron transfer process to proton transfer. We investigated this approach some years ago in a porphyrin-quinone dyad wherein the quinone bore a carboxylic acid proton donor. These interests have led us to investigate proton transfer in 2-hydroxyphenyl-lapazole (**7**). The molecule was found<sup>9</sup> to



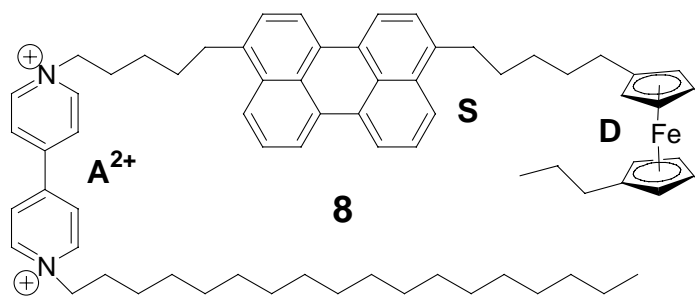
undergo Excited State Intramolecular Proton Transfer (ESIPT) in the protic solvents methanol, 2-propanol and 1-octanol at room temperature. The proton that resides on the phenolic group in the ground state migrates to the nitrogen in the excited state, producing zwitterionic species. Investigation of the kinetics of this process, using time-resolved single photon counting and transient absorption spectroscopy, indicated the presence of three different

excited-state species. These results are very different from those already reported for **7** in non-protic solvents, where it was found that the ESIPT process attains equilibrium during the lifetime of the excited state. Factor analysis of the steady state spectra supports the conclusions drawn from the kinetic results. The difference in behavior as a function of solvent is attributed to two factors that depend on the stronger solute-solvent interactions in the case of the protic solvents: 1) The slight slowing down of the process of proton transfer, which prevents equilibrium from being established during the lifetime of the excited singlet state, and 2) The weakening of the intramolecular hydrogen bond, which allows rotation of the hydroxyphenyl moiety.

#### D. Interfacing artificial reaction centers to electronic surfaces

Many of the artificial photosynthetic reaction centers produced by our group and others are capable of generating long-lived charge-separated states in high quantum yield when in fluid solution. Utilization of the energy stored in these states requires coupling them to another process. For example, in the liposome work described above, the charge-separated state powers transmembrane ion transport via a redox loop. Another possible method for harnessing the energy produced by the artificial reaction centers is to attach the molecules to conducting or semiconducting surfaces in such a way that electrons may be transferred into or out of the electronic material, generating an electrical current. We have carried out two investigations that may lead to progress in this area.

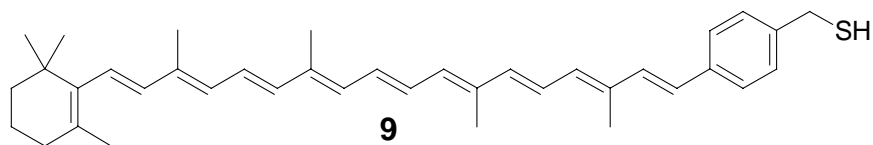
We have established a collaboration with the group of Professor Masamichi Fujihira, at the Tokyo Institute of Technology. The Fujihira group has synthesized triad molecules such as **8**, and used them as components of a photoelectrochemical cell. The molecule consists of a viologen-based electron acceptor ( $A^{2+}$ ), a perylene photosensitizer (S), and a ferrocene donor moiety (D). The triads form stable mixed monolayers at the air-water interface with arachidic acid, in which the donor-acceptor systems are oriented. These layers can be deposited onto a gold electrode using the Langmuir-Blodgett technique, and the resulting sensitized electrodes generate current in a photoelectrochemical cell. The Fujihira group has demonstrated the



photoelectrochemical effect, but understanding its basis requires a knowledge of the various electron and energy transfer pathways that are available following light absorption. We have now studied the new amphiphilic  $A^{2+}$ -S-D triad **8** and its reference compounds, S-D,  $A^{2+}$ -S, and S type molecules (synthesized by the Fujihira

group), using time-resolved transient absorption spectroscopy.<sup>7</sup> Intramolecular electron transfer reactions were initiated by photo-excitation of the S moiety, and a long-lived final charge separated state,  $A^+-S-D^+$ , was formed. Although the yield of the initial charge separated state,  $A^+-S^+-D$ , was very high (0.93), the overall yield of the final charge separated state was relatively low (0.03). The rate of the back electron transfer from  $A^+$  to  $S^+$  was observed to be two times lower than that of the forward electron transfer from S to  $A^{2+}$ , suggesting that with suitable molecular engineering, the yield of long-lived charge separation in such triads could be improved substantially. This would require increasing the electronic coupling between S and D, and/or slowing the recombination of  $A^+-S^+-D$  in some fashion. The Fujihira group is preparing new molecules to investigate this possibility.

The formation of self-assembled monolayers (SAMs) from organosulfur compounds on metal surfaces has been a topic of great interest over the past two decades. The majority of these investigations concern the self-assembly of various alkanethiols and dialkyl disulfides on gold surfaces. Currently there is increasing interest in studying the properties of electroactive SAMs for potential applications in solar energy conversion and molecular devices. Our group has previously shown that a synthetic carotenoid containing a thiol group, 7'-apo-7'-(4-mercaptomethylphenyl)- $\beta$ -carotene (**9**), could be embedded into a docosanethiol SAM on Au. Using a dilute mole fraction of **9** in the SAM we were able to measure the electrical properties of



single molecules in an insulating matrix. We found that carotenoid molecules were over 1 million times more conductive than the surrounding alkane chain, suggesting that the carotenoids act as a molecular wire. Lowell Kispert and his group have been able to observe photoinduced electron injection from carotenoids with related structures into nanoparticulate  $TiO_2$ , leading to photocurrents. In the context of these studies, we have collaborated with the Kispert group to study the properties of pure self-assembled monolayers of **9** on gold surfaces.<sup>6</sup> The stability, packing density, optical absorption, and hydrophobicity of the monolayers were investigated

with x-ray photoelectron spectroscopy (XPS), Fourier-transform infrared reflection-absorption spectroscopy (FTIR-RAS), UV-Vis spectroscopy, spectroscopic ellipsometry and contact angle measurements. The XPS and spectroscopic ellipsometry measurements reveal that the saturation coverage is  $\sim 4 \times 10^{14}$  molecules of **9** per  $\text{cm}^{-2}$  and the film thickness is  $\sim 20$  Å, respectively. The FTIR-RAS and contact angle measurements suggest that the polyene chains are packed well enough to create a hydrophobic interface.

#### **E. Medically-related spin-offs of artificial photosynthesis research**

A major role of carotenoids in photosynthesis is photoprotection from singlet oxygen. Carotenoids rapidly quench chlorophyll triplet states by triplet-triplet energy transfer, precluding formation of singlet oxygen. They can also scavenge singlet oxygen that may be present. Our research group has been interested in mimicking this photoprotective behavior in artificial photosynthetic systems, and studying the structural prerequisites for rapid energy transfer quenching of tetrapyrrole triplet states by carotenoids. It occurred to us that carotenoid photoprotection might also be applicable to a problem encountered in the medical use of porphyrin derivatives as tumor localizing agents. Certain porphyrins localize in tumor tissue. If the area is irradiated with light absorbed by the porphyrin, porphyrin fluorescence is observed, and the fluorescence delineates the tumor tissue. Unfortunately, most fluorescent porphyrins have a high yield of triplet states, which are excellent sensitizers for production of highly toxic singlet oxygen. Thus, the use of porphyrins for imaging purposes has been limited. If a carotenoid could be covalently linked to a porphyrin tumor visualization agent, then rapid quenching of the porphyrin triplet state could prevent singlet oxygen damage.

Consequently, we have provided some carotenoid and carotenoporphyrin materials to medical researchers for investigation of their applicability as photoprotected tumor localizing agents.<sup>13-15</sup> For example, a carotenopyropheophorbide dyad has been investigated for the discrimination of adenocarcinoma tissue from normal mammary tissue in dogs. Active uptake of the dyad into diseased tissue was observed. The tumor tissue was readily observed by monitoring the fluorescent image generated by external irradiation of the animal with a 778 nm or 660 nm laser beam. These studies allow some of our synthetic molecules to do “double duty” by contributing to our solar energy research, and at the same time to medical research.

#### **F. Publications since last progress report based on DOE research**

1. “Active Transport of  $\text{Ca}^{++}$  by an Artificial Photosynthetic Membrane”, I. M. Bennett, H. M. Vanegas-Farfano, A. Primak, P. A. Liddell, L. Otero, L. Sereno, J. J. Silber, A. L. Moore, T. A. Moore and D. Gust, *Nature*, **420**, 398-401 (2002).
2. “Stepwise Sequential and Parallel Photoinduced Charge Separation in a Porphyrin-Triquinone Tetrad,” J. Springer, G. Kodis, L. de la Garza, A. L. Moore, T. A. Moore and D. Gust, *J. Phys. Chem. A*, **107**, 3567-3575 (2003).
3. “1,4,5,8-Tetramethoxyanthracene,” J. W. Springer, T. A. Moore, A. L. Moore, D. Gust and T. L. Groy, *Acta Cryst.*, **58**, o1145-o1146 (2002).
4. “The Gold Porphyrin First Excited Singlet State,” J. Andréasson, G. Kodis, S. Lin, A. L. Moore, T. A. Moore, and D. Gust, *Photochem. Photobiol.*, **76**, 47-50 (2002).

5. "Ultrafast Energy Transfer from a Carotenoid to a Chlorin in a Simple Artificial Photosynthetic Antenna," A. N. Macpherson, P. A. Liddell, D. Kuciauskas, D. Tatman, T. Gillbro, D. Gust, T. A. Moore, and A. L. Moore, *J. Phys. Chem. B.*, **106**, 9424-9433 (2002).
6. "A Thiol-Substituted Carotenoid Self-Assembles on Gold Surfaces," D. Liu, G. J. Szulczewski, L. D. Kispert, A. Primak, T. A. Moore, A. L. Moore, and D. Gust, *J. Phys. Chem. A.*, **106**, 2933-2936 (2002).
7. "Dynamics of Photoinduced Electron Transfer in an Amphiphilic A<sup>2+</sup>-S-D Triad Molecule," M. Sakomura, S. Lin, T. A. Moore, A. L. Moore, D. Gust, and M. Fujihira, *J. Phys. Chem. A.*, **106**, 2118-2226 (2002).
8. "High Efficiency Energy Transfer from Carotenoids to a Phthalocyanine in an Artificial Photosynthetic Antenna," E. Mariño-Ochoa, R. Palacios, G. Kodis, A. N. Macpherson, T. Gillbro, D. Gust, T. A. Moore and A. L. Moore, *Photochem. Photobiol.*, **76**, 116-121 (2002).
9. "Excited State Acidity of Bifunctional Compounds. 8. Competitive Kinetics Between Solvent Reorientation and Proton Transfer during ESIPT of 2-Hydroxyphenyl-Lapazole in Protic Solvents," C. E. M. Carvalho, A. S. Silva, I. M. Brinn, A. V. Pinto, M. C. F. R. Pinto, S. Lin, T. A. Moore, D. Gust, and M. Maeder, *Phys. Chem. Chem. Phys.*, **4**, 3383-3389 (2002).
10. "Efficient Energy Transfer and Electron Transfer in an Artificial Photosynthetic Antenna-Reaction Center Complex," G. Kodis, P. A. Liddell, L. de la Garza, P. C. Clausen, J. S. Lindsey, A. L. Moore, T. A. Moore, and D. Gust, *J. Phys. Chem. A.*, **106**, 2036-2048 (2002). (DOE support via J. S. Lindsey)
11. "Mimicking Photosynthetic Solar Energy Transduction," D. Gust, T. A. Moore, and A. L. Moore, *Accounts of Chemical Research*, **34**, 40-48 (2001).
12. "Covalently Linked Systems Containing Porphyrin Units," D. Gust, A. L. Moore, and T. A. Moore, In *Electron Transfer in Chemistry, Vol. 3, Biological and Artificial Supramolecular Systems*, V. Balzani, Ed., Wiley-VCH: Weinheim, pp 272-336 (2001).
13. "Synthesis of a Carotenobenzoporphyrin from a *Meso*-Diphenylporphyrin," P. A. Liddell, X. Zárate, A. L. Moore, T. A. Moore, and D. Gust, *Tetrahedron Letters*, **41**, 9661-9665 (2000).
14. "Localisation and Accumulation of a New Carotenoporphyrin in Two Primary Tumour Models," J. T. H. M. van den Akker, O. C. Speelman, H. J. van Staveren, A. L. Moore, T. A. Moore, D. Gust, W. M. Star, and H. J. C. M. Sterenborg, *J. Photochem. Photobiol., B: Biology*, **54**, 108-115 (2000).
15. "Pharmacokinetics of ICG and HPPH-car for the Detection of Normal and Tumor Tissue Using Fluorescence, Near-infrared Reflectance Imaging: A Case Study," M. Gurfinkel, A. B. Thompson, W. Ralston, T. L. Troy, A. L. Moore, T. A. Moore, D. Gust, D. Tatman, J. S. Reynolds, B. Muggenbeurg, K. Nikula, R. Pandey, R. H. Mayer, D. J. Hawrysz, and E. M. Sevick-Muraca, *Photochem. Photobiol.* **72**, 94-102 (2000).

16. "Intramolecular Photoinduced Electron Transfer Reactions of Porphyrins," D. Gust and T. A. Moore, In *The Porphyrin Handbook*, Vol. 8, K. M. Kadish, K. M. Smith and R. Guilard, Eds., Academic Press: New York, pp 153-190 (2000).
17. "Novel and Biomimetic Functions of Carotenoids in Artificial Photosynthesis," T. A. Moore, A. L. Moore and D. Gust, *Adv. Photosynth.*, **8**, 327-339 (1999).
18. "An Artificial Photosynthetic Membrane," D. Gust, T. A. Moore and A. L. Moore, *Zeitschrift für Physikalische Chemie*, **213**, 149-155 (1999).



