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Project Title: Photoinitiated Electron Transfer in Multichromophoric Species: Synthetic Tetrads and Pentads Featuring Diquinone Moieties

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Introduction

This project involves the design, synthesis and photophysical study of complex molecular systems engineered to achieve long lived charge separated states by a biomimetic, photoinitiated multistep electron transfer process. The use of these artificial systems to investigate different electron and energy transfer strategies will allow the evolution of more efficient molecular devices for the gathering of light energy and its transformation into chemical potential energy.

The three major aspects of the work emphasized in the initial proposal are:

- i. Design and synthesis of molecular devices incorporating new quinone moieties.
- ii. Synthesis and spectroscopic studies of molecular tetrads and pentads featuring modified porphyrin-diquinone linkages. These systems are related to ones prepared earlier in this project.
- iii. New photochemical and photophysical investigations of tetrads and pentads, including the development of methods for harvesting the energy stored in long-lived charge separated states.

Progress in each of these areas during the second period of this project is summarized below.

Design and synthesis of molecular devices incorporating new quinone moieties.

A series of compounds is being prepared in order to investigate the possibility of coupling a proton transfer process to an electron transfer process. The premise is that rapid intramolecular proton transfer to a quinone anion radical (formed by photoinitiated electron transfer from an attached porphyrin) might increase the lifetime of the intermediate charge separated state, and thus allow more efficient competition of subsequent forward electron transfer with the recombination reaction. The first system we have synthesized in order to test this hypothesis is porphyrin-quinone **1**. Fluorescence decay studies have shown that the first excited singlet state lifetime of **1**

in CH_2Cl_2 is *ca.* 100 ps, which is the same as that of reference compound 2. The lifetimes are also identical in butyronitrile (1.5 ns) and benzonitrile (500 ps). Femtosecond transient absorption studies designed to determine the lifetimes of the charge-separated states have begun using benzonitrile as the solvent.

A different system is being examined in parallel with this study. Porphyrin-quinone **1** has proven to be difficult to handle in that it is almost impossible to keep the quinone moiety in the oxidized form. Since alcohols are also proton donors, we have prepared triad **3**, which bears a side chain with an -OH group. This molecule was synthesized according to Scheme I. The fluorescence lifetime of **3** in CH_2Cl_2 is 105 ps, which is essentially identical to that found for an analogous triad lacking the quinone alcohol side chain. Thus, the change in the quinone structure has evidently not altered the thermodynamic driving force for the electron transfer (and therefore the energy of the $\text{P}^{+\bullet}\text{Q}^{-\bullet}$ state). In preliminary experiments, flash photolysis studies of **3** on the nanosecond time scale indicated that the carotenoid radical cation ($\text{C}^{+\bullet}$) is being formed with a quantum yield approximately 1.5 times larger than that for the reference triad. This increase in the quantum yield for the final charge separated state in **3** is clearly in the direction expected for stabilization via proton transfer.

In order to further investigate these interesting results, new systems such as **4**, **5**, and **6**, which feature quinones with substituents capable of forming internal hydrogen bonding within a six membered ring are being designed. Some of the components are already synthesized.

Scheme I

In another facet of this project, tetrads and pentads bearing new interquinone linkages are being prepared. One aspect of this work involves modification of the bicyclic bridge between the naphthoquinone and benzoquinone moieties of the original pentad (**10** see page 9). The product of synthetic Scheme II features a keto group protected as a diethylketal (**7**) which has replaced the CH_2 group of the norbornadiene bridge. In a model system recently prepared, the keto group has been deprotected by acid catalyzed hydrolysis to yield compound **8**, which is stable at room temperature. Base catalyzed hydrolysis of **7**, coupling to a porphyrin, and deprotection of the quinones will afford a triad with the modified bridge between the quinones. In a similar fashion, various tetrads can be constructed.

One reason for choosing a keto group in the bridge in **8** is that it provides a synthetic "handle" for introducing other functionalities. For example, by a Wittig reaction of a derivative of ketone **8** and the phosphonium salt of bromodiphenylmethane derivatives systems such as **9** can be synthesized. The R_1 groups can be either electron donor or acceptor substituents. After the synthesis of these molecules has been completed, the rate of electron transfer between the quinones as a function of the electron density of the bridging system will be determined.

Scheme II

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Molecular tetrads and pentads featuring a modified porphyrin-diquinone linkage.

Three systems which use a photochemically initiated electron transfer strategy to produce long lived charge separated species have now been prepared. In the final charge-separated states, the positive and negative charges are separated by as much as 80 Å. These compounds have been designed to explore the electronic factors controlling the balance between the useful forward and energy-wasting recombination electron transfer reactions. These processes may be visualized in general terms as shown in Scheme III. In a molecular pentad consisting of three electron donor (D) and two electron acceptor (A) moieties, the first excited singlet state of D₁ transfers an electron to the attached acceptor A₁ to form an initial charge separated state (Step 2). This process can go

on via steps 3 and 4 to initiate an electron transfer cascade which ultimately yields a long lived $D_3^{+*}D_2D_1A_1A_2^{-*}$ species. Competing with these two steps is charge recombination by step 5, which generates the neutral ground state and dissipates stored energy as heat. In the series of compounds under investigation, D_1 and D_2 are free base and metallated porphyrins, respectively, D_3 is a carotenoid polyene, and A_1 and A_2 are naphthoquinones and benzoquinones, respectively.

Scheme III

In the initial pentad system prepared in our laboratories in 1990, **10**, fluorescence lifetime measurements yielded a rate for step 2 of $7.1 \times 10^8 \text{ s}^{-1}$, which corresponds to a quantum yield of 0.85. This step is undoubtedly the yield limiting step, since the overall yield for the final charge separated state, $D_3^{+*}D_2D_1A_1A_2^{-*}$, was 0.83.

In order to increase the yield of step 2, and ideally the overall yield, the linkage between the free base porphyrin and the naphthoquinone has now been altered to increase the electronic coupling. The CH_2 group was eliminated and the amide linkage was reversed. In this compound, pentad **11**, the rate of the initial electron transfer reaction was found by fluorescence decay studies to be increased *ca.* 30 fold to $2.1 \times 10^{10} \text{ s}^{-1}$, which indicates a quantum yield of 0.99.

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The quantum yield for the final charge separated state $D_3^{+*}D_2D_1A_1A_2^{-*}$, however, was reduced to 0.38 in this molecule. Our interpretation of this result is that the increased electronic coupling between the porphyrin and the quinone which leads to the greatly enhanced rate for the initial electron transfer (step 2) also increases the recombination reaction 5 so that the forward steps 3 and 4 cannot prevail.

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Clearly, what is needed is an intermediate degree of electronic coupling. In the ideal molecule, the rate of step 2 will be reduced, relative to that in **11**, but still rapid enough to give a high quantum yield of the initial charge separated state. At the same time, the reduced coupling must also slow step 5 significantly. Pentad **12**, which has a methylene spacer inserted between D_1 and A_1 in pentad **11**, was designed to meet these requirements. The synthesis of pentad **12** has not been completed, but data for triad **13**, which is essentially a precursor of **12**, has been obtained (the preparation of **13** is described in Scheme IV). Fluorescence lifetime measurements on triad **13**, which has the new linkage, gave a rate of $2.2 \times 10^9 \text{ s}^{-1}$ for step 2. This allows

calculation of a quantum yield of 0.95. Thus, as expected, the reduction in the electronic coupling has resulted in a significant decrease in the rate of the initial electron transfer step, but still preserves an almost quantitative quantum yield. This suggests that the yield of the long lived charge separated state in pentad **12** may turn out to be optimal.

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When completed, the study of this series of compounds will demonstrate the control of electron transfer direction at a branch point by electronic coupling effects. Taken together with our previous work on the thermodynamic control of electron transfer at an analogous branch point, these principles make it possible to rationally design successful photoelectrical energy converting devices at the molecular level.

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Scheme IV

New photochemical and photophysical investigations of tetrads and pentads.

The achievement of long-lived, energetic charge separation in high quantum yield presents the challenge of harvesting the stored chemical potential. Several approaches are currently under investigation. One involves the incorporation of pentads or other molecular devices into monolayers prepared on conducting or semiconducting electrodes. We are making good progress on an approach mentioned in last year's report, which described the synthesis of porphyrin species bearing isonitrile side chains which are known to bind strongly to gold surfaces. Indeed, monolayers of these porphyrins linked to a gold surface can be visualized using scanning tunneling microscopy (STM). Monolayers of a single porphyrin and a porphyrin dyad prepared under conditions such that either compound could be linked to the gold surface were scanned in the STM using the same tip. Images of particles resembling porphyrins were observed. At low coverage we obtained a markedly larger average particle size ($395 \text{ \AA}^2$) for diporphyrins than for monoporphyrins ($121 \text{ \AA}^2$), which strongly supports our assignment of these images to the two porphyrin species. The particle size distributions are broad, but the images show a characteristic variation of contrast with tip bias, suggesting that the heterogeneity is due to different molecular conformations rather than contamination. We also find evidence of ordered structures at high coverages. These preliminary data indicate that the images are of use in determining the coverage, mechanism of attachment, and to some extent, electronic properties of a molecular adsorbate in an environment appropriate for the operation of practical energy converting molecular devices. The initial report of this work has now appeared in *Langmuir*.

In summary, the year has seen considerable progress in the synthesis of complex molecular devices designed to investigate several important aspects of photoinitiated electron transfer in multichromophoric species. During the next year, these syntheses will be completed, and the spectroscopic studies necessary to complete the work will be performed.

Publications and presentations based on this work.

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4. "Photosynthetic Model Systems," D. Gust and T. A. Moore, *Topics in Current Chemistry*, **159**, 103-151 (1991).
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6. "Synthesis of Carotenoporphyrin Models for Photosynthetic Energy and Electron Transfer," D. Gust, T. A. Moore, A. L. Moore and P. A. Liddell, *Methods in Enzymology*, in press (1992).

7. "Multistep Electron and Energy Transfer in Artificial Photosynthesis," D. Gust and T. A. Moore, In: *The Photosynthetic Reaction Center, Volume II*, J. Deisenhofer and J. R. Norris, eds. (New York: Academic Press), in press.
8. "Photoinitiated Electron Transfer in Synthetic Tetrads and Pentads," D. Gust, T. A. Moore and A. L. Moore, Fifteenth DOE Solar Photochemistry Research Conference, Snowmass Village, Colorado, June, 1991.
9. "Photoinitiated Energy and Electron Transfer in a Covalently Linked Porphyrin Dyad," L. S. Leggett, D. Gust, T. A. Moore, A. Moore, G. Seely, J. DeGraziano, R. Hermant, T. Causgrove, R. Alden and P. Craig, 27th Western Regional ACS Meeting-FACSS/Pacific Conference, 13. Anaheim, CA, October, 1991.
10. "Photoinitiated Electron Transfer in Porphyrin Dyads," P. K. Kerrigan, A. L. Moore, T. A. Moore, D. Gust, G. Seely and Janice M. DeGraziano, 27th Western Regional ACS Meeting-FACSS/Pacific Conference, Anaheim, CA, October, 1991.
11. "Multicomponent Molecular Systems Which Mimic Photosynthetic Electron and Energy Transfer," D. Gust, T. A. Moore and A. L. Moore, The 10-Year Anniversary Symposium of the Japan-US Cooperative Photoconversion and Photosynthesis Research Program, Okazaki, Japan, December, 1991.
12. "Photosynthesis by Organic Photochemists," T. A. Moore, A. L. Moore and D. Gust, 3er. Encuentro Latinoamericano de Fotoquímica y Fotobiología, Mar del Plata, Argentina, October, 1991.
13. "Mimicry of Photosynthetic Energy and Electron Transfer," D. Gust, T. A. Moore and A. L. Moore, Fourth Annual Conference of the Inter-American Photochemical Society, Clearwater Beach, FL, January, 1992.

14. "Multistep Electron Transfer Strategies for Artificial Photosynthesis," D. Gust, Symposium on Electron Transfer Processes in Chemistry and Biology, Centre for Photomolecular Sciences, Imperial College, London, June, 1991.
15. "Synthetic Models for Reaction Centers," D. Gust, Gordon Research Conference on Photosynthesis: Biophysical Aspects, Hanover, New Hampshire, July 28 - August 2, 1991.
16. "Formation of the Pigment Triplets States and Singlet Oxygen by Pyropheophorbide-Porphyrin-Carotene Triads", A. A. Krasnovsky Jr., A. L. Moore, T. A. Moore, D. Gust and P. A. Liddell, Gordon Conference on Carotenoids, Oxnard, California, March 8-13, 1992.
17. "Carotenoids in Model Photosynthetic Systems", T. A. Moore, Gordon Conference on Carotenoids, Oxnard, California, March 8-13, 1992.
18. "Resonance Raman Studies of Caroteno-Tetratolylporphyrin Dyads", M. H. Wall, A. L. Moore, T. A. Moore, D. Gust, P. A. Liddell and M. R. Ondrias, 203rd ACS National Meeting, San Francisco, California, April 4-10, 1992.

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