

TECHNICAL PROGRESS REPORT

**Award Number:** DE-FG02-87ER13791

**Project Title:** Photoinitiated Electron Transfer in Multi-chromophoric Species - Synthetic Tetrads and Pentads

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**MASTER**

## II. Technical Progress Report

A. Overall Research Goal. As discussed in detail in the original proposal document, this research project involves the design, synthesis and study of molecules which mimic many of the important aspects of photosynthetic electron and energy transfer. Solar energy conversion via photosynthesis is the ultimate energy source for essentially all life. In addition, most of mankind's energy needs are met by coal, oil, and other fossil fuels which are the result of ancient photosynthesis. Because photosynthesis is one of the most durable and, in its early steps, most efficient solar conversion "technologies", an understanding of the details of the process is crucial. This research project will lead to a better understanding of the energy conserving steps of photosynthesis via the study of synthetic model systems which abstract features of the natural photosynthetic apparatus. The knowledge gained from such studies could be used to design artificial photosynthetic systems which employ the basic physics and chemistry of photosynthesis to help meet mankind's energy needs.

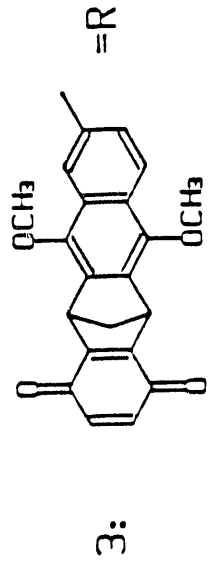
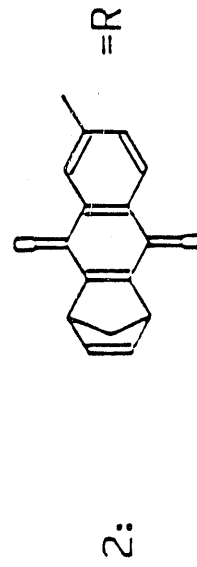
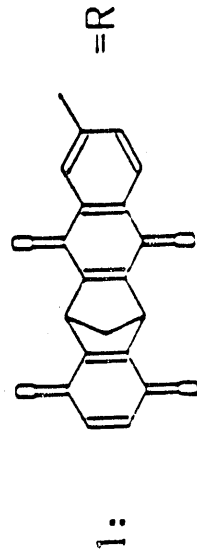
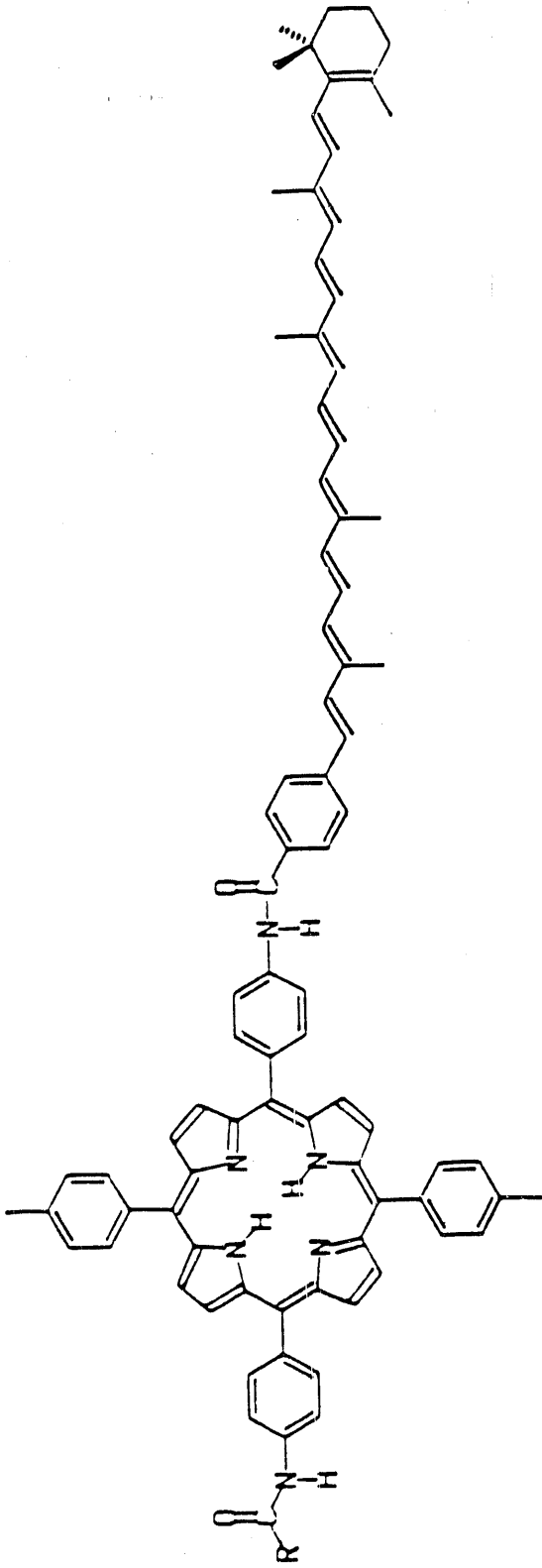
More specifically, the proposed models are designed to mimic the following aspects of natural photosynthetic multistep electron transfer: electron donation from a tetrapyrrole excited singlet state, electron transfer between tetrapyrroles, electron transfer from tetrapyrroles to quinones, and electron transfer between quinones with different redox properties. In addition, they will model carotenoid antenna function in photosynthesis

(singlet-singlet energy transfer from carotenoid polyenes to chlorophyll) and carotenoid photoprotection from singlet oxygen damage (triplet-triplet energy transfer from chlorophyll to carotenoids).

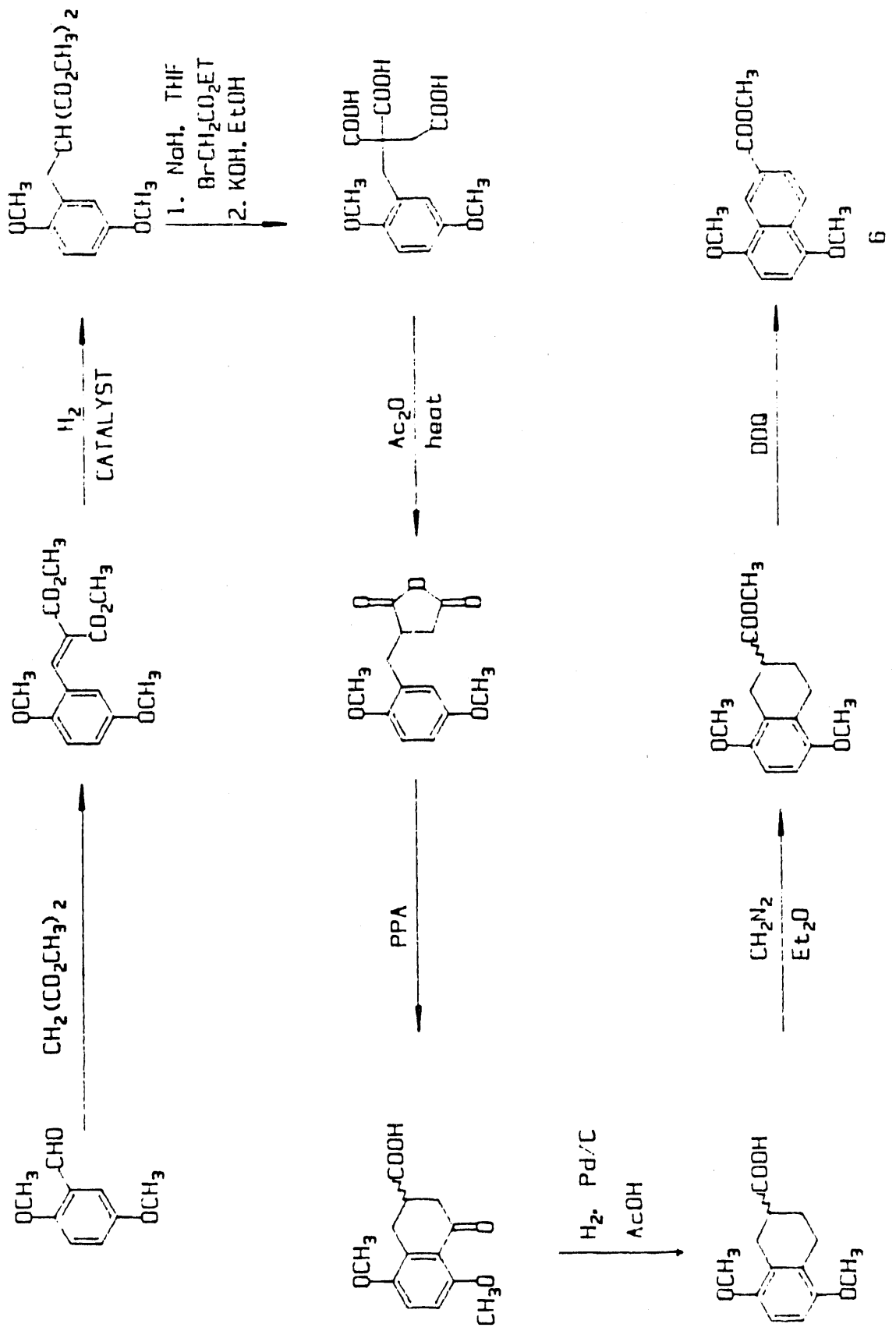
**B. Progress To Date.** The initial goal of the project was to prepare and study a molecular tetrad consisting of a porphyrin (P) linked to both a carotenoid polyene (C) and a diquinone moiety ( $Q_A-Q_B$ ). This goal has now been achieved with the synthesis of C-P- $Q_A-Q_B$  species 1. Understanding the photophysics of 1 also required the preparation of model compounds 2 and 3. It will be noted that 1 features a relatively rigid structure due to the short covalent linkages between the chromophores, the partial double bond character of the amides, and the bicyclic moiety linking the quinones. This prevents folding of the molecule which in turn could short-circuit both photodriven electron transfer and charge recombination. In addition, the molecule has been designed so that the final benzoquinone is a better electron acceptor than the naphthoquinone. This will favor the desired sequential electron transfers.

The synthetic route used for 1 is outlined in Scheme I. The preparation of 2 was achieved as shown in Scheme II, which begins with one of the intermediates obtained during the synthesis of 1. Model compound 3 required a more circuitous route (Scheme III).

Long-lived photoinitiated charge separation in 1-3 may be investigated using transient absorption spectroscopy on the nanosecond time scale. Such investigations have been begun with our laser transient absorption spectrometer at ASU. Excitation of

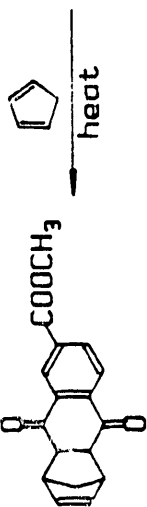
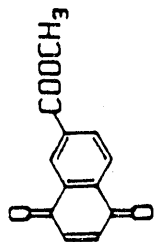


SCHEME 1

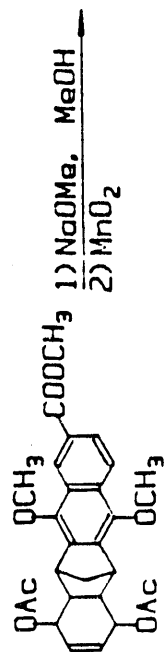
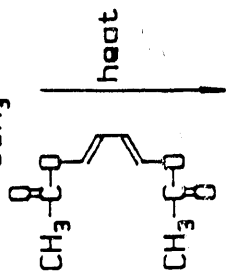
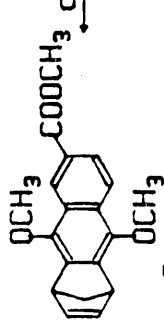


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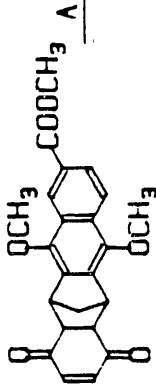
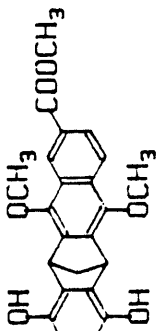
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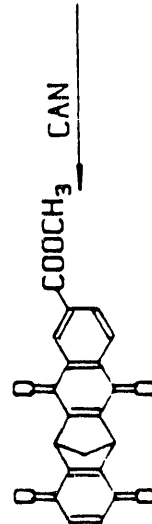
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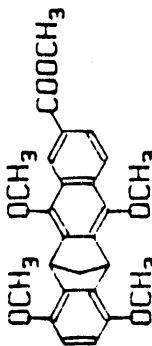
1) NaOMe, MeOH  
2) MnO<sub>2</sub>

Al<sub>2</sub>O<sub>3</sub>

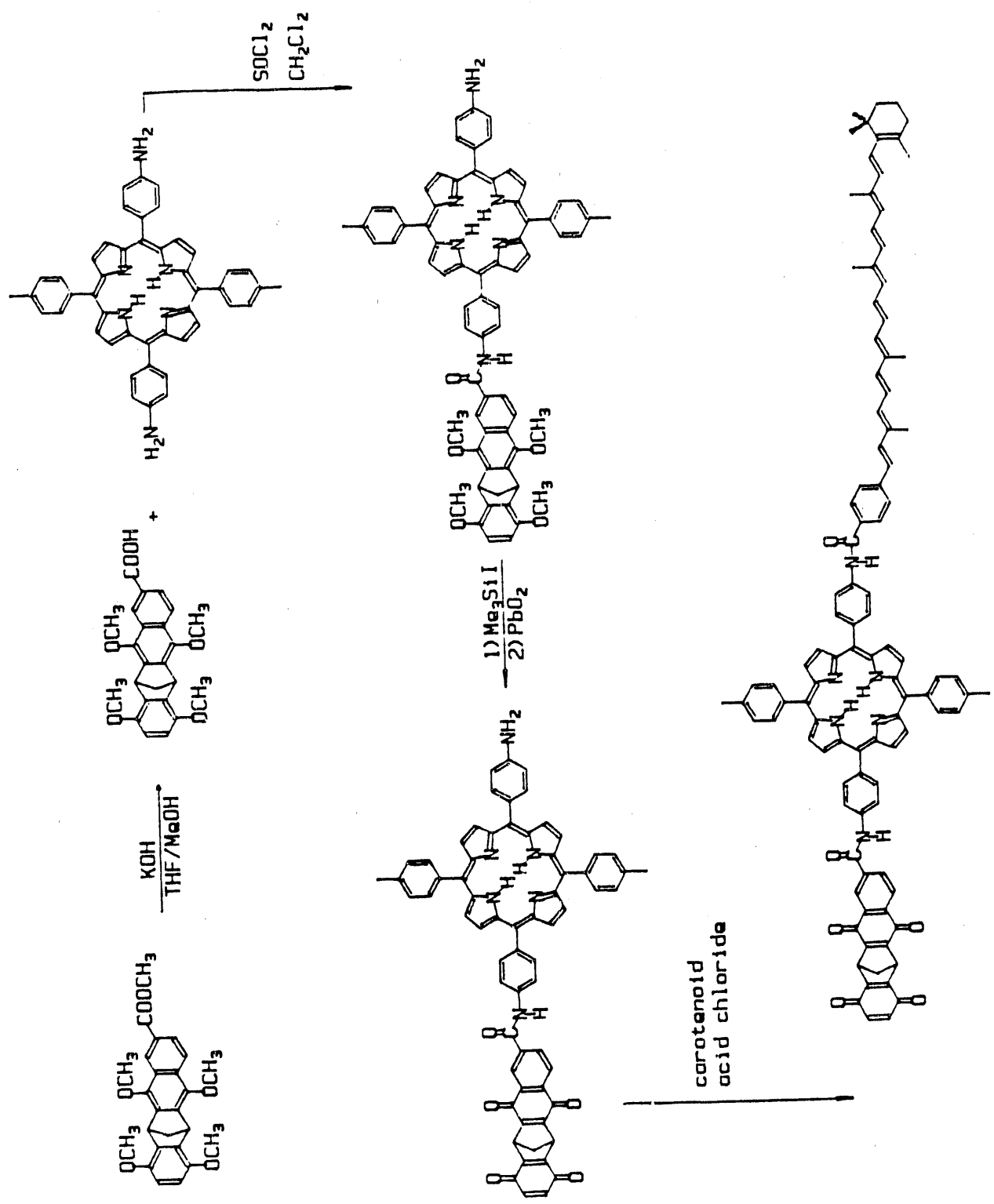
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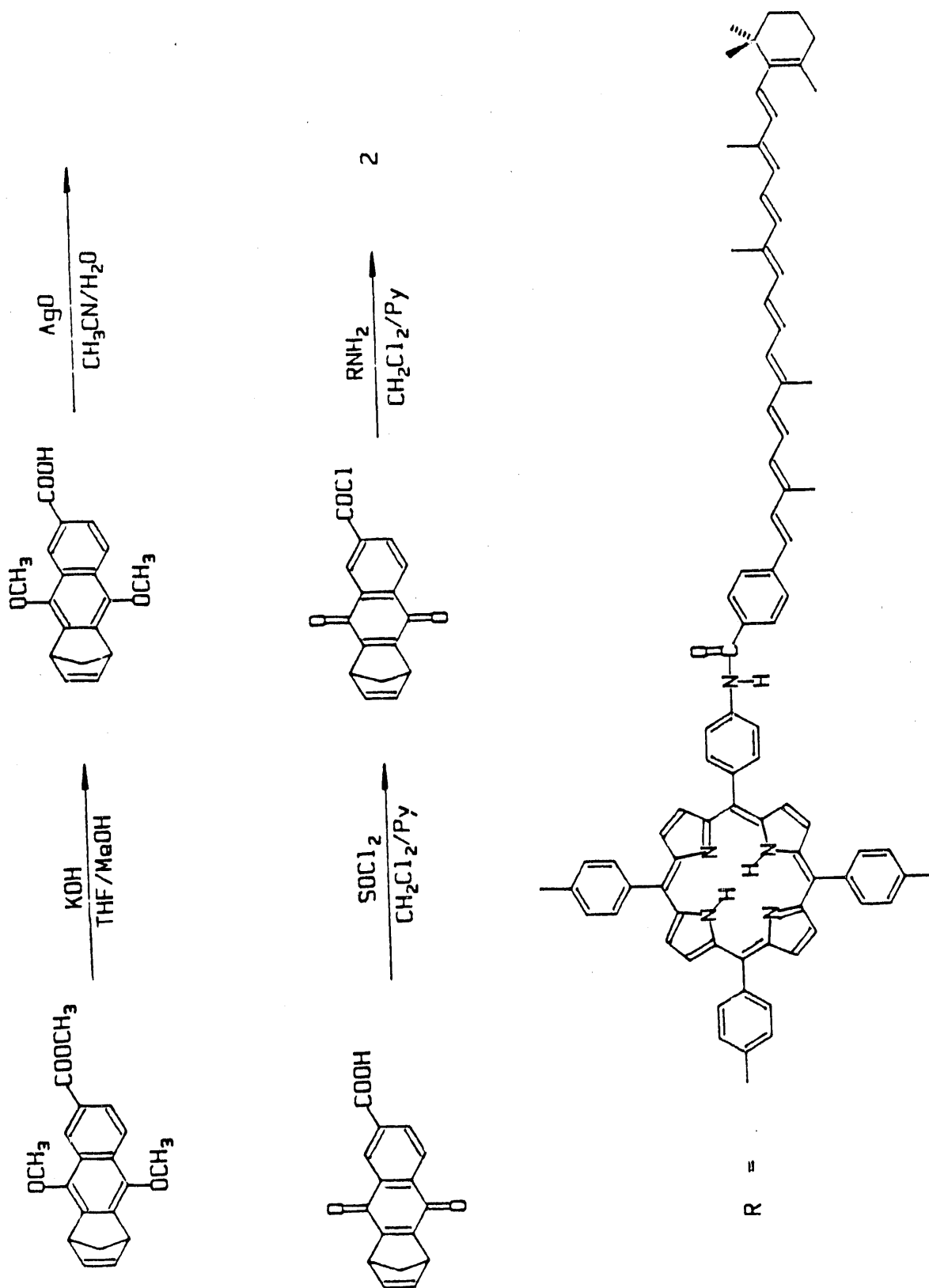
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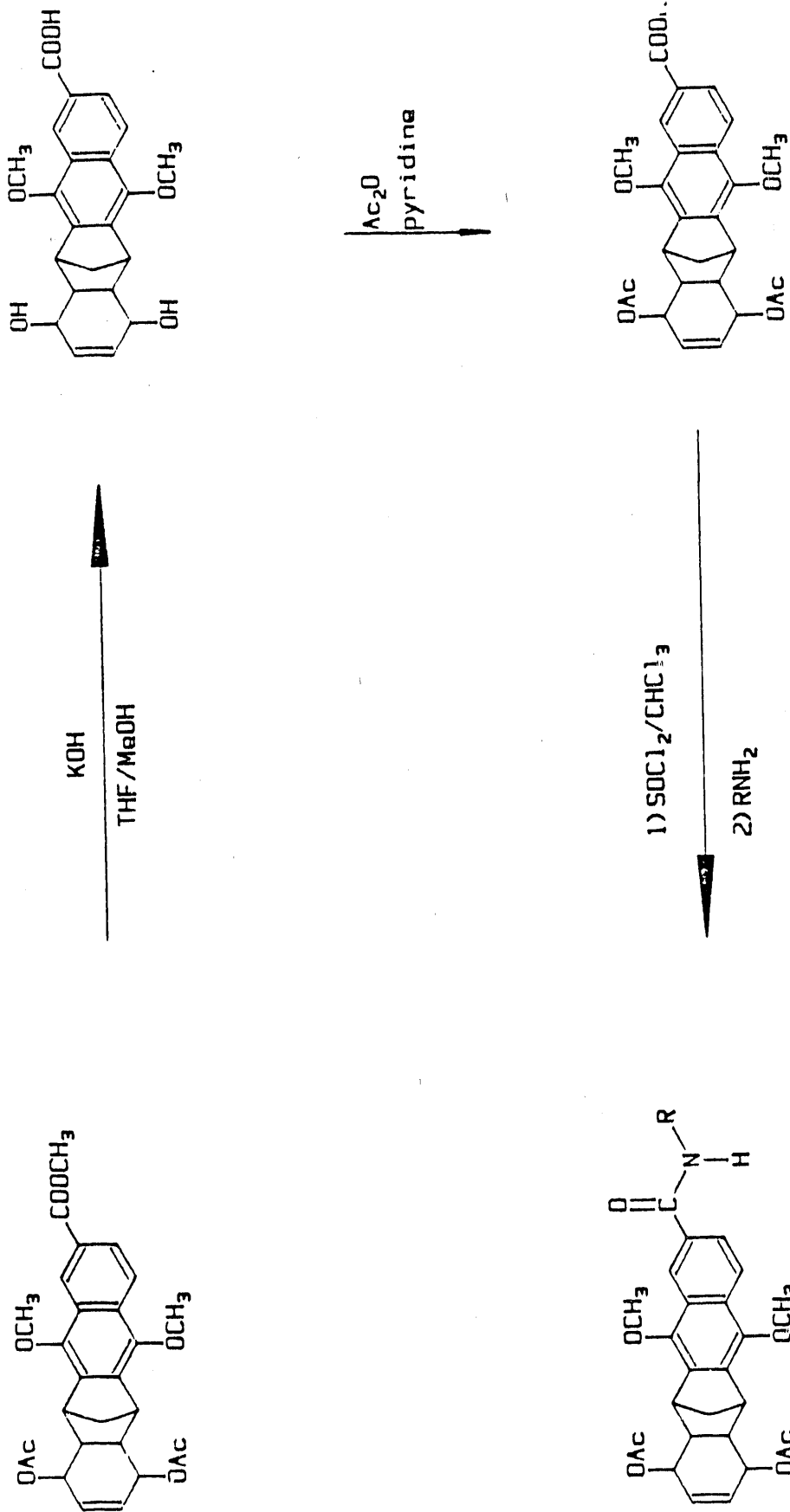


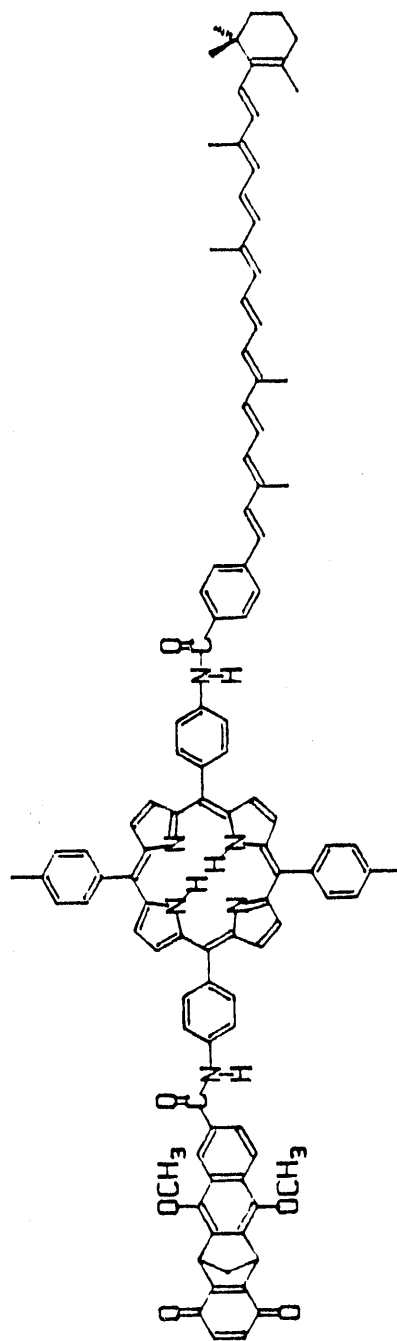
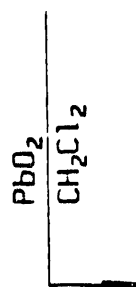
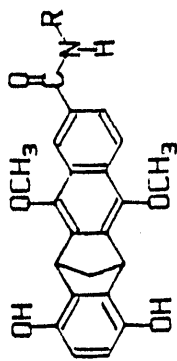
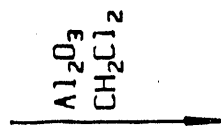
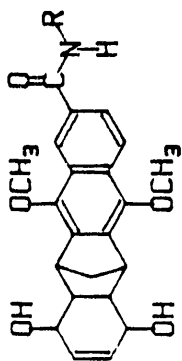
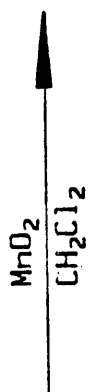
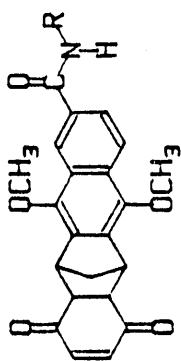
SCHEME II





SCHEME III





a dichloromethane solution of 1 with a ca. 15 ns pulse of light at 590 nm resulted in the observation of a transient absorption with a maximum at 970 nm and a lifetime of 460 ns (Figure 1). The spectrum of this transient revealed that it was due to a carotenoid radical cation. By analogy with other systems studied in our laboratories, we may ascribe this transient to the species  $C^+ \cdot -P-Q_A-Q_B^- \cdot$ . Thus, excitation of tetrad 1 does indeed lead to the formation of a long-lived charge-separated state. The quantum yield of this state was calculated to be 0.23 at ambient temperatures. Cooling the sample to 240 K resulted in an increase in quantum yield to 0.50.

A reasonable pathway for the formation of  $C^+ \cdot -P-Q_A-Q_B^- \cdot$  is shown in Figure 2. Excitation of the porphyrin generates the first excited singlet state, which donates an electron to the naphthoquinone to yield  $C-P^+ \cdot -Q_A^- \cdot -Q_B$  (step 2). By analogy with the triad systems previously studied in our laboratories,  $C-P^+ \cdot -Q_A^- \cdot -Q_B$  may go on to produce a second charge-separated state  $C^+ \cdot -P-Q_A^- \cdot -Q_B$  (step 4), which in turn undergoes a third electron transfer to yield the final  $C^+ \cdot -P-Q_A-Q_B^- \cdot$  species. The  $C-P^+ \cdot -Q_A^- \cdot -Q_B$  state may undergo an additional reaction in which an electron is transferred between quinones to yield  $C-P^+ \cdot -Q_A-Q_B^-$  (step 3). This species may also go on to give the final  $C^+ \cdot -P-Q_A-Q_B^- \cdot$  species. The high quantum yield for the final charge separated state in 1 may be attributed in part to the fact that two electron transfer pathways (steps 3 and 4) compete with charge recombination of the initial  $C-P^+ \cdot -Q_A^- \cdot -Q_B$  species, rather than just one, as in triad-type systems.

Figure 1

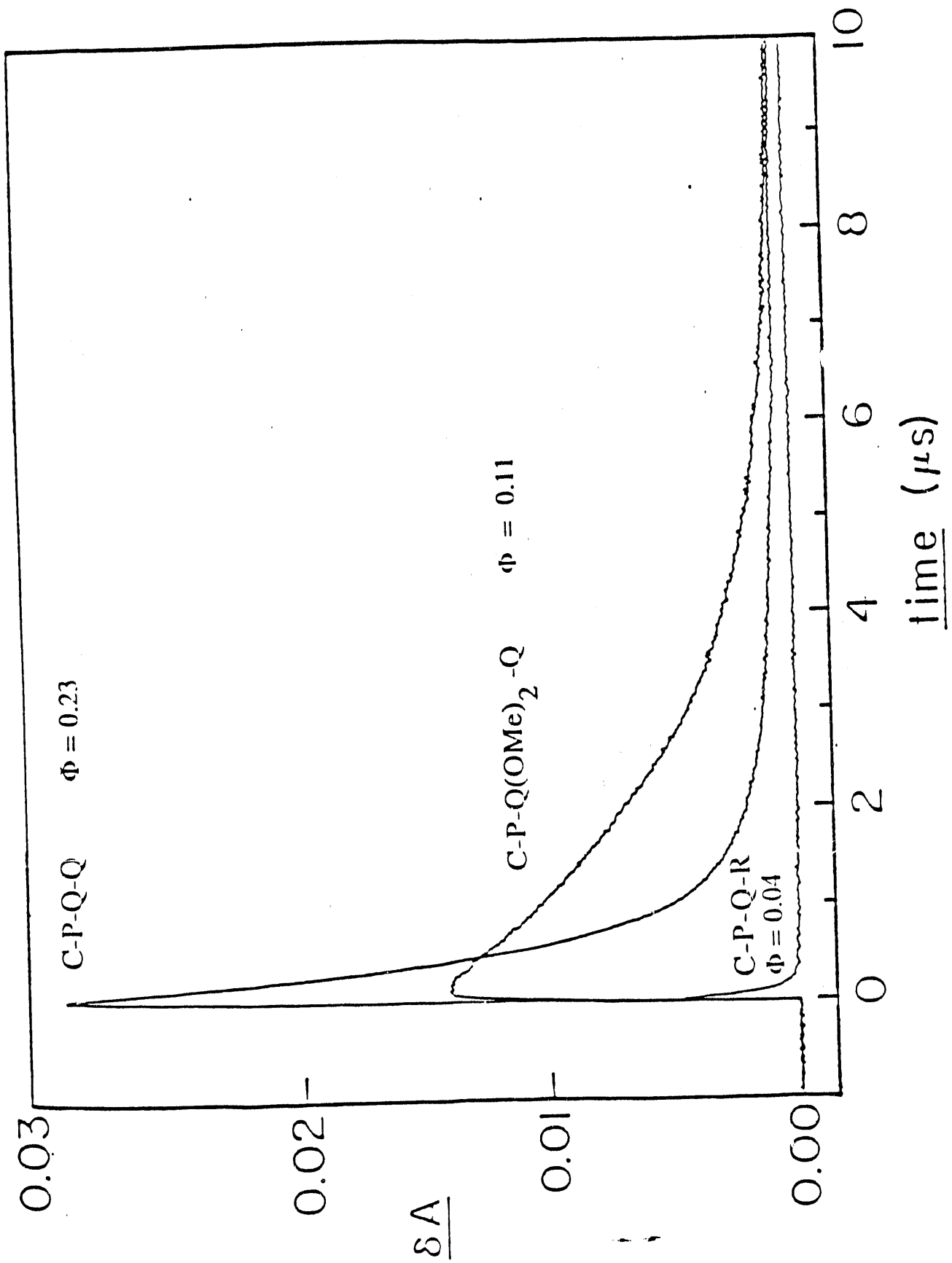
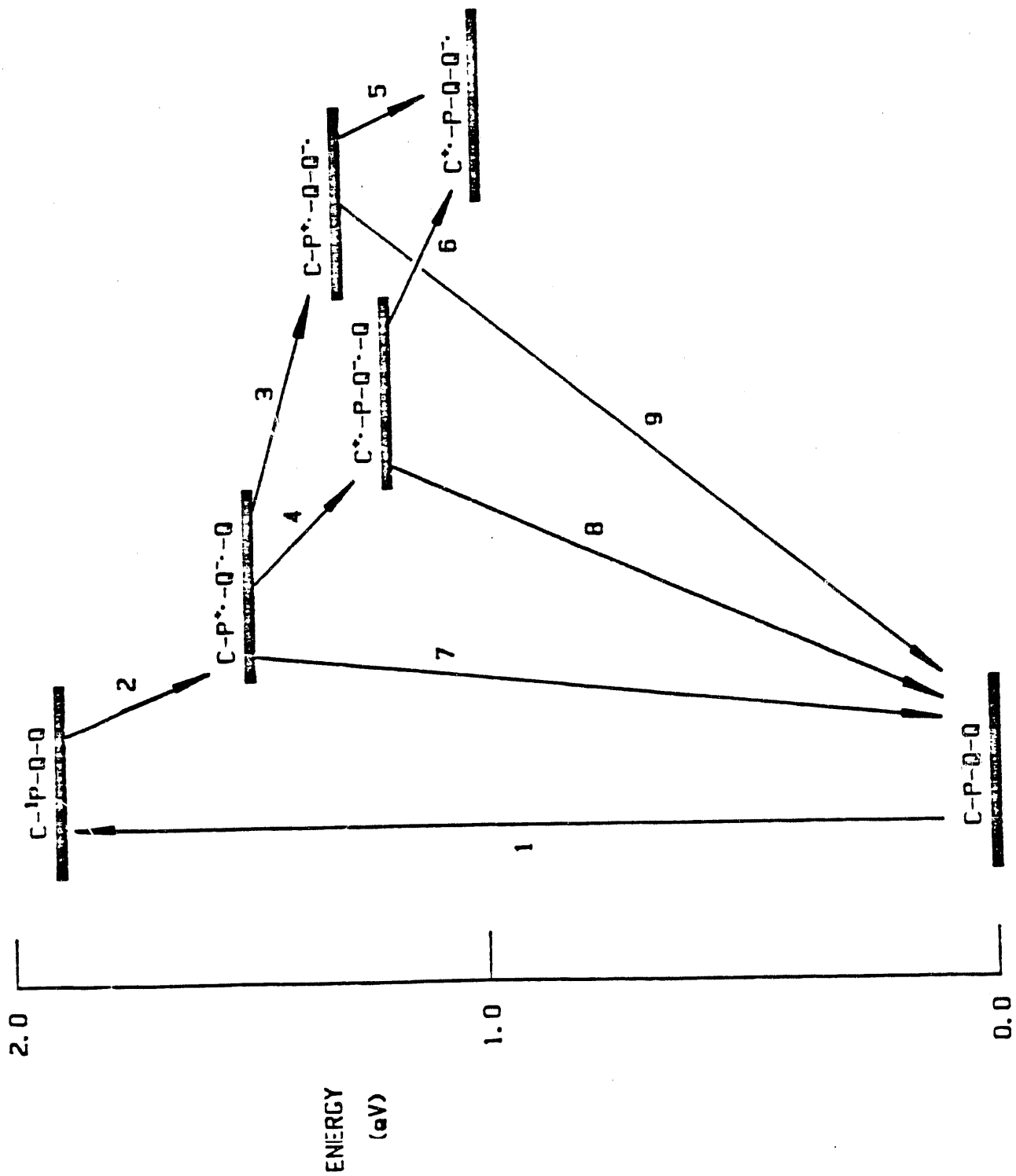


Figure 2



Information concerning the rates of the initial photodriven electron transfers in 1 - 3 may be obtained from picosecond fluorescence decay measurements. Because the single photon counting spectrometer for determination of fluorescence lifetimes is still under construction at ASU, such measurements were performed in collaboration with coworkers at the University of Leuven, Belgium, and the Muséum National d'Histoire Naturelle in Paris, France. The electron transfer rate constant  $k_{et}$  is given by  $(1/\tau_f) - (1/\tau_0)$ , where  $\tau_f$  is the fluorescence lifetime of the tetrad or other molecule in question, and  $\tau_0$  is the lifetime of a model system with similar photophysics, but which lacks the electron transfer step. Measurements on 1, 2, and 3 yielded  $k_{et}$  values of  $\geq 2 \times 10^{10}$ ,  $1.2 \times 10^{10}$ , and  $9.6 \times 10^8 \text{ s}^{-1}$ , respectively. The value for 1 is only a lower limit because it corresponds to a lifetime for the porphyrin first excited singlet state (ca. 50 ps) which is close to the time resolution of the spectrometer used.

The energies of the various charge-separated states relative to the ground state have been estimated on the basis of electrochemical (cyclic voltammetric) studies of model systems. The results are as shown in Figure 2, and have not been corrected for any coulombic stabilization effects. The Figure shows that the intermediate  $C-P^{+\cdot}-Q_A-Q_B^{-\cdot}$  and  $C^{+\cdot}-P-Q_A^{-\cdot}-Q_B$  states are nearly equal in energy, and that the final  $C^{+\cdot}-P-Q_A-Q_B^{-\cdot}$  species preserves about 1 eV of the 1.9 eV inherent in the porphyrin first excited singlet state.

The synergistic effects of multiple electron transfers in 1 may best be illustrated by comparison of the results for 1 with those for related model systems 2 and 3. As shown in Figure 1, triad 2, which lacks benzoquinone  $Q_B$ , also undergoes photodriven charge separation to yield a final charge-separated state  $C^{\bullet+}-P-Q^{\bullet-}$ . However, the quantum yield for this state is only 0.04, and the lifetime is only about 70 ns. Thus, the addition of  $Q_B$  in 1 greatly increases both the quantum yield and the lifetime of charge separation. The fluorescence lifetime results demonstrate that the quantum yield for the initial charge separation step (step 2) in each of these molecules is very high ( $>0.98$ ). However, in 2, only one subsequent electron transfer (analogous to step 4) competes with charge recombination (step 7) to yield  $C^{\bullet+}-P-Q^{\bullet-}$ . This competition is not very effective, and thus limits the quantum yield. In 1, there are two electron transfers competing with the back reaction, and both of these pathways ultimately lead to product. The quantum yield is therefore increased. The longer lifetime noted for 1 relative to 2 may be ascribed to the enhanced donor-acceptor separation in 1. Direct electron transfer from  $Q_B$  to C should be slow because of the large distance involved, and a multistep charge recombination would require slow endergonic electron transfer to yield either  $C-P^{\bullet+}-Q_A-Q_B^{\bullet-}$  or  $C^{\bullet+}-P-Q_A^{\bullet-}-Q_B$  followed by direct recombination of these states or a second endergonic electron transfer to yield  $C-P^{\bullet+}-Q_A^{\bullet-}-Q_B$ .

Tetrad 3 also yields a charge-separated state upon porphyrin excitation. The  $C^{\bullet+}-P-Q_A(OMe)_2-Q_B^{\bullet-}$  species is formed with a

quantum yield of 0.11 and lives for 1.9  $\mu$ s in methylene chloride (Figure 1). The quantum yield for 3 is reduced relative to that for 1 in part because the initial photodriven electron transfer must occur in one long-range step to form  $C-P^{+\cdot}-Q_A(OMe)_2-Q_B^{-\cdot}$  rather than two short range (and therefore faster and more efficient) steps as in 1. The additional thermodynamic driving force in 3 evidently cannot compensate for the increased separation. This is clear from the fluorescence lifetime results, which show that photodriven electron transfer in 3 is more than 20 times slower than in 1. The overall quantum yield in 3 is further limited by the fact that the step analogous to step 5 does not compete especially well with charge recombination of  $C-P^{+\cdot}-Q_A(OMe)_2-Q_B^{-\cdot}$ .

It is surprising that the rate of photodriven electron transfer in 3 is as great as it is. Simple electron transfer theories predict an exponential dependence of electron transfer rates on donor-acceptor separation. Calculations based on the donor-acceptor distance in 3 and the quantitative dependence of electron transfer on distance found for other porphyrin-quinone systems<sup>1-4</sup> suggest that the quantum yield of formation of  $C-P^{+\cdot}-Q_A(OMe)_2-Q_B^{-\cdot}$  should be near zero. It seems likely, then, that the dimethoxynaphthalene  $\pi$ -electron system and perhaps the bicyclic bridge are playing some role in the electron transfer process. Recent studies have suggested that both aromatic systems and  $\sigma$ -bonds may facilitate electron transfer under some circumstances.<sup>5-8</sup>



The somewhat longer lifetime for 3 relative to 1 may be related to the fact that 1 may recombine via a pathway involving the reverse of step 6, whereas this mechanism is precluded for 3.

These preliminary findings for 1 - 3 have been reported in a communication to the Journal of the American Chemical Society, and have been presented at a variety of meetings and seminars (see attached list). Graduate Student Larry O. Harding received a travel award from the American Society for Photobiology to allow presentation of the work at the Society's meeting in Colorado Springs in March.

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8. Heitele, H.; Michel-Beyerle, M. E. J. Am. Chem. Soc. 1985, 107, 8286-8288.

### III. Publications and Presentations Resulting From This Work.

1. "Photoinitiated Charge Separation in a Carotenoid-Porphyrin-Diquinone Tetrad: Enhanced Quantum Yields via Multistep Electron Transfers," Devens Gust, Thomas A. Moore, Ana L. Moore, Donna Barrett, Larry O. Harding, Lewis R. Makings, Paul A. Liddell, F. C. De Schryver, M. Van der Auweraer, René V. Bensasson and Michel Rougée, J. Am. Chem. Soc. 1988, 110, 321-323.
2. "Carotenoporphyrin Quinone Triads and Tetrads as Reaction Center Mimics: Strategies for Control of Electron Transfer Rates," Devens Gust and Thomas A. Moore, Japan-US Information Exchange Seminar: Chemical Approach to the Photosynthetic Reaction Center, held in Lake Biwa, Japan, January 10-14, 1988.
3. "Enhanced Quantum Yields in Reaction Center Models via Multistep Electron Transfers," Devens Gust, International Minisymposium on Synthetic Model Approach to Photosynthetic Reaction Center, ISIR, Osaka University, January 16, 1988.
4. "Mimicry of Photosynthetic Charge Separation in a Carotenoid-Porphyrin-Diquinone Molecular Tetrad," Devens Gust, Thomas A. Moore, Ana L. Moore, Donna Barrett, Larry O. Harding, Lewis R. Makings and Paul A. Liddell, 1988 Biophysical Society Meeting, Phoenix, Arizona, Feb. 28-Mar. 3, 1988.
5. "Mimicry of Photosynthetic Charge Separation - Multistep Electron Transfer Reactions in a Carotenoid-Porphyrin-Diquinone Molecular Tetrad," Larry O. Harding, Ana L. Moore, Donna Barrett, Lewis R. Makings, Paul A. Liddell, Devens Gust and Thomas A. Moore, 16th Annual Meeting of the American Society for Photobiology, Colorado Springs, CO, Mar. 13-17, 1988; Photochem. Photobiol. 1988, 47S, 17S.

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