TECHNICAL PROGRESS REPORT

1987-1990

Award Number: DE-FG02-87ER13791

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

Project Directors: J. Devens Gust, Jr. and Thomas A. Moore

Institution: Department of Chemistry, Arizona State University

Date: 14 February 1990

DISCLAIMER

MASTER

Technical Progress Report, 1987-1990

A. Overall Research Goals

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 is leading 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 these 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 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 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). The initial phase of the project involved

the synthesis and photochemical study of molecular tetrads of the form C-P-Q-Q and pentads C-

P-P-Q-Q. This has now been accomplished.

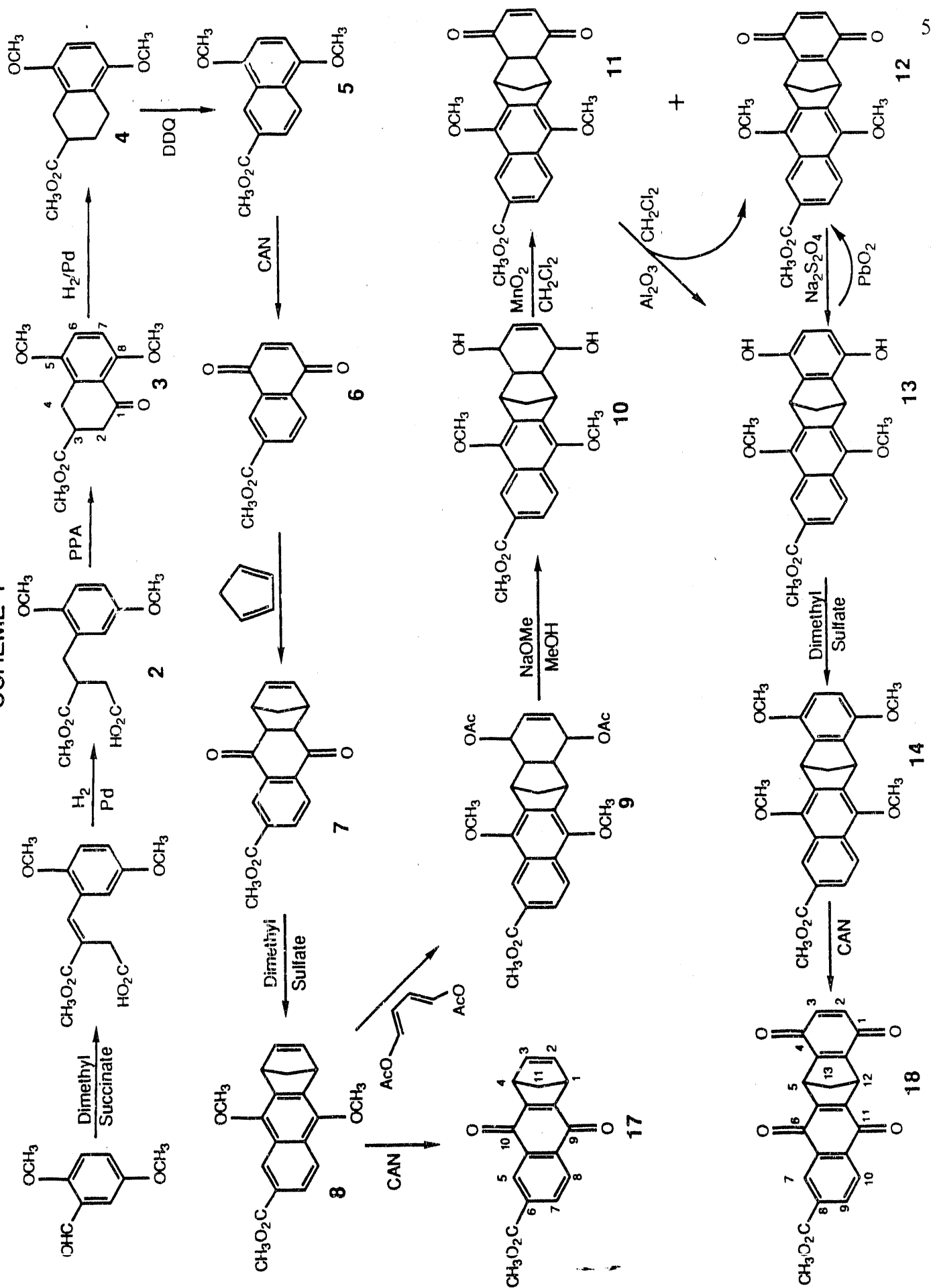## B.   C-P-Q-Q Tetrad and Related Molecules

1.   **Synthesis.** The first goal of the research was to prepare and study molecular

tetrad **1**, which consists of a porphyrin (P) linked to both a carotenoid polyene (C) and a

diquinone moiety (Q_A-Q_B).

1
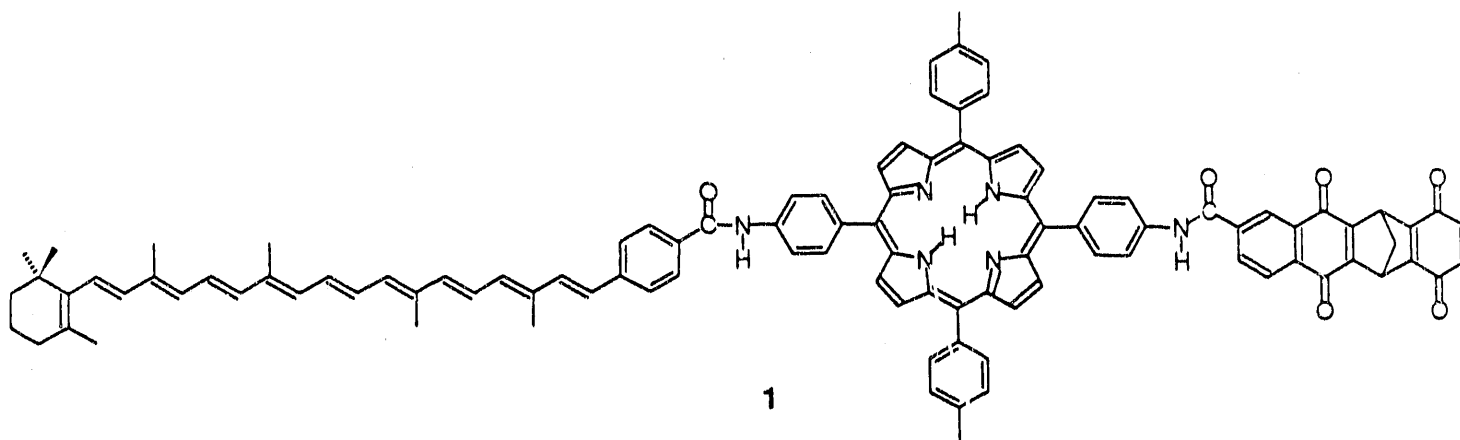
Several closely related synthetic routes for the preparation of **1** were developed. The best of

these is illustrated in Scheme I. To begin, the diquinone ring system was built up by making use

of the fact that quinones are relatively good dienophiles in the Diels-Alder reaction. The

diquinone moiety, protected as the tetramethoxy derivative **14**, was then linked to the porphyrin

via the acid chloride. At this point, the protecting methyl groups were removed and the resulting

hydroquinones oxidized to the diquinone system. Finally, the sensitive carotenoid moiety was

attached via an amide linkage.

Understanding the photophysics of **1** also required the preparation of model compounds **2**

and **3**. The preparation of **2** was achieved as shown in Scheme II. The synthesis begins with **8**,

SCHEME 1

Tetrad 1

SCHEME II

7

2

3
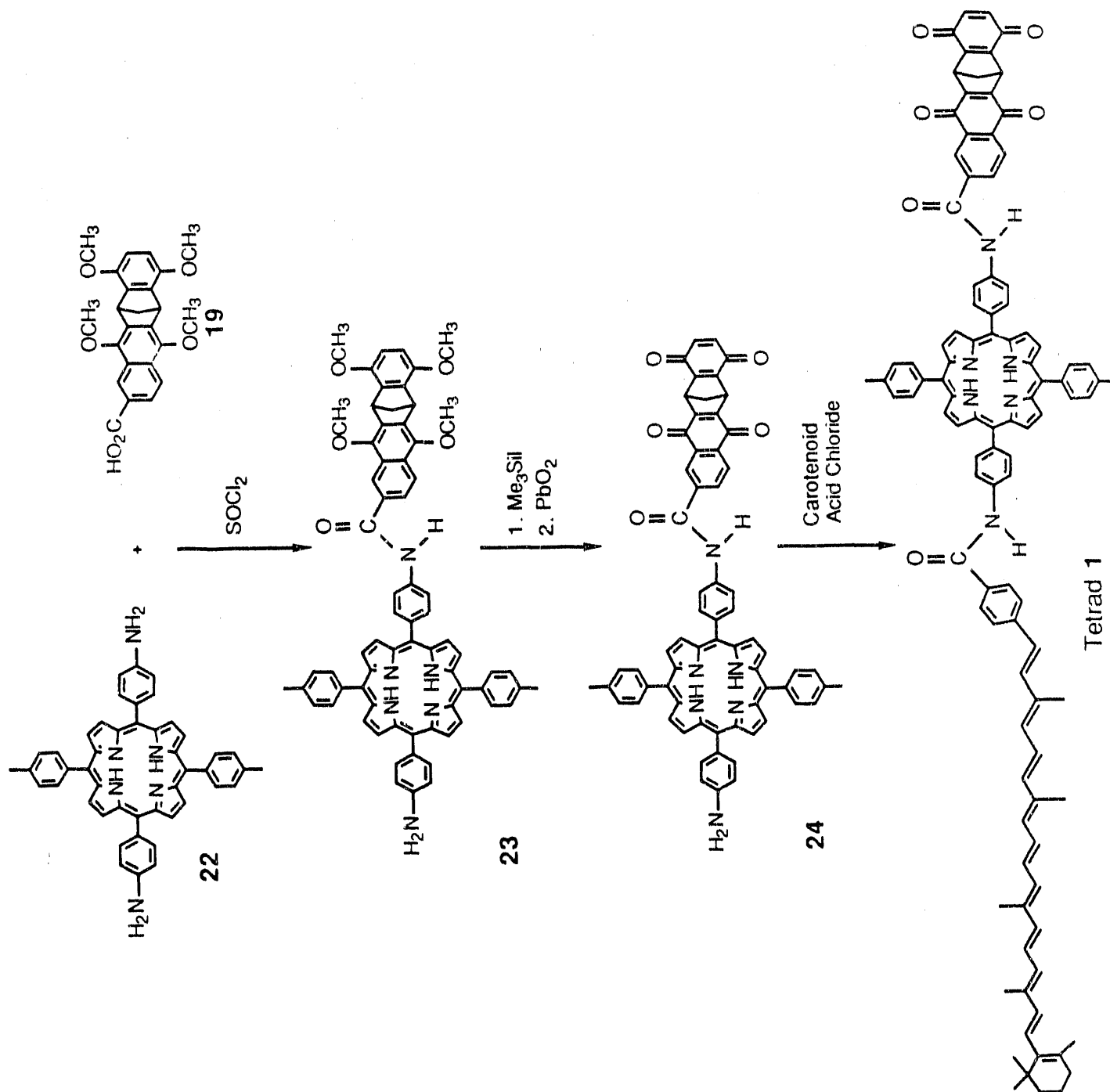
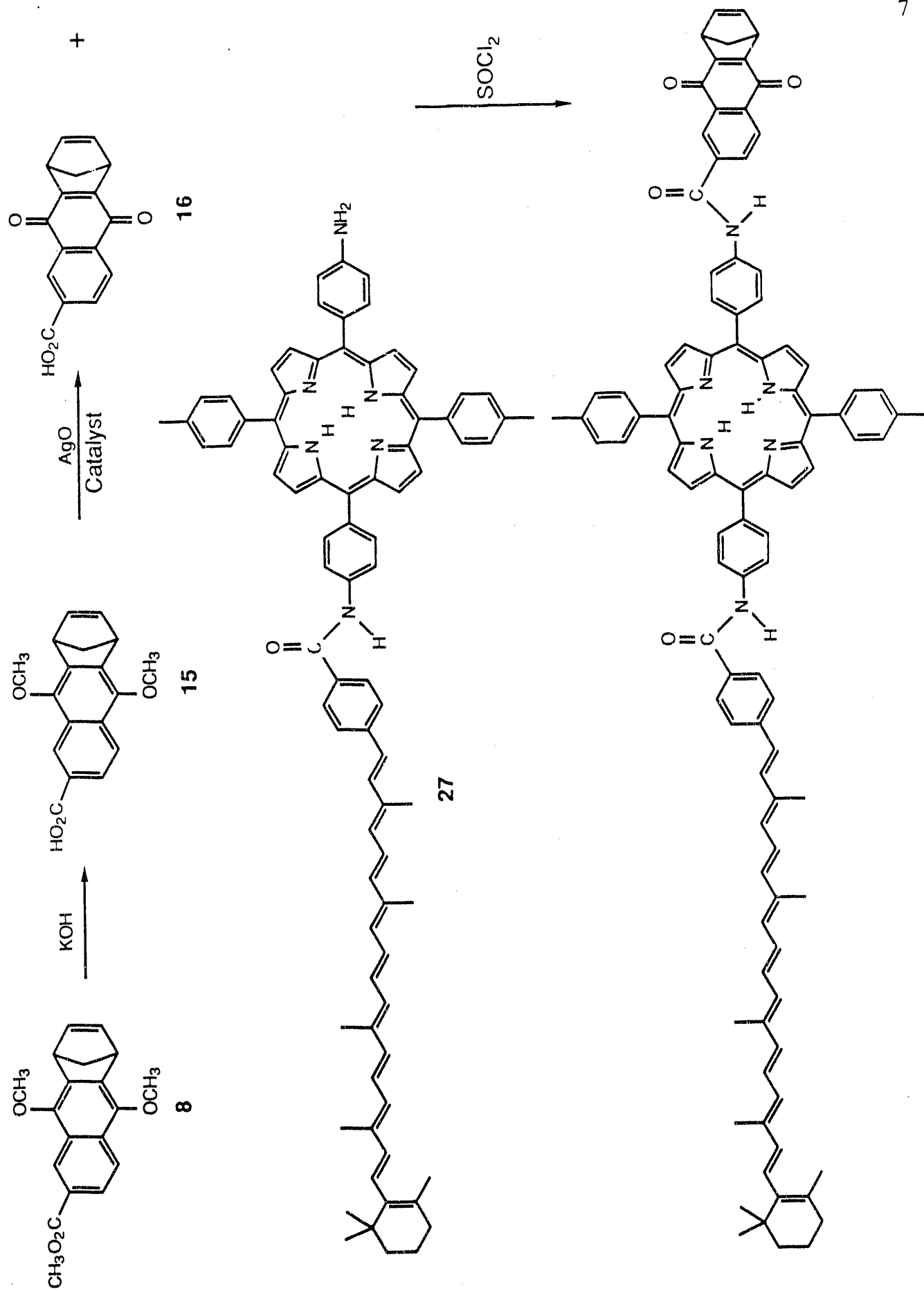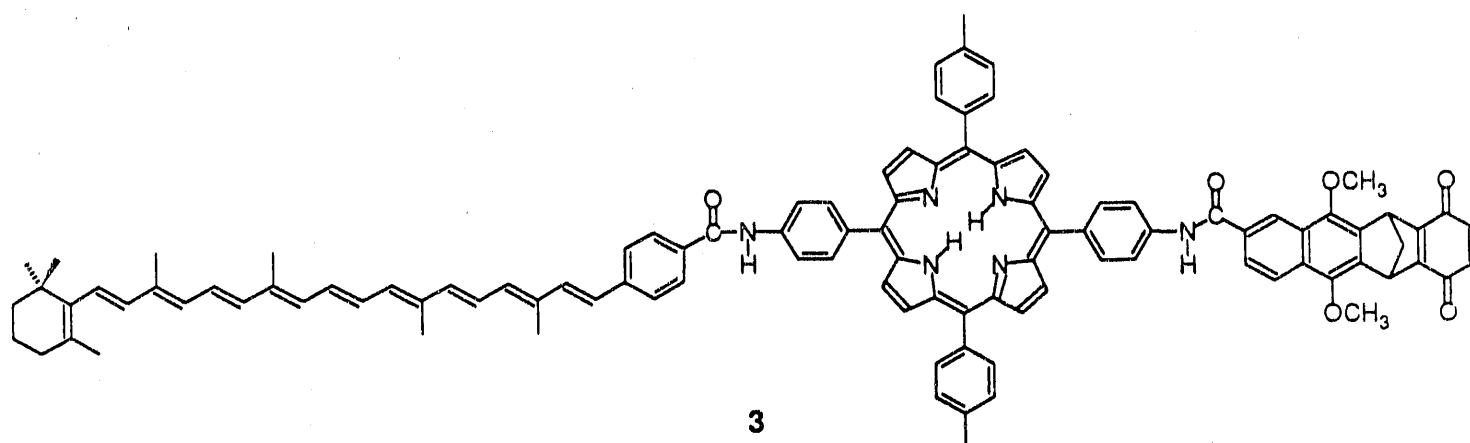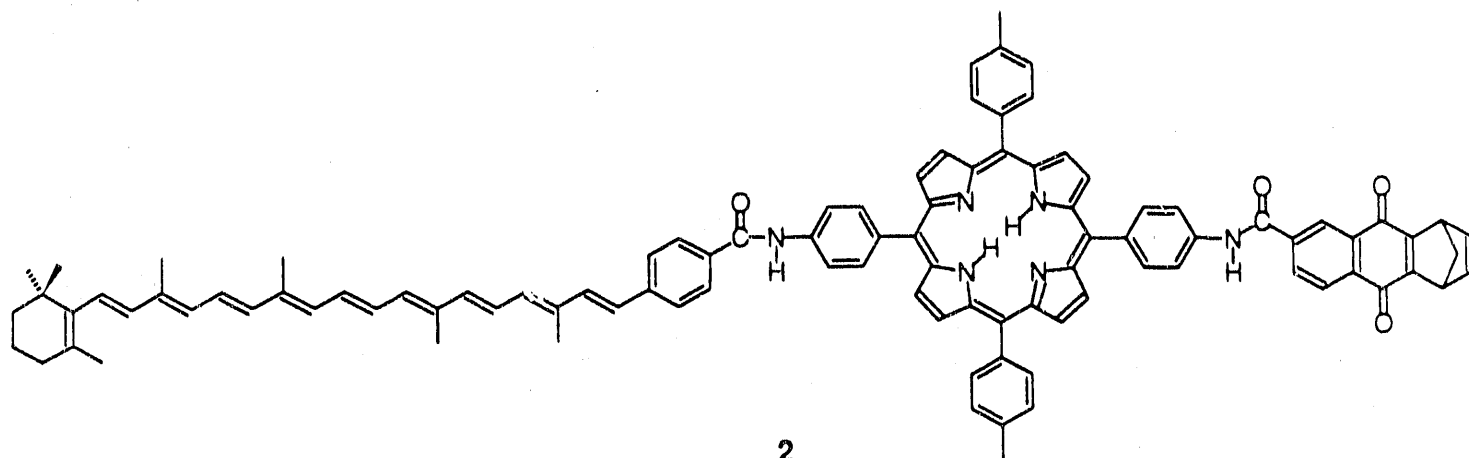which was prepared during the synthesis of the tetrad itself (Scheme I). Triad **3**, on the other hand, required a more circuitous route (Scheme III).

The details of the preparation of molecules **1** - **3** and related model compounds and precursors, including **14**, were published in a special <u>Tetrahedron</u> Symposium in Print issue.[1]

2. **Photochemistry.** Long-lived photoinitiated charge separation in **1** - **3** was investigated using transient absorption spectroscopy on the nanosecond time scale.[2] Excitation of a dichloromethane solution of **1** with a 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

SCHEME III

1. MnO$_2$
2. Al$_2$O$_3$

PbO$_2$

29

30

Figure 1

$c^{\cdot+}-P-Q_A-Q_B^{\cdot-}$

$c^{\cdot+}-P-Q_A(OMe)_2-Q_B^{\cdot-}$

$c^{\cdot+}-P-Q_A^{\cdot-}$

time (μs)
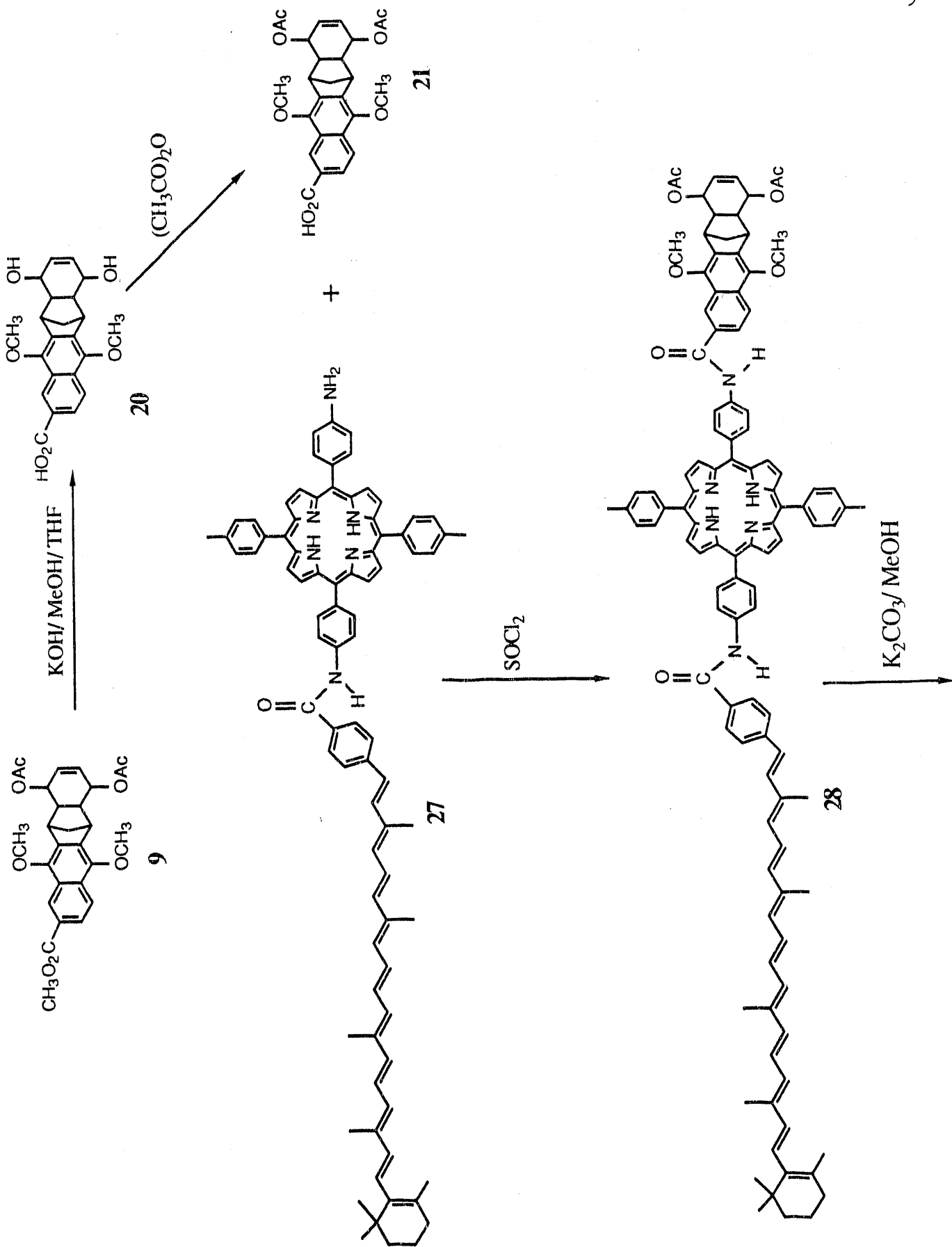
analogy with other systems studied in our laboratories, we may ascribe this transient to the species $C^{\cdot+}$-P-Q_A-$Q_B^{\cdot-}$. The quantum yield of this long-lived charge separated state was found to be 0.23 at ambient temperatures. Cooling the sample to 240 K resulted in an increase in quantum yield to 0.50.

The proposed pathway for the formation of $C^{\cdot+}$-P-Q_A-$Q_B^{\cdot-}$ is shown in Figure 2. The energies of the va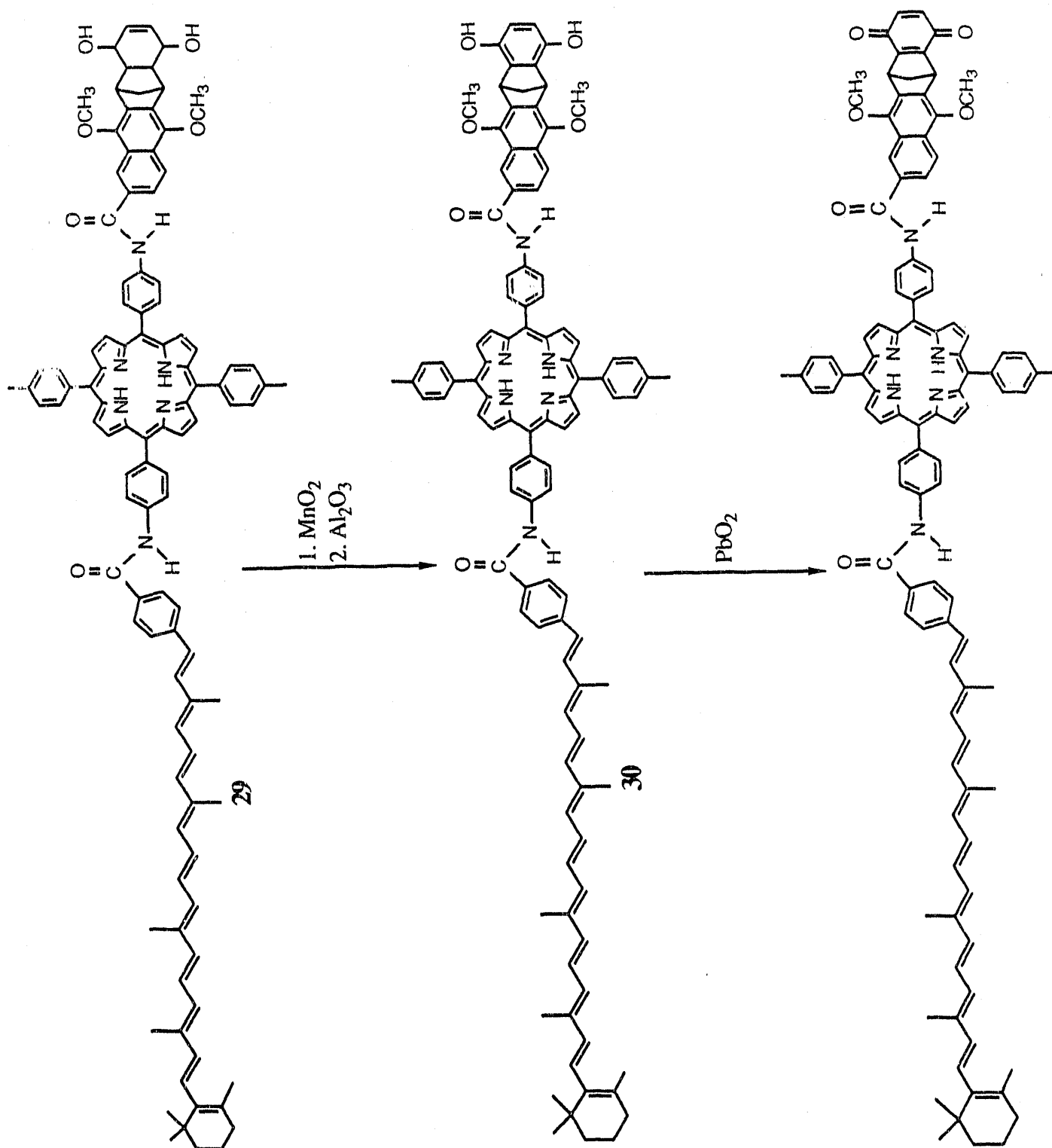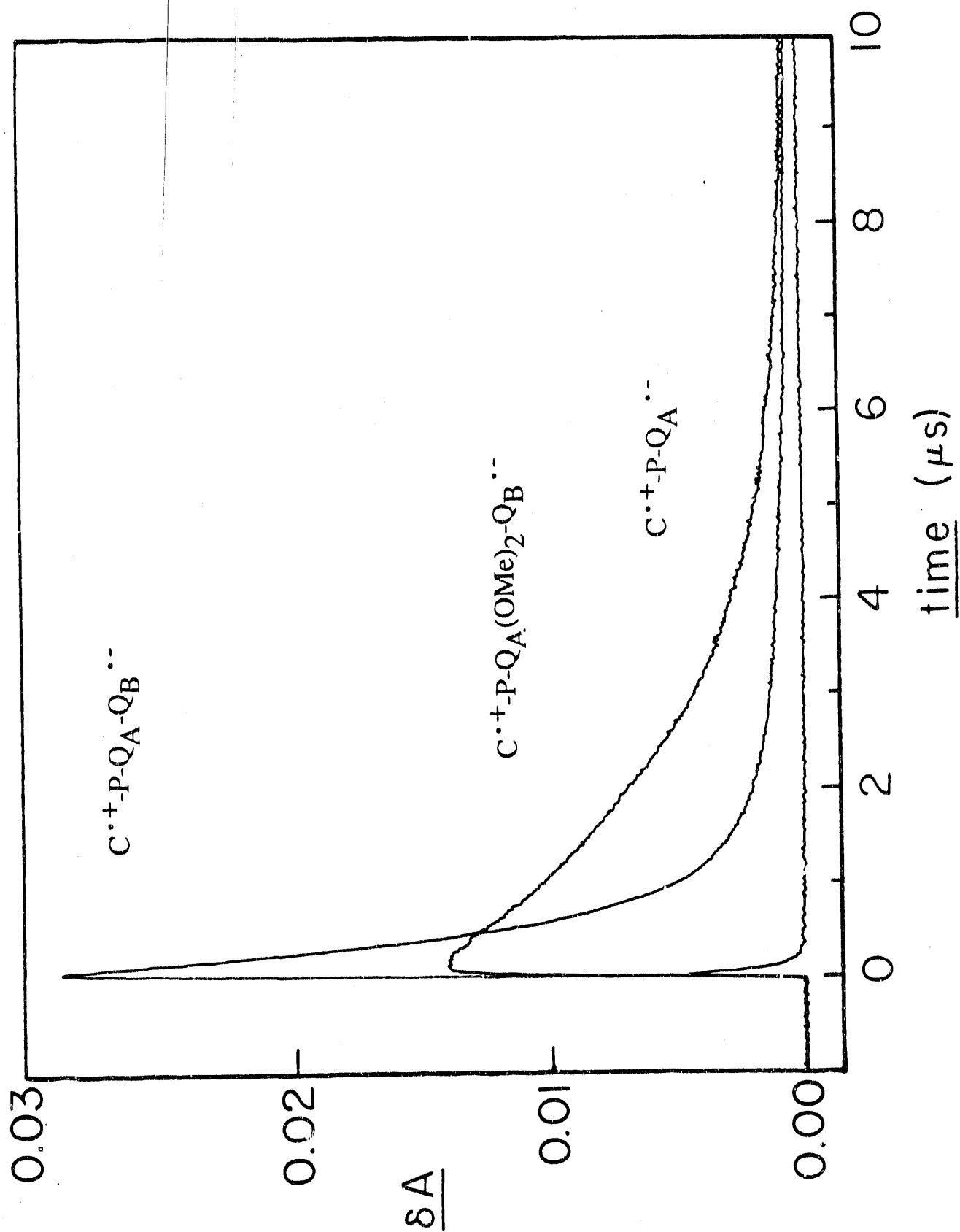rious charge-separated states in the figure are estimated on the basis of cyclic voltammetric studies of model systems,[1] and have not been corrected for any coulombic stabilization effects. Excitation of the porphyrin moiety generates the first excited singlet state, which donates an electron to the 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-$Q_B^{\cdot-}$ (step 3). This species may also go on to give the final $C^{\cdot+}$-P-Q_A-$Q_B^{\cdot-}$ species. The relatively 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 (step 7), rather than just one, as in triad-type systems.

The rate constant for the photodriven electron transfer step 2 may be determined by using the relationship:

$$\underline{k}_2 = (1/\tau) - (1/\tau_0)$$

Figure 2
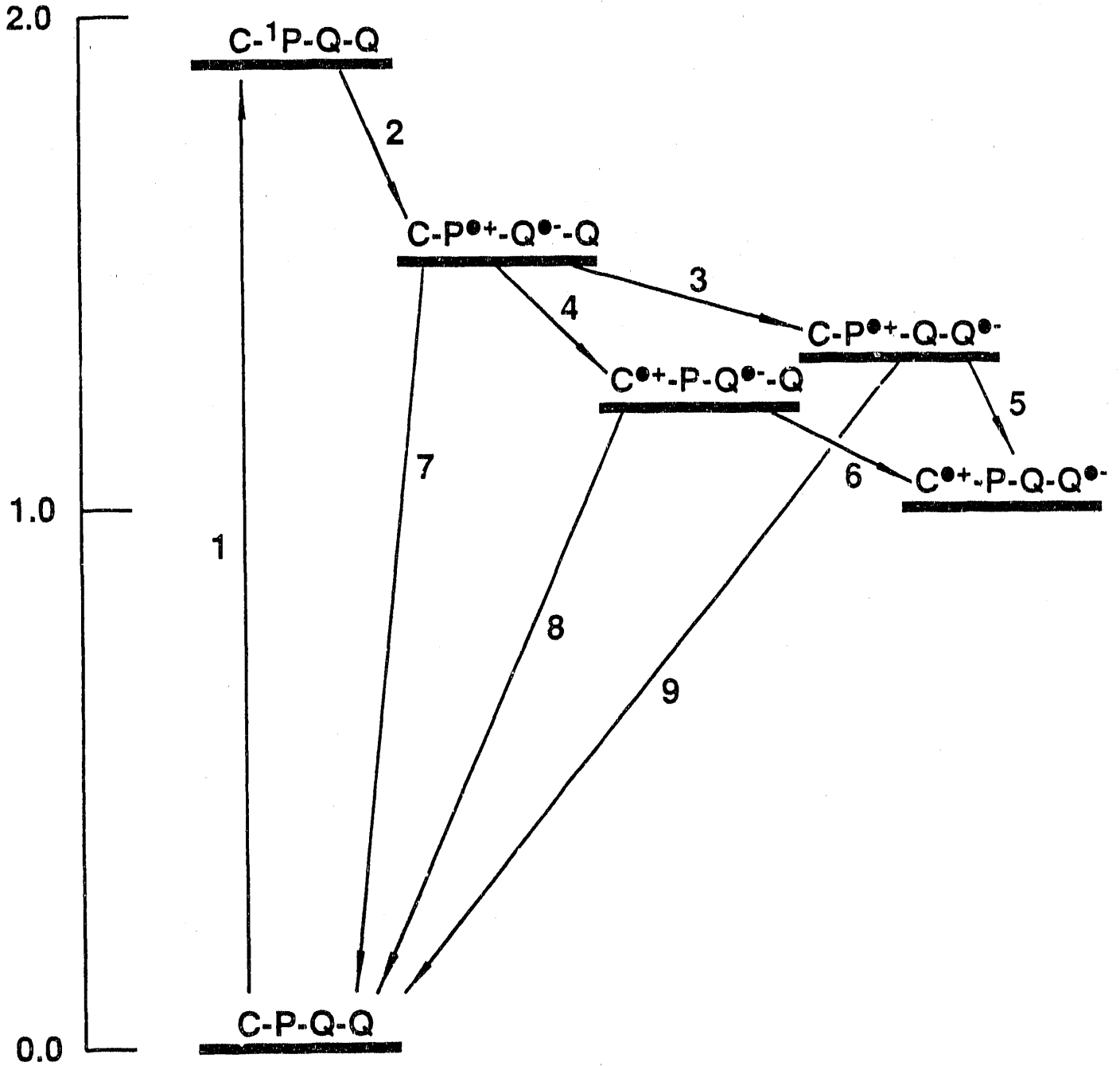
where τ is the measured fluorescence lifetime of **1** and τ_0 is the lifetime of a model compound which has essentially the same photophysics as **1**, but which lacks the electron transfer step. Initial attempts to determine k_2 yielded only a lower limit because the electron transfer was too fast to measure using the equipment which was available.[2] The construction of a picosecond time correlated single photon counting fluorescence spectrometer has now been completed with support from the DOE University Instrumentation Program. This state-of-the-art instrument uses an ultrafast Hamamatsu R2809U-01 microchannel-plate photomultiplier tube as the detector, and has an overall instrument response function of about 35 ps. Thus, fluorescence decays of less than 10 ps may be reliably deconvoluted from the response function.

Using this instrumentation, we measured the fluorescence decay for a solution of tetrad **1** in dichloromethane. The results are shown in Figure 3, which indicates that the significant component of the decay (>99%) was exponential with a lifetime of 15 ps. Suitable model systems lacking electron transfer to the quinone have lifetimes of 3.4 ns. Therefore, a value of 6.6×10^{10} s^{-1} may be calculated for k_2 using the above equation.

The quantum yield of the initial $C\text{-}P^{\cdot+}\text{-}Q_A^{\cdot-}\text{-}Q_B$ charge-separated state (Φ_2) may be calculated from:

$$\Phi_2 = k_2 \times \tau$$

Given that τ equals 15 ps for **1**, Φ_2 is 0.99. Thus, the photoinitiated electron transfer step is extremely efficient.

It will be noted from Figure 2 that the final $C^{\cdot+}\text{-}P\text{-}Q_A\text{-}Q_B^{\cdot-}$ state is not only long lived and formed with a reasonable quantum yield, but also preserves a significant fraction of the excitation energy of the porphyrin as chemical potential. The porphyrin first excited singlet state

15

Figure 3

Spectrum no.: 1888   Prompt no.: 1889   Date: 3-FEB-89
Subst.: CPQQ   Shift: -1.777

Excitation: 590.0 nm   Emission: 652.0 nm
X2glob: 1.035   X2: 1.035   Time/channel: 0.0021 ns
T(1): 0.015 T(2): 0.138 T(3): 1.998
A(1): 92.148 A(2): 0.427 A(3): 0.456

lies at 1.9 eV, based on the absorption and emission spectra, and the final charge separated state at about 1 eV.

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 the benzoquinone Q_B, also undergoes photodriven charge separation, and yields a final charge separated state $C^{\cdot+}\text{-}P\text{-}Q_A{}^{\cdot-}$. However, the quantum yield for this state is only 0.04, and the lifetime only about 70 ns. Thus, the addition of Q_B in **1** greatly increases both the quantum yield and the lifetime of charge separation. Fluorescence decay studies demonstrate that the quantum yield for the initial charge separation step in **1** and **2** is essentially unity. However, in **2**, only one subsequent electron transfer (analogous to step 4 in Figure 2) competes with charge recombination (step 7) to yield $C^{\cdot+}\text{-}P\text{-}Q_A{}^{\cdot-}$. 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. One of these steps, 3, is relatively efficient, and 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 (such as was observed in some triad systems[3]) would require slow endergonic electron transfer to yield either $C\text{-}P^{\cdot+}\text{-}Q_A\text{-}Q_B{}^{\cdot-}$ or $C^{\cdot+}\text{-}P\text{-}Q_A{}^{\cdot-}\text{-}Q_B$ followed by direct recombination of these states or a second endergonic electron transfer to yield $C\text{-}P^{\cdot+}\text{-}Q_A{}^{\cdot-}\text{-}Q_B$.

Triad **3** also yields a charge-separated state upon porphyrin excitation. The $C^{\cdot+}\text{-}P\text{-}Q_A(OMe)_2\text{-}Q_B{}^{\cdot-}$ species is formed with a quantum yield of 0.11 and lives for 1.9 μs in

dichloromethane (Figure 1). The quantum yield of the final state in **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$^{\bullet+}$-Q$_A$(OMe)$_2$-Q$_B$$^{\bullet-}$ rather than two short-range (and therefore faster and more efficient) steps as in **1**. The additional thermodynamic driving force in **3** evidently cannot compensate for the increased separation. This is clear from fluorescence lifetime studies, which yield a rate constant for the initial electron transfer of 9.6×10^8 s^{-1}. Thus, electron transfer in **1** is more than 60 times faster than in **3**. The overall quantum yield in **3** is further limited by the fact that the step analogous to step 5 in Figure 2 does not compete very well with charge recombination of C-P$^{\bullet+}$-Q$_A$(OMe)$_2$-Q$_B$$^{\bullet-}$.

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[4-7] suggest that the quantum yield of formation of C-P$^{\bullet+}$-Q$_A$(OMe)$_2$-Q$_B$$^{\bullet-}$ should be near zero. It seems likely, then, that the dimethoxynaphthalene π-electron system and perhaps the bicyclic bridge are playing some role in the electron transfer process.

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 in Figure 2, whereas a similar mechanism is precluded for **3**.

The zinc analog of **1** was also prepared, and its photochemistry investigated. A fluorescence lifetime for the C-^{1}P$_{Zn}$-Q$_A$-Q$_B$ state of 5 ps was determined. This corresponds to an electron transfer rate constant of 2.0×10^{11} s^{-1} as calculated using appropriate model

compounds. The quantum yield of $C\text{-}P_{Zn}{}^{\bullet+}\text{-}Q_A{}^{\bullet-}\text{-}Q_B$ is again essentially quantitative. The

enhanced photoinitiated electron transfer rate constant for the zinc tetrad results from the fact that

zinc substitution in the porphyrin not only raises the energy of the first excited singlet state to

≈ 2.1 eV (vs. 1.9 eV for the free base), but also lowers the energy of $P^{+\bullet}$ by 210 meV relative to

the free base porphyrin. Thus the thermodynamic driving force for the electron transfer is greatly

increased, relative to **1**.

The quantum yield of the final $C^{\bullet+}\text{-}P_{Zn}\text{-}Q_A\text{-}Q_B{}^{\bullet-}$ state is only 70% of that for the free

base analog. This result is also reasonable. Lowering the energy of $P^{+\bullet}$ will lower the

thermodynamic driving force for steps 4 and 5 in Figure 2, and therefore slow down these steps.

The driving force for charge recombination reactions 7 and 9 will also be decreased, but as these

reactions likely fall in the Marcus inverted region, this may well lead to an increase in the rates

of these reactions. The net result of all of these effects can only be an overall decrease in the

quantum yield of the final charge separated state, as is observed. This net negative effect of zinc

substitution on quantum yield in spite of an overall increase in driving force for charge

separation is an excellent example of the subtle interplay of competing and sequential electron

transfer steps which make these complex molecular devices both interesting and challenging to

study.

    3.   **FT-EPR Studies.** It will be seen from the above discussions that in the tetrads,

the main evidence for the formation of the final charge separated states (e.g. $C^{\bullet+}\text{-}P\text{-}Q_A\text{-}Q_B{}^{\bullet-}$)

comes from direct spectroscopic observation of the carotenoid radical cation coupled with

arguments based on the behavior of various model systems. Direct spectroscopic detection of the

quinone radical anion by optical methods is difficult in these complex systems due to its low

extinction coefficient. This problem is not restricted to our tetrads and pentads, but is endemic to all of the porphyrin-quinone electron transfer work in the literature. Recognizing this to be the case, we have undertaken an investigation of photoinduced electron transfer in tetrad 1 using the Fourier transform electron paramagnetic resonance (FT-EPR) technique. This work has been carried out collaboratively with Dr. Haim Levanon of the Hebrew University of Jerusalem, Dr. James Norris and Dr. Michael Bowman of Argonne National Laboratory, and coworkers. These scientists are recognized experts in the application of this and other magnetic resonance techniques to the study of photosynthetic electron transfer.

A major advantage of the FT-EPR technique is that when combined with pulsed laser excitation, it allows complete EPR spectral information to be determined for relatively short lived species such as the charge separated states of the tetrad. For example, the spectrum resulting from Fourier transformation of the free induction decay obtained following a microwave pulse 44 ns after excitation of the porphyrin with a 591 nm laser pulse is shown in Figure 4a. Analysis of the spectrum yielded the stick spectrum shown in Figure 4b, which is very similar to that of the radical anion of a model benzoquinone bearing the norbornene moiety (Figure 4c). Thus, the presence of the quinone radical anion is verified.

Although observation of the carotenoid radical cation was precluded in this experiment because of its large linewidth, a two-pulse, electron spin echo experiment allowed simultaneous detection of both the carotenoid radical cation and the benzoquinone radical anion. Additional experiments demonstrated that the electron spin polarization detected was due to a small degree of electron spin-spin interaction between the quinone radical anion and the carotenoid radical cation, and that the electron transfer reaction must have proceeded from a singlet excited state
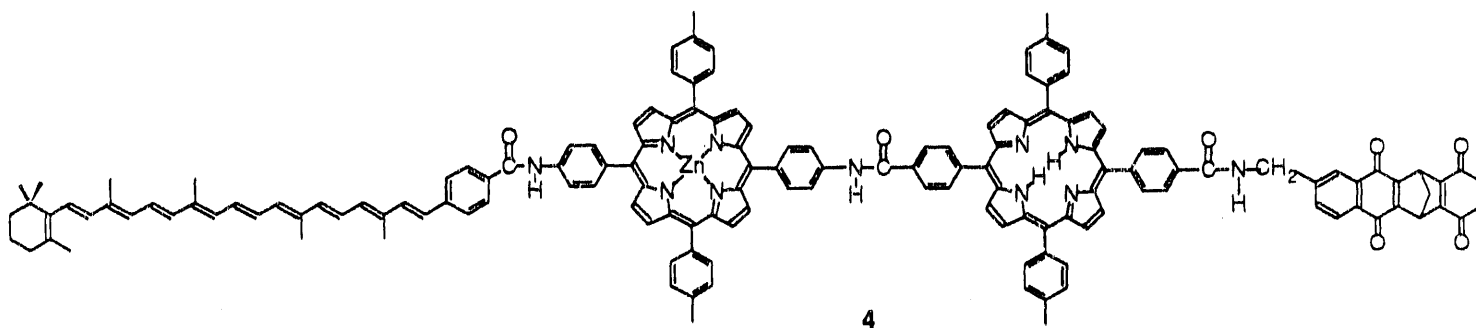
Figure 4

a) FT-EPR spectra of the tetrad (T=240 K) in dichloromethane. Microwave pulse is 44 ns after the laser pulse (591 nm, ~1 mJ/pulse). Positive going signals correspond to absorption and negative to emission.

b) Frequencies of the 12 hyperfine lines as determined from LP analysis.

c) Frequencies of the 12 hyperfine lines from the model quinone

precursor. This work has now been submitted for publication in the Journal of the American

Chemical Society.[8]

These very interesting results demonstrate that the FT-EPR technique is ideally suited for

the study of long-lived charge separated states such as those found for the tetrads and pentads (to

be discussed below). The method not only complements optical spectroscopic investigations of

the course of the electron transfer reactions, but can also provide valuable information

concerning the degree of electronic interaction of the two radical ions.
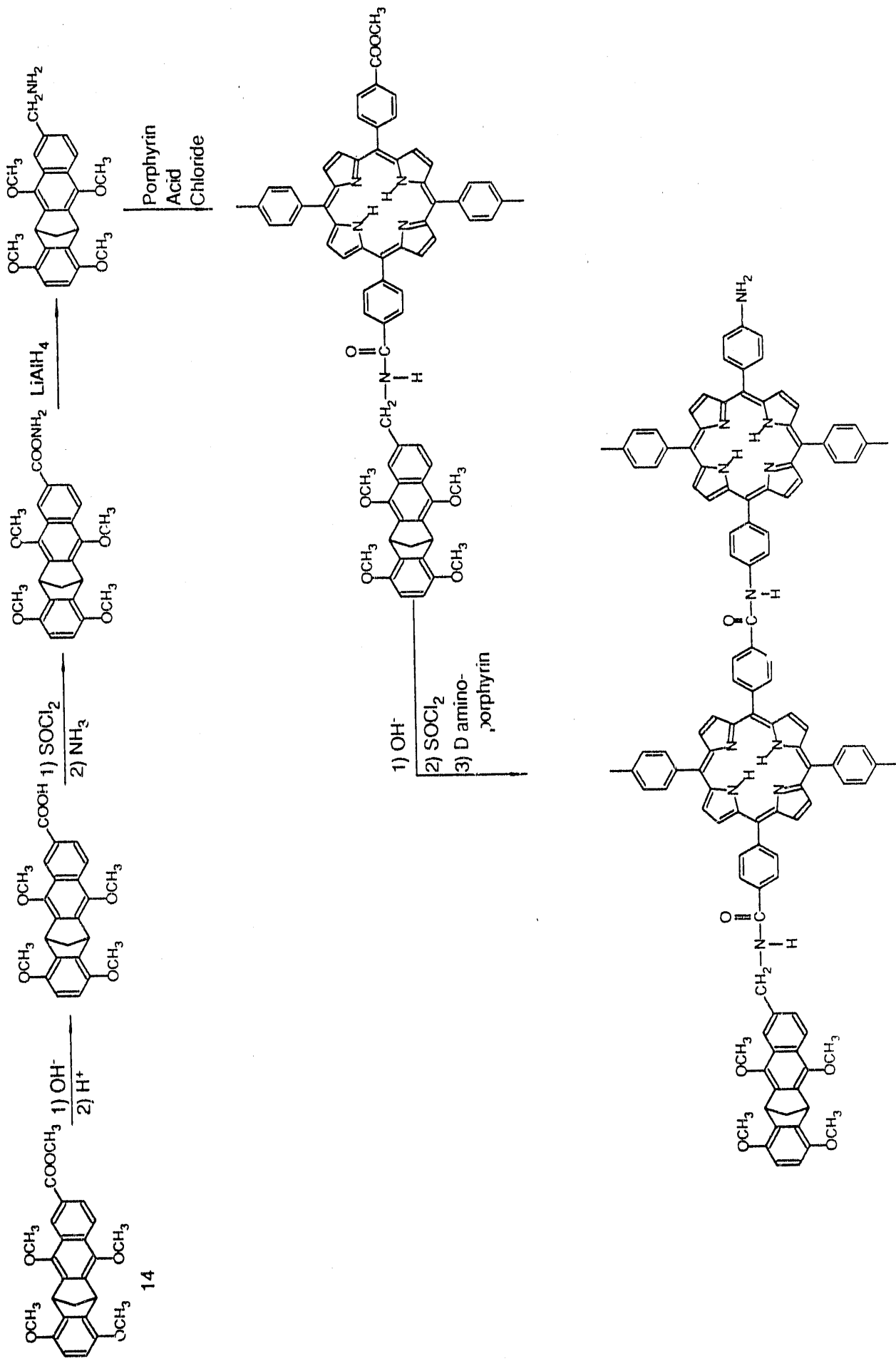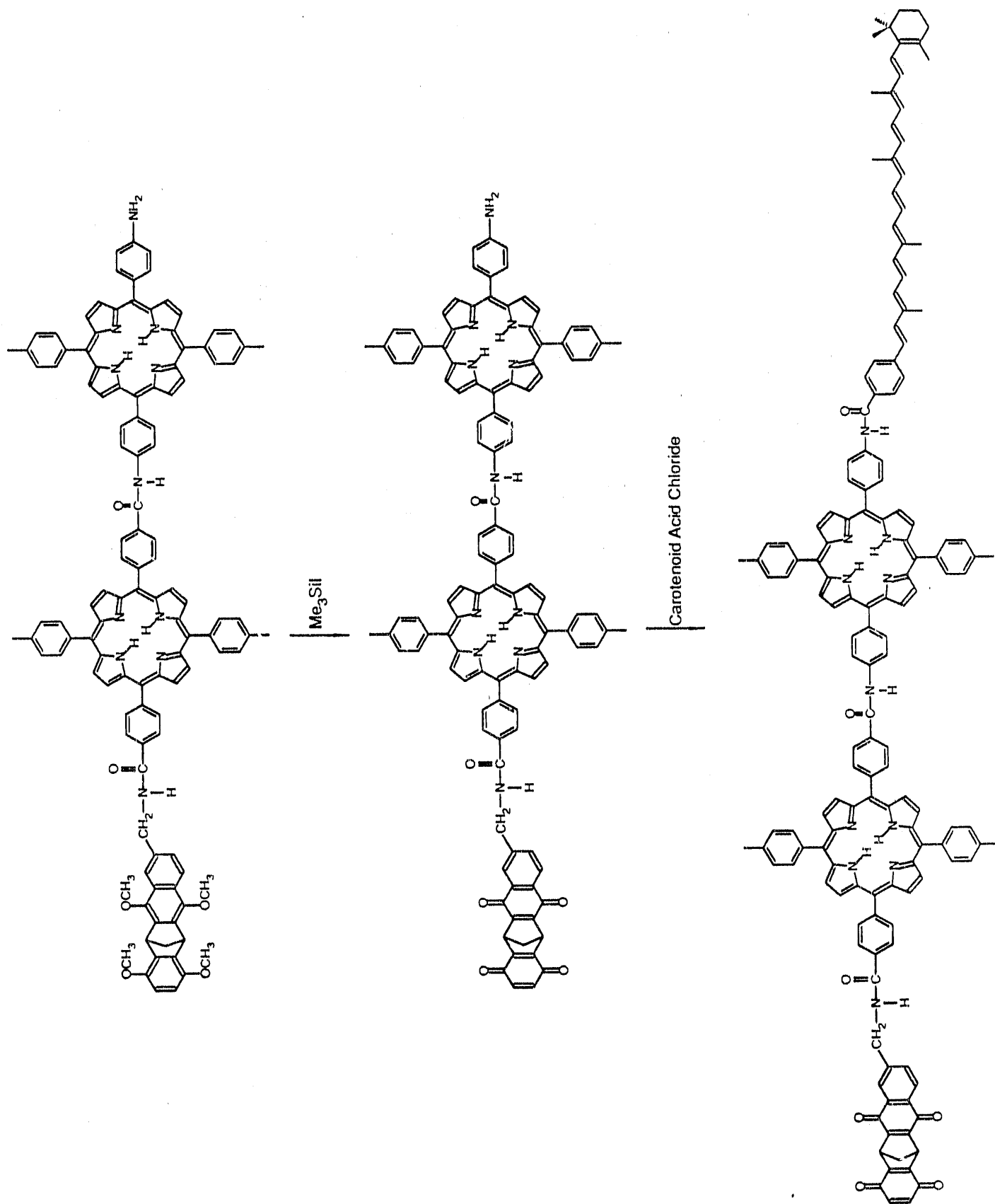
C.   C-P-P-Q-Q Pentad

The successful synthesis and photochemical study of the tetrad and related systems

discussed above led to the design and preparation of $C-P_{Zn}-P-Q_A-Q_B$ pentad 4 and its free base

analog 5. The synthesis of the new diquinone moiety began with the protected form of the

4

diquinone 14, whose preparation was shown in Scheme I. As shown in Scheme IV, the methyl

ester group of 14 was elaborated into a benzyl amine derivative, and this was linked to a

porphyrin via an amide bond. Attachment of a second free base porphyrin followed by

deprotection of the diquinone and linkage of the carotenoid polyene gave 5. Alternatively,

linkage of a zinc carotenoporphyrin to the aminoporphyrin bearing the protected diquinone

yielded 4.

Scheme IV

Me$_3$Sil

Carotenoid Acid Chloride

The absorption spectrum of **4** in chloroform is nearly identical to the sum of the spectra of unlinked model chromophores. The fluorescence emission spectrum in the same solvent has maxima at 655 and 718 nm. These bands are typical of emission from free base porphyrins, but the emission is quenched, relative to model carotenoporphyrin compounds which lack the diquinone moiety. In addition, a very weak band, characteristic of emission from a zinc porphyrin, appears at 611 nm. The quenching of the steady-state fluorescence suggests that in common with those of **1 - 3** and other porphyrin-quinone systems, the free base porphyrin singlet state is being quenched by electron transfer to the quinone to generate $C\text{-}P_{Zn}\text{-}P^{\bullet\,+}\text{-}Q_A{}^{\bullet\,-}\text{-}Q_B$. In addition, the lack of strong emission from the zinc porphyrin moiety of **4** is consistent with rapid singlet energy transfer to the free base porphyrin. Time resolved fluorescence studies were undertaken in order to investigate these possibilities.

Fluorescence decay curves were obtained by the single photon counting technique using the instrument mentioned above. The results for **4** in chloroform are shown in Figure 5. The sample was excited at 590 nm, and emission decay curves were taken at 14 wavelengths. All 14 decays were fit simultaneously to four exponentials ($\chi^2 = 1.12$) using a global analysis technique, and the decay components in Figure 5 have been scaled according to their relative amplitudes. The two major components of the decay had lifetimes of 0.039 and 1.2 ns. (The two minor components represent impurities, or conceivably a minor conformer in the case of the 4.6 ns decay.)

In order to discuss the origins of these decay components, it is useful to refer to Figure 6, which depicts the relevant high-energy states of **4** and some of the pathways available for their interconversion. The excited singlet state energies were calculated from the absorption and
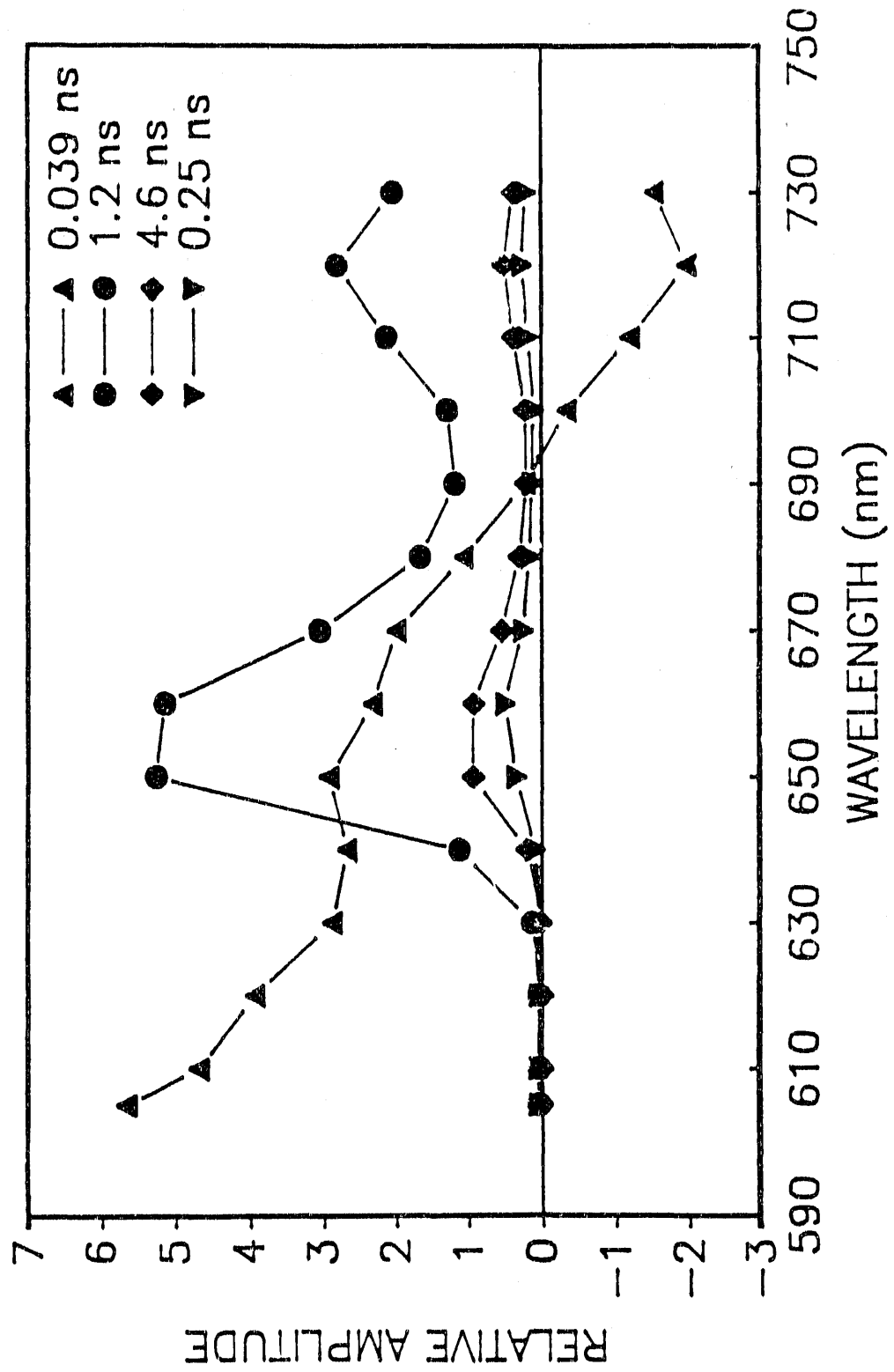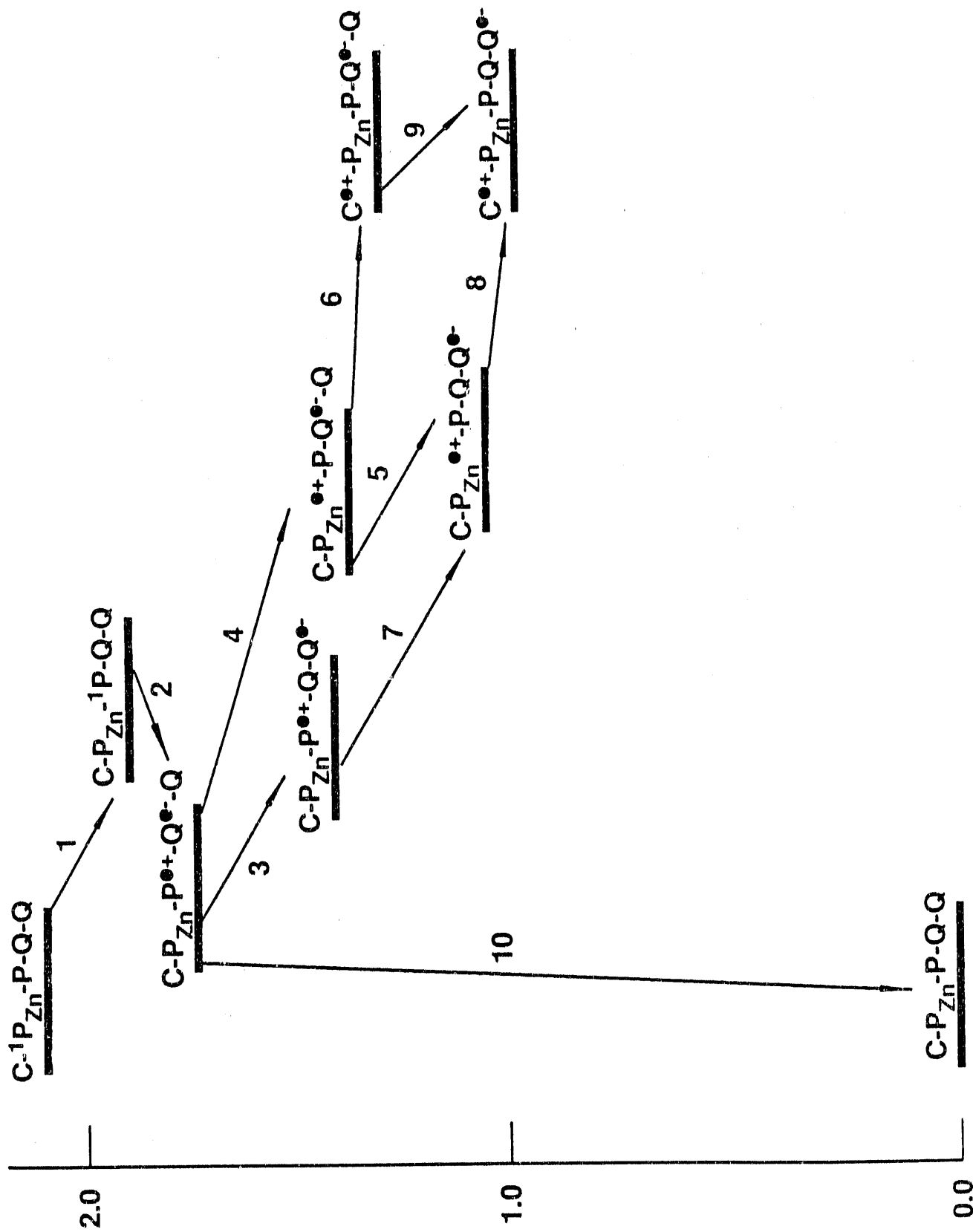
Figure 5

Figure 6

fluorescence emission spectra. The energies of the various charge separated states were estimated from cyclic voltammetric studies of models for the components of the pentad (carotenoid, porphyrins, diquinone).

Returning to the time resolved fluorescence spectrum, we see that the 39 ps component comprises essentially the sole emission in the 610 nm region where only the zinc porphyrin fluoresces, and manifests itself as a growth in the 710 nm region, where most of the emission comes from the free base porphyrin. The decay in the 610 nm region reflects the decay of the zinc porphyrin singlet state, and the corresponding rise in emission intensity in the red signifies the population of the free base porphyrin singlet state by energy transfer from P_{Zn} (step 1 in Figure 6). A model carotenoid-bearing zinc porphyrin, in which there is no possibility of such energy transfer, has a singlet lifetime of 370 ps. Thus, if it is assumed that the addition of the free base porphyrin serves only to introduce the possibility of energy transfer, the singlet energy transfer rate constant $\underline{k}_1$ may be calculated as follows:

$$\underline{k}_1 = (1/0.039 \times 10^{-9}) - (1/0.37 \times 10^{-9}) = 2.3 \times 10^{10} \text{ s}^{-1}$$

The quantum yield for energy transfer, given by $\underline{k}_1/(1/0.039 \times 10^{-9})$, is 0.90.

The 1.2 ns component has a spectrum consistent with emission from the free base porphyrin. Singlet states of similar porphyrins, with or without an attached zinc porphyrin moiety but lacking attached quinones, have lifetimes of 7.8 ns. The addition of the quinone opens up a new pathway for decay of the porphyrin singlet state: electron transfer to the quinone to generate $C-P_{Zn}-P^{\cdot+}-Q_A^{\cdot-}-Q_B$ (step 2 in Figure 6). As in the tetrad species discussed above, the rate constant for this photoinitiated electron transfer may therefore be estimated as:

$$\underline{k}_2 = (1/\tau) - (1/\tau_o)$$

where τ is the fluorescence lifetime of the free base porphyrin singlet state and τ_0 is the lifetime of a model compound with photophysics similar to **4**, but which lacks the electron transfer step (i.e., 7.8 ns). Thus, $\underline{k_2}$ equals 7.1×10^8 s^{-1}. The corresponding quantum yield is $\underline{k_2}/(1/\tau)$, or 0.85.

Given the formation of C-P_{Zn}-P$^{\bullet+}$-$Q_A$$^{\bullet-}$-$Q_B$, studies of simpler but related molecular devices such as **1 - 3** suggest that two secondary electron transfer reactions, steps 3 and 4 in Figure 6, should compete with charge recombination to the ground state (step 10). Step 3 involves electron transfer from the naphthoquinone moiety to the benzoquinone (a better electron acceptor) to yield C-P_{Zn}-P$^{\bullet+}$-Q_A-$Q_B$$^{\bullet-}$. Two subsequent electron transfers (steps 7 and 8) lead to a final charge-separated state C$^{\bullet+}$-P_{Zn}-P-Q_A-$Q_B$$^{\bullet-}$. Alternatively, step 4, which involves electron transfer from the zinc porphyrin to the free base radical cation, generates C-$P_{Zn}$$^{\bullet+}$-P-$Q_A$$^{\bullet-}$-$Q_B$, which can also decay to C$^{\bullet+}$-P_{Zn}-P-Q_A-$Q_B$$^{\bullet-}$ by two different pathways. Thus, the pentad has been constructed so that all of the likely electron transfer pathways converge to the same final C$^{\bullet+}$-P_{Zn}-P-Q_A-$Q_B$$^{\bullet-}$ state, in which the electron and the hole are located at opposite ends of the molecule.

Transient absorption studies on the ns time scale reveal that this state is indeed produced. Excitation of the free base porphyrin moiety of **4** in chloroform solution at 650 nm resulted in the observation of a long-lived transient (Figure 7) which was identified by its spectrum (λ_{max} = 970 nm) as the carotenoid radical cation.[9] This transient represents C$^{\bullet+}$-P_{Zn}-P-Q_A-$Q_B$$^{\bullet-}$. The decay was fit as a single exponential to yield a lifetime of 55 μs. The quantum yield of the charge separated state, estimated by the comparative method,[10] was ~0.83. Thus, the yield of the final state from C-P_{Zn}-P$^{\bullet+}$-$Q_A$$^{\bullet-}$-$Q_B$ is essentially quantitative. Determination of the

Figure 7
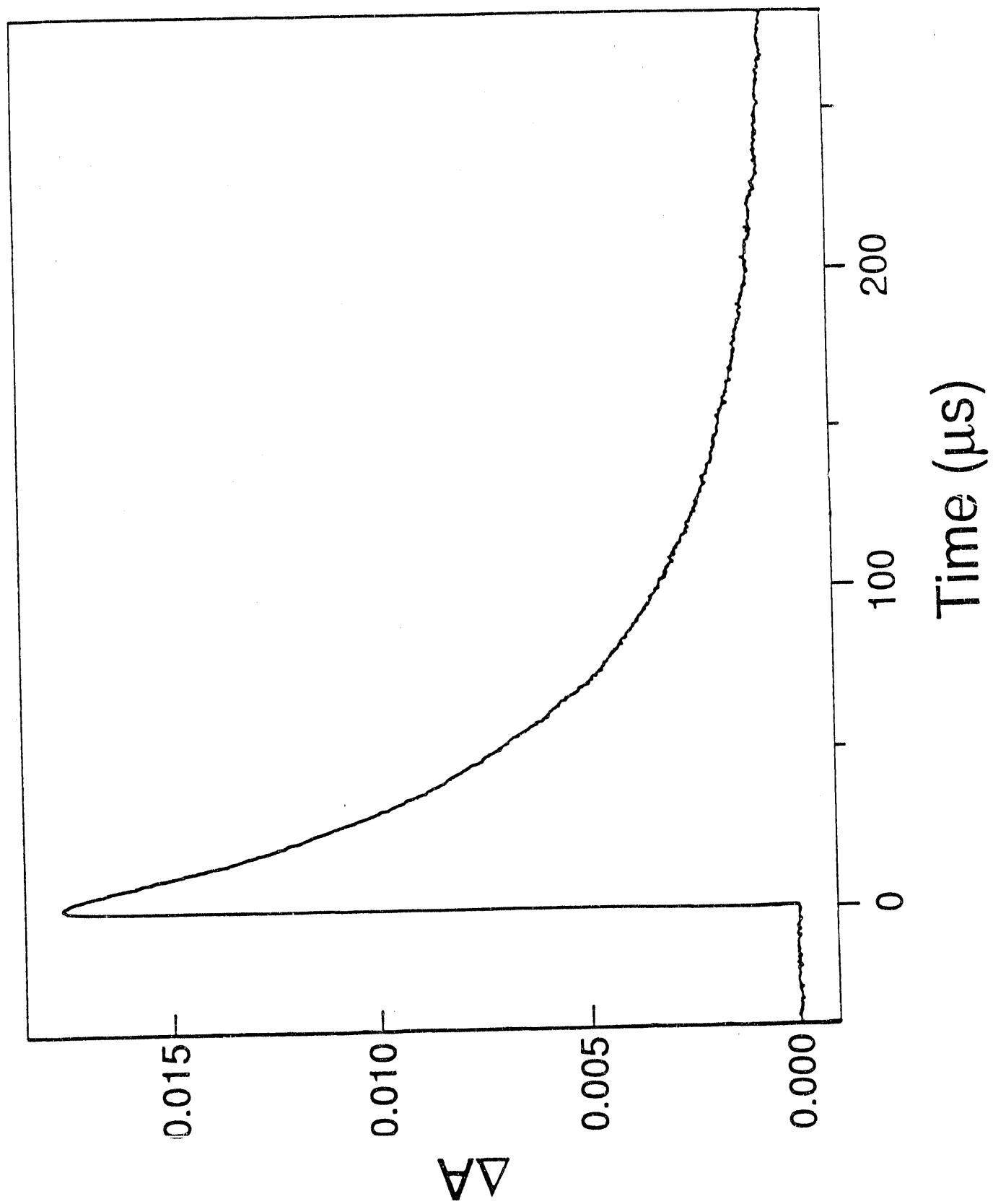
relative contributions of the various electron transfer pathways in Figure 6 to the total yield must await transient absorption studies on the ps time scale. However, comparison of the results for 4 with those for our earlier model systems suggests that it is the thermodynamically favorable interporphyrin electron transfer step 4 which is mainly responsible for the enhanced quantum yield of charge separation for 4. This pathway, which competes well with the initial charge recombination, was not available in the previous systems.

Pentad 4 shows similar behavior in dichloromethane solution. The rate constant for energy transfer is essentially unchanged at 2.5×10^{10} s^{-1}, but the rate constant for step 2 is reduced to 2.9×10^8 s^{-1}. Consequently, the quantum yield of this step is reduced to 0.71. Such a decrease in the rate constant for photoinitiated electron transfer upon changing the solvent from chloroform to dichloromethane has been reported in porphyrin-quinone dyad systems.[11] Transient absorption studies with excitation at 650 nm show that the subsequent electron transfer steps yield $C^{\cdot+}\text{-}P_{Zn}\text{-}P\text{-}Q_A\text{-}Q_B^{\cdot-}$ with a quantum yield of ~0.60. The lifetime of the final state, however, is increased to ~200 μs.

It is interesting to note that 5, in which both porphyrins are present as the free base, also demonstrates photoinitiated electron transfer to yield a long-lived charge separated state. In this case the quantum yield of $C^{\cdot+}\text{-}P\text{-}P\text{-}Q_A\text{-}Q_B^{\cdot-}$ in dichloromethane is only 0.15, but the lifetime of this state is ~340 μs. There are two reasons for the reduced quantum yield for this molecule relative to 4. In the first place, although the rate constant for step 2 (2.3×10^8 s^{-1}) is similar to that found for 4, the quantum yield for this step is reduced to 0.35 because of an increased rate of decay of the porphyrin singlet by other pathways. In addition, the interporphyrin electron

transfer step 4 competes less efficiently with charge recombination because the $C\text{-}P^{\bullet+}\text{-}P\text{-}Q_A^{\bullet-}\text{-}Q_B$ state is destabilized by ~0.2 eV relative to $C\text{-}P_{Zn}^{\bullet+}\text{-}P\text{-}Q_A^{\bullet-}\text{-}Q_B$.

Although tetrad **1**, pentad **4** and related molecules differ significantly in structure from natural reaction centers, they do mimic several aspects of photosynthetic energy conversion. These include rapid singlet energy transfer to the primary donor, triplet energy transfer to the carotenoid, and a multistep electron transfer strategy which achieves efficient long range and long lived charge separation. There remain many important unanswered questions concerning natural photosynthesis which these artificial systems do not address or fail to mimic. However, the results for pentad **4** do demonstrate that compounds can be designed in which electron transfer following photoexcitation occurs over several redox centers with a yield of near unity while conserving more than one half of the excited state energy of the primary donor. Thus, it appears that there is no a priori reason why the essential features of photosynthetic solar energy conversion cannot ultimately be reproduced successfully using man-made molecular devices.[12]

D. References and Notes

1. Gust, D.; Moore, T. A.; Moore, A. L.; Seely, G.; Liddell, P.; Barrett, D.; Harding, L. O.; Ma, X. C.; Lee, S.-J.; Gao, F. Tetrahedron 1989, 45, 4867-4891.

2. Gust, D.; Moore. T. A.; Moore, A. L.; Barrett, D.; Harding, L. O.; Makings, L. R.; Liddell, P. A.; De Schryver, F. C.; Van der Auweraer, M.; Bensasson, R. V.; Rougèe, M. J. Am. Chem. Soc. 1988, 110, 321-323.

3. Gust, D.; Moore, T. A. Science 1989, 244, 35-41.

4. Gust, D.; Moore, T. A.; Liddell, P. A.; Nemeth, G. A.; Makings, L. R.; Moore, A. L.; Barrett, D.; Pessiki, P. J.; Bensasson, R. V.; Rougèe, M.; Chachaty, C.; De Schryver, F. C.; Van der Auweraer, M.; Holzwarth, A. R.; Connolly, J. S. J. Am. Chem. Soc. 1987, 109, 846-856.

5. Wasielewski, M.; Niemczyk, M. P.; in Porphyrins - Excited States and Dynamics; Gouterman, M., Rentzepis, P. M., Straub, K. D., Eds.; ACS Symposium Series 321: American Chemical Society: Washington, DC 1986; pp 154-165.

6. Joran, A. D.; Leland, B. A.; Geller, G. G.; Hopfield, J. J.; Dervan, P. B. J. Am. Chem. Soc. 1984, 106, 6090-6092.

7. Leland, B. A.; Joran, A. D.; Felker, P. M.; Hopfield, J. J.; Zewail, A. H.; Dervan, P. B. J. Phys. Chem. 1985, 89, 5571-5573.

8. Hasharoni, K.; Levanon, H.; Tang, J.; Bowman, M. K.; Norris, J. R.; Gust, D.; Moore, T. A.; Moore, A. L. J. Am. Chem. Soc., submitted for publication.

9. At 960 nm, the transient signal rises to ~90% of its maximum value with the response time of the instrument, and reaches the peak value within several microseconds.

10. R. Bensasson, C. R. Goldschmidt, E. J. Land and T. G. Truscott, Photochem. Photobiol. 1978, 28, 277. Quantum yields are based on published extinction coefficients for transient species (carotenoid radical cations and porphyrin triplet states) which are not accurately known.

11. J. A. Schmidt, A. Siemiarczuk, A. C. Weedon and J. R. Bolton, J. Am. Chem. Soc. 1985, 107, 6112; For a comprehensive review, see J. S. Connolly and J. R. Bolton, in Photoinduced Electron Transfer, Part D., M. A. Fox and M. Channon, Eds. (Elsevier, Amsterdam, 1988), chap. 6.2.

12. G. Ciamician, Science 1912, 36, 385.

Publications and Meeting Presentations Resulting from this Project

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, Biophysical Journal **1988**, 53, 271a.

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, Photochem. Photobiol. **1988**, 47S, 17S.

6. "Long-Lived, Photoinitiated Charge Separation in a Carotenoid-Porphyrin-Quinone Molecular Tetrad," Devens Gust, Thomas A. Moore, Ana L. Moore, Donna Barrett, Larry O. Harding, Lewis R. Makings and P. A. Liddell, Proceedings of the Twelfth DOE Solar Photochemistry Research Conference, 1988, 139.

7. "Carotenoporphyrin-Quinone Triads and Tetrads as Reaction Center Mimics: Control of Electron Transfer Rates," Ana L. Moore, Thomas A. Moore, Devens Gust, Larry O. Harding, Susan Hatlevig, Lewis R. Makings, Donna Barrett and Paul A. Liddell, Abstracts of the XII IUPAC Symposium on Photochemistry, 1988, 416-417.

8. "Strategies for Enhancing Quantum Yields in Model Photosynthetic Reaction Centers," Devens Gust, Electron Donor-Acceptor Gordon Conference, Wolfeboro, NH, August, 1988.

9. "Multicomponent Molecular Devices for Photoinitiated Electron Transfer," Devens Gust and Thomas A. Moore, 196th National Meeting of the American Chemical Society, Los Angeles, CA, September, 1988.

10. "A Carotenoid-Porphyrin-Diquinone Tetrad: Synthesis, Electrochemistry and Photoinitiated Electron Transfer," Devens Gust, Thomas A. Moore, Ana L. Moore, Gilbert Seely, Paul A.

Liddell, Donna Barrett, Larry O. Harding, Xiaochun C. Ma, Seung-Joo Lee and Feng Gao, Tetrahedron, **1989,** 45, 4867-4891.

11. "Mimicking Photosynthesis," Devens Gust and Thomas A. Moore, Science **1989,** 244, 35-41.

12. "Synthetic Multichromophoric Systems as Reaction Center Mimics. Fine Tuning of Electron Transfer Rates," Thomas A. Moore, Devens Gust, Ana L. Moore, Larry O. Harding, Seung-Joo Lee, Feng Gao, Xiaochun C. Ma., and Robert E. Belford, Photochem. Photobiol. **1989,** 49S, 61S.

13. "Photoinitiated 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, Paul A. Liddell, Xiaochun C. Ma., Seung-Joo Lee, and Feng Gao, Proceedings of the Thirteenth DOE Solar Photochemistry Research Conference, 1989, 59-61.

14. "Mimickry of Photosynthetic Energy and Electron Transfer," Devens Gust, Gordon Conference on Organic Photochemistry, Andover, NH, 1989.

15. "Multistep Photoinduced Electron Transfer in Porphyrin-Based Tetrad Compounds," Devens Gust, Thomas A. Moore, ANa L. Moore, Xiaochun Ma, Robert E. Belford, David K. Luttrull, and Feng Gao, The 1989 International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 1989, Abstracts, Phys 173.

16. "Mimicking the Triplet Energy Transfer Relay of Rb. Sphaeroides," Thomas A. Moore, Devens Gust, Ana L. Moore, Lewis R. Makings, Robert E. Belford, Paul A. Liddell, and Peter J. Pessiki, The 1989 International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 1989, Abstracts, Orgn 128.

17. "Efficient Multistep Photoinitiated Electron Transfer in a Molecular Pentad," Devens Gust, Thomas A. Moore, Ana L. Moore, Seung-Joo Lee, Edith Bittersmann, David K. Luttrull, Aden A. Rehms, Janice M. DeGraziano, Xiaochun C. Ma, Feng Gao, Robert E. Belford, and Todd T. Trier, Science, in press.

18. "Association of Chlorophyll with Inverted Micelles of Dodecylpyridinium Iodide in Toluene," Gilbert R. Seely, Xiaochun C. Ma., Ronald A. Nieman, and Devens Gust, J. Phys. Chem., in press.

19. "Photosynthetic Model Systems," Devens Gust and Thomas A. Moore, Topics in Current Chemistry, in press.

20. "Singlet Photochemistry in Model Photosynthesis: Identification of Charge Separated Intermediates by Fourier Transform and CW EPR Spectroscopies," Kobi Hasharoni, Haim Levanon, Jau Tang, Michael K. Bowman, James R. Norris, Devens Gust, Thomas A. Moore, and Ana L. Moore, J. Am. Chem. Soc., submitted for publication.

END

DATE
FILMED
5/07/92