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Photodriven Electron Transfer in Triad Molecules: A Two-Step Charge Recombination Reaction

Devens Gust,* Thomas A. Moore,* Lewis R. Makings, Paul A. Liddell, Gregory A. Nemeth, and Ana L. Moore

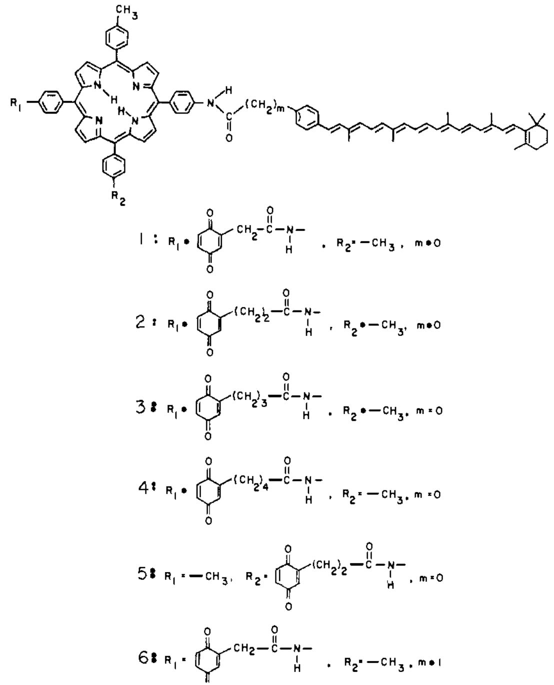
Contribution from the Department of Chemistry, Arizona State University, Tempe, Arizona 85287. *Received May 23, 1986*

Abstract: Excitation of carotenoid–porphyrin–quinone (C–P–Q) triad molecules initiates a two-step electron transfer to yield a final charge separated state of the form $\mathrm{C^{\bullet+}{-}P{-}Q^{\bullet-}}$. This state has a very long lifetime in solution (10^{-7}–10^{-6} s), and the nature of the ultimate charge recombination reaction has not previously been investigated. Nanosecond transient absorption spectroscopic studies have been performed on a series of such triad molecules wherein the nature of the linkages joining the porphyrin to the quinone and/or carotenoid moieties is varied systematically. The results reveal that charge recombination in $\mathrm{C^{\bullet+}{-}P{-}Q^{\bullet-}}$ does not occur in a single step but rather via an unusual two-step electron transfer involving an intermediate $\mathrm{C{-}P^{\bullet+}{-}Q^{\bullet-}}$ species. The temperature dependence is consistent with the formation of $\mathrm{C{-}P^{\bullet+}{-}Q^{\bullet-}}$ via a thermally activated process, and measurements over the range 221–296 K yield $\Delta H^{\ddagger} = 2.7$ kcal/mol and $\Delta S^{\ddagger} = -20$ cal/(deg·mol). The transient absorption measurements also reveal that the quantum yield of the $\mathrm{C^{\bullet+}{-}P{-}Q^{\bullet-}}$ state is a function of three electron transfer rate constants and that it can therefore be maximized by controlling the ratios of these rate constants to one another and to the rates of other pathways which depopulate the relevant excited states.

A key step in natural photosynthesis is photodriven electron transfer to generate an energetic charge-separated state. No less important is the strategy developed by photosynthetic organisms to prevent rapid charge recombination and consequent waste of the chemical potential of the charge-separated state as heat. Plants achieve this goal by using a series of electron-transfer reactions which rapidly move the electron and the positive charge through a series of acceptors and donors and thereby separate the charges in space and regenerate the photocatalytic center. We recently reported the synthesis and study of a group of carotenoid–porphyrin–quinone triad molecules which form long-lived photogenerated charge-separated states via a biomimetic two-step electron transfer.[1-6] These high-energy states live for microseconds in some solvents, but eventually they decay back to the ground state. An understanding of the factors leading to the long lifetimes of the charge-separated states requires in turn an understanding of the nature of the decay process. We have therefore prepared a series of triad molecules in which the structures are varied in a systematic way and studied the rates of decay of the charge-separated states using nanosecond transient absorption spectroscopy.

The molecules under study, **1–6**, consist of tetraarylporphyrins (P) covalently linked to carotenoid polyenes (C) and quinones (Q). Within the series **1–4**, the linkage between the porphyrin and the quinone has been varied by the addition of methylene spacers. Triad **6** is the analogue of **1** in which a methylene group has been inserted between the carotenoid polyene and the porphyrin moiety, whereas **5** is an analogue of **2** in which the carotenoid and quinone are linked to the porphyrin in the 5,10 relationship, rather than the 5,15 arrangement common to **2** and the other members of the series.

Absorption of light by these molecules leads to the series of events diagrammed in Scheme I. Excitation of the porphyrin moiety leads to the porphyrin first excited singlet state $\mathrm{C{-}^{1}P{-}Q}$ (step 1). The initial electron transfer (step 2) produces the intermediate charge-separated state $\mathrm{C{-}P^{\bullet+}{-}Q^{\bullet-}}$, whose decay is partitioned between a return to the ground state via the back electron transfer reaction step 3 and formation of a final charge-separated state $\mathrm{C^{\bullet+}{-}P{-}Q^{\bullet-}}$ via electron donation from the carotenoid moiety to the porphyrin radical cation in step 4. In the case of **1**, the lifetime of the final $\mathrm{C^{\bullet+}{-}P{-}Q^{\bullet-}}$ state was found to range from a few hundred nanoseconds in methylene chloride to a few microseconds in acetonitrile.[1]



The rate constants for the initial electron transfer (step 2) can be determined by measuring the fluorescence decay times of triads and related model compounds. Such studies with **1–4** have revealed that electron-transfer rates within this series range from 1.5×10^{8} to 97×10^{8} s^{-1} in dichloromethane and depend approximately exponentially upon the donor–acceptor separation for most members of the series.[7] The yield of $\mathrm{C^{\bullet+}{-}P{-}Q^{\bullet-}}$ and

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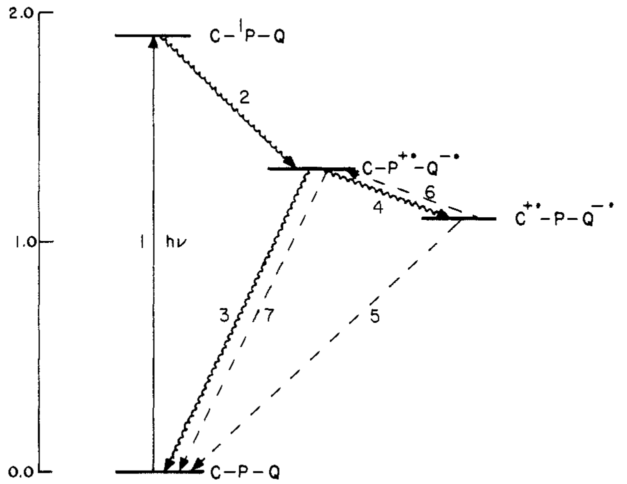
Scheme I



the lifetime of this state can be obtained by using nanosecond transient absorption spectroscopy. Such measurements are especially convenient and unambiguous with the triads because the carotenoid radical cation has a very strong $(\epsilon \simeq 1 \times 10^{5}\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1})$[8] and characteristic absorption band with a maximum at about 970 nm. The results of measurements of this type for compounds **1–6** are reported below.

Experimental Section

The preparation and characterization of **1–6** have been reported elsewhere, as have the solution conformations of these molecules (and therefore the intramolecular donor–acceptor distances) as determined from 400-MHz ^{1}H NMR studies.[7] Transient absorption spectra at ambient temperature were obtained in 1-cm rectangular cuvettes with 10^{-5} M solutions of the triads in dichloromethane which had been stored over potassium carbonate in order to remove traces of acid. Samples were purified by thin-layer chromatography immediately prior to use. Studies of decay rate as a function of temperature were performed by immersing the sample cuvette in an optical Dewar containing acetone. The temperature of the acetone bath, as measured by a thermocouple in contact with the sample cuvette, was adjusted with solid carbon dioxide. Temperature variations during the course of a measurement were within ±2 K.

The pulsed excitation source was a Lambda Physik FL 2000 dye laser using Rhodamine 6G pumped by a Lambda Physik EMG 50 E xenon chloride excimer laser at 308 nm. The output of the dye laser consisted of a series of ≃5-mJ, 20-ns pulses at 590 nm with a repetition rate of ≃10 Hz. The continuous probe beam was orthogonal to the pump beam and was generated by a 12 V, 100 W quartz–halogen tungsten lamp equipped with a 750 nm long-pass filter to prevent photolysis. Detection was via a UDP PIN 10D silicon photodiode equipped with a 10 nm bandpass filter. Detection was usually at the maximum of the carotenoid cation absorption at 970 nm. Amplification was via a Comlinear CLC100 (rise time of 0.75 ns) followed by two CLC103 amplifiers (rise time of 2.5 ns), and digitization was by a 200-MHz LeCroy TR8828B fast waveform digitizer. Signal averaging was performed with an IBM PC computer. A digital back-off circuit was employed.[9]

Results

Representative decay curves for the radical cations of **1–4** are shown in Figure 1. The curves depict the relative intensities of the radical cation absorptions for solutions having the same optical density at the 590 nm pump wavelength. The absorption spectra of **1–4** are identical in the visible region, within experimental error, and do not differ significantly from a simple sum of the absorption spectra of carotenoid and porphyrin model systems. The 590 nm laser pulse excites the corresponding porphyrin Q band.

The decay curves are not quite exponential. They consist of a major, monoexponential short component superimposed on a minor, long-lived component, one manifestation of which is a slight base line shift at this short time scale. The amplitude of the long-lived component increases, relative to the short component, with increasing concentration, and may be ascribed to the bimolecular electron transfer

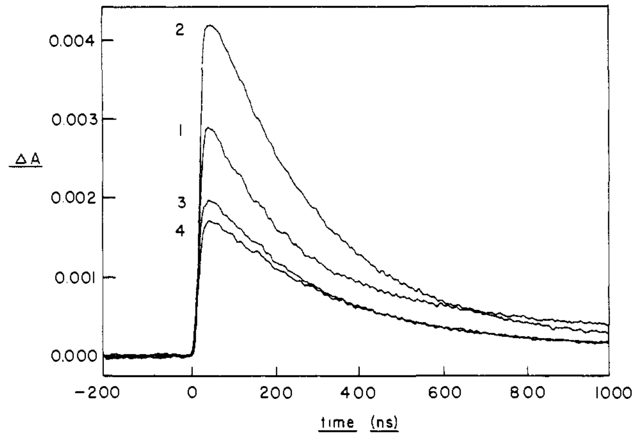


Figure 1. Typical transient absorption decays of the carotenoid radical cation of **1–4** (970 nm) in dichloromethane following excitation by a 20-ns, 590-nm laser pulse. Relative ΔA values reflect relative quantum yields of $C^{\bullet+}$–P–$Q^{\bullet-}$ (see text).

Table I. Quantum Yield and Lifetime of $C^{\bullet+}$–P–$Q^{\bullet-}$ in CH_2Cl_2

molecule	lifetime (ns) 295 K	rel quantum yield 295 K	rel quantum yield 220 K[a]
1	298	1.00	2.50
2	283	1.44	3.09
3	315	0.65	1.04
4	335	0.56	0.48
5	285	1.47	3.20
6	1010		

[a] Calculated by assuming that the extinction coefficient of the carotenoid radical cation at 970 nm is independent of temperature.

$$C^{\bullet+}\text{–P–}Q^{\bullet-} + \text{C–P–Q} \rightarrow C^{\bullet+}\text{–P–Q} + \text{C–P–}Q^{\bullet-}$$

The short-lived component is independent of concentration and must represent unimolecular charge recombination. At sufficiently low concentrations, the decay curves are a good approximation to a single exponential, and decay times for the short-lived component could be obtained by a three-parameter curve-fitting procedure. The lifetimes of the $C^{\bullet+}$–P–$Q^{\bullet-}$ states for **1–6** measured in this way at ambient temperature (295 K) are listed in Table I.

Also listed in the table are the relative quantum yields of the $C^{\bullet+}$–P–$Q^{\bullet-}$ states based on that for triad **1**. Previous work has shown that the quantum yield of $C^{\bullet+}$–P–$Q^{\bullet-}$ in **1** varies from 0 to >0.25, depending upon the solvent and temperature.[1,4] In dichloromethane at ambient temperatures, the yield is ≃0.04. Thus, the absolute quantum yields in Table I range from ≃0.02 to ≃0.11. The absolute quantum yield calculations were based upon published extinction coefficients for excited states and are therefore somewhat uncertain.[1] The relative quantum yields in the table do not suffer from this problem, and thus they allow meaningful comparisons among the various triads. Triads **1** and **2** have the highest quantum yields, and these yields increase significantly at low temperatures. The yields for **3** and **4**, however, are relatively insensitive to temperature.

The lifetimes of the charge-separated states are also temperature dependent. The decay rate for the $C^{\bullet+}$–P–$Q^{\bullet-}$ state of **2** in methylene chloride was measured at 11 temperatures in the range 221–296 K. A plot of the data obtained in the form ln (k/T) vs. $1/T$ is shown in Figure 2. A linear least-squares fit (R^2 = 98.8%) allows calculation[10] of the activation parameters for the decay process: $\Delta H^{\ddagger}$ = 2.7 kcal/mol and $\Delta S^{\ddagger}$ = −20 cal/(deg·mol) (assuming a transmission coefficient of unity and $k_7 \gg k_4$).

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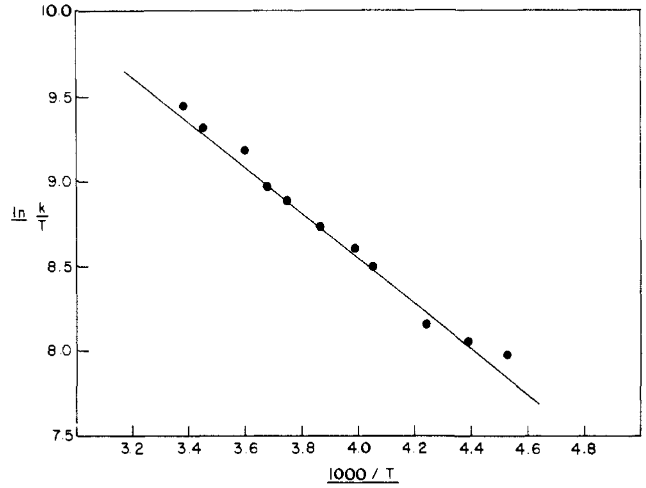

Figure 2. Plot of ln (k/T) vs. $1/T$ for triad **2** in dichloromethane solution. The solid line is the least-squares best fit for the data points shown and yields the activation parameters reported in the text. The experimental error in the measurement of k was ±10%, and that for T was ±2 K (see Experimental Section).

Measuring the decay rate at significantly lower temperatures has not been possible because the formation of $C^{\bullet+}$–P–$Q^{\bullet-}$ in a frozen glass has not been observed. For example, excitation of 1 in butyronitrile solution at ambient temperatures leads to the formation of $C^{\bullet+}$–P–$Q^{\bullet-}$ in good yield with a lifetime of 1.6 μs. When the same solution is frozen as a glass at 77 K, however, no carotenoid cation absorption is observed. Disappearance of the carotenoid cation is accompanied by appearance of strong porphyrin fluorescence. This suggests that the lack of observation of $C^{\bullet+}$–P–$Q^{\bullet-}$ in the glass is a consequence of the failure of the initial charge separation (step 2). This conclusion has been confirmed by fluorescence lifetime studies of 1 and its relatives.[11]

Discussion

The Decay of $C^{\bullet+}$–P–$Q^{\bullet-}$. Most electron-transfer theories predict that the electron-transfer rate will depend strongly on donor–acceptor orbital overlap, and therefore on donor–acceptor separation and orientation.[12-20] In the absence of nonspherical electron distributions, through-bond effects, or other complicating factors, the distance dependence is expected to be exponential. Such a distance dependence is indeed observed for the initial photodriven electron transfer (step 2 in Scheme I) in **1**–**4**.[7] The rate decreases by a factor of ca. 65 as one goes from 1 to 4 methylene spacers separating the porphyrin and quinone moieties. Decay of $C^{\bullet+}$–P–$Q^{\bullet-}$ by direct electron transfer from the quinone radical anion to the carotenoid radical cation (step 5 in Scheme I) would also be expected to show a strong distance dependence. The data in Table I reveal, however, that the lifetime of the $C^{\bullet+}$–P–$Q^{\bullet-}$ state in **1**–**4** is essentially independent of the nature of the porphyrin–quinone linkage (ca. 300 ns for all four compounds). ^{1}H NMR data have shown that the average separation of the quinone and porphyrin, and therefore of the quinone and carotenoid moieties, increases by ≃4 Å in this series of molecules.[7] Thus, the observed lack of dependence of electron-transfer rate on distance is puzzling.

One explanation for this apparent anomaly might be that even though the average carotenoid–quinone separation changes considerably in the series, molecular motions during the rather long lifetime of the $C^{\bullet+}$–P–$Q^{\bullet-}$ state somehow average to yield essentially the same average electron-transfer distance and orientation for each of the four molecules, and for **5** (see below). Such a coincidence would be unlikely.

An alternative, and much more reasonable, explanation for the experimental observations is that the charge recombination reaction does not occur by the direct route (step 5) but rather via a two-step electron transfer. The first step is an endergonic transfer from the neutral porphyrin moiety of $C^{\bullet+}$–P–$Q^{\bullet-}$ to the carotenoid cation to yield C–$P^{\bullet+}$–$Q^{\bullet-}$ (step 6 in the scheme). This slow, rate-determining step is followed by rapid electron transfer from the quinone radical anion to the porphyrin radical cation to yield the neutral ground state (step 7). One of the consequences of this mechanism is that the rate-determining step involves only porphyrin–carotenoid electron transfer and should therefore be independent of the quinone radical anion and the porphyrin–quinone separation, to a first approximation. Because the porphyrin–carotenoid separation does not change through the series **1**–**4**, the lifetimes of the $C^{\bullet+}$–P–$Q^{\bullet-}$ state should be essentially equivalent for all four molecules, as observed.

Triad **5** provides one test of the proposed mechanism. In this molecule, the carotenoid has been moved from the 5,15 relationship to the quinone on the porphyrin macrocycle to the 5,10 relationship. This change brings the carotenoid much closer to the quinone moiety.[7] For example, the distance from the quinone ring to the carotenoid aryl group is decreased from ≃25 Å in **2** to ≃18 Å in **5**. If the back reaction were direct via step 5, this change in structure would result in a dramatic shortening of the lifetime of $C^{\bullet+}$–P–$Q^{\bullet-}$. As seen in Table I, the charge-separated states in **2** and **5** have identical lifetimes, within the experimental error of ±20 ns.

If the proposed two-step mechanism is correct, then changing the distance between the porphyrin and the carotenoid polyene *should* affect the lifetime of the $C^{\bullet+}$–P–$Q^{\bullet-}$ state, because porphyrin-to-carotenoid electron transfer is the rate-determining step. Indeed, triad **6**, which features a methylene spacer between the carotenoid and porphyrin moieties, has a lifetime for the final charge-separated state of about 1 μs, which is about three times that observed for the other five compounds in dichloromethane (Table I).

The proposed charge recombination mechanism requires a thermally activated step (step 6), and the lifetime of the charge-separated state should be temperature dependent. As noted above, such a temperature dependence is observed. The measured $\Delta H^{\ddagger}$ (2.7 kcal/mol) and $\Delta S^{\ddagger}$ (−20 cal/(deg·mol)) yield $\Delta G^{\ddagger}$ = 8.6 kcal/mol at 295 K. This is comparable to the free energy difference of ca. 6 kcal/mol between the C–$P^{\bullet+}$–$Q^{\bullet-}$ and $C^{\bullet+}$–P–$Q^{\bullet-}$ states as roughly estimated from the electrochemically determined redox potentials of the carotenoid, quinone, and porphyrin moieties.[7] The relatively large apparent negative entropy of activation is a result of assuming a transmission coefficient κ in the Eyring equation of 1.0. Alternatively, the data may be equally well accommodated by reducing κ, in accord with current theories for nonadiabatic electron transfer.[12,14-16,18-20]

It should be noted that although step 6 would appear to be the reverse of step 4, and step 7 equivalent to step 3, this may not actually be the case. Steps 2, 3, and 4 are all very fast (undoubtedly on the ns time scale or faster), and as a result the charge-separated states will all be singlet biradicals, to the extent that there is interaction between the unpaired electrons. Steps 5, 6, and 7, on the other hand, would occur on the hundreds of nanoseconds or microsecond time scale. During this time, there is ample opportunity for singlet–triplet transitions, and as a result, some of the biradicals should be present as triplets. This would presumably have little effect on the rate of step 6, which is slow in any case. However, it could conceivably result in a difference in rates for step 3 and step 7 (which includes any effect of triplet

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biradicals on the lifetime of C–P$^{\bullet+}$–Q$^{\bullet-}$).

Relative Quantum Yields. Even though fluorescence decay studies have shown that the initial electron-transfer step is faster for triad **1** than for **2–4**,[7] the data in Table I reveal that the highest quantum yield of the C$^{\bullet+}$–P–Q$^{\bullet-}$ state is attained for triad **2**. This observation may be rationalized by examination of Scheme I. Assuming that the electron-transfer rates measured via fluorescence decay studies reflect the formation of C–P$^{\bullet+}$–Q$^{\bullet-}$,[7] the quantum yield of this intermediate depends upon the ratio of the rate of step 2 (k_2) to the rate of decay of the porphyrin first excited singlet state by all other pathways. The quantum yield of the final C$^{\bullet+}$–P–Q$^{\bullet-}$ state, however, depends not only on that ratio but also on the ratio of step 3 to step 4 (k_3/k_4). In the case of **2**, k_2 is in fact reduced by a factor of 11 relative to **1**. However, the observed rate (8.3×10^8 s^{-1}) is still fast enough to achieve a quantum yield of 0.75 for C–P$^{\bullet+}$–Q$^{\bullet-}$ (vs. 0.97 for **1**).[7] The decrease in rate for **1** is, of course, related to the decreased coupling of the π electron systems which results from the insertion of an additional methylene spacer group. This same decrease in orbital overlap, however, should also decrease the rate of the back reaction (step 3) relative to **1**. On the other hand, the rate of step 4, which does not involve porphyrin-to-quinone electron transfer, should be essentially the same for both **1** and **2**. Thus, the relatively small decrease in quantum yield of C–P$^{\bullet+}$–Q$^{\bullet-}$ for **2** is evidently more than offset by a decrease in k_3/k_4, and the quantum yield of C$^{\bullet+}$–P–Q$^{\bullet-}$ for **2** is greater than that for **1**.

The same considerations apply to triads **3** and **4**. However, in these cases, the rates of step 2 are relatively slow, and the quantum yields of C–P$^{\bullet+}$–Q$^{\bullet-}$ have dropped to 0.57 and 0.34, respectively.[7] Apparently, any additional decrease in k_3/k_4 for these molecules cannot overcome the decrease in quantum yield of step 2, and the quantum yield of C$^{\bullet+}$–P–Q$^{\bullet-}$ drops. Quantitatively, the drop in quantum yield of C$^{\bullet+}$–P–Q$^{\bullet-}$ is not proportional to the decrease for C–P$^{\bullet+}$–Q$^{\bullet-}$, and the overall quantum yield is lower than would be expected if k_3/k_4 were approaching zero. Clearly, transient absorption data on the picosecond time scale will be necessary to determine directly the relative decay rates and to detect any alternative decay pathways.

The arguments given above suggest that the main factor controlling the quantum yield for **1** and **2** is the ratio k_3/k_4, whereas the yield of **3** and **4** is also affected strongly by the rate of step 2 relative to that of the depopulation of the porphyrin first excited singlet state by other pathways. Support for this interpretation is provided by the quantum yield data at 220 K (Table I). Cooling to 220 K more than doubles the quantum yield of C$^{\bullet+}$–P–Q$^{\bullet-}$ for **1** and **2**, but it has little effect on the corresponding quantum yields for **3** and **4**. Also, it was previously reported that addition of tetra-*n*-butylammonium tetrafluoroborate to a dichloromethane solution of **1** greatly increased the quantum yield of C$^{\bullet+}$–P–Q$^{\bullet-}$.[1] The same is observed for **2**. Addition of this salt to solutions of **3** or **4**, on the other hand, produced essentially no change in quantum yield. These results suggest that the factors controlling the quantum yield of C$^{\bullet+}$–P–Q$^{\bullet-}$ differ for the two sets of molecules.

The studies of triad-type porphyrin-based molecules reported here and previously[1-7,21] have begun to reveal some of the factors which are important in biological multistep electron-transfer reactions. Indeed, studies of bacterial reaction centers have shown that the electron transfer back reaction involves in part a thermally activated reversal of the forward electron-transfer process.[22-24] As exemplified by the thermally activated two-step charge recombination reaction discussed above, the possibility for multiple forward and backward electron-transfer processes in model systems opens up new opportunities for fine-tuned control of photodriven charge separation and adds considerably to the complexity of the analysis of experimental results. Both this complexity and the ability to maximize the system for an optimal balance among the various electron-transfer and energy-transfer processes are greatly magnified in photosynthetic reaction centers themselves.

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Registry No. **1**, 90463-28-8; **2**, 104977-30-2; **3**, 104994-68-5; **4**, 104994-69-6; **5**, 104994-52-7; **6**, 104977-31-3.

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