Structural Effects on Photoinduced Electron Transfer in Carotenoid−Porphyrin−Quinone Triads

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meso-Polyarylporphyrins are often used as components of molecules that mimic photosynthetic reaction centers by carrying out photoinduced electron-transfer reactions. Studies of these systems have raised questions concerning the role of alkyl substituents at the "*β*-pyrrolic" positions on the porphyrin periphery in limiting $\pi-\pi$ overlap between the macrocycle and the aryl rings. The degree of overlap affects electronic coupling and, therefore, the rates of electron-transfer reactions. There is also evidence that when the linkages joining porphyrins to electron-acceptor or -donor moieties contain amide bonds, the sense of the amide linkage may strongly affect electron-transfer rate constants. In this study, three carotenoid−porphyrin−quinone molecular triads and various model compounds have been prepared, and electron-transfer has been studied using time-resolved emission and absorption techniques. The results show that steric hindrance due to methyl groups at the *β*-pyrrolic positions reduces electron-transfer rate constants by a factor of $\sim 1/5$. In addition, amide-containing donor−acceptor linkages having the nitrogen atom attached to the porphyrin *meso*-aryl ring demonstrate electron-transfer rate constants ~ 30 times larger than those for similar linkages with the amide reversed, after correction for thermodynamic effects.

Introduction

A large number of model systems for light-induced charge separation in photosynthetic reaction centers have been reported in recent years. Most consist of porphyrins covalently linked to quinones or other electron acceptors.[1−6] Spectroscopic study of these materials has revealed much about the dependence of electron-transfer rates on donor−acceptor coupling, thermodynamic driving force, solvent, and temperature. These investigations have raised a number of interesting unresolved questions.

For example, in most of these systems, electron transfer is mediated by the covalent linkage joining the donor and acceptor moieties. Many of the model systems involve a porphyrin *meso*-aryl ring in this linkage. In porphyrins with unsubstituted "*β*-pyrrolic" peripheral positions (*cf.* structure **3**), these aryl rings make angles ≥45° but <90° with the mean porphyrin plane.[7−14] Thus, conjugation between the ring and the macrocycle π-electron system can play a role in the donor−acceptor electronic interaction, which in turn affects the electron-transfer rate.[15] A number of investigators have attempted to limit this conjugative interaction by placing alkyl groups at the *β*-pyrrolic positions (*cf.* **1**).[9−11,16−27] The idea is that the steric effect of these groups forces the aryl ring to be orthogonal to the porphyrin, and thus eliminates $\pi-\pi$ interactions. There are factors that argue against complete orthogonality; the porphyrin macrocycle might distort significantly due to the steric hindrance, rotational motion on an appropriate time scale about the single bond joining the aryl ring to the macrocycle might significantly populate conformations with $\pi-\pi$ overlap, and solution conformations might not demonstrate true orthogonality, as this would force the system to forgo all resonance stabilization.

A second question involves the role of amide bonds in the donor−acceptor linkages. It has been found that a porphyrin linked to a benzoquinone derivative by an amide group having the nitrogen bonded to the porphyrin *meso*-aryl ring (as in **1**)

undergoes photoinduced electron transfer 12 times more rapidly than a related porphyrin−quinone dyad in which the amide linkage has been reversed.[28,29] A theoretical explanation for this difference has been reported,[30] but it is not clear whether this is a general phenomenon.

In order to further investigate these questions, we have prepared and studied the photochemistry of carotene (C) porphyrin (P) quinone (Q) triads **1**−**3** and model compounds **4**−**10**. Triads **1** and **3** differ in that **1** has sterically demanding methyl groups in the porphyrin *β*-pyrrolic positions, whereas **3** does not. Triads **1** and **2** differ only in the sense of the amide bond joining the porphyrin and the carotenoid polyene.

Results

Synthesis. The porphyrin moieties employed in the synthesis of **1**, **2**, **4**−**6**, and **10** (Charts 1−3) were prepared using a modification of the MacDonald [2+2] cyclization.[31,32] The carotenoid, quinone, and *meso*-polyarylporphyrins were prepared using methods previously developed in our laboratories (see Experimental Section). All molecules were characterized using NMR and mass spectrometric methods.

Electrochemistry. Cyclic voltammetric studies were carried out in order to estimate the energetics of electron-transfer in the three triads. The first reduction potential of a model for the quinone in the triads, 6-phenylcarbamyl-1,4-naphthoquinone, is −0.58 V vs SCE. The first oxidation potential of a model for the carotenoid moiety of triads **1** and **3** is +0.65 V,[33] whereas that for a model for the carotenoid moiety of **2** is +0.47 V.[34] The first oxidation potential for a model for the porphyrin moiety of **3**, 5,15-bis(4-acetamidophenyl)-10,20-bis(4-methylphenyl)-porphyrin, is +0.93 V. A model for the octaalkylporphyrin moiety found in **2** is oxidized at +0.87 V, whereas a model for that of **1** has a first oxidation potential of +0.84 V.

Steady-State Absorption Spectra. The absorption spectra of triads **1**−**3** are shown in Figure 1. The absorption maxima in the 440−540 nm region are due mainly to the carotenoid
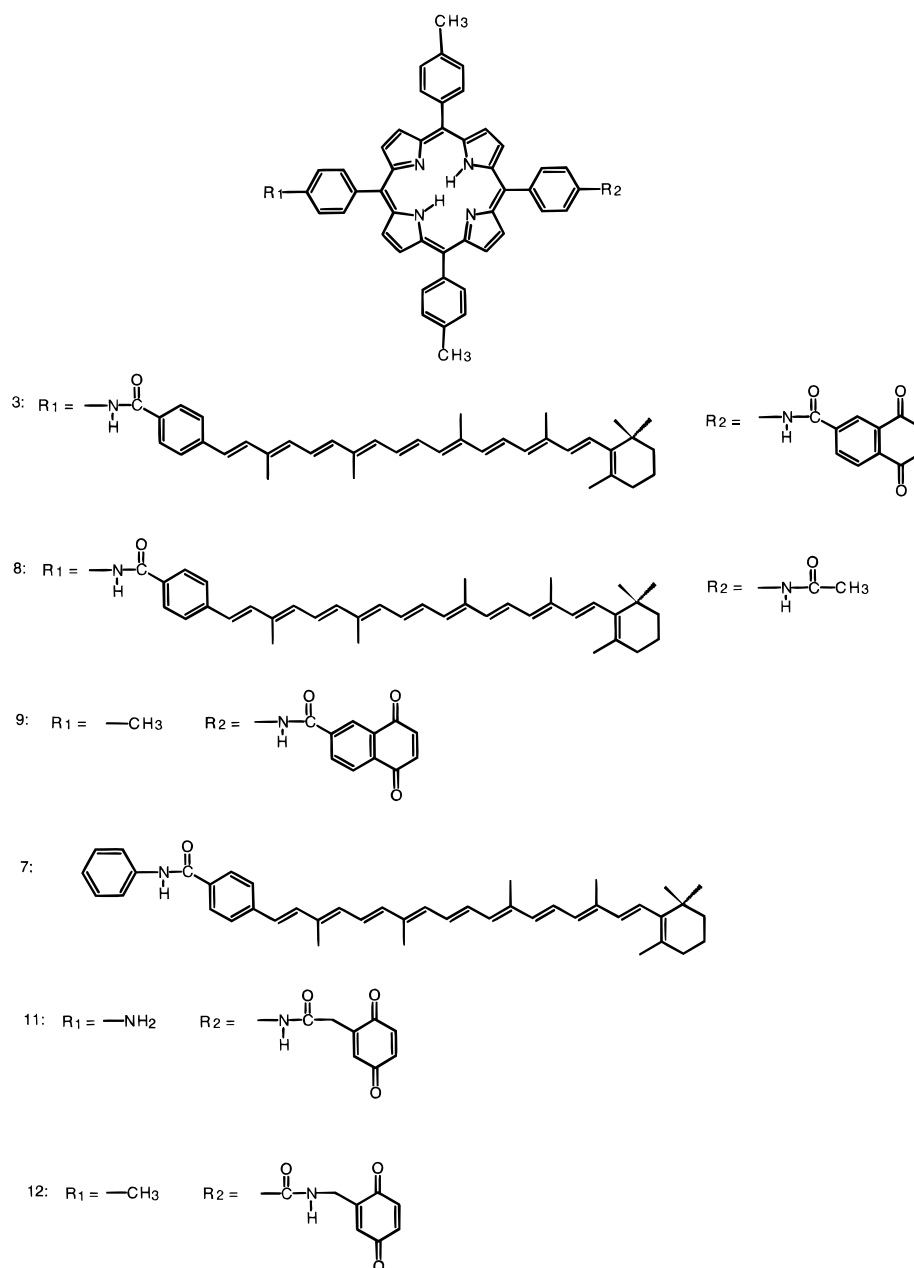

CHART 1
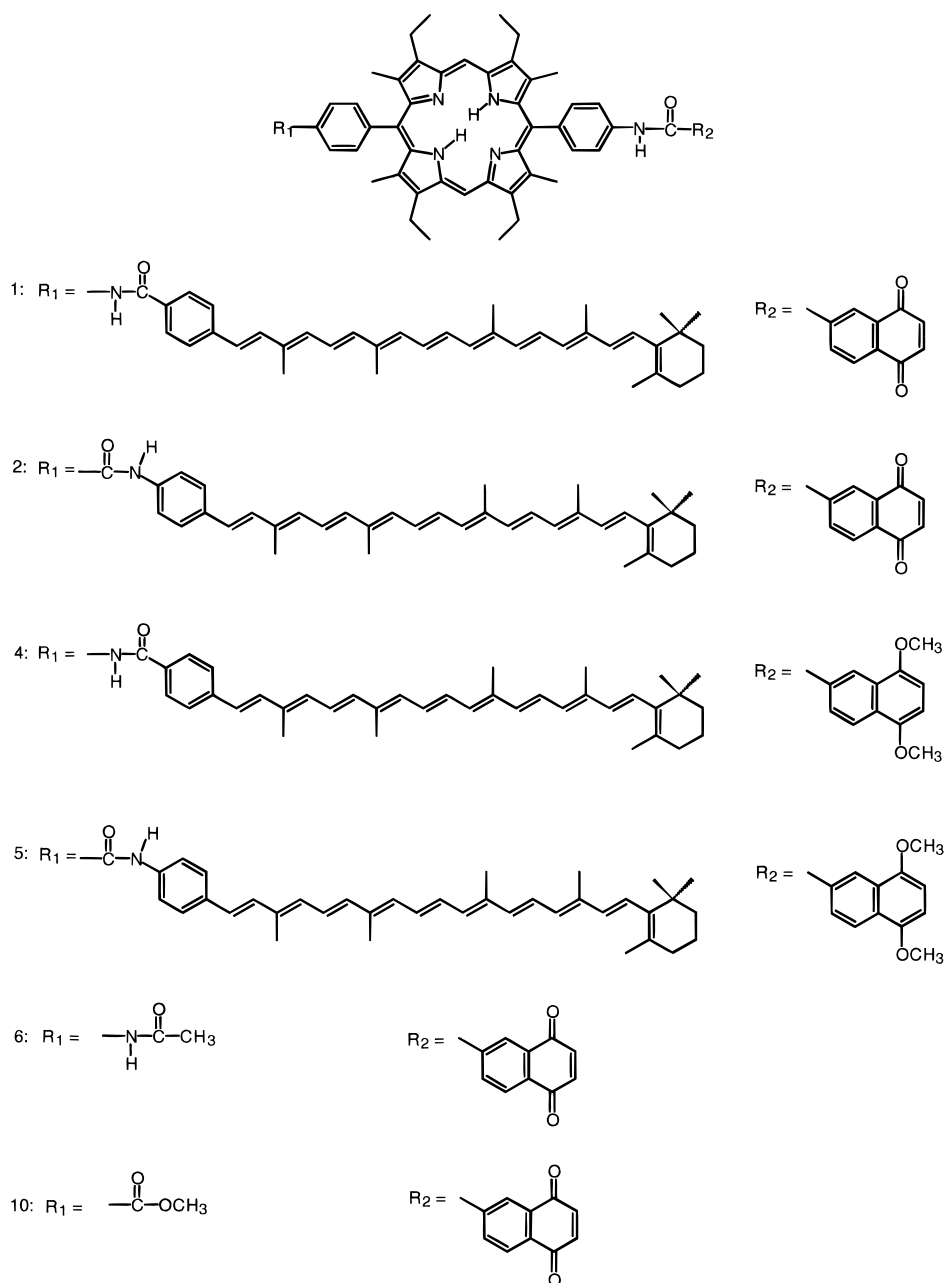
polyene, as shown by the absorption spectrum of model carotene **7**, which has bands at 521 and 490 nm and a shoulder at ∼460 nm. Model porphyrin−quinone dyad **6** has Q-band maxima at 627, 576, 540, and 508 nm, and a Soret band at 413 nm. Triad **1** has maxima at 630, 574, 492, and 415 nm and shoulders in the 520 and 460 nm regions; its spectrum is nearly a linear combination of those of the two model compounds. Thus, there is no evidence from the absorption spectrum for strong electronic interaction between the chromophores. Similarly, **2** has maxima at 628, 575, 514, 488, and 415 nm. Triad **3** has maxima at 651, 592, 520, 490, and 427 nm. The shift in the absorption maxima and relative amplitudes of **3** with respect to **1** and **2** is due to the different substitution pattern of the porphyrin: 5,-15-bis(4-acetamidophenyl)-10,20-bis(4-methylphenyl)porphyrin has maxima at 648, 592, 552, 526, and 418 nm in dichloromethane solution. Model compounds **4** and **5** have absorption spectra that are virtually identical to those of **1** and **2**, respectively, in the visible region.

Fluorescence Spectra and Lifetimes. The steady-state fluorescence emission spectra of triads **1** and **2** and porphyrin−quinone dyad **6** in benzonitrile solution, with excitation at 590

nm, are all similar, with maxima at 632 and 698 nm. Triad **3** has emission maxima at 661 and 725 nm under these conditions. The fluorescence quantum yields in all cases were ∼0.001, as determined using the comparative method with *meso*-tetraphenylporphyrin as the standard ($\Phi = 0.11$). Thus, the porphyrin first excited singlet states of **1**−**3** and **6** are strongly quenched by the attached quinone.

The quenching was investigated further by time-resolved fluorescence studies using the single-photon-timing method (Table 1). An ∼1×10^{-5} M solution of triad **1** in benzonitrile was excited with 9 ps laser pulses at 590 nm, and the fluorescence was measured as a function of time at 8 wavelengths in the 635−760 nm region. The decays were analyzed globally as two exponential components ($\chi^2 = 1.14$); the results are shown as decay-associated spectra in Figure 2a. The only significant decay component has a lifetime of 103 ps. A similar result was obtained for **2** (Figure 2b); global analysis of the decays at seven wavelengths in the 635−740 nm region ($\chi^2 = 1.14$) gave a major component with a lifetime of 87 ps. The fluorescence lifetime studies of **3** were performed at eight wavelengths in the 650−735 nm region, and global analysis

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CHART 2

3: R₁ =

8: R₁ =   R₂ =

9: R₁ = —CH₃   R₂ =

7:

11: R₁ = —NH₂   R₂ =

12: R₁ = —CH₃   R₂ =

($\chi^2 = 1.10$) gave a lifetime of 110 ps for the significant component (Figure 2c). Model porphyrin−quinone dyad **6** also displays one major decay component of 85 ps, as determined from global analysis of data at five wavelengths in the 630−720 nm region ($\chi^2 = 1.09$). Similar experiments with dyad **10** yield a fluorescence decay time constant of 102 ps.
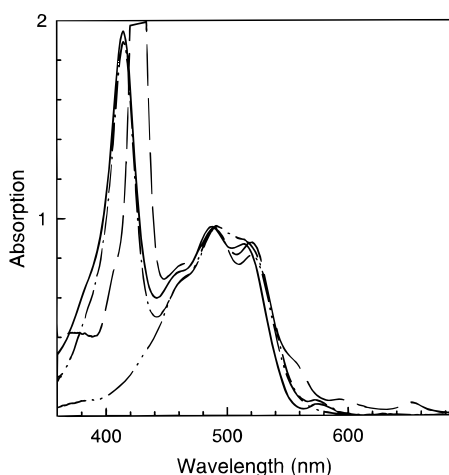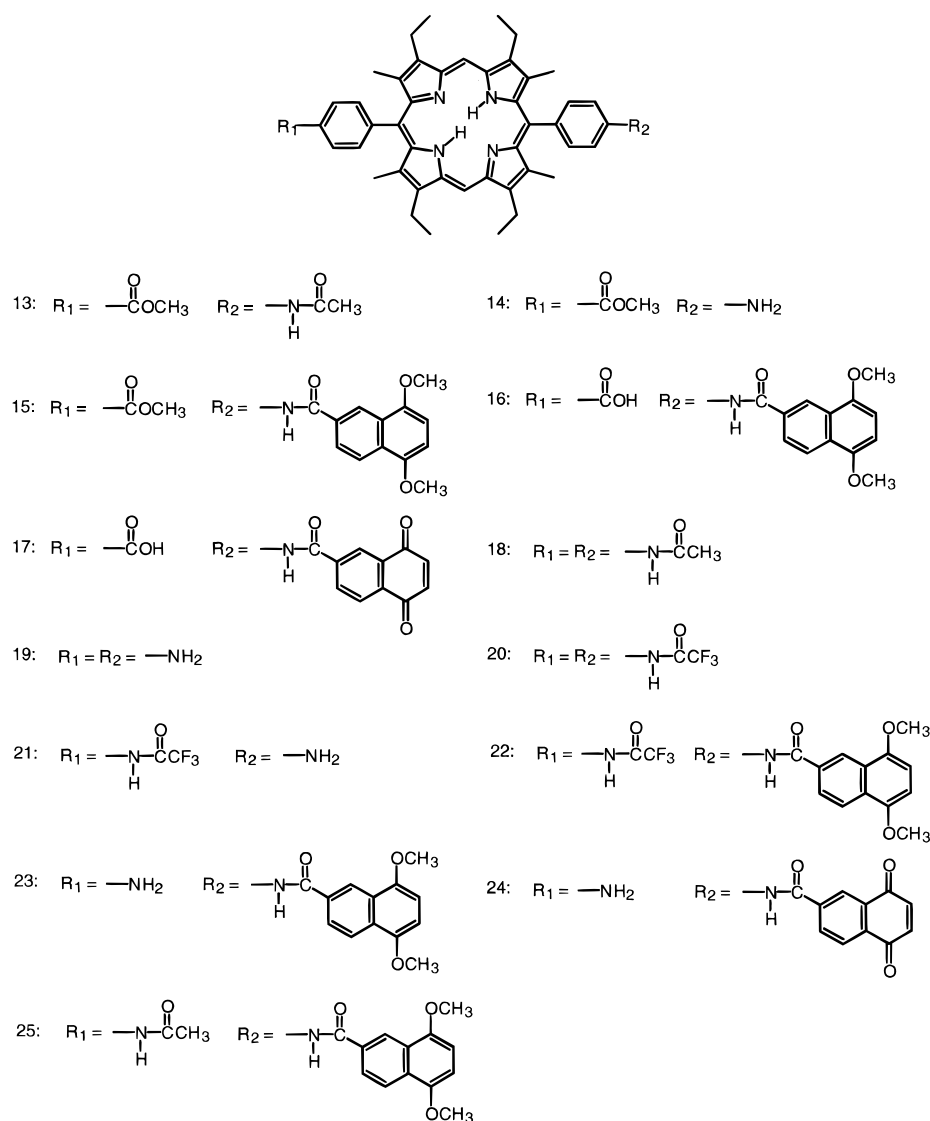
The fluorescence decays of model carotenoporphyrins **4**, **5**, and **8** in benzonitrile were monoexponential, with time constants of 6.2, 7.0, and 2.2 ns, respectively (Table 1). Thus, the first excited singlet states of all the porphyrins bearing quinone moieties are strongly quenched. Such quenching has been observed in many porphyrin−quinone dyads and found to be due to photoinduced electron transfer that yields a porphyrin radical cation and quinone radical anion. As typical lifetimes for porphyrin first excited singlet states are ∼10 ns, the porphyrin singlet states are slightly quenched by the attached carotenoid in **4**, **5**, and **8**. The mechanism of this quenching has been discussed elsewhere.[36]

Nanosecond Transient Absorption Spectroscopy. In the triads, the C−P•⁺−Q•⁻ charge-separated states resulting from quenching of the porphyrin first excited singlet state may evolve

by electron transfer from the carotenoid polyene to the porphyrin radical cation to yield C•⁺−P−Q•⁻. This possibility was investigated in **1**−**3** using transient absorption techniques. Excitation of an ∼3 × 10⁻⁵ M solution of triad **1** in benzonitrile with a 5-ns laser pulse at 630 nm, where only the porphyrin is excited, led to a strong absorption with a maximum at 950 nm that is ascribed to the carotenoid radical cation.[33] This absorption decayed monoexponentially with a lifetime of 310 ns (Figure 3). Thus, the C•⁺−P−Q•⁻ state is indeed formed. Similar results were obtained for **2**, whose carotenoid radical cation has an absorption maximum at 986 nm and a lifetime of 260 ns. Excitation of **3** under the same conditions gave rise to a carotenoid radical cation with its absorption maximum at 950 nm and a lifetime of 67 ns (Figure 3).

Figure 3 shows the decays of the carotenoid radical cations of the C•⁺−P−Q•⁻ states of solutions of **1**−**3** with equal ground-state absorbance at the 630-nm excitation wavelength. Quantum yields were calculated using the comparative method with the *meso*-tetraphenylporphyrin triplet state ($\Phi_T = 0.67$, ($\epsilon_T − \epsilon_G)_{440}$ = 6.8×10^4 L mol⁻¹ cm⁻¹) as the standard. Using an extinction coefficient for the carotenoid radical cation of 1.6×10^5 L mol⁻¹

CHART 3

13: R_1 = —COCH₃ R_2 = —NHCCH₃ (with carbonyl)

14: R_1 = —COCH₃ R_2 = —NH₂

15: R_1 = —COCH₃ R_2 = —NHC(=O)-naphthalene(OCH₃)₂

16: R_1 = —COH R_2 = —NHC(=O)-naphthalene(OCH₃)₂

17: R_1 = —COH R_2 = —NHC(=O)-naphthoquinone

18: R_1 = R_2 = —NHCCH₃ (with carbonyl)

19: R_1 = R_2 = —NH₂

20: R_1 = R_2 = —NHCCF₃ (with carbonyl)

21: R_1 = —NHCCF₃ (with carbonyl) R_2 = —NH₂

22: R_1 = —NHCCF₃ (with carbonyl) R_2 = —NHC(=O)-naphthalene(OCH₃)₂

23: R_1 = —NH₂ R_2 = —NHC(=O)-naphthalene(OCH₃)₂

24: R_1 = —NH₂ R_2 = —NHC(=O)-naphthoquinone

25: R_1 = —NHCCH₃ (with carbonyl) R_2 = —NHC(=O)-naphthalene(OCH₃)₂

Figure 1. Absorption spectra of triads **1** (—·—), **2** (—), and **3** (- - -) and model carotenoid **7** (—··—) in benzonitrile solution. The spectra have been normalized at the maximum of the carotenoid absorption in the 480–490 nm region. Note that the Soret band of **3** has been truncated.

cm^{-1} at the absorption maximum, the quantum yields of C$^{\bullet+}$–P–Q$^{\bullet-}$ for **1**, **2**, and **3** were estimated to be 0.057, 0.063, and 0.044, respectively.

Subpicosecond Transient Absorption Spectroscopy. Time-resolved absorption experiments on a faster time scale were

TABLE 1: Porphyrin Excited Singlet State Lifetimes in Benzonitrile As Determined from Time-Resolved Fluorescence Studies

compound	τ_1 (ns)[a]	compound	τ_1 (ns)[a]
1	0.10	**5**	7.0
2	0.087	**6**	0.085
3	0.110	**8**	2.2
4	6.2	**10**	0.10

[a] In some cases, minor decay components were also observed (see text).

necessary in order to obtain kinetic information concerning the formation of C$^{\bullet+}$–P–Q$^{\bullet-}$. Excitation of an $\sim 1 \times 10^{-4}$ M solution of **1** in benzonitrile with 200 fs laser pulses at 590 nm led to the appearance of the spectrum shown in Figure 4. This spectrum, taken 20 ps after the laser flash, shows a positive transient absorbance over the entire 600–1100 nm region. The absorption in the shorter-wavelength part of the spectrum is due mainly to the porphyrin first excited singlet state and includes a minimum at 698 nm that is due to stimulated emission. The strong positive absorption at 954 nm arises from the carotenoid radical cation. Thus, both C–^{1}P–Q and C$^{\bullet+}$–P–Q$^{\bullet-}$ are present in the solution at this time. Similar results were obtained for **2** and **3**, except, of course, for the shifts in the absorption and stimulated emission maxima due to changes in porphyrin or carotenoid structure.

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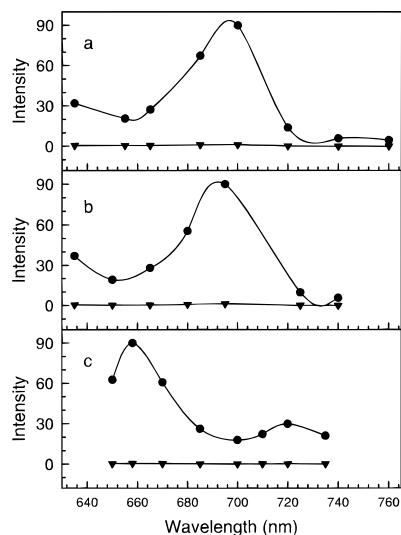
Figure 2. Fluorescence decay-associated spectra for triads in benzonitrile following excitation at 590 nm. (a) Triad **1**: (●), 103 ps; (▼), 5.8 ns. (b) Triad **2**: (●), 87 ps; (▼), 5.2 ns. (c) Triad **3**: (●), 110 ps, (▼), 1.8 ns.
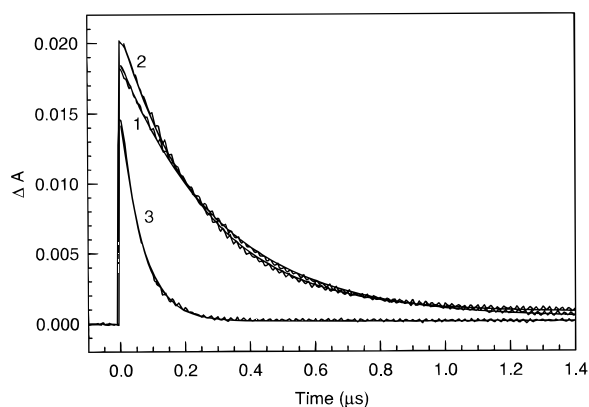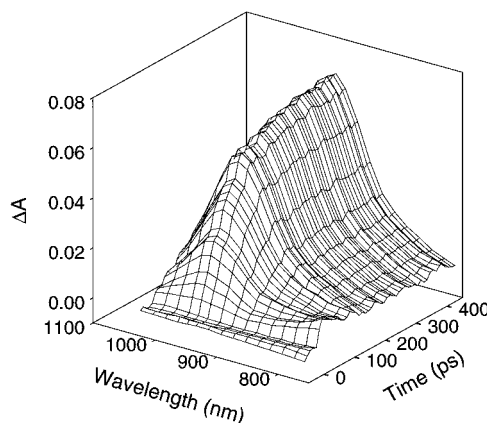

Figure 3. Decay of the carotenoid radical cation transient absorption in solutions of triads **1**−**3** in benzonitrile following excitation with a 5-ns laser pulse at 630 nm. The solutions had equal absorbance at the excitation wavelength. The smooth curves are single-exponential least-squares fits to the experimental decays. The lifetimes are 310 ns for **1** (measured at 970 nm), 260 ns for **2** (measured at 970 nm), and 67 ns for **3** (measured at 950 nm).
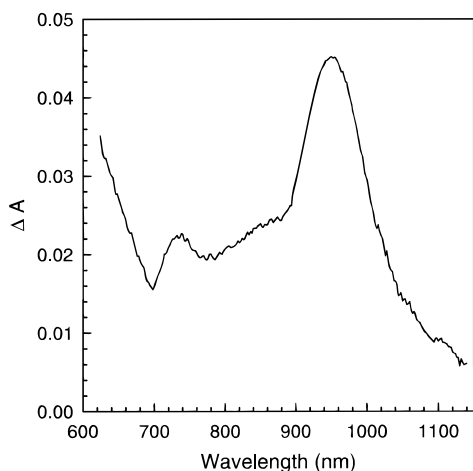

Figure 4. Transient absorption spectrum of triad **1** taken 20 ps after excitation of a benzonitrile solution with a 200 fs laser pulse at 590 nm.

The rise times of the transients were also investigated. Figure 5 shows the formation of the carotenoid radical cation absorption in **3** following laser excitation as described above. Global analysis of these data in the 850−1044 nm region (97 kinetic

Figure 5. Rise of the transient absorption of the carotenoid radical cation of triad **3** as a function of wavelength and time following excitation of a benzonitrile solution with a 200 fs laser pulse at 590 nm.
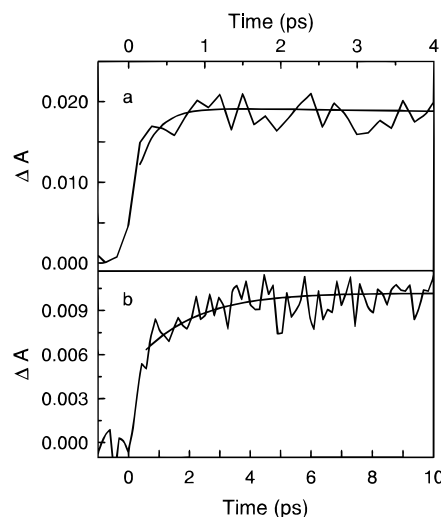

Figure 6. (a) Transient absorption at 654 nm following excitation of a 2×10^{-4} M solution of porphyrin−quinone dyad **9** in benzonitrile with a 150−200 fs laser pulse at 590 nm. The prompt absorption is due to the porphyrin first excited singlet state. The smooth curve is a theoretical exponential fit to the slower part of the rise with a time constant of 0.24 ps. (b) Transient absorption at 698 nm following excitation of a 1×10^{-4} M solution of porphyrin−quinone dyad **10** in benzonitrile with a 150−200 fs laser pulse at 590 nm. The prompt absorption is due to the porphyrin first excited singlet state. The smooth curve is a theoretical exponential fit to the slower part of the rise with a time constant of 1.9 ps.

traces) yielded a monoexponential rise time of 90 ps. Similar ∼90-ps rise times were determined for triads **1** and **2**.

The transient absorption of **2** was also examined in the 624−850 nm region, with excitation as discussed above. The data show a transient that is consistent with the absorption of the porphyrin first excited singlet state with a lifetime of ∼100 ps, which is close to the 90-ps value noted above. In the shorter-wavelength region of this spectrum a contribution from a transient decay with a time constant of 12 ps was also observed. This likely represents the decay of the carotenoid first excited singlet state, as some carotenoid is excited at 590 nm. The observed lifetime is typical of such singlet states.

Additional information was obtained by studying the transient absorption spectra of porphyrin−quinone dyads **9** and **10**. Figure 6a shows the rise of the transient absorption at 654 nm of an ∼1×10^{-4} M benzonitrile solution of dyad **9** following excitation with a 590-nm, 150−200-fs laser pulse. The transient absorption features a prompt rise with the laser pulse, due to the porphyrin first excited singlet state, followed by a slower increase with a time constant of 0.24 ps. Similar measurements
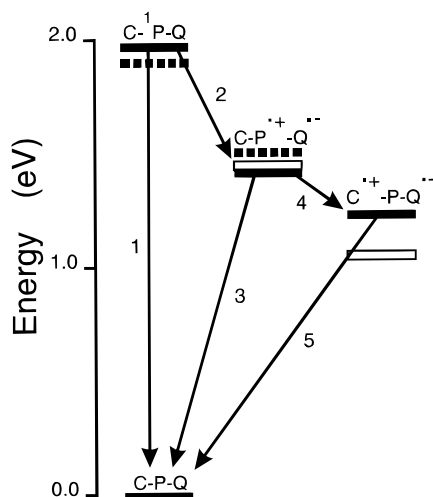
Figure 7. Energies of the relevant states of the triads and interconversion pathways. The solid bars show the energies for triad **1**. Where the energies differ significantly from those of **1**, the dashed bars show the energies for **3**, and the hollow bars show the energies for **2**.

at 698 nm on dyad **10** showed a prompt rise of the porphyrin first excited singlet state and a slower rising component of 1.9 ps (Figure 6b). These rise times are considerably shorter than the porphyrin first excited singlet state lifetimes, for reasons that will be discussed below.

Discussion

Photoinduced Electron Transfer. It is clear from the spectroscopic data that excitation of the porphyrin moieties of triads **1**−**3** results in the formation of long-lived C•+−P−Q•− charge-separated states. The pathways leading to these states may be discussed with reference to Figure 7. The singlet-state energies are estimated from the wavenumber average of the longest-wavelength absorption maximum and the shortest-wavelength emission maximum. The energies of the charge-separated states are based on the electrochemical results reported above. No corrections have been made for Coulombic effects, but such effects should be small in a polar solvent such as benzonitrile.

Upon excitation, the C−1P−Q state of **1** may decay by the usual photophysical processes of intersystem crossing, fluorescence and internal conversion, and through quenching by the carotenoid. The sum of the rate constants for these processes is k_1 and may be approximated by the reciprocal of the 6.2 ns lifetime of model compound **4**, which contains no quinone moiety. Thus, k_1 is 1.6×10^8 s^{-1}. (See also Table 2.) Competing with decay of C−1P−Q by these routes is photoinduced electron transfer to the quinone to produce C−P•+−Q•− (step 2 in the figure). The rate constant for step 2 is given by eq 1, where τ is the lifetime of the porphyrin first excited singlet state as determined from the time-resolved fluorescence studies.

$$k_2 = (1/\tau) - k_1 \qquad (1)$$

For **1**, τ is 103 ps, and k_2 equals 9.5×10^9 s^{-1}. The quantum yield of C−P•+−Q•− ($\Phi_2 = k_2 \times \tau$) is 0.98.

The C−P•+−Q•− state can decay by charge-recombination step 3, or by electron transfer from the carotenoid to the porphyrin radical cation to produce C•+−P−Q•−. The subpicosecond transient absorption kinetic experiments on **1** report a rise time for the carotenoid radical cation of 90 ps, which is within experimental error of the 103 ps fluorescence lifetime. (The fluorescence lifetime data were obtained with a better signal-to-noise ratio, and are deemed more accurate at these

long lifetimes than the results from the transient absorption experiments.) In addition, the transient spectra (Figure 4) show the presence of both C−1P−Q and C•+−P−Q•− at the same time. These results show that formation of C−P•+−Q•− is slower than its conversion to C•+−P−Q•− (($k_3 + k_4$) > k_2).

In order to obtain values for k_3 and k_4, we turn to the transient absorption results. Recall that the 1P−Q state in dyad **10** has a lifetime of 102 ps in benzonitrile, as determined from time-resolved fluorescence studies. This relatively long lifetime explains the apparent lack of decay of the transient absorption in Figure 6b. What, then, is responsible for the 1.9 ps rise time of the transient absorption of **10**? A reasonable explanation is suggested by eq 2,[37] which is the expression governing the

$$[P^{\bullet+} - Q^{\bullet-}] = k_2[^1P - Q]_0[k_3 - k_2]^{-1}[\exp[-k_2t] - \exp[-k_3t]] \quad (2)$$

concentration of P•+−Q•− as a function of time after laser excitation. In this expression, k_2 and k_3 are rate constants for charge separation and charge recombination (Figure 7) and t is the time after formation of the porphyrin first excited singlet state with an initial concentration of $[^1P-Q]_0$. It is apparent from this equation that the reciprocal of the greater of k_2 or k_3 will appear as the rise time constant of the transient. The fluorescence results show that the time constant for formation of P•+−Q•− is ~100 ps. Therefore, the 1.9 ps rise time must represent the lifetime of P•+−Q•−, and k_3 equals 5.3×10^{11} s^{-1}. The decay of the charge-separated state is much faster than its formation. Similar kinetic behavior has been observed in other porphyrin−quinone dyads.[37] The structural and energetic similarities of **6**, **10**, and **1** suggest that k_3 has a value of ~5.3 $\times 10^{11}$ s^{-1} in triad **1** as well. The quantum yield of the final C•+−P−Q•− state in **1**, $\Phi_{fin} = 0.057$, is given by eq 3.

$$\Phi_{fin} = \Phi_2 \frac{k_4}{k_3 + k_4} \qquad (3)$$

Substituting the values for Φ_2, Φ_{fin}, and k_3 given above yields a value for k_4 of 3.3×10^{10} s^{-1}. Ultimately, C•+−P−Q•− decays by charge recombination with a rate constant of 3.2×10^6 s^{-1}, as determined from the 310 ns lifetime (Figure 3). Quantum yields and rate constants for triad **1** are summarized in Table 2.

The spectroscopic data for triad **2** may be analyzed in a similar fashion. The value of k_1, based on the 7.0 ns fluorescence lifetime of the porphyrin moiety of dyad **5**, is 1.4 $\times 10^8$ s^{-1}. This value, coupled with the 87-ps fluorescence lifetime of the porphyrin first excited singlet state in triad **2**, yields a k_2 value of 1.1×10^{10} s^{-1} (eq 1) and a quantum yield Φ_2 of 0.96. The k_3 value for **2** is assumed to be equal to 5.3 $\times 10^{11}$ s^{-1}, on the basis of the transient absorption results for dyad **10**. Given the Φ_{fin} value of 0.063 for **2**, eq 3 yields a k_4 of 3.7 $\times 10^{10}$ s^{-1}. The rate constant for charge recombination to the ground state is 3.8×10^6 s^{-1}, as calculated from the lifetime of the carotenoid radical cation.

In triad **3**, k_1 equals 4.6×10^8 s^{-1}, from the 2.2 ns lifetime of the porphyrin first excited singlet state in dyad **8**. The lifetime of C−1P−Q in the triad is 110 ps, based on the time-resolved fluorescence results. Thus, eq 2 gives a k_2 value of 8.6×10^9 s^{-1} and a Φ_2 of 0.95. The transient absorption results for dyad **9** yielded a rise time of 0.24 ps for the absorption at 654 nm. As discussed above for **1**, the reciprocal of this rise time, 4.2×10^{12} s^{-1}, is k_3. This value and the 0.044 quantum yield for C•+−P−Q•− yields a k_4 of 2.0×10^{11} s^{-1} (eq 3). This value is similar to the value of ~1 $\times 10^{11}$ s^{-1} reported for the corresponding process in a triad with an identical carotenoid-

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TABLE 2: Rate Constants and Quantum Yields for Triads 1−3 in Benzonitrile

compound	k_1 (s^{-1})	k_2 (s^{-1})	k_3 (s^{-1})	k_4 (s^{-1})	k_5 (s^{-1})	$\Phi_{C-P^{\bullet+}-Q^{\bullet-}}$	$\Phi_{C^{\bullet+}-P-Q^{\bullet-}}$
1	1.6×10^8	9.5×10^9	5.3×10^{11}	3.3×10^{10}	3.2×10^6	0.98	0.057
2	1.4×10^8	1.1×10^{10}	5.3×10^{11}	3.7×10^{10}	3.8×10^6	0.96	0.063
3	4.6×10^8	8.6×10^9	4.2×10^{12}	2.0×10^{11}	1.5×10^7	0.95	0.044

to-porphyrin linkage.[37] Charge recombination step 5 in triad **3** occurs with a rate constant of 1.5×10^7 s^{-1} (Table 2).

Effect of Steric Hindrance. Electron-transfer rates in the triads will be discussed in terms of eq 4, which was developed for nonadiabatic electron-transfer reactions.[38−40] The electron-

$$k_{et} = \sqrt{(\pi/\hbar^2 \lambda k_B T)}|V|^2 \exp[-(\Delta G° + \lambda)^2/4\lambda k_B T] \quad (4)$$

transfer rate constant is k_{et}. The preexponential factor includes the electronic matrix element V that describes the coupling of the reactant state with that of the product. In addition to Planck's constant $\hbar$, Boltzmann's constant k_B, and the absolute temperature T, this factor also includes the reorganization energy for the reaction, λ. The reorganization energy is associated with the nuclear motions necessary to carry the molecule from the initial to the final state. The exponential term includes not only λ, but also the standard free energy change for the reaction, $\Delta G°$. It will be noted that eq 4 predicts an increase in rate with thermodynamic driving force (the "normal" region) up to a maximum when $-\Delta G° = \lambda$, and a decrease in rate as the standard free energy change becomes more negative in the "inverted" region.

Equation 4 indicates that electron-transfer rates in the three triads are governed by the electronic coupling, the reorganization energy, and the free energy change. In a solvent such as benzonitrile, most of the reorganization energy is due to solvent reorganization. This fact, coupled with the structural similarity of triads **1−3**, suggests that λ will be essentially the same for all three molecules under the conditions of this study. Thus, differences in electron-transfer rates will be determined by the electronic coupling V and the free energy change $\Delta G°$.

Triads **1** and **3** differ in that **1** features hindering methyl groups at the β-pyrrolic positions, whereas **3** does not. As discussed earlier, this steric hindrance may affect electronic coupling through the covalent bonds joining the various moieties. However, the two triads also differ slightly in free energy change values. For example, although the photoinduced electron-transfer rate constants k_2 for **1** and **3** are nearly identical (Table 2), the free energy change for step 2 in Figure 7 is −0.55 eV for **1** and −0.39 eV for **3**. Several studies of the effect of free energy change on photoinduced electron-transfer rate constants in porphyrin−quinone systems have been reported. Two of these[41,42] have reported electron-transfer rate constant and free energy change data for porphyrin-quinone dyads in butyronitrile solution that are correlated well by eq 4 or its semiclassical analog. In both cases, Marcus theory predicts that a change in $\Delta G°$ from −0.39 eV to −0.55 eV will result in a rate increase by a factor of 6. The structural and energetic similarities between these dyads[41,42] and the porphyrin−quinone moieties of **1−3** suggest that the shapes of the rate *vs* free energy change curves for compounds such as **1−3** should be similar to those in these other studies. Thus, the rate constant for photoinduced electron-transfer k_2 in **1** should be about 6 times larger than the corresponding value for **3**, or ~5×10^{10} s^{-1} on the basis of thermodynamic differences alone. In fact, k_2 for **1** is only 9.5×10^9 s^{-1}. The steric hindrance resulting from methyl groups at the β-pyrrolic positions slows photoinduced charge separation by a factor of ~$1/5$.

Turning now to charge shift reaction step 4 in Figure 7, it will be noted from Table 2 that the rate constant k_4 for triad **3** is about 6 times larger than that for **1**. The free energy change

for this step in **3** is −0.28 eV, whereas it is −0.19 eV for **1**. The reference cited above predicts that for this change in driving force, k_4 in **1** should be about 0.2 times that of k_4 in **3**, or 4×10^{10} s^{-1}, only on the basis of the changes in driving force. In fact, it is 3.3×10^{10} s^{-1}. Thus, the steric factors have little effect on the electron-transfer rate constant for step 4.

Charge recombination of the C−P$^{\bullet+}$−Q$^{\bullet-}$ state by step 3 in Figure 7 is about 8 times faster for **3**, where the free energy change is −1.51 eV, than for triad **1**, where the free energy change is −1.42 eV. Electron transfer in this region of free energy change occurs slightly in the inverted region, near the maximum of the rate vs free energy change curve. Semiclassical refinements of eq 4 which take into account quantized vibrational states of the system show a less-pronounced falloff of rate with increasing driving force in the inverted region.[43,44] There is little experimental data available in this region, but that which is available suggests that electron-transfer rates have relatively little dependence on free energy change.[41,45] Thus, the 0.09 eV difference in free energy change for step 3 in triads **1** and **3** is expected to have relatively little effect on rate. The factor of 8 in rate constant for this step is probably attributable mostly to the steric effect on electronic coupling.

Effect of the Linkage. The effect of reversal of the amide linkage on the rates of electron transfer can be assessed by comparison of triads **1** and **2**, which differ only in the direction of this linkage. The rate constants for photoinduced electron transfer step 2 are virtually identical for the two molecules. This is reasonable, as the free energy change is nearly the same, and electronic coupling between the porphyrin and quinone moieties is also identical. Similarly, the rate constants for charge recombination by step 3 are assumed to be identical at 5.3×10^{11} s^{-1} because of the structural similarities. Table 2 indicates that the rate constant for charge shift from the carotenoid polyene to the porphyrin radical cation, step 4 in Figure 7, is only 1.1 times larger in triad **2** than in triad **1**. This would seem to suggest that the sense of the amide linkage has almost no effect on electron-transfer rates. However, there is also a thermodynamic difference in the two molecules. The free energy change for step 4 in **1** is 0.19 eV, whereas that for **2** is 0.40 eV. By using the rate vs free energy change correlation cited above, it can be calculated that on thermodynamic grounds alone, step 4 in triad **2** should be ~35 times faster than that in triad **1**, whereas it is actually only 1.1 times faster. Thus, reversing the amide linkage from the direction in **1** to the sense in **2** slows electron transfer by a factor of ~1/30.

Charge Recombination of C$^{\bullet+}$−P−Q$^{\bullet-}$. The rate constants for charge recombination of the final C$^{\bullet+}$−P−Q$^{\bullet-}$ states of the triads, k_5, are virtually identical for **1** and **2**, whereas k_5 for **3** is about 4 times greater. As with charge separation and charge shift reactions in these triads, the rates of charge recombination will be determined by thermodynamics and electronic coupling factors. In triads **1** and **3**, the ionic species in the C$^{\bullet+}$−P−Q$^{\bullet-}$ states are identical, with the same free energy change for charge recombination to the ground state, but the recombination rates differ by a factor of 4. This suggests that charge recombination is not a direct, "through space" electron transfer, but rather involves the bridging porphyrin moiety in some way.

A previously studied set of C−P−Q triads features a carotenoporphyrin moiety identical to that in **3** bonded to benzoquinone by linkages containing various numbers of methylene groups.[28] Studies of this series suggested that charge

recombination is a two-step process occurring by a slow, thermally activated conversion of C•+−P−Q•− to C−P•+−Q•− followed by rapid charge recombination. It is unlikely that this mechanism is correct for **3** because the lifetime of C•+−P−Q•− in **3** is substantially shorter than those of the related triads, even though they all share the same carotenoporphyrin structure. Stronger porphyrin−quinone electronic coupling in **3** relative to that in these other triads evidently allows more rapid charge recombination by another pathway, such as a superexchange process involving the porphyrin and associated linkages.

Similarly, charge recombination in **1** and **2** cannot be controlled solely by the thermodynamics of the conversion of C•+−P−Q•− to C−P•+−Q•−, because these molecules have similar C•+−P−Q•− lifetimes even though the free energy change for this reaction is quite different for the two molecules (Figure 7). Although complete understanding of charge recombination in **1**−**3** must await further studies, it is clear that recombination is slower in the molecules that feature alkyl groups in the β-pyrrolic positions flanking the aryl rings. Thus, steric effects are likely to play some role in the recombination process, presumably by affecting electronic coupling among the carotenoid, porphyrin, and quinone moieties.

Conclusions

These studies have allowed investigation of the effect of steric hindrance to *meso* aryl ring rotation by alkyl groups at the β-pyrrolic peripheral positions on electron-transfer rate constants. Methyl groups flanking the aryl groups force them to assume a larger angle with respect to the mean porphyrin plane, and this decreases the $\pi-\pi$ overlap between the macrocycle and the *meso* substituents. The decreased overlap decreases the electronic coupling *V* between electron donor and acceptor, and this in turn reduces the electron transfer rate constant. The effect is relatively small. For the electron-transfer reactions studied here, the average reduction in electron-transfer rate constant was a factor of only ∼$^1/_5$. This result suggests that the flanking groups do not in fact succeed at keeping the aryl groups completely orthogonal to the macrocyclic plane. This is consistent with recent ^{13}C spin−lattice relaxation time studies which indicate that even in the presence of flanking groups, the *meso* aryl rings still undergo oscillatory motions on the subnanosecond time scale.[46]

This series of triads also allowed investigation of the effect of the sense of the amide link in **1** and **2** on electron-transfer rate constants. After correction for free energy change effects, it was found that the amide linkage in **1** increases the electron-transfer rate constant by a factor of about 30 relative to the linkage in **2**. Earlier work has shown that photoinduced electron transfer from porphyrin to quinone in dyad **11** in dichloromethane solution[28] is 12 times faster than the comparable process in dyad **12**.[29] The linkages in the dyads differ from those in the triads in that the dyads involve an additional methylene group. These rate differences indicate that in both sets of molecules, the electronic coupling for linkages in which the nitrogen atom of the amide is attached to the porphyrin *meso* aryl group is stronger than that in the linkages where the amide carbonyl is linked directly to the *meso* aryl ring. INDO-CI calculations of electronic coupling for dyads **11** and **12** have shown a factor of 2.7 in the expected direction.[30]

Experimental Section

Synthesis. Triad **3**,[37] dyad **8**,[37] and carotenoid **7**[33] have been reported in the literature.

5-(4-Acetamidophenyl)-15-(4-carbomethoxyphenyl)-2,8,12,-18-tetraethyl-3,7,13,17-tetramethylporphyrin (**13**) *and 5,15-bis(4-acetamidophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tet-*

*ramethylporphyrin (**18**)* were prepared from bis(4-ethyl-3-methyl-2-pyrrolyl)methane, 4-carbomethoxybenzaldehyde, and 4-acetamidobenzaldehyde using the method of Maruyama and co-workers.[47] Porphyrin **13** was obtained in 31% yield: ^{1}H-NMR (300 MHz, CDCl₃) δ −2.42 (2H, brs, −NH), 1.76 (12H, t, *J* = 8 Hz, 2-CH₃, 8-CH₃, 12-CH₃, 18-CH₃), 2.32 (3H, s, CH₃C(O)), 2.46 (6H, s, 13-CH₃, 17-CH₃), 2.51 (6H, s, 3-CH₃, 7-CH₃), 4.01 (8H, q, *J* = 8 Hz, 2-CH₂, 8-CH₂,12-CH₂, 18-CH₂), 4.13 (3H, s, −OCH₃), 7.46 (1H, s, −NH), 7.86 (2H, d, *J* = 8 Hz, 5Ar3,5-H), 7.92 (2H, d, *J* = 8 Hz, 5Ar2,6-H), 8.17 (2H, d, *J* = 8 Hz, 15Ar3,5-H), 8.44 (2H, d, *J* = 8 Hz, 15Ar2,6-H), 10.24 (2H, s, 10-CH, 20-CH); MS *m/z* 746 (M + 1)⁺; UV/vis (CH₂Cl₂) 408, 508, 542, 576, 628 nm. Porphyrin **18** was obtained in 17% yield: ^{1}H-NMR (300 MHz, CDCl₃) δ −2.42 (2H, brs, −NH), 1.77 (12H, t, *J* = 8 Hz, 2-CH₃, 8-CH₃, 12-CH₃, 18-CH₃), 2.38 (3H, s, CH₃C(O)), 2.53 (12H, s, 3-CH₃, 7-CH₃, 13-CH₃, 17-CH₃), 4.02 (8H, q, *J* = 8 Hz, 2-CH₂, 8-CH₂, 12-CH₂, 18-CH₂), 7.92 (4H, d, *J* = 8 Hz, 5Ar3,5-H, 15Ar3,5-H), 8.02 (4H, d, *J* = 8 Hz, 5Ar2,6-H, 15Ar2,6-H), 10.22 (2H, s, 10-CH, 20-CH); MS *m/z* 745 (M + 1)⁺; UV/vis (CH₂Cl₂) 410, 508, 542, 576, 628 nm. In addition, 5,15-bis(4-carbomethoxyphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin was obtained from the reaction in 17% yield.

*Porphyrin **14**.* A mixture of 100 mg (0.134 mmol) **13,** 15 mL of trifluoroacetic acid, and 25 mL of concentrated hydrochloric acid was stirred under nitrogen at 90 °C for 18 h. The reaction mixture was cooled and poured into chloroform containing 15% methanol. The organic layer was washed with water until neutral, and the solvent was removed by distillation under reduced pressure. The resulting solid acid was suspended in dichloromethane and treated with excess diazomethane in diethyl ether. The reaction mixture was stirred for **5** min, and the solvent was distilled at reduced pressure. The resulting solid was dissolved in dichloromethane, and the organic solution was washed with dilute sodium carbonate solution. The solvent was distilled at reduced pressure, and the crude product was recrystallized from a mixture of dichloromethane and methanol to yield 87 mg of **14** (92% yield): ^{1}H-NMR (300 MHz, CDCl₃) δ −2.42 (2H, brs, −NH), 1.76 (6H, t, *J* = 8 Hz, 12-CH₃, 18-CH₃), 1.77 (6H, t, *J* = 8 Hz, 2-CH₃, 8-CH₃), 2.32 (3H, s, CH₃C-(O)), 2.46 (6H, s, 13-CH₃, 17-CH₃), 2.51 (6H, s, 3-CH₃, 7-CH₃), 4.01 (4H, q, *J* = 8 Hz, 12-CH₂, 18-CH₂), 4.02 (4H, q, *J* = 8 Hz, 2-CH₂, 8-CH₂), 4.13 (3H, s, −OCH₃), 7.06 (2H, d, *J* = 8 Hz, 5Ar3,5-H), 7.79 (2H, d, *J* = 8 Hz, 5Ar2,6-H), 8.19 (2H, d, *J* = 8 Hz, 15Ar3,5-H), 8.43 (2H, d, *J* = 8 Hz, 15Ar2,6-H), 10.22 (2H, s, 10-CH, 20-CH); MS *m/z* 704 (M + 1)⁺; UV/vis (CH₂Cl₂) 410, 508, 542, 576, 628 nm.

*Porphyrin **15**.* A mixture of 6-carboxy-1,4-dimethoxynaphthalene (49 mg, 0.23 mmol), 2-chloro-4,6-dimethoxy-1,3,5-triazine (40 mg, 0.23 mmol), and *N*-methylmorpholine (25 μL, 0.21 mmol) in 10 mL of dichloromethane was stirred at room temperature under a nitrogen atmosphere for 3 h. To the resulting pale yellow solution were added porphyrin **14** (100 mg, 0.142 mmol), *N*-methylmorpholine (25 μL, 0.23 mmol), and 4-(*N*,*N*-dimethylamino)pyridine (26 mg, 0.21 mmol). The resulting solution was stirred for 20 h under a nitrogen atmosphere and then added to a mixture of dichloromethane and 1 M aqueous hydrochloric acid. The green organic layer was separated and washed with dilute sodium bicarbonate solution, and the solvent was distilled at reduced pressure. Recrystallization of the resulting solid from dichloromethane/methanol gave 112 mg of **15** (85%): ^{1}H-NMR (300 MHz, CDCl₃) δ −2.40 (2H, brs, −NH), 1.78 (12H, t, *J* = 8 Hz, 2-CH₃, 8-CH₃, 12-CH₃, 18-CH₃), 2.46 (6H, s, 13-CH₃, 17-CH₃), 2.60 (6H, s, 3-CH₃, 7-CH₃), 4.04 (14H, m, 2-CH₂, 8-CH₂, 12-CH₂, 18-CH₂, ArOCH₃), 4.13 (3H, s, −OCH₃), 6.84 (2H, AB, *J* = 9

Electron Transfer in C−P−Q Triads

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Hz, naphthyl 2,3-H), 8.07−8.21 (7H, m, 5Ar3,5-H, 5Ar2,6-H, 15Ar3,5-H, naphthyl 7-H), 8.44 (3H, m, 15Ar2,6-H, naphthyl 8-H), 8.90 (1H, s, naphthyl 5-H), 10.25 (2H, s, 10-CH, 20-CH); MS m/z 917 (M)$^+$; UV/vis (CH$_2$Cl$_2$) 408, 508, 542, 576, 628 nm.

Dyad 10. A solution of 100 mg (0.109 mmol) of **15** in 18 mL of dichloromethane was cooled to 0 °C and stirred under a nitrogen atmosphere as 1.1 mL (1.1 mmol) of 1 M boron tribromide in dichloromethane was added. The mixture was stirred for 20 min and then warmed to room temperature and stirred for 4 h. The mixture was diluted with dichloromethane and washed with water, dilute aqueous sodium bicarbonate, and aqueous sodium periodate. The organic layer was separated, dried over sodium sulfate, and filtered. The solvent was removed from the filtrate by distillation at reduced pressure, and the residue was chromatographed on silica gel (toluene containing 10−12% ethyl acetate) to yield 47 mg of **10** (49% yield): ^{1}H-NMR (300 MHz, CDCl$_3$) δ −2.45 (2H, brs, −NH), 1.78 (12H, t, $J = 8$ Hz, 2-CH$_3$, 8-CH$_3$, 12-CH$_3$, 18-CH$_3$), 2.47 (6H, s, 13-CH$_3$, 17-CH$_3$), 2.58 (6H, s, 3-CH$_3$, 7-CH$_3$), 4.02 (8H, m, 2-CH$_2$, 8-CH$_2$, 12-CH$_2$, 18-CH$_2$), 4.13 (3H, s, −OCH$_3$), 6.94 (2H, s, naphthyl 2,3-H), 8.12 (1H, d, $J = 8$ Hz, naphthyl 8-H), 8.13 (4H, brs, 5Ar2,3,5,6-H), 8.21 (2H, d, $J = 8$ Hz, 15Ar3,5-H), 8.28 (1H, brs, −NH), 8.39 (1H, dd, $J = 8$, 2 Hz, naphthyl 7-H), 8.45 (2H, d, $J = 8$ Hz, 15Ar2,6-H), 8.49 (1H, d, $J = 2$ Hz, naphthyl 5-H), 10.24 (2H, s, 10-CH, 20-CH); MS m/z 890 (M + 2)$^+$; UV/vis (CH$_2$Cl$_2$) 408, 508, 542, 576, 628 nm.

Model Triad 5. A 0.200-g portion (0.218 mmol) of porphyrin **15** was dissolved in 50 mL of tetrahydrofuran and 10 mL of methanol, and the solution was stirred under a nitrogen atmosphere as 2.5 mL of 10% aqueous potassium hydroxide was added dropwise. The mixture was warmed to 40 °C and stirred for 16 h. The reaction mixture was diluted with a 10% solution of methanol in chloroform, and the organic layer was washed with dilute aqueous citric acid and with water. The solvent was evaporated at reduced pressure to yield 181 mg of **16** (92% yield).

This acid (100 mg, 0.111 mmol) was suspended in 20 mL of dichloromethane under a nitrogen atmosphere. With stirring, 14 μL (0.12 mmol) of N-methylmorpholine and 22 mg (0.12 mmol) of 2-chloro-4,6-dimethoxy-1,3,5-triazine was added, and stirring was continued for 8 h. To the solution were added 56 mg (0.11 mmol) of 7′-apo-7-(4-aminophenyl)-β-carotene,[48] 14 μL (0.12 mmol) of *N*-methylmorpholine, and 14 mg (0.11 mmol) of 4-(*N,N*-dimethylamino)pyridine, and stirring was continued for 18 h. The reaction mixture was then diluted with dichloromethane and washed with dilute aqueous citric acid followed by aqueous sodium bicarbonate. The organic layer was dried with sodium sulfate and filtered. The solvent was removed from the filtrate by distillation at reduced pressure and the resulting material was chromatographed on silica gel (dichloromethane containing 1−2% acetone) to give 46 mg of **5** (30% yield): ^{1}H-NMR (300 MHz, CDCl$_3$) δ −2.40 (2H, brs, −NH), 1.04 (6H, s, Car 16-CH$_3$, Car 17-CH$_3$), 1.43−1.49 (2H, m, Car 2-CH$_2$), 1.57−1.65 (2H, m, Car 3-CH$_2$), 1.73 (3H, s, Car 18-CH$_3$), 1.78 (12H, m, 2-CH$_3$, 8-CH$_3$, 12-CH$_3$, 18-CH$_3$), 1.98 (3H, s, Car 19-CH$_3$), 1.99 (3H, s, Car 20-CH$_3$), 2.01 (3H, s, Car 20′-CH$_3$), 2.01 (2H, m, Car 4-CH$_2$), 2.09 (3H, s, Car 19′-CH$_3$), 2.47 (6H, s, 13-CH$_3$, 17-CH$_3$), 2.59 (6H, s, 3-CH$_3$, 7-CH$_3$), 4.02 (8H, m, 2-CH$_2$, 8-CH$_2$, 12-CH$_2$, 18-CH$_2$), 4.02 (3H, s, −OCH$_3$,), 4.07 (3H, s, −OCH$_3$), 6.1−7.0 (14H, m, Car =CH), 6.85 (2H, AB, $J = 8$ Hz, naphthyl 2,3-H), 7.55 (2H, d, $J = 8$ Hz, Car 1′,5′-H), 7.80 (2H, d, $J = 8$ Hz, Car 2′,4′-H), 8.05−8.30 (10H, m, 5Ar2,3,5,6-H, 15Ar2,3,5,6-H, naphthyl 7-H, −NH), 8.43 (1H, d, $J = 8$ Hz, naphthyl 8-H), 8.43 (1H, s, −NH), 8.91 (1H, d, $J = 2$ Hz, naphthyl 5-H), 10.26 (2H, s,

10-CH, 20-CH); MS m/z 1392 (M$^+$); UV/vis (CH$_2$Cl$_2$) 408, 450 (sh), 480, 510, 574, 628 nm.

Triad 2. A suspension of acid **16** (180 mg, 0.199 mmol) in 25 mL of chloroform was stirred at 0 °C under a nitrogen atmosphere as 3 mL of 1 M boron tribromide in dichloromethane was added. After stirring for 2 h, the mixture was diluted with a mixture of chloroform and methanol, washed with water until neutral, washed with dilute aqueous sodium periodate, and washed again with water. The solvent was distilled from the organic layer under vacuum to produce **dyad 17** in 82% yield.

Dyad **17** (120 mg, 0.137 mmol) was suspended in 25 mL of benzene and 0.11 mL (1.4 mmol) of pyridine. The mixture was stirred under a nitrogen atmosphere and 50 μL (0.69 mmol) of thionyl chloride was added. Stirring was continued for 1 h, and the solvent was removed by distillation at reduced pressure. The residue was dissolved in 20 mL of benzene, which was removed by distillation at reduced pressure, and 30 mL of dichloromethane, 0.11 mL of pyridine (1.4 mmol), and 76 mg (0.15 mmol) of 7′-apo-7-(4-aminophenyl)-β-carotene were added. After stirring the reaction mixture for 20 min in a nitrogen atmosphere, it was diluted with 200 mL dichloromethane and washed with aqueous sodium bicarbonate, aqueous sodium periodate, and aqueous sodium bicarbonate once again. The organic layer was dried over sodium sulfate and filtered, and the solvent was distilled under reduced pressure. Chromatography on silica gel (dichloromethane containing 2−2.5% acetone) gave triad **2** in 31% yield: ^{1}H-NMR (300 MHz, CDCl$_3$) δ −2.42 (2H, brs, −NH), 1.04 (6H, s, Car 16-CH$_3$, Car 17-CH$_3$), 1.43−1.49 (2H, m, Car 2-CH$_2$), 1.57−1.65 (2H, m, Car 3-CH$_2$), 1.73 (3H, s, Car 18-CH$_3$), 1.78 (12H, m, 2-CH$_3$, 8-CH$_3$, 12-CH$_3$, 18-CH$_3$), 1.98 (3H, s, Car 19-CH$_3$), 1.99 (3H, s, Car 20-CH$_3$), 2.01 (3H, s, Car 20′-CH$_3$), 2.01 (2H, m, Car 4-CH$_2$), 2.09 (3H, s, Car 19′-CH$_3$), 2.46 (6H, s, 13-CH$_3$, 17-CH$_3$), 2.57 (6H, s, 3-CH$_3$, 7-CH$_3$), 4.02 (8H, m, 2-CH$_2$, 8-CH$_2$, 12-CH$_2$, 18-CH$_2$), 6.1−7.0 (14H, m, Car =CH), 7.01 (2H, s, naphthyl 2,3-H), 7.54 (2H, d, $J = 8$ Hz, Car 1′,5′-H), 7.78 (2H, d, $J = 8$ Hz, Car 2′,4′-H), 8.10 (4H, brs, 5Ar2,3,5,6-H), 8.12−8.23 (5H, m, 15Ar2,3,5,6-H, naphthyl 8-H), 8.30 (1H, s, −NH), 8.43 (1H, dd, $J = 8$, 2 Hz, naphthyl 7-H), 8.57 (1H, d, $J = 2$ Hz, naphthyl 5-H), 10.25 (2H, s, 10-CH, 20-CH); MS-(FAB) m/z 1361.7575 (calcd for (M + H)$^+$, 1361.7571); UV/vis (CH$_2$Cl$_2$) 410, 450 (sh), 478, 510, 576, 626 nm.

Porphyrin 19. Porphyrin **18** (1.10 g, 1.48 mmol) was dissolved in 300 mL of concentrated hydrochloric acid and refluxed under a nitrogen atmosphere for 17 h. The mixture was cooled, water was added, and the solution was extracted with chloroform until the aqueous phase was almost colorless. The combined organic extracts were washed with aqueous sodium bicarbonate and dried over sodium sulfate, and the solvent was distilled under vacuum. The resulting solid was pure **19**, obtained in quantitative yield: ^{1}H-NMR (300 MHz, CDCl$_3$) δ −2.42 (2H, brs, −NH), 1.77 (12H, t, $J = 8$ Hz, 2-CH$_3$, 8-CH$_3$, 12-CH$_3$, 18-CH$_3$), 2.61 (12H, s, 3-CH$_3$, 7-CH$_3$, 13-CH$_3$, 17-CH$_3$), 4.03 (8H, q, $J = 8$ Hz, 2-CH$_2$, 8-CH$_2$, 12-CH$_2$, 18-CH$_2$), 7.06 (4H, d, $J = 8$ Hz, 5Ar3,5-H, 15Ar3,5-H), 7.80 (4H, d, $J = 8$ Hz, 5Ar2,6-H, 15Ar2,6-H), 10.22 (2H, s, 10-CH, 20-CH); MS m/z 662 (M + 2)$^+$; UV/vis (CH$_2$Cl$_2$) 410, 508, 542, 576, 628 nm.

Porphyrin 20. Porphyrin **19** (1.00 g, 1.51 mmol) was dissolved in 500 mL of dichloromethane and 15 mL of pyridine, and the solution was stirred under a nitrogen atmosphere and cooled to 0 °C. Trifluoroacetic anhydride (5 mL, excess) was added dropwise, and the mixture was stirred for 20 min, diluted with dichloromethane, washed with aqueous citric acid, aqueous sodium bicarbonate, and aqueous sodium carbonate, and dried over sodium sulfate. The solvent was distilled at reduced

pressure, and the residue was chromatographed on silica gel (dichloromethane containing 1−3% acetone). The crude **20** from the column was recrystallized from a mixture of dichloromethane and methanol to yield 0.84 g of pure **20** (65% yield): ^{1}H-NMR (300 MHz, CDCl$_3$) δ −2.42 (2H, brs, −NH), 1.78 (12H, t, $J = 8$ Hz, 2-CH$_3$, 8-CH$_3$, 12-CH$_3$, 18-CH$_3$), 2.52 (12H, s, 3-CH$_3$, 7-CH$_3$, 13-CH$_3$, 17-CH$_3$), 4.02 (8H, q, $J = 8$ Hz, 2-CH$_2$, 8-CH$_2$, 12-CH$_2$, 18-CH$_2$), 8.00 (4H, d, $J = 8$ Hz, 5Ar3,5-H, 15Ar3,5-H), 8.13 (4H, d, $J = 8$ Hz, 5Ar2,6-H, 15Ar2,6-H), 8.20 (1H, brs, −NH), 10.25 (2H, s, 10-CH, 20-CH); MS m/z 853 (M + 1)$^+$; UV/vis (CH$_2$Cl$_2$) 408, 508, 542, 576, 628 nm.

Porphyrin 21. Porphyrin **20** (120 mg, 0.141 mmol) was dissolved in 20 mL of tetrahydrofuran and 10 mL of methanol and stirred under a nitrogen atmosphere as 3 mL of a 10% aqueous solution of potassium hydroxide was added. Stirring was continued for 2.5 h, and the reaction mixture was diluted with dichloromethane and washed twice with water and then with aqueous sodium bicarbonate. The solvent was removed by distillation at reduced pressure, and the residue was chromatographed on silica gel (dichloromethane containing 0.5−5% acetone) to give 38 mg of **21** (36% yield) as well as starting material **20** and porphyrin **19**, both of which could be recycled to yield more **21**: ^{1}H-NMR (300 MHz, CDCl$_3$) δ −2.42 (2H, brs, −NH), 1.76 (12H, t, $J = 8$ Hz, 2-CH$_3$, 8-CH$_3$, 12-CH$_3$, 18-CH$_3$), 2.49 (6H, s, 13-CH$_3$, 17-CH$_3$), 2.60 (6H, s, 3-CH$_3$, 7-CH$_3$), 3.98−4.05 (8H, m, 2-CH$_2$, 8-CH$_2$, 12-CH$_2$, 18-CH$_2$), 7.05 (2H, d, $J = 8$ Hz, 5Ar3,5-H) 7.78 (2H, d, $J = 8$ Hz, 5Ar2,6-H), 7.94 (2H, d, $J = 8$ Hz, 15Ar3,5-H), 8.09 (2H, d, $J = 8$ Hz, 15Ar2,6-H), 8.20 (1H, brs, −NH), 10.22 (2H, s, 10-CH, 20-CH); MS m/z 757 (M + 1)$^+$; UV/vis (CH$_2$Cl$_2$) 410, 508, 542, 576, 628 nm.

Porphyrin 22. A mixture of 6-carboxy-1,4-dimethoxynaphthalene (46 mg, 0.20 mmol), 2-chloro-4,6-dimethoxy-1,3,5-triazine (37 mg, 0.21 mmol), and *N*-methylmorpholine (23 μL, 0.21 mmol) in 15 mL of dichloromethane under a nitrogen atmosphere was stirred at 0 °C for 5 min and then at room temperature for 2.5 h. To the resulting pale yellow solution was added porphyrin **21** (100 mg, 0.132 mmol), *N*-methylmorpholine (23 μL, 0.21 mmol), and 4-(*N*,*N*-dimethylamino)pyridine (24 mg, 0.20 mmol). The resulting solution was stirred for 20 h under a nitrogen atmosphere. Dilute aqueous sodium bicarbonate (10 mL) was added, and the mixture was stirred for an additional 3 h. The mixture was then diluted with 200 mL of dichloromethane; washed with dilute sodium bicarbonate solution, dilute aqueous citric acid, and dilute sodium bicarbonate; dried over sodium sulfate; and filtered; and the solvent was distilled at reduced pressure. Recrystallization of the resulting solid from dichloromethane/methanol gave 109 mg of **22** (85%): ^{1}H-NMR (300 MHz, CDCl$_3$) δ −2.41 (2H, brs, −NH), 1.77 (6H, t, $J = 8$ Hz, 12-CH$_3$, 18-CH$_3$), 1.78 (6H, t, $J = 8$ Hz, 2-CH$_3$, 8-CH$_3$), 2.51 (6H, s, 13-CH$_3$, 17-CH$_3$), 2.59 (6H, s, 3-CH$_3$, 7-CH$_3$), 4.02 (8H, m, 2-CH$_2$, 8-CH$_2$, 12-CH$_2$, 18-CH$_2$), 4.07 (6H, s, ArOCH$_3$), 6.85 (2H, AB, $J = 9$ Hz, naphthyl 2,3-H), 7.97 (2H, d, $J = 8$ Hz, 15Ar3,5-H), 8.00−8.18 (6H, m, 5Ar3,5-H, 5Ar2,6-H, 15Ar2,6-H), 8.20 (1H, dd, $J = 9,2$ Hz, naphthyl 7-H), 8.24 (1H, brs, -NH), 8.43 (2H, m, naphthyl 8-H, −NH), 8.90 (1H, d, $J = 2$ Hz, naphthyl 5-H), 10.24 (2H, s, 10-CH, 20-CH); MS m/z 971 (M + 1)$^+$; UV/vis (CH$_2$Cl$_2$) 408, 508, 542, 576, 628 nm.

Porphyrin 23. To a stirred solution of porphyrin **22** (0.300 g, 0.309 mmol) in 80 mL of tetrahydrofuran and 40 mL of methanol under a nitrogen atmosphere was added 12 mL of a 10% aqueous solution of potassium hydroxide. The mixture was stirred for 48 h, and about half of the solvent was removed by distillation at reduced pressure. The remainder was diluted

with dichloromethane, washed with water, dried over sodium sulfate, and filtered. The solvent was removed by distillation at reduced pressure, and the residue was recrystallized from dichloromethane and methanol to give 0.261 g of **23** (96% yield): ^{1}H-NMR (300 MHz, CDCl$_3$) δ −2.40 (2H, brs, −NH), 1.78 (12H, t, $J = 8$ Hz, 2-CH$_3$, 8-CH3, 12-CH$_3$, 18-CH$_3$), 2.59 (6H, s, 13-CH$_3$, 17-CH$_3$ or 3-CH$_3$, 7-CH$_3$), 2.61 (6H, s, 3-CH$_3$, 7-CH$_3$ or 13-CH$_3$, 17-CH$_3$), 4.01, (6H, s, ArOCH$_3$), 4.01−4.06 (8H, m, 2-CH$_2$, 8-CH$_2$, 12-CH$_2$, 18-CH$_2$), 6.83 (2H, AB, $J = 9$ Hz, naphthyl 2,3-H), 7.06 (2H, d, $J = 8$ Hz, 15Ar3,5-H), 7.79 (2H, d, $J = 8$ Hz, 15Ar2,6-H), 8.14 (4H, AB, $J = 8$ Hz, 5Ar2,3,5,6-H), 8.19 (1H, dd, $J = 9$, 2 Hz, naphthyl 7-H), 8.42 (1H, d, $J = 9$ Hz, naphthyl 8-H,), 8.43 (1H, brs, −NH), 8.90 (1H, d, $J = 2$ Hz, naphthyl 5-H), 10.23 (2H, s, 10-CH, 20-CH); MS m/z 874 (M + 1)$^+$; UV/vis (CH$_2$Cl$_2$) 408, 508, 542, 576, 628 nm.

Model Triad 4. To a 50-mL flask under a nitrogen atmosphere were added 46 mg (0.086 mmol) of 7′-apo-7′-(4-carboxyphenyl)-β-carotene,[49] 12 mL of dichloromethane, 10 μL (0.091 mmol) of *N*-methylmorpholine, and 16 mg (0.091 mmol) of 2-chloro-4,6-dimethoxy-1,3,5-triazine. The mixture was stirred for 2 h, and 50 mg (0.057 mmol) of porphyrin **23** was added, along with 10 μL (0.091 mmol) of *N*-methylmorpholine and 11 mg (0.091 mmol) of 4-(*N*,*N*-dimethylamino)pyridine. After the mixture was stirred for 17 h, aqueous sodium bicarbonate was added, and the mixture stirred for 1.5 h. Dichloromethane was added, and the resulting mixture was washed with water, dilute aqueous citric acid, and dilute aqueous sodium bicarbonate. Sodium sulfate was used to dry the organic phase, and after filtering, the solvent was distilled at reduced pressure. Chromatography of the residue on silica gel (dichloromethane containing 1−2% acetone) gave crude product, which was recrystallized from dichloromethane and methanol to give 57 mg of **4** (71% yield): ^{1}H-NMR (300 MHz, CDCl$_3$) δ −2.40 (2H, brs, −NH), 1.04 (6H, s, Car 16-CH$_3$, Car 17-CH$_3$), 1.43−1.52 (2H, m, Car 2-CH$_2$), 1.57−1.68 (2H, m, Car 3-CH$_2$), 1.73 (3H, s, Car 18-CH$_3$), 1.78 (12H, m, 2-CH$_3$, 8-CH$_3$, 12-CH$_3$, 18-CH$_3$), 1.99 (3H, s, Car 19-CH$_3$), 2.00 (3H, s, Car 20-CH$_3$), 2.01 (3H, s, Car 20′-CH$_3$), 2.01 (2H, m, Car 4-CH$_2$), 2.10 (3H, s, Car 19′-CH$_3$), 2.56 (6H, s, 13-CH$_3$, 17-CH$_3$), 2.59 (6H, s, 3-CH$_3$, 7-CH$_3$), 4.02 (3H, s, ArOCH$_3$), 4.02 (8H, m, 2-CH$_2$, 8-CH$_2$, 12-CH$_2$, 18-CH$_2$), 4.07, (3H, s, ArOCH$_3$), 6.1−6.8 (13H, m, Car =CH−), 6.84 (2H, AB, $J = 9$ Hz, naphthyl 2,3-H), 7.07 (1H, d, $J = 16$ Hz, Car 8′-H), 7.62 (2H, d, $J = 8$ Hz, Car 1′,5′-H), 7.97−8.23 (12H, m, Car 2′,4′-H, 5Ar2,3,5,6-H, 15Ar2,3,5,6-H, naphthyl 7-H, -NH), 8.42 (1H, d, $J = 9$ Hz, naphthyl 8-H,), 8.44 (1H, brs, −NH), 8.90 (1H, brs, naphthyl 5-H), 10.24 (2H, s, 10-CH, 20-CH); MS m/z 1393 (M + H)$^+$; UV/vis (CH$_2$Cl$_2$) 410, 450 (sh), 484, 512, 574, 626 nm.

Porphyrin 25. To porphyrin **23** (100 mg, 0.114 mmol) in 30 mL of dichloromethane was added 2 mL (excess) of acetic anhydride and 0.100 g (excess) of 4-(*N*,*N*-dimethylamino)-pyridine. The mixture was stirred for 15 min, dilute aqueous sodium bicarbonate was added, and stirring was continued for 2 h. The organic layer was separated and washed twice with water, and the solvent was distilled at reduced pressure. Recrystallization of the residue from chloroform and methanol gave 102 mg of **25** (97% yield): ^{1}H-NMR (300 MHz, CDCl$_3$) δ −2.42 (2H, brs, −NH), 1.76 (6H, t, $J = 8$ Hz, 12-CH$_3$, 18-CH$_3$), 1.78 (6H, t, $J = 8$ Hz, 2-CH$_3$, 8-CH$_3$), 2.34 (3H, s, CH$_3$C-(O)) 2.52 (6H, s, 13-CH$_3$, 17-CH$_3$), 2.59 (6H, s, 3-CH$_3$, 7-CH$_3$), 3.98−4.06 (8H, m, 2-CH$_2$, 8-CH$_2$, 12-CH$_2$, 18-CH$_2$), 4.01 (3H, s, ArOCH$_3$), 4.06 (3H, s, ArOCH$_3$), 6.84 (2H, AB, $J = 8$ Hz, naphthyl 2,3-H), 7.49 (1H, s, −NH), 7.87 (2H, d, $J = 8$ Hz, 15Ar3,5-H), 7.99 (2H, d, $J = 8$ Hz, 15Ar2,6-H), 8.09 (2H, d, $J = 8$ Hz, 5Ar3,5-H or 5Ar2,6-H), 8.15 (2H, d, $J = 8$ Hz,

Electron Transfer in C−P−Q Triads

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5Ar2,6-H or 5Ar3,5-H), 8.19 (1H, dd, J = 8, 2 Hz, naphthyl 7-H), 8.42 (1H, d, J = 8 Hz naphthyl 8-H), 8.45 (1H, s, −NH), 8.90 (1H, d, J = 2 Hz, naphthyl 5-H), 10.23 (2H, s, 10-CH, 20-CH); MS m/z 916 (M + 1)$^+$; UV/vis (CH$_2$Cl$_2$) 410, 508, 542, 576, 628 nm.

Dyad 6. Porphyrin **25** (90 mg, 0.098 mmol) was mixed with 25 mL of dichloromethane, and the suspension was cooled to 0 °C and stirred under a nitrogen atmosphere. A 1 M solution of boron tribromide in dichloromethane (1 mL, excess) was added, and the mixture was stirred for 5 h. Chloroform was added, followed by methanol, and the resulting solution was washed with water, aqueous sodium periodate, and aqueous sodium bicarbonate. Methanol was added to the organic phase, and the chloroform was removed by distillation at reduced pressure. A solid precipitated and was chromatographed on deactivated silica gel (1% water added) (dichloromethane and 5−10% acetone) to yield 67 mg of **6** (77% yield): H-NMR (300 MHz, CDCl$_3$) δ −2.44 (2H, brs, −NH), 1.77 (12H, t, J = 8 Hz, 2-CH$_3$, 8-CH$_3$, 12-CH$_3$, 18-CH$_3$), 2.36 (3H, s, CH$_3$C(O)) 2.53 (6H, s, 13-CH$_3$, 17-CH$_3$), 2.57 (6H, s, 3-CH$_3$, 7-CH$_3$), 4.01 (8H, q, J = 8 Hz, 2-CH$_2$, 8-CH$_2$, 12-CH$_2$, 18-CH$_2$), 6.91 (2H, s, naphthyl 2,3-H), 7.52 (1H, brs, −NH), 7.90 (2H, d, J = 8 Hz, 15Ar3,5-H), 8.01 (2H, d, J = 8 Hz, 15Ar2,6-H), 8.12 (1H, d, J = 8 Hz, naphthyl 8-H), 8.13 (4H, brs, 5Ar2,3,5,6-H), 8.32 (1H, brs, −NH), 8.40 (1H, dd, J = 8, ∼2 Hz, naphthyl 7-H), 8.49 (1H, brs, naphthyl 5-H), 10.21 (2H, s, 10-CH, 20-CH); MS m/z 888 (M + 2)$^+$; UV/vis (CH$_2$Cl$_2$) 410, 508, 542, 576, 628 nm.

Porphyrin 24. Porphyrin **23** (150 mg, 0.171 mmol) was mixed with 20 mL of dichloromethane, and the suspension was cooled to 0 °C and stirred under a nitrogen atmosphere. A 1 M solution of boron tribromide in dichloromethane (1.5 mL, excess) was added dropwise, and the mixture was stirred for 10 min at 0 °C and for 2 h at ambient temperature. Chloroform was added, followed by methanol, and the resulting solution was washed with water, aqueous sodium bicarbonate, aqueous sodium periodate, and aqueous sodium bicarbonate. The chloroform was removed by distillation at reduced pressure, and the residue was chromatographed on silica gel (dichloromethane and 3−5% acetone) to give 110 mg of **24** (76% yield): H-NMR (300 MHz, CDCl$_3$) δ −2.44 (2H, brs, −NH), 1.78 (12H, t, J = 8 Hz, 2-CH$_3$, 8-CH3, 12-CH$_3$, 18-CH$_3$), 2.58 (6H, s, 3-CH$_3$, 7-CH$_3$), 2.62 (6H, s, 13-CH$_3$, 17-CH$_3$), 4.03 (8H, q, J = 8 Hz, 2-CH$_2$, 8-CH$_2$, 12-CH$_2$, 18-CH$_2$), 6.83 (2H, s, naphthyl 2,3-H), 7.07 (2H, d, J = 8 Hz, 15Ar3,5-H), 7.81 (2H, d, J = 8 Hz, 15Ar2,6-H), 7.99 (1H, d, J = 8 Hz, naphthyl 8-H), 8.13 (5H, m, 5Ar2,3,5,6-H, −NH), 8.30 (1H, dd, J = 8, 2 Hz, naphthyl 7-H), 8.36 (1H, d, J = 2 Hz, naphthyl 5-H), 10.21 (2H, s, 10-CH, 20-CH); MS m/z 845 (M + 1)$^+$; UV/vis (CH$_2$Cl$_2$) 410, 508, 542, 576, 628 nm.

Triad 1. To a 100-mL flask under a nitrogen atmosphere were added 95 mg (0.18 mmol) of 7′-apo-7′-(4-carboxyphenyl)-β-carotene,[49] 20 mL of dichloromethane, 20 μL (0.19 mmol) of N-methylmorpholine, and 33 mg (0.19 mmol) of 2-chloro-4,6-dimethoxy-1,3,5-triazine. The mixture was stirred for 3 h and then added to a flask containing a solution of 100 mg (0.118 mmol) of porphyrin **24** in dichloromethane, along with 20 μL (0.19 mmol) of N-methylmorpholine and 23 mg (0.19 mmol) of 4-(N,N-dimethylamino)pyridine. After the solution was stirred for 2 h, aqueous sodium bicarbonate was added, and the mixture was stirred for 30 min. Dichloromethane was added and the organic layer was separated. The aqueous layer was extracted with dichloromethane to remove additional colored material. The combined organic extracts were washed with dilute aqueous sodium periodate and dilute aqueous sodium bicarbonate. Sodium sulfate was used to dry the organic phase, and after filtering, the solvent was distilled at reduced pressure.

Chromatography of the residue on silica gel (dichloromethane containing 2−4% acetone) gave 27 mg of **1** (17% yield): ^{1}H-NMR (300 MHz, CDCl$_3$) δ −2.44 (2H, brs, −NH), 1.04 (6H, s, Car 16-CH$_3$, Car 17-CH$_3$), 1.44−1.54 (2H, m, Car 2-CH$_2$), 1.57−1.68 (2H, m, Car 3-CH$_2$), 1.73 (3H, s, Car 18-CH$_3$), 1.76 (12H, t, J = 8 Hz, 2-CH$_3$, 8-CH3, 12-CH$_3$, 18-CH$_3$), 1.99 (3H, s, Car 19-CH$_3$), 2.00 (3H, s, Car 20-CH$_3$), 2.01 (3H, s, Car 20′-CH$_3$), 2.01 (2H, m, Car 4-CH$_2$), 2.10 (3H, s, Car 19′-CH$_3$), 2.57 (12H, s, 3-CH$_3$, 7-CH$_3$, 13-CH$_3$, 17-CH$_3$), 4.00 (8H, m, 2-CH$_2$, 8-CH$_2$, 12-CH$_2$, 18-CH$_2$), 6.1−6.8 (13H, m, Car ═CH−), 6.82 (2H, brs, naphthyl 2,3-H), 7.05 (1H, d, J = 15 Hz, Car 8′-H), 7.60 (2H, d, J = 8 Hz, Car 1′,5′-H), 7.99 (2H, d, J = 8 Hz, Car 2′,4′-H) 8.07 (5 H, brs, 15Ar2,3,5,6-H, naphthyl 8-H), 8.13 (4H, brs, 5Ar2,3,5,6-H), 8.20 (1H, brs, −NH), 8.34 (2H, m, naphthyl 7-H, −NH), 8.43 (1H, brs, naphthyl 5-H), 10.19 (2H, s, 10-CH, 20-CH); MS(FAB) m/z 1361.7567 (calcd for (M + H)$^+$, 1361.7571); UV/vis (CH$_2$Cl$_2$) 410, 450 (sh), 484, 510, 574, 628 nm.

Dyad 9. A 120-mg portion (0.0179 mmol) of 5-(4-aminophenyl)-10,15,20-(4-methylphenyl)porphyrin was dissolved in 15 mL of dichloromethane and 54 mg (0.23 mmol) of 6-carboxy-1,4-dimethoxynaphthalene and 4.0 mg (0.036 mmol) of 4-(N,N-dimethylamino)pyridine were added. The mixture was stirred under a nitrogen atmosphere, and 55 mg (0.27 mmol) of dicyclohexylcarbodiimide was added. The mixture was stirred for a total of 48 h, with three periodic additions of 30-mg portions of dicyclohexylcarbodiimide. The mixture was then washed with dilute aqueous citric acid and dilute aqueous sodium bicarbonate, dried with sodium sulfate, and filtered. The solvent was distilled at reduced pressure and the crude produce was chromatographed on silica gel (dichloromethane containing 1% acetone), and the resulting protected dyad recrystallized from dichloromethane and methanol (132 mg, 83% yield).

The protected dyad (100 mg, 0.113 mmol) was dissolved in 30 mL dichloromethane and stirred under a nitrogen atmosphere as 1.13 mL of 1 M boron tribromide in dichloromethane (1.13 mmol) was added dropwise. After 3 h, the solution was diluted with dichloromethane and washed with dilute aqueous sodium bicarbonate, aqueous sodium periodate, and again with aqueous sodium bicarbonate. After the solution was dried with sodium sulfate, the solvent was distilled at reduced pressure, and the residue was chromatographed on silica gel (dichloromethane containing 1% acetone) to give 84 mg dyad **9** (86% yield): ^{1}H NMR (300 MHz, CDCl$_3$) δ −2.90 (2H, s, −NH), 2.70 (9H, s, ArCH$_3$), 6.66 (2H, s, naphthyl 2,3-H), 7.56 (6H, d, J = 8 Hz, 10,15,20Ar3,5-H), 7.74 (1H, d, J = 8 Hz, naphthyl 8-H), 8.05 (2H, d, J = 8 Hz, 5Ar3,5-H), 8.12 (7H, m, 10,15,20-Ar2,6-H, naphthyl 5-H), 8.16 (1H, dd, J = 8, 2 Hz, naphthyl 7-H), 8.27 (2H, d, J = 8 Hz, 5Ar2,6-H), 8.84−8.93 (8H, m, pyrrole-H); MS m/z 857 (M + 1)$^+$; UV/vis (CH$_2$Cl$_2$) 418, 518, 554, 594, 650 nm.

Instrumental Techniques. The ^{1}H NMR spectra were recorded on Varian Unity spectrometers at 300 or 500 MHz. Unless otherwise specified, samples were dissolved in deuteriochloroform with tetramethylsilane as an internal reference. High-resolution mass spectra were obtained on a Kratos MS 50 mass spectrometer operating at 8 eV in FAB mode. Other mass spectra were obtained on a Varian MAT 311 spectrometer operating in EI mode or a matrix-assisted laser desorption/ionization time-of-flight spectrometer (MALDI-TOF). Ultraviolet−visible spectra were measured on a Shimadzu UV2100U UV-VIS spectrometer, and fluorescence spectra were measured on a SPEX Fluorolog using optically dilute samples and corrected. Cyclic voltammetric measurements were carried out with a Pine Instrument Company Model AFRDE4 potentiostat. The electrochemical measurements were performed in benzoni-

trile at ambient temperatures with a glassy carbon working electrode, a Ag/Ag$^+$ reference electrode, and a platinum wire counter electrode. The electrolyte was 0.1 M tetra-*n*-butylammonium hexafluorophosphate, and ferrocene was employed as an internal reference redox system.

Fluorescence decay measurements were performed on ~1 × 10^{-5} M solutions by the time-correlated single photon counting method. The excitation source was a cavity-dumped Coherent 700 dye laser pumped by a frequency-doubled Coherent Antares 76s Nd:YAG laser.[50] The instrument response function was 35 ps, as measured at the excitation wavelength for each decay experiment with Ludox AS-40.

Nanosecond transient absorption measurements were made with excitation from an Opotek optical parametric oscillator pumped by the third harmonic of a Continuum Surelight Nd: YAG laser. The pulse width was ~5 ns, and the repetition rate was 10 Hz. The detection portion of the spectrometer has been described elsewhere.[51]

Transient absorption measurements on the subpicosecond time scale were made using the pump−probe technique. The sample was dissolved in purified solvent and the resulting solution was circulated by magnetic stirring in a cuvette having a 2-mm path length in the beam area. Excitation was at 590 nm with 150−200 fs, 30 μJ pulses at a repetition rate of 540 Hz. The signals from the continuum-generated white-light probe beam were collected by an optical spectrometric multichannel analyzer with a dual diode array detector head.[52]

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