of the upper empty set. Note the close correspondence between this picture and that used to describe the bonding in $\mathrm{Rh_3(CNR)_{12}}^{3+}$[22] and stacked trimer units of $(\mathrm{Pt(CN)_4}^{2-})_3$[23] with the filled 6s orbital of thallium(I) having similar characteristics to the filled d_{z^2} orbital in planar d^8 complexes. The strong 27 000-$\mathrm{cm^{-1}}$ absorption is assigned to a spin and symmetry allowed $a_{1g} \rightarrow a_{2u}$ transition. The molecular orbital diagram accounts for the occurrence of this feature at lower energies than the s → p transition in Tl(I) or the $d_{z^2} \rightarrow p,\pi$ transition in $\mathrm{Pt(CN)_4}^{2-}$. On the basis of its long lifetime, the luminescence is assigned to the spin forbidden $a_{2u} \rightarrow a_{1g}$ process (phosphorescence).

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Supplementary Material Available: Tables of atomic positional parameters, bond distances, bond angles, anisotropic thermal parameters, and data collection parameters for $\mathrm{Tl_2Pt(CN)_4}$ (3 pages); tables of observed and calculated structure factors for $\mathrm{Tl_2Pt(CN)_4}$ (4 pages). Ordering information is given on any current masthead page.

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Photoinitiated Charge Separation in a Carotenoid-Porphyrin-Diquinone Tetrad: Enhanced Quantum Yields via Multistep Electron Transfers

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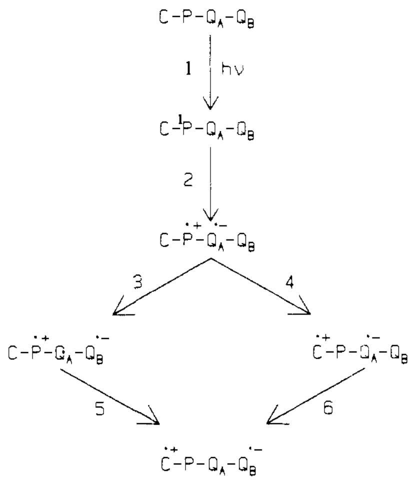
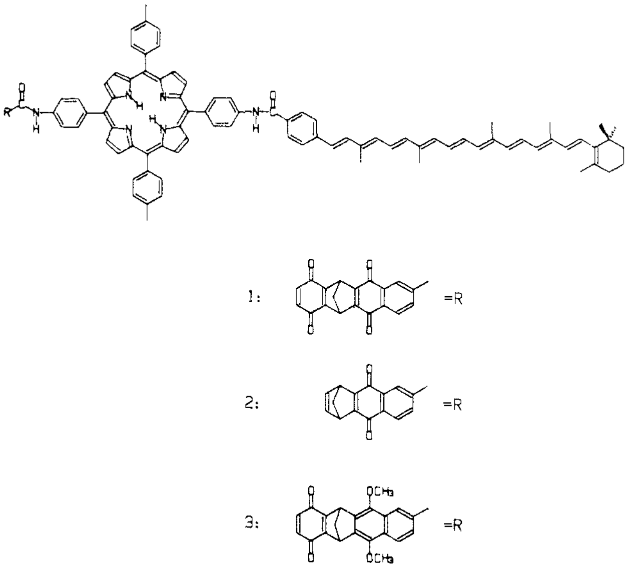
Scheme I





Photosynthesis converts light to chemical potential energy in the form of long-lived charge separation across a bilayer membrane. Recombination of the charge-separated state is prevented by the large distance between the final electron donor and acceptor. Because the quantum yield of a single long-range electron transfer across the bilayer would be vanishingly small, reaction centers employ a series of electron-transfer steps, each of which occurs over a short distance with high yield. Synthetic carotenoid-porphyrin-quinone triad molecules[1-8] and other molecular systems[9-12] which begin to model this approach have recently been reported. In photosynthetic bacteria, the charge separation sequence includes electron donation from a bacteriopheophytin to a quinone which then transfers an electron to a second quinone. An elegant molecule that models such electron transfer has been prepared,[12] although it did not reproduce the long-lived charge separation characteristic of the natural system. We now report the synthesis of a tetrachromophoric molecule **1** consisting of a porphyrin (P) covalently linked to both a carotenoid polyene (C) and a rigid diquinone moiety ($\mathrm{Q_A}$-$\mathrm{Q_B}$), excitation of which pro-

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duces a long-lived (460 ns in dichloromethane, 4 μs in acetonitrile) charge-separated state $C^{\bullet+}$–P–Q_A–$Q_B^{\bullet-}$ with a quantum yield of 0.23 at ambient temperatures and 0.50 at 240 K. Comparison of these results with those for related triads **2** and **3** clearly demonstrates that although the tetrad is a considerably more complex molecular device, the additional electron-transfer steps lead to an increased quantum yield of long-lived, high-energy charge-separated states.

Excitation of **1**[13] in dichloromethane at 295 K resulted in the observation of the transient spectrum (λ_{max} = 970 nm) of a carotenoid radical cation (ϕ = 0.23,[14] τ = 460 ns, Figure 1). On the basis of the evidence presented below and by analogy with related systems[1-9,11,12,15-17] this cation spectrum may be ascribed to the species $C^{\bullet+}$–P–Q_A–$Q_B^{\bullet-}$. A reasonable pathway for the formation of this charge-separated state is shown in Scheme I, although direct observation of all of the proposed intermediate species must await picosecond transient absorption studies. The porphyrin first excited singlet state donates an electron to Q_A to form C–$P^{\bullet+}$–$Q_A^{\bullet-}$–Q_B (step 2).[1-9,12,15-17] The rate constant for step 2 (as determined by a comparison of the porphyrin fluorescence decay of **1** with that of related model compounds in which no electron transfer is possible) was found to be $\geq 2 \times 10^{10}$ s^{-1}. Although C–$P^{\bullet+}$–$Q_A^{\bullet-}$–Q_B should tend to rapidly undergo charge recombination,[1-9] two additional electron transfers, steps 3 and 4, compete with the back reaction and lead to two new intermediate charge-separated states which decay to $C^{\bullet+}$–P–Q_A–$Q_B^{\bullet-}$ via steps 5 and 6. Step 3 is exergonic by ~180 mV, as shown by cyclic voltammetric studies of the diquinone moiety, and step 4 is analogous to electron-transfer reactions observed in C–P–Q triads.[1-8]

The synergistic effects of multiple electron transfers in **1** are revealed by comparison with model systems. Triad **2** resembles **1** but lacks quinone Q_B. The carotenoid radical cation transient obtained upon excitation of **2** (Figure 1) represents $C^{\bullet+}$–P–$Q^{\bullet-}$, which is formed with a quantum yield of ca. 0.04 and decays with a lifetime of ca. 70 ns. Thus, addition of the second quinone in **1** has resulted in both a greatly enhanced quantum yield and a much longer lifetime for the final charge-separated state. Because the quantum yield for the initial photodriven electron transfer is high (>0.98) for both molecules, the low overall quantum yield for **2** demonstrates that the electron transfer analogous to step 4 does not compete effectively with charge recombination of C–$P^{\bullet+}$–$Q^{\bullet-}$. With **1**, the rate of step 4 would be expected to be essentially the same as for **2**. But, with **1** step 3 also competes with charge recombination to yield C–$P^{\bullet+}$–Q_A–$Q_B^{\bullet-}$. Since both this species and $C^{\bullet+}$–P–$Q_A^{\bullet-}$–Q_B would be expected to have relatively long lifetimes, steps 5 and 6 should be very efficient. The enhanced lifetime for **1** is doubtless a result of the increased donor–acceptor separation in $C^{\bullet+}$–P–Q_A–$Q_B^{\bullet-}$ relative to $C^{\bullet+}$–P–$Q^{\bullet-}$. Direct electron transfer from the quinone to the carotenoid will be slow because the long, rigid molecule prevents close approach of these two moieties. A multistep charge recombination reaction[7] would require slow endergonic electron transfer to return to $C^{\bullet+}$–P–$Q_A^{\bullet-}$–Q_B and/or C–$P^{\bullet+}$–Q_A–$Q_B^{\bullet-}$ followed by either direct charge recombination or an additional endergonic step to reach C–$P^{\bullet+}$–$Q_A^{\bullet-}$–Q_B.

A second tetrad, **3**, yields $C^{\bullet+}$–P–$Q_A(OMe)_2$–$Q_B^{\bullet-}$ upon excitation (Figure 1). This charge-separated state is formed with a lower quantum yield (0.11) than is the final state in **1**, but the lifetime is somewhat longer (1.9 μs). The higher quantum yield for **1** may be ascribed to the additional electron-transfer steps. The initial charge separation in **3** must occur directly from C–^{1}P–$Q_A(OMe)_2$–Q_B to yield C–$P^{\bullet+}$–$Q_A(OMe)_2$–$Q_B^{\bullet-}$ with a quantum yield of 0.77 as calculated from fluorescence decay measurements (rate constant for step 2 = 9.6×10^8 s^{-1}). The overall quantum yield is further limited by slow electron transfer from the carotenoid moiety which must compete with rapid recombination to the ground state. In **1**, however, the reduced donor–acceptor separation leads to a faster electron transfer rate and a higher quantum yield for the initial electron transfer (>0.98) in spite of the reduced exergonicity due to the substitution of a naphthoquinone for a benzoquinone. Once formed, C–$P^{\bullet+}$–$Q_A^{\bullet-}$–Q_B may attain the final state by either of two pathways which compete with charge recombination, as discussed above.

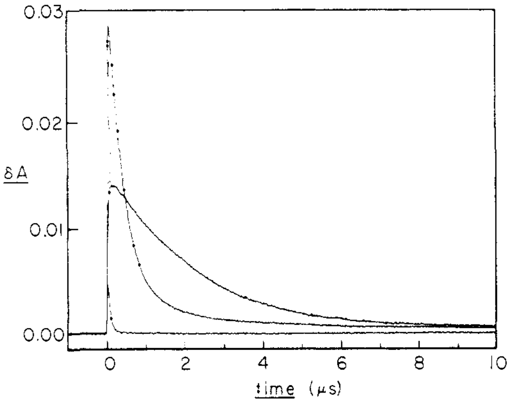

Figure 1. Transient absorption (980 nm) of ca. 1×10^{-4} M solutions of **1** (upper trace), **2** (lower trace), and **3** (middle trace) in dichloromethane at ambient temperature following laser excitation[7] with 15-ns pulses of 590-nm light. Curves have been normalized to the same absorption at the excitation wavelength so that relative transient absorption reflects relative quantum yield. These decay curves display a major, short-lived, exponential component due to unimolecular charge recombination superimposed on a minor, long-lived, concentration-dependent component presumably due to electron transfer between the intramolecular charge-separated state and a neutral molecule.[7] The lifetimes given in the text were determined from decays measured in dilute solutions which could be fit satisfactorily as single exponentials.

Examination of the results for some other systems in which porphyrins are linked to benzoquinone derivatives[8,15-17] would suggest that electron transfer from the porphyrin first excited singlet state to the quinone in **3** should be very slow at such large donor–acceptor separations and that the quantum yield should be insignificant. The relatively high quantum yield actually observed likely indicates the participation of the dimethoxynaphthalene π-electron system and perhaps the bicyclic bridge in the electron-transfer process. The involvement of both σ and π orbitals in electron-transfer reactions has recently been reported.[18-22]

It is not surprising that the final charge-separated states in **1** and **3** have somewhat different lifetimes, as the molecules differ structurally and have different pathways available for recombination (e.g., **1**, but not **3**, could recombine via the reverse of step 6).

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(13) The synthesis and characterization by mass, UV–vis, and nuclear magnetic resonance spectrometry of the molecules discussed in this paper will be reported elsewhere.

(14) Quantum yields are based on published extinction coefficients for transient species (carotenoid radical cations and porphyrin triplet states) which are not accurately known.[3]

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Evidence for the Generation of α-Carboxy-α-hydroxy-*p*-xylylene from *p*-(Bromomethyl)mandelate by Mandelate Racemase

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Mandelate racemase [EC 5.1.2.2] from *Pseudomonas putida* catalyzes the interconversion of (*R*)- and (*S*)-mandelates and requires only a divalent cation (e.g., Mg^{2+}) for this reaction that presumably proceeds via a carbanionic intermediate.[1] Concern over the intermediacy of such a high-energy carbanion[2] and our recent interest in the generation of quino dimethane derivatives[3] have prompted us to synthesize *p*-(bromomethyl)mandelate (**1**) and evaluate its reaction with mandelate racemase. We report here that reaction of **1** with the racemase uniquely affords *p*-methylbenzoylformate (**4**) and bromide elimination. These findings, consonant with our previous work on a related system,[3] provide a strong argument for the intermediacy of the carbanion **2** and of the unusual *p*-xylylene derivative **3** (Scheme I).

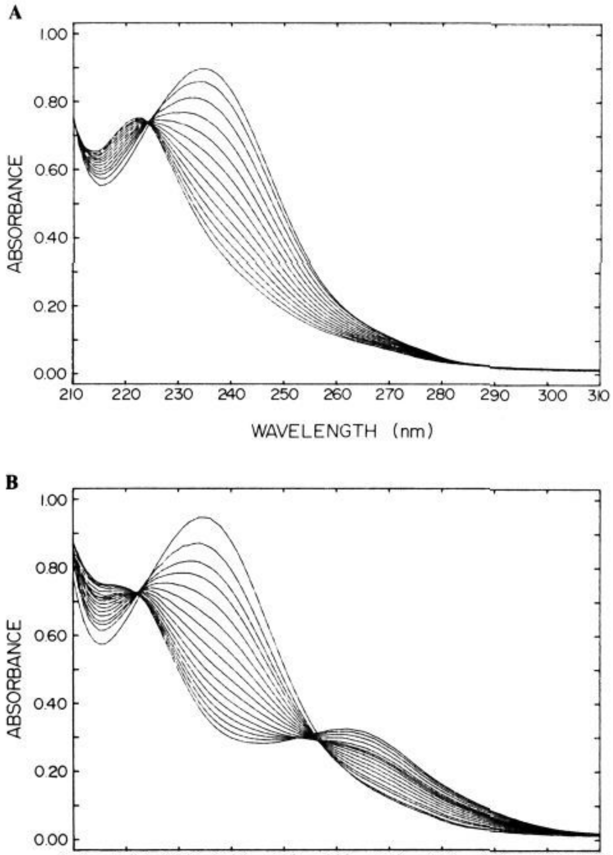
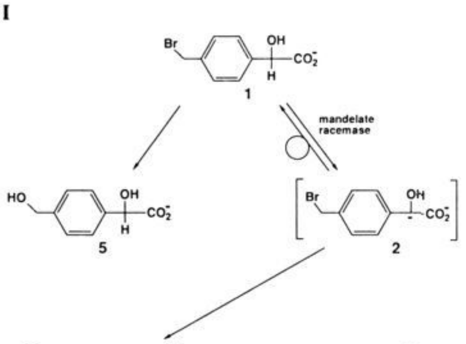


Figure 1. UV spectra (1-mm pathlength) of the chemical and enzymatic reactions of *p*-(bromomethyl)mandelate (**1**; 1 mM; λ_{max} 235 nm) in 0.1 M MES (pH 6.0) and 1 mM $MgCl_2$: (a) solvolysis (5-min intervals) and (b) reaction with mandelate racemase (2.6 units, 4-min intervals).

Scheme I



p-(Bromomethyl)mandelate[4] (**1**) is subject to a facile buffer-dependent solvolysis to *p*-(hydroxymethyl)mandelate (**5**). At pH 6.0 (0.1 M MES buffer, 1 mM $MgCl_2$) the $t_{1/2}$ is approximately 65 min, and UV analysis (Figure 1a) reveals the smooth first-order decay of **1** (1 mM; λ_{max} 235 nm) and the formation of **5** (λ_{max} 222 nm) with a sharp isosbestic point at 224 nm.[5] Addition of mandelate racemase (2.6 units)[6] to an identical mixture afforded a more complex spectral change (Figure 1b), the most striking feature being the formation of a new product (λ_{max} 264 nm) in

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(4) Ethyl-*p*-(bromomethyl)benzoylformate (1 g) (Barnish, I. T.; Cross, P. E.; Danielewicz, J. C.; Dickinson, R. P.; Stopher, D. A. *J. Med. Chem.* **1981**, *24*, 399) was treated with sodium borohydride (3 equiv) in ethanol (90 mL total volume) under N_2 for 90 min at 0 °C. Workup afforded ethyl *p*-(bromomethyl)mandelate (0.85 g, 84% yield): ^1H NMR ($CDCl_3$) δ 7.5 (4 H, s), 5.3 (1 H, s), 4.8 (2 H, s), 4.4 (2 H, q), 1.6 (3 H, t). Hydrolysis in refluxing 10% HBr gave **1** as light orange solid (100% yield); mp 140–42 °C; UV (H_2O) λ_{max} = 235 nm, ϵ = 7050 M^{-1} cm^{-1}; ^1H NMR (acetone-d_6) δ 7.5 (4 H, q), 5.3 (1 H, s), 4.7 (2 H, s); EI mass spectrum *m*/*e* (rel intensity) 246, 244 (M^+, 1.39, 0.92), 201, 199 ($M^+ - COOH$, 22.61, 23.02), 165 ($M^+ - Br$, 14.8) 120 ($M^+ - Br - COOH$, 30.77). A satisfactory microanalysis was obtained (±0.4 of calculated values). Stock solutions of **1** were freshly prepared in ethanol and were quite stable at 0 °C.

(5) The identification of **5** was established by ^1H NMR and HPLC comparison with an authentic sample.[4] The conversion of **1** to **5** was also monitored by ^1H NMR (D_2O). No exchange of the methine proton was detected.

(6) Mandelate racemase (510 units/mg) was isolated according to Hegeman (Hegeman, G. D. *Methods Enzymol.* **1970**, *17A*, 670). Activity was measured by circular dichroism: Sharp., T. R.; Hegeman, G. D.; Kenyon, G. L. *Anal. Biochem.* **1979**, *94*, 329.