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A CAROTENOID-PORPHYRIN-DIQUINONE TETRAD: SYNTHESIS, ELECTROCHEMISTRY AND PHOTOINITIATED ELECTRON TRANSFER

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Abstract

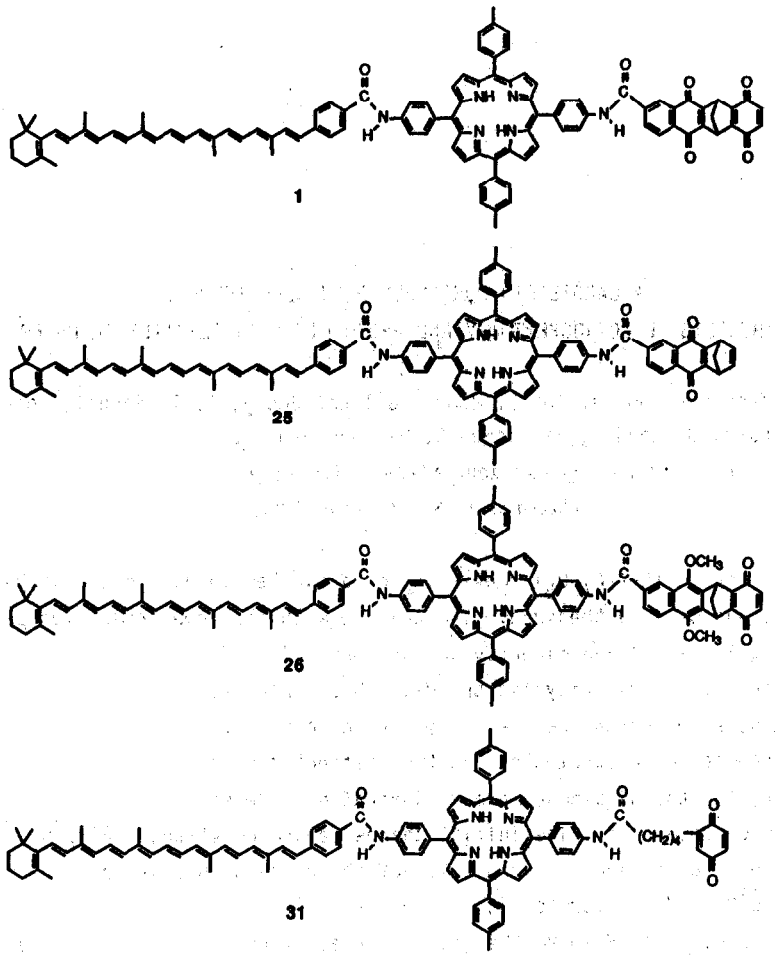
A molecular tetrad (C-P-Q_A-Q_B) consisting of a carotenoid polyene, a porphyrin and a diquinone moiety has been synthesized. The quinone with the lower reduction potential, the naphthoquinone (Q_A), was linked directly to the porphyrin and the benzoquinone (Q_B) was attached in series by a rigid bicyclic bridge. This arrangement was designed to promote a biomimetic sequential electron transfer from the porphyrin to Q_A, and on to Q_B.

Cyclic voltammetric measurements show two distinct reduction steps at -0.65 and -0.46 V (vs. SCE) for the diquinone moiety, indicating independence of the benzoquinone and the naphthoquinone components. The initial charge separated state, C-P^{+}-$Q_A^{\cdot -}$-Q_B, is formed within 15 ps of excitation and lies about 1.6 eV above the ground state. The final charge separated state C^{+}-P-Q_A-Q_B^{-} is formed with a quantum yield of 0.23 at room temperature (0.5 at 240 K) and lies ca. 1.1 eV above the ground state. Both parallel and sequential mechanisms for the electron transfer processes are elucidated from studies with model triads which feature a carotenoid, a porphyrin and only one of the components of the diquinone moiety.

Introduction

Sequential electron transfer originating from the excited singlet state of the bacteriochlorophyll special pair and following the increasing reduction potentials of bacteriopheophytin, quinone A (Q_A) and finally quinone B (Q_B) serves to move an electron across the plasma membrane in bacterial photosynthesis. This is the primary energy transduction process in which light energy is converted to electrical-chemical potential. Although this process occurs with a quantum yield of $\geq$ 0.98, the energy loss in terms of redox potential is substantial. In fact, only 30-40% of the energy of the excited state of the bacteriochlorophyll in the special pair (1.43 eV) is conserved as redox potential after the above-mentioned electron transfer processes.[1]

In order to investigate the primary electron transfer steps in photosynthetic membranes we have previously synthesized a number of triad molecules, which consist of porphyrin or chlorophyll-based macrocycles linked to quinones and carotenoid pigments, and have studied them using a variety of spectroscopic, photochemical, and electrochemical



methods.[2-5] Recently, we have reported[6] on the photodriven charge separation and electron transfer in a carotenoid-porphyrin-diquinone tetrad (1) (C-P-Q_A-Q_B) which was designed to mimic sequential electron transfer similar to that described above for bacterial reaction centers. Detailed studies of the rates and energetics of the individual electron transfer steps in this tetrad and its derivatives should yield new information about electron transfer in reaction centers and about the fundamental constraints on energy conserved vis-à-vis the overall quantum yield.

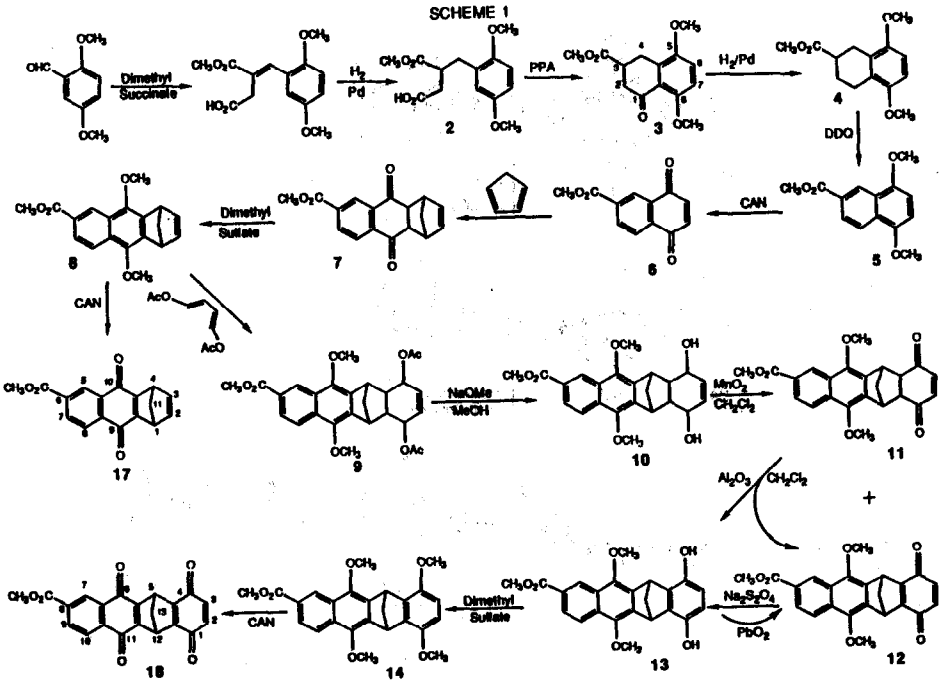
We report herein the strategy for the synthesis of tetrad 1 and related compounds along with an electrochemical study of the rigid diquinone species and other model systems from which the energies of the states involved in the sequential electron transfer can be estimated. The participation of intermediate charge-separated states in systems designed to optimize the yield and the intramolecular redox potential during sequential electron transfer processes is discussed.

Results and Discussion

Synthesis. The tetrad was designed so that it could be synthesized by linking three structural units, the carotenoid polyene, the porphyrin, and the diquinone moiety, via amide bonds. The quinone with the lower reduction potential, the naphthoquinone, was placed nearer the porphyrin than the benzoquinone in order to favor sequential electron transfer from porphyrin to Q_A to Q_B. The rigid bicyclic bridge between the quinone moieties and the amide linkages, which have partial double bond character, were employed to constrain the molecule to linear conformations, thereby preventing the quinones or carotenoid from folding back across the porphyrin and short-circuiting the electron transfer process.[7,8]

The synthetic steps followed in the preparation of the diquinone moiety are presented in Scheme 1. Naphthoquinone **6** was prepared in six steps from 2,5-dimethoxybenzaldehyde.[9,10] A Diels-Alder cycloaddition with **6** and cyclopentadiene was used to generate the norbornene spacer and new dienophile **7**, which, after aromatization to yield **8**, was used in a second Diels-Alder reaction with trans,trans-1,4-diacetoxy-1,3-butadiene to produce the pentacyclic ester **9**.[11] This compound has the basic framework required for the synthesis of the diquinone **18**. The benzoquinone portion was obtained by a transesterification reaction of **9** which yielded ester **10**, a subsequent oxidative step with manganese dioxide which gave the diketone **11**, and aromatization by treatment with basic alumina. The hydroquinone, **13**, could be oxidized to the quinone form **12** with lead dioxide, or protected as the

SCHEME 1

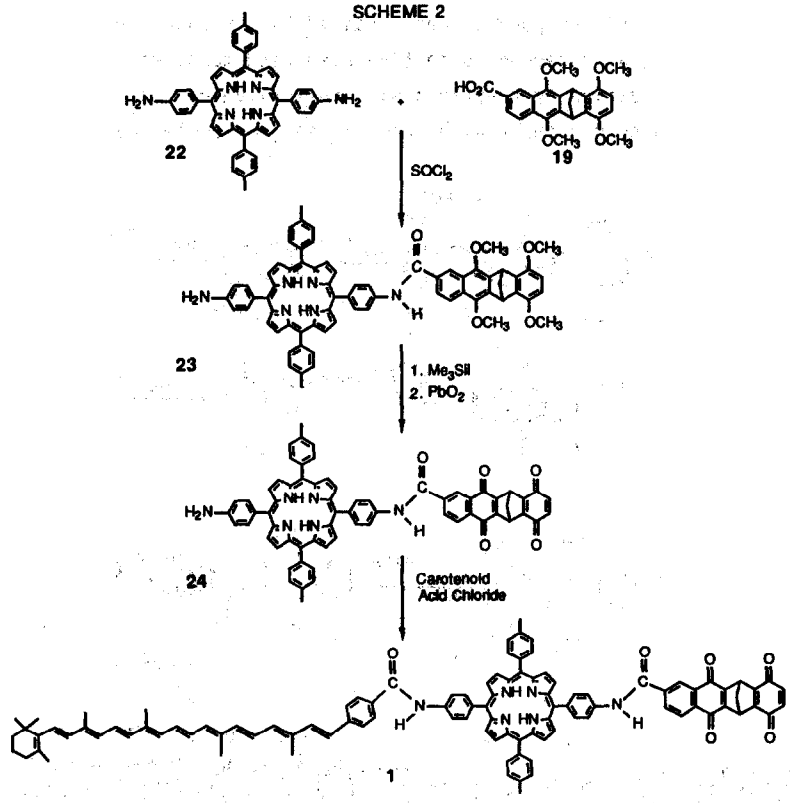


tetramethoxy ester, **14**, by treatment with dimethyl sulfate. It was this fully protected form which was actually employed in the synthesis of the diquinone ester, **18**, by reaction with ceric ammonium nitrate, and also in the preparation of the tetrad **1**.

Attempts to hydrolyze esters **12** or **18** to produce the required acids for the direct assembly of the tetrad failed; only polymeric products were obtained. In order to avoid this problem, the quinones were deprotected after the diquinone precursor was attached to the porphyrin. As shown in Scheme 2, the acid chloride of the protected acid, **19**, was allowed to react with an excess of porphyrin **22**[4] to afford the monosubstitution product **23**. The removal of the methyl protecting groups with iodotrimethylsilane followed by oxidation with lead dioxide gave **24** in the diquinone form. The coupling of **24** with the acid chloride of 4-(β-apo-7'-carotenyl)benzoic acid[12] yielded the tetrad **1**.

A similar synthetic approach was employed in the synthesis of triads **25** and **26**. In the case of **25**, it was possible to directly couple the acid chloride of the naphthoquinone

SCHEME 2

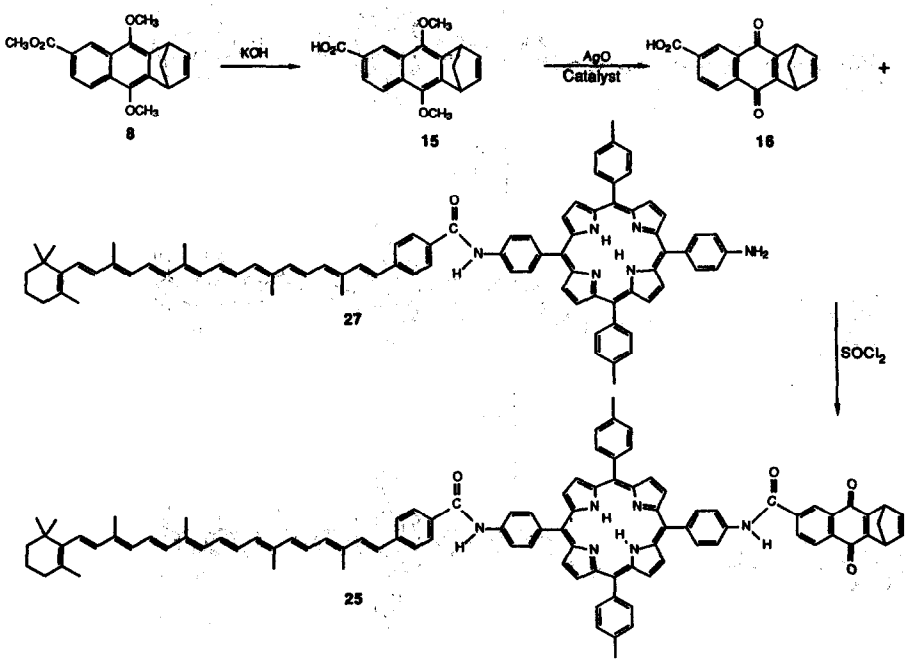


moiety to the carotenoporphyrin **27**[4] (Scheme 3). For the synthesis of triad **26** (Scheme 4), the ester **9** was hydrolyzed to the 1,4-dihydroxy-6,11-dimethoxy acid **20**. The hydroxyl groups were reprotected as esters to yield **21**, which was then coupled to the carotenoporphyrin as in the case of **25**. The final steps of the deprotection of the benzoquinone to generate triad **26** followed the synthetic sequence used in Scheme 1. The synthesis of triad **31** was previously reported.[4]

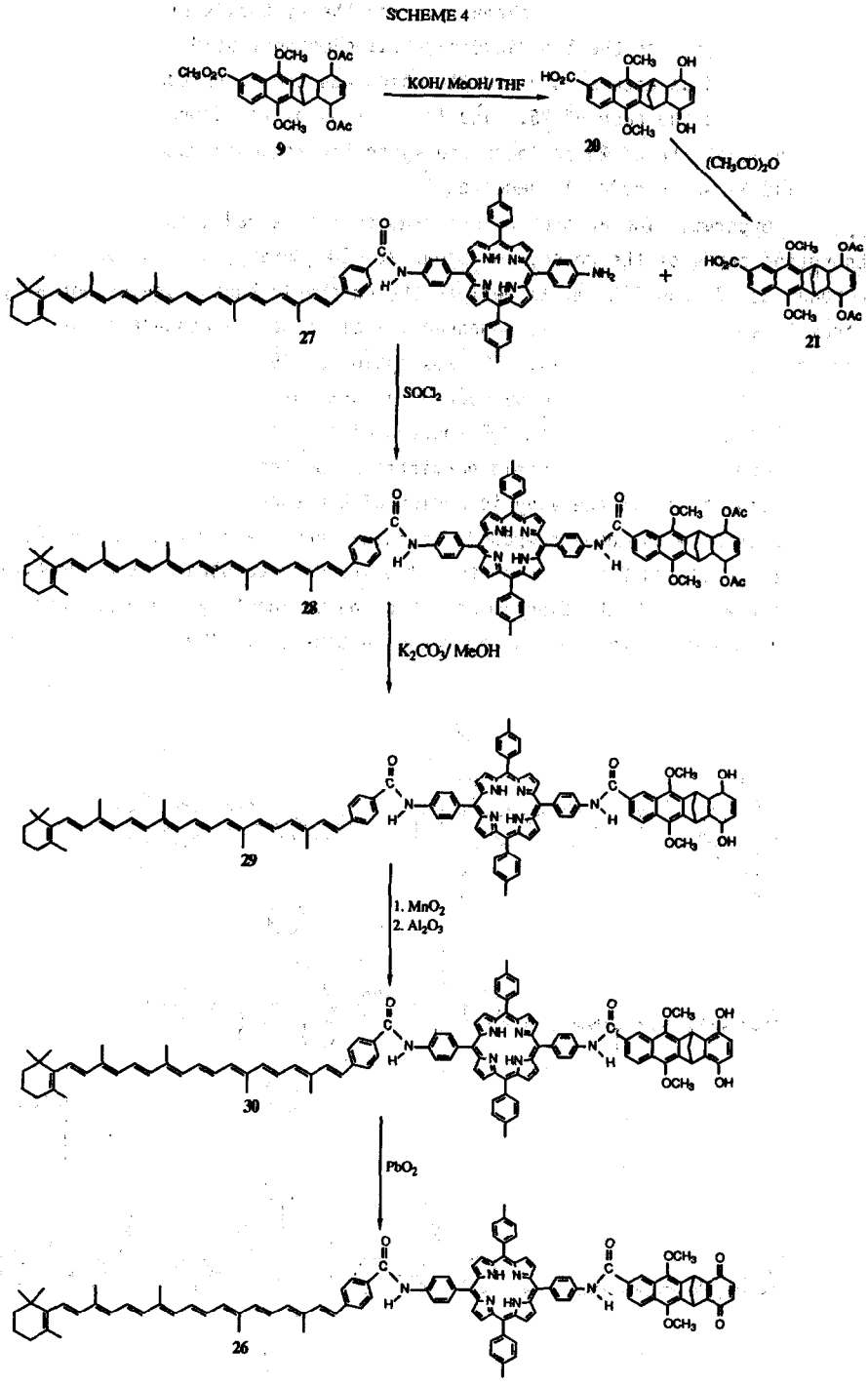
Absorption Spectrum. The absorption spectrum of the tetrad **1** is shown in Figure 1. Typical absorption bands of the porphyrin appear at 420 (Soret), 592 and 652 nm. The carotenoid bands at 478 and 512 nm, as well as the porphyrin bands, are essentially unchanged from those of unlinked model compounds, indicating the absence of strong interactions between the chromophores. The absorption at 259 nm corresponds to the benzoquinone, and it is absent in the hydroquinone forms of the tetrad and triad **26**.

NMR Spectral Assignments. The ^{1}H NMR spectra of the tetrad, triads and precursors were obtained at 400 MHz. The high field permitted a complete assignment of all resonances, including those in the vinylic region of the spectrum. The resonances were assigned by comparisons with model compounds, single-frequency decoupling, and COSY homonuclear shift-correlated 2-D experiments. The standard carotenoid and porphyrin numbering systems are used in the Experimental Section to identify the resonances.[4] The quinone and precursors were numbered as indicated in Scheme 1. The spectral assignments

SCHEME 3



SCHEME 4



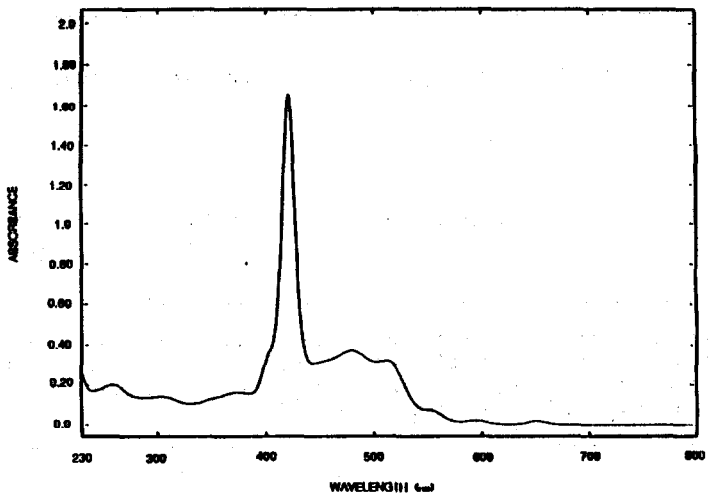


Figure 1. Absorption spectrum of tetrad **1** in dichloromethane solution.

for the tetrad, triads and carotenoporphyrins in the carotenoid and porphyrin regions are in agreement with our previously published assignments for related triads and carotenoporphyrins.[4,13]

The oxidation state of the benzoquinone moiety can be easily identified by the chemical shifts of H-2 and H-3. Both protons are isochronous in the complete series of compounds, showing a singlet between 6.61 and 6.68 ppm. The hydroquinone form, however, exhibits a marked upfield shift for the resonances of H-2 and H-3, which appear as a singlet at 6.33-6.40 ppm.

Electrochemical Measurements. In order to investigate the redox properties of the two quinone moieties of the tetrad, cyclic voltammetric measurements were carried out with diquinone ester **18**, the two corresponding monoquinone esters **12** and **17**, and 2,5-dimethoxybenzoquinone (DMQ). The results, presented in Table 1 and Figure 2, show two distinct reduction steps for the diquinone ester **18**. The two halves of diquinone **18** are reduced at potentials 0.056 and 0.031 V more positive than the model monoquinones **12** and **17**. The relatively small degree of perturbation indicates that the benzoquinone and the naphthoquinone components are essentially electrochemically independent.

Cyclic voltammetric measurements of carotenoporphyrins, triads and model compounds[14] have demonstrated that the redox potentials of the covalently linked chromophores are little changed from those of their unlinked counterparts. Therefore, if one ignores coulombic stabilization, the measured reduction potentials of the model quinones and the oxidation potentials of the carotenoid and porphyrin moieties can be used to estimate the energies of the charge separated states of the tetrad and triad molecules. The results are shown in Scheme 5.

The energy of $\dot{C}^{+}$P-Q_A-$Q_B^{\bullet -}$ obtained in this way (1.1 eV) is about the same as that of the $\dot{C}^{+}$P-$(CH_2)_4$-$Q_B^{\bullet -}$ state of triad **31**,[4] and *ca.* 60% of the energy originally stored in the

Table 1. One-electron reduction potentials[a] vs. internal ferrocene.

Quinone:	DMQ	12	17	18
$\bar{E}_{CV}$ (V):	-1.158 (-0.76)	-0.920 (-0.52)	-1.079 (-0.68)	-0.864 (-0.46) -1.048 (-0.65)

[a] Cyclic voltammetry potentials for one-electron reduction of the quinone as a ca. 10^{-3} M solution in dichloromethane, against internal ferrocene reference, and extrapolated to zero scanning rate. The numbers in parentheses correspond to the reduction potentials vs. SCE obtained by adding 0.40 to the ferrocene values.[15]

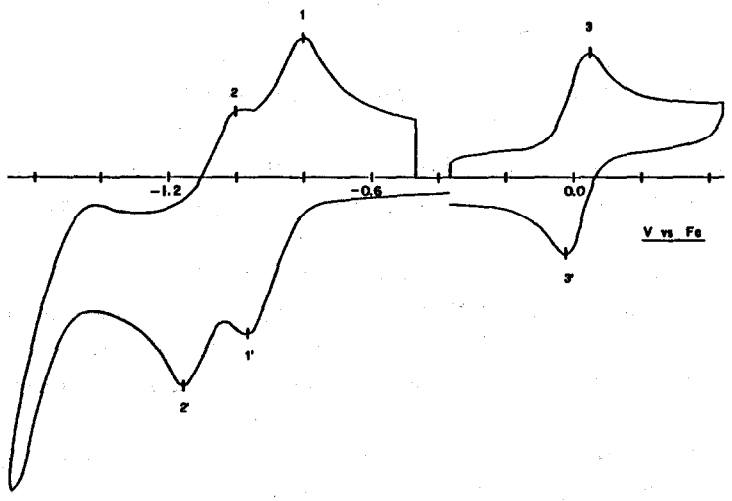
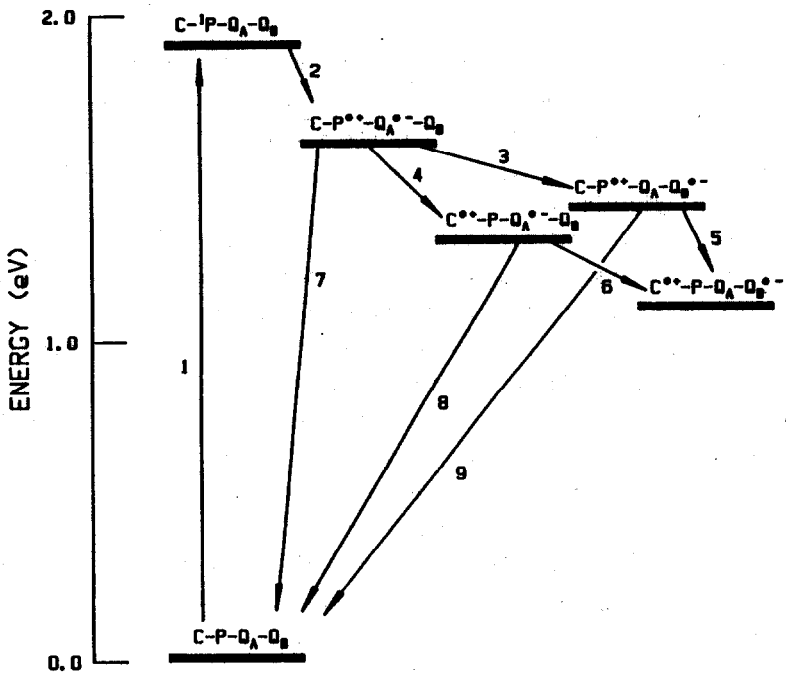


Figure 2. Cyclic voltammogram of diquinone **18** obtained in 1,2-dichloroethane containing 0.1 M $(CH_3CH_2CH_2CH_2)_4NPF_6$, scanned at 0.2 V/s. The cathodic waves 1' and 2' indicate reversible one-electron steps in the reduction of the quinone; 3 indicates the reversible oxidation of the internal reference ferrocene.

singlet state of the porphyrin (1.9 eV) is conserved in these final charge separated states. The initial charge separated state, $C\text{-}\dot{P}^{+}\text{-}Q_A^{\bullet -}\text{-}Q_B$, lies about 1.6 eV above the ground state.

Photoinitiated electron transfer. Scheme 5 also presents the sequence of electron transfer events which follows excitation of tetrad **1** in dichloromethane solution, as deduced from nanosecond transient absorption and picosecond fluorescence lifetime studies.[6] The porphyrin first excited singlet state donates an electron to the adjacent naphthoquinone to yield $C\text{-}P^{\bullet +}\text{-}Q_A^{\bullet -}\text{-}Q_B$ (step 2). Two subsequent electron transfer reactions,

SCHEME 5



steps 3 and 4, compete with charge recombination (step 7) to yield two new intermediate states, both of which can either undergo an additional electron transfer step to generate the same final $C^{\bullet+}$-P-Q_A-$Q_B^{\bullet-}$ state (steps 5 and 6), or suffer recombination (steps 8 and 9). The final charge separated state, $C^{\bullet+}$-P-Q_A-$Q_B^{\bullet-}$, is formed with a quantum yield of 0.23 at room temperature and a lifetime of 460 ns.[6] At 240 K, the quantum yield increases to 0.50. Similar studies on triad **25** have shown that $C^{\bullet+}$-P-$Q_A^{\bullet-}$ is formed with a quantum yield of ~ 0.04; its lifetime is only ~ 70 ns. Triad **26** forms $C^{\bullet+}$-P-$Q_A(OMe)_2$-$Q_B^{\bullet-}$ with a quantum yield of 0.11 and a lifetime of 1.9 μs.[6]

Although the quantum yield of the final state at ambient temperature is quite respectable for a model system, the natural photosynthetic apparatus operates with a quantum yield of essentially one for comparable steps. Thus, it is of interest to identify the steps in Scheme 5 for which the quantum yield for forward electron transfer is less than optimal. From fluorescence lifetime studies,[6] the initial step to form C-$\dot{P}^+$-$\dot{Q}_A^-$-Q_B occurs with a quantum yield of ~ 1.0. Therefore, the yield of $\dot{C}^+$-P-Q_A-$\dot{Q}_B^-$ is given by eq. 1.

$$\Phi_3 \cdot \Phi_5 + \Phi_4 \cdot \Phi_6 = 0.23 \qquad \text{eq. 1}$$

The second product in eq. 1 must be < 0.04 because a step analogous to 4 occurs with a yield of 0.04 in triad **25**, which lacks step 3. Thus, the product $\Phi_3 \cdot \Phi_5$ must be ≥ 0.19. Quantitatively, one can show that $k_3/k_4 \geq 7.5$ if one assumes that the rate constant for recombination from the state C-$\dot{P}^+$-$\dot{Q}_A^-$-Q_B is the same in tetrad **1** and triad **25**. Thus at least 88% of the overall yield of 0.23 for $\dot{C}^+$-P-Q_A-$\dot{Q}_B^-$ must derive from steps 3 and 5.

It is interesting to note that both tetrad **1** and a previously studied C-P-Q triad **31** have final charge separated states of about the same energy. Although the porphyrin and benzoquinone moieties of **1** are separated by two more carbon-carbon bonds than are those of **31**, the yield of the final charge-separated state in **1** is greater by a factor of about 10 at ambient temperature. The additional electron transfer steps in **1** act in several ways to bring this increase about. First, in the tetrad, charge recombination from the initial C-$\dot{P}^+$-$Q_A^{\bullet-}$-Q_B state at 1.6 eV is more exergonic than that from C-$\dot{P}^+$-$Q_B^{\bullet-}$ in **31** at ~ 1.45 eV. To the extent that the processes fall in the Marcus inverted region for electron transfer,[16-21] this should make recombination from this state relatively slow for **1**. Second, the process C-$\dot{P}^+$-$Q_A^{\bullet-}$-Q_B → C-$\dot{P}^+$-Q_A-$Q_B^{\bullet-}$ (step 3) competes well with charge recombination and dramatically lowers the quantum yield of recombination relative to **31**, which lacks an analogous step.

Triad **26** serves to illustrate the importance of the intervening medium or linkage, in this case the -$Q_A(OMe)_2$- moiety, in both the forward and reverse electron transfer processes. From studies of electron transfer in a series of analogs of triad **31**,[4] the initial photodriven electron transfer rate constant, $\underline{k}_{et}$, was found to be exponentially dependent upon donor-acceptor separation. Using the dependency found in this study (or, for that matter, any of the published data for similar sytems),[18,22] one calculates that $\underline{k}_{et}$ would be $\ll 10^8$ s^{-1} in triad **2**, and this in turn implies that the quantum yield for the formation of C-$\dot{P}^+$-$Q_A(OMe)_2$-$\dot{Q}_B^-$ should be vanishingly small. In fact, the quantum yield for this step is 0.77, with $\underline{k}_{et} = 9.6 \times 10^8$ s^{-1}. Superexchange, the promotion of electron transfer via the involvement of orbitals of the linking group in the mixing of the donor and acceptor orbitals, has been invoked[23-26] in other systems and could account for the increased electronic coupling in triad **26** relative to that in triad **31**.

Charge recombination from the state C-$\dot{P}^+$-$Q_A(OMe)_2$-$\dot{Q}_B^-$ in **26** must also be unusually rapid, as illustrated by the fact that the yield of $\dot{C}^+$-P-$Q_A(OMe)_2$-$\dot{Q}_B^-$ is only 0.11, even though the initial charge separation occurs with a yield of 0.77. This means that the yield of the final step from C-$\dot{P}^+$-$Q_A(OMe)$-$\dot{Q}_B^-$ must be only 0.11/0.77 = 0.14. This result can be interpreted in terms of the lifetime of the precursor state involving the porphyrin radical cation and the rate of electron donation by the carotenoid species, which are common elements in triad **26** and tetrad **1**. Since the electron donation step from the carotenoid should occur at about the same rate in both cases, the lifetime of C-$\dot{P}^+$-$Q_A(OMe)_2$-$\dot{Q}_B^-$ in **26** must be significantly shorter than that of C-$\dot{P}^+$-Q_A-$\dot{Q}_B^-$ in **1** in order to

account for the reduced quantum yield. The shorter lifetime of $C\text{-}\dot{P}^{+}\text{-}Q_A(OMe)_2\dot{Q}_B^{-}$ is due to faster charge recombination in this species. Conversely, it is not possible to assign a yield of 0.14 (from electron donation by the carotene in triad **26**) to step 5 (Scheme 5) for tetrad **1** because the product $\Phi_3 \cdot \Phi_5$ would be ≥ 0.19 in eq. 1. In this respect, triad **26** is not a good model for the analogous electron transfer in tetrad **1**. As in the case of charge separation discussed above, this fast charge recombination process is undoubtedly a consequence of the coupling provided by orbitals of the linking moiety, which involves a fully aromatic dimethoxynaphthalene system in the case of **26**, but a naphthoquinone in **1**.

Conclusions

An important principle regarding long-lived, photoinitiated charge separation spanning distances of several nm begins to emerge. In the case of triad **26**, a reasonable yield of the initial charge separated state over a substantial distance was achieved because of the favorable electronic coupling between donor and acceptor provided in part by the linkage. However, the same favorable electronic coupling ensured that charge recombination was also fast so that the subsequent step was not very efficient. In tetrad **1**, however, an even higher yield of electron transport over the same distance was observed, and the subsequent step 5 was much more efficient. In other words, in these systems two fast, short range electron transfer steps are much more desirable than one long step both in terms of the quantum yields of the intermediates being formed and their lifetimes, which in turn help determine the efficiency of subsequent electron transfer processes. These results serve to illustrate strategies for improving the yield of long distance electron transfer in systems which conserve a substantial fraction of the photon energy as intramolecular redox potential. It is expected that continued work along these lines will better define the relationships between the yield of primary charge separation and the efficiency of transfer to secondary electron carriers in these systems and make possible the further optimization of energy conversion.

Experimental Section

Synthesis. ^1H NMR spectra were obtained on a Bruker AM-400 spectrometer and refer to ca. 1% solutions in deuteriochloroform. Mass spectra were obtained on a Varian MAT 311.

3-Carbomethoxy-4-(2,5-dimethoxyphenyl)-3-butenoic acid. A solution of 2,5-dimethoxybenzaldehyde (70.0 g, 420 mmol) and dimethyl succinate (60 mL, 459 mmol) in t-butyl alcohol (250 mL) was added dropwise, over one half hour, to a stirred, refluxing solution of potassium t-butoxide (58.0 g, 517 mmol) in t-butyl alcohol (300 mL) under nitrogen. The reaction mixture was refluxed for an additional 40 min, and then allowed to cool to room temperature. Most of the t-butyl alcohol was removed by distillation under vacuum and the resulting yellow suspension was acidified with 4M aqueous HCl and extracted with ether. The ether layer was extracted with a cold 10% aqueous sodium carbonate solution, which was then acidified with cold 4M HCl to give a yellow oil. The oil was extracted into chloroform. Drying (Na_2SO_4), removal of the solvent by distillation under

vacuum, and recrystallization (methanol) gave the desired product as a yellow solid in 80% yield: m.p. 128-129°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.52 (2 H, s, H-2), 3.77 (3 H, s, OCH_3-5, Ar), 3.79 (3 H, s, OCH_3-2, Ar), 3.85 (3 H, s, CO_2CH_3), 6.83 (1 H, d, J = 9.8 Hz, H-3, Ar or H-4, Ar), 6.90 (1 H, d, J = 9.8 Hz, H-4, Ar or H-3, Ar), 6.89 (1 H, s, H-6, Ar), 7.98 (1 H, s, H-4); MS m/e 280 (M^+).

3-Carbomethoxy-4-(2,5-dimethoxyphenyl)-butanoic acid (2). To a solution of 3-carbomethoxy-4(2,5-dimethoxyphenyl)-3-butenoic acid (15.0 g, 53 mmol) in methanol (180 mL) that had been thoroughly degassed with argon was added 5% palladium on carbon (1.8 g) in small portions. The mixture was then hydrogenated at 40 psi. Analysis by TLC indicated consumption of the starting material after 20 h. The reaction mixture was filtered through celite, the solvent was evaporated under reduced pressure, and the residue was recrystallized (methanol-water) to give a white solid in essentially quantitative yield: m.p. 92-93°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (1 H, dd, J = 17.3, 9.4 Hz, H-2 or H-2'),2.69 (1 H, dd, J = 17.3, 9.4Hz, H-2' or H-2), 2.77 (1 H, dd, J = 13.3, 6.4 Hz, H-4 or H-4'), 3.03 (1 H, dd, J = 13.3, 7.4 Hz, H-4' or H-4), 3.14-3.19 (1 H, m, H-3), 3.66 (3 H, s, CO_2CH_3), 3.73 (3 H, s, OCH_3-5, Ar), 3.75 (3 H, s, OCH_3-2, Ar), 6.66 (1 H, d, J = 2.8, H-3, Ar or H-4, Ar), 6.74 (1 H, d, J = 2.8 Hz, H-4, Ar or H-3, Ar), 6.75 (1 H, s, H-6); MS m/e 282 (M^+).

3-Carbomethoxy-3,4-dihydro-2H-5,8-dimethoxy-1-oxo-naphthalene (3). The half-ester 2 (13.0 g, 46 mmol) was mechanically stirred with polyphosphoric acid (250.0 mL) at 85 °C under nitrogen. TLC analysis indicated 95% completion of the reaction after 20 min. The hot reaction mixture was immediately poured into ice-cold water (500 mL) with vigorous stirring to give a creamy suspension. The suspension was filtered, and the filtrate was extracted with chloroform (3 x 200 mL). Drying (Na_2SO_4) and evaporation of the solvent at reduced pressure gave a green-yellow solid which was combined with the residue from the filtration and dried for several hours under vacuum. The resulting solid, which was obtained in 89% yield, was promptly used in next step, as it decomposed with time: m.p. 126-128°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.75-2.92 (3 H, m, H-2 or H-2', H-4 and H-4'), 3.03-3.09 (1 H, m, H-3), 3.38 (1 H, ddd, J = 15.8, 3.4, 1.7 Hz, H-2' or H-2), 3.73 (3 H, s, CO_2CH_3), 3.83 (3 H, s, OCH_3-5), 3.87 (3 H, s, OCH_3-8), 6.82 (1 H, d, J = 9.0 Hz, H-6 or H-7), 7.02 (1 H, d, J = 9.0 Hz, H-7 or H-6); MS m/e 264 (M^+).

2-Carbomethoxy-5,8-dimethoxy-1,2,3,4-tetrahydronaphthalene (4). To a solution of the keto-ester 3 (11.0 g, 42 mmol) in acetic acid (250 mL) was added 10% palladium on carbon (3.0 g) in small portions. The mixture was then hydrogenated at 50 psi and 40 °C for 60 min. TLC analysis showed complete conversion of the starting material. The reaction mixture was filtered through celite. Distillation of the solvent at reduced pressure resulted in an oil which was crystallized from methanol to yield 4 in 85% yield: m.p. 66-69.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69-1.82 (1 H, m, H-3 or H-3'), 2.17-2.23 (1 H, m, H-3' or H-3), 2.51-2.64 (1 H, m, H-2), 2.65 (1 H, dd, J = 11.0, 1.5 Hz, H-4 or H-4'), 2.72 (1 H, d, J = 10.8 Hz, H-4' or H-4), 2.93 (1 H, m, J = 17.2, 5.4, 2.2 Hz, H-1 or H-1'), 3.10 (1 H,

m, J = 17.2, 3.0 Hz, H-1' or H-1), 3.73 (3 H, s, CO_2CH_3), 3.77 (3 H, s, OCH_3-5), 3.78 (3 H, s, OCH_3-8), 6.63 (2 H, s, H-6 and H-7); MS m/e 250 (M^+).

6-Carbomethoxy-1,4-dimethoxynaphthalene (5). To a stirred solution of 4 (23.0 g, 92 mmol) in dry benzene (250 mL) that had been saturated with nitrogen was added 2,3-dichloro-5,6-dicyanobenzoquinone (40.0 g, 176 mmol) in one portion. The mixture was warmed to 40 °C and stirred for 72 h under nitrogen. The reaction mixture was cooled to room temperature and vacuum filtered, and the solvent was evaporated at reduced pressure to yield an oil which was chromatographed on a fast alumina column eluted with pure chloroform. The resulting product was recrystallized (methanol) to give 13.8 g (61%) of 5 as a white solid: m.p. 115-116 °C, lit. m.p. 115-117 °C;[9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96 (3 H, s, CO_2CH_3), 3.97 (3 H, s, OCH_3-1), 3.98 (3 H, s, OCH_3-4), 6.74 (1 H, d, J = 8.4 Hz, H-2 or H-3), 6.81 (1 H, d, J = 8.4 Hz, H-2 or H-3), 8.08 (1 H, dd, J = 8.8, 1.8 Hz, H-7), 8.24 (1 H, d, J = 8.8 Hz, H-8), 8.97 (1 H, d, J = 1.8 Hz, H-5); MS m/e 246 (M^+).

6-Carbomethoxy-1,4-naphthoquinone (6). A solution of ceric ammonium nitrate (28.7 g, 52 mmol) in water (50 mL) was added, over 5 min, to a stirred solution of the ester 5 (4.3 g, 17 mmol) in acetonitrile (50 mL) at room temperature. The resulting suspension was stirred for an additional 5 min and poured into water (100 mL). Extractive workup ($CHCl_3$, 6 x 100 mL) and removal of the solvent by evaporation under reduced pressure gave a yellow solid which was recrystallized from ethanol to yield 6 in 81% yield: m.p. 94-95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99 (3 H, s, CO_2CH_3), 7.05 (2 H, s, H-2 and H-3), 8.18 (1 H, d, J = 7.7 Hz, H-8), 8.41 (1 H, dd, J = 7.7, 1.8 Hz, H-7), 8.74 (1 H, d, J = 1.8 Hz, H-5); MS m/e 216 (M^+).

6-Carbomethoxy-1,4,4a,9a-tetrahydro-1,4-methanoanthracene-9,10-dione (7). Cyclopentadiene, obtained by cracking (fractional distillation) of dicyclopentadiene (25 mL), was added dropwise to a stirred solution of 6 (6.0 g, 28 mmol) in toluene (100 mL) at room temperature. Analysis by TLC showed complete conversion of starting material in 10 min. Extractive workup (chloroform-water), drying (Na_2SO_4), and removal of the solvent by evaporation at reduced pressure gave a tan oil which was crystallized from methanol to give 7 as an off-white solid in 88% yield: m.p. 114-116°C; ^{1}H NMR (400 MHz $CDCl_3$) δ 1.53 (1 H, d, J = 8.6 Hz, H-11 or H-11'), 1.58 (1 H, d, J = 8.6 Hz, H-11' or H-11), 3.49 (2 H, t, J = 2.0 Hz, H-4a and H-9a), 3.66-3.67 (2 H, m, H-1 and H-4), 3.96 (3 H, s, CO_2CH_3), 5.96 (2 H, t, J =1.5 Hz, H-2 and H-3), 8.29 (1 H, d, J = 8.1 Hz, H-8), 8.31 (1 H, dd, J = 8.1, 1.6 Hz, H-7), 8.64 (1 H, d, J = 1.6 Hz, H-5); MS m/e 282 (M^+).

6-Carbomethoxy-1,4-dihydro-9,10-dimethoxy-1,4-methanoanthracene (8). To a stirred, refluxing solution of the diketone 7 (1.0 g, 3.5 mmol) in dry acetone (20 mL) was slowly added dimethyl sulfate (1.0 mL) over a five minute period. A 10% methanolic KOH solution was then added dropwise by syringe (each drop was accompanied by a transient purple coloration), until no more purple discharges could be seen. An inert atmosphere was continuously maintained. The resulting pale yellow suspension was dissolved in 2M aqueous HCl (20 mL) and extracted with dichloromethane (4 x 50 mL). The organic layer was dried (Na_2SO_4), the solvent was removed by evaporation at reduced pressure, and the resulting oil

was crystallized from methanol to give 93 mg (85%) of **8** as a tan solid: m.p. 88-90°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.14 (1 H, d, J = 7.6 Hz, H-11 or H-11'), 2.23 (1 H, d, J = 7.6 Hz, H-11' or H-11), 3.92 (3 H, s, OCH_3-9), 3.94 (3 H, s, OCH_3-10), 3.98 (3 H, s, CO_2CH_3), 4.27-4.29 (2 H, m, H-1 and H-4), 6.72 (1 H, dt, J = 6.0, 5.2 Hz, H-2 or H-3), 6.73 (1 H, dt, J = 6.0, 5.2 Hz, H-2 or H-3), 8.01 (1 H, dd, J = 8.8, 1.5 Hz, H-7), 8.04 (1 H, d, J = 8.8 Hz, H-8), 8.78 (1 H, d, J = 1.5 Hz, H-5); MS m/e 310 (M^+).

8-Carbomethoxy-1,4-diacetoxy-6,11-dimethoxy-1,4,4a,5,12,12a-hexahydro-5,12-methanonaphthacene (9). Tetracyclic ester **8** (1.5 g, 4.8 mmol), trans, trans-1,4-diacetoxy-1,3-butadiene (1.0 g, 5.8 mmol) and a small amount of hydroquinone (ca. 60 mg) were thoroughly dried, ground, and loaded into a 41 mm thick-walled pyrolysis tube. The tube was flushed with argon, sealed, and heated at 140 °C for 30 h. Analysis by TLC showed complete conversion of the ester. The crude product was purified by flash column chromatography (silica gel, 1% ethyl acetate in toluene), and crystallized (acetone-hexane) to yield **9** in 90% yield as a white solid: m.p. 185-188 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.90 (1 H, dt, J = 10.3, 1.1 Hz, H-13 or H-13'), 2.04 (1 H, dt, J = 10.3, 1.1 Hz, H-13' or H-13), 2.18 (6 H, s, CH_3CO_2-1 and CH_3CO_2-4), 2.20 (2 H, m, H-4a and H-12a), 3.69 (1 H, d, J = 1.1 Hz, H-5 or H-12), 3.72 (1 H, d, J = 1.1 Hz, H-12 or H-5), 3.97 (6 H, s, OCH_3-6 and OCH_3-11),4.02 (3 H, s, CO_2CH_3-8), 5.27 (2 H, dt, J = 8.1, 2.9 Hz, H-1 and H-4), 5.74 (2 H, d, J = 0.9 Hz, H-2 and H-3), 8.03 (1 H, dd, J = 8.8, 1.6 Hz, H-9), 8.11 (1 H, d, J = 8.8 Hz, H-10), 8.82 (1 H, d, J = 1.6 Hz, H-7); MS m/e 480 (M^+).

8-Carbomethoxy-1,4-dihydroxy-6,11-dimethoxy-1,4,4a,5,12,12a-hexahydro-5,12-methanonaphthacene (10). A mixture of the triester **9** (1.3 g, 2.7 mmol), sodium methoxide (440 mg, 8 mmol) and dry methanol (20 mL) was stirred at room temperature under an argon atmosphere for 24 h. Analysis by TLC indicated two products. The reaction was diluted with dichloromethane and washed with 5% aqueous HCl (100 mL) and water (50 mL). Drying (Na_2SO_4) and evaporation of the solvent at reduced pressure gave an off-white solid in almost quantitative yield. Column chromatography (silica gel, 3% MeOH/$CHCl_3$) afforded two products which were identified from ^{1}H NMR and mass spectral data as diastereomeric forms of **10**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.76 (1 H, d, J = 9.6 Hz, H-13 or H-13'), 2.09 (2 H, s, H-4a and H-12a), 2.62 (1 H, d, J = 9.6 Hz, H-13' or H-13), 2.74 (2 H, br s, OH-1 and OH-4), 3.83 (1 H, s, H-5 or H-12), 3.85 (1 H, s, H-12 or H-5), 3.97 (3 H, s, OCH_3-11), 3.99 (3 H, s, OCH_3-6), 4.04 (3 H, s, CO_2CH_3-8), 4.55 (2 H, s, H-1 and H-4), 6.36 (2 H, s, H-2 and H-3), 8.01 (1 H, d, J = 8.6 Hz, H-9), 8.09 (1 H, d, J = 8.6 Hz, H-10), 8.70 (1 H, s, H-7); MS m/e 396 (M^+).

8-Carbomethoxy-6,11-dimethoxy-4a,5,12,12a-tetrahydro-5,12-methanonaphthacene-1,4-dione (11). The mixture of diastereomers of **10** (400 mg, 1 mmol) and excess activated manganese dioxide was stirred in very dry dichloromethane (25 mL) under argon for 5 days. Small additional amounts of manganese dioxide were added periodically over that period. The original pale yellow solution of the starting material was seen to change slowly to a permanent orange. TLC analysis indicated about 90% completion of the reaction. The reaction mixture was filtered through celite and concentrated to an oil. Flash column

chromatography (silica gel, $CHCl_3$) yielded a major yellow fraction and a minor red fraction. Further purification by HPLC was followed by mass spectral and ^1H NMR analysis which identified the red fraction as 8-carbomethoxy-5,12-dihydro-6,11-dimethoxy-5,12-methanonaphthacene-1,4-dione (**12**): ^1H NMR (400 MHz, $CDCl_3$) δ 2.45 (1 H, dt, J = 8.5, 1.3 Hz, H-13 or H-13'), 2.55 (1 H, dt, J = 8.5, 1.3 Hz, H-13' or H-13), 3.96 (3 H, s, CO_2CH_3-8), 4.03 (3 H, s, OCH_3-11), 4.08 (3 H, s, OCH_3-6), 4.91 (1 H, t, J = 1.3 Hz, H-5 or H-12), 4.93 (1 H, t, J = 1.3 Hz, H-12 or H-5), 6.60 (2 H, s, H-2 and H-3), 8.05 (1 H, dd, J = 8.8, 1.6 Hz, H-9), 8.08 (1 H, d, J = 8.8 Hz, H-10), 8.78 (1 H, d, J = 1.6 Hz, H-7); MS m/e 390 (M^+). The yellow fraction was the desired product **11** (60%). ^1H NMR (400 MHz, $CDCl_3$) δ 1.69 (1 H, dt, J = 10.2, 1.5 Hz, H-13 or H-13'), 1.81 (1 H, dt, J = 10.2, 1.5 Hz, H-13' or H-13), 2.92 (2 H, dd, J = 8.8, 1.2 Hz, H-4a and H-12a), 4.02 (3 H, s, CO_2CH_3-8), 4.08 (3 H, s, OCH_3-11), 4.14 (3 H, s, OCH_3-6), 4.28 (1 H, d, J = 1.4 Hz, H-5 or H-12), 4.31 (1 H, d, J = 1.4 Hz, H-12 or H-5), 6.89 (2 H, s, H-2 and H-3), 8.05 (1 H, dd, J = 8.8, 1.7 Hz, H-9), 8.14 (1 H, d, J = 8.8 Hz, H-10), 8.85 (1 H, d, J = 1.7 Hz, H-7); MS m/e 392 (M^+).

8-Carbomethoxy-5,12-dihydro-1,4-dihydroxy-6-11-dimethoxy-5,12-methanonaphthacene (13). A mixture of the diketone **11** (240 mg, 0.6 mmol) and excess base-washed alumina was stirred with anhydrous dichloromethane (25 mL) at room temperature, under argon, for six days. The reaction progress was monitored throughout this period by TLC, and more alumina was added as required. There was a gradual color change from yellow, through orange, to purple. When no more change was observed, the reaction mixture was filtered through celite and the solvent was removed by evaporation under reduced pressure to give a brown solid which was purified by flash chromatography (silica gel, $CHCl_3$) to give two main fractions. The top, minor, red fraction was identified from the mass spectrum and ^1H NMR analysis as **12**, and the bottom, major, tan fraction gave the desired product **13** in 60% yield: ^1H NMR (400 MHz, $CDCl_3$) δ 2.28 (1 H, dt, J = 8.2, 1.3 Hz, H-13 or H-13'), 2.32 (1 H, dt, J = 8.2, 1.3 Hz, H-13' or H-13), 3.89 (3 H, s, CO_2CH_3-8), 4.03 (3 H, s, OCH_3-11), 4.10 (3 H, s, OCH_3-6), 4.92 (1 H, t, J = 1.1 Hz, H-5 or H-12), 4.96 (1 H, t, J = 1.1 Hz, H-12 or H-5), 6.33 (2 H, s, H-2 and H-3), 7.94 (1 H, dd, J = 8.8, 1.7 Hz, H-9), 8.04 (1 H, d, J = 8.8 Hz, H-10), 8.62 (1 H, d, J = 1.7 Hz, H-7), 8.86 (2 H, s, OH-1 and OH-4); MS m/e 392 (M^+).

Quinone **12** was reduced to hydroquinone **13** by the dropwise addition of a 0.02M aqueous sodium dithionite solution to a stirred solution of the quinone in freshly distilled tetrahydrofuran. The red color of the starting material was gradually bleached as the reaction progressed. At the complete loss of color, the reaction was quenched with a 5% aqueous HCl solution. Extractive workup ($CHCl_3$) and concentration gave a light brown solid which was characterized and identified as **13** above.

8-Carbomethoxy-5,12-dihydro-1,4,6,11-tetramethoxy-5,12-methanonaphthacene (14). A mixture of hydroquinone **13** (140 mg, 0.36 mmol), dimethyl sulfate (173 μL, 1.8 mmol) and excess anhydrous potassium carbonate was stirred in dry acetone (30 mL) in an argon atmosphere for 24 h. TLC analysis indicated consumption of starting material (ca. 95%).

The reaction mixture was diluted with water (50 mL), extracted with chloroform (6 x 100 mL), and dried (Na_2SO_4), and the solvent was evaporated to yield a brown solid. Flash chromatography (silica gel, CH_2Cl_2) gave 120 mg (80%) of **14** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (1 H, dt, J = 7.7, 1.3 Hz, H-13 or H-13'), 2.44 (1 H, dt, J = 7.7, 1.3 Hz, H-13' or H-13), 3.77 (6 H, s, OCH_3-1 and OCH_3-4), 3.91 (3 H, s, CO_2CH_3-8), 4.03 (3 H, s, OCH_3-11), 4.07 (3 H, s, OCH_3-6), 4.98 (1 H, d, J = 1.5 Hz, H-5 or H-12), 5.00 (1 H, d, J = 1.5 Hz, H-12 or H-5), 6.52 (2 H, s, H-2 and H-3), 7.95 (1 H, dd, J = 8.8, 1.5 Hz, H-9), 8.02 (1 H, d, J = 8.8 Hz, H-10), 8.73 (1 H, d, J = 1.5 Hz, H-7); MS m/e 420 (M^+).

6-Carboxy-1,4-dihydro-9,10-dimethoxy-1,4-methanoanthracene (15). A mixture of the ester **8** (500 mg, 1.6 mmol), methanol (12 mL), 10% aqueous potassium hydroxide (6 mL) and freshly distilled tetrahydrofuran (18 mL) was stirred at room temperature for 5 h. Analysis by TLC indicated consumption of the starting material. The reaction mixture was quenched with a 2M aqueous HCl solution (100 mL) and extracted with dichloromethane. Drying (Na_2SO_4) and removal of the solvent by evaporation under reduced pressure gave **15** as a tan solid in quantitative yield: ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.11 (1 H, d, J = 7.8 Hz, H-11 or H-11'), 2.20 (1 H, d, J = 7.8 Hz, H-11 or H-11'), 3.93 (3 H, s, OCH_3-9), 3.98 (3 H, s, OCH_3-10), 4.34 (1 H, s, H-1), 4.38 (1 H, s, H-4), 6.85 (2 H, m, H-2 and H-3), 7.94 (1 H, dd, J = 8.6, 1.6 Hz, H-7), 8.00 (1H, d, J = 8.6 Hz, H-8) 8.59 (1 H, d, J = 1.6 Hz, H-5); MS m/e 296 (M^+).

6-Carboxy-1,4-dihydro-1,4-methanoanthracene-9,10-dione (16). A mixture of the acid **15** (50 mg, 0.169 mmol), pyridine-2,6-dicarboxylic acid N-oxide[10,27] (154 mg, 0.84 mmol), and silver(II) oxide (40 mg, 0.32 mmol) was stirred in an acetonitrile-water mixture (5 mL, 2.5:1) at 0°C for 5 min. TLC analysis showed complete conversion of starting material. The reaction mixture was filtered through celite, diluted with water (20 mL), and extracted with chloroform (2 x 20 mL). Drying (Na_2SO_4) and evaporation of the solvent at reduced pressure gave a crude yellow solid which was recrystallized from methanol to give 18 mg (40%) of **16** as a bright yellow solid: ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$) δ 2.32 (1 H, dt, J = 7.2, 1.4 Hz, H-11 or H-11'), 2.38 (1 H, dt, J = 7.2, 1.4 Hz, H-11 or H-11'), 4.24 (1 H, t, J = 1.8 Hz, H-1), 4.25 (1 H, t, J = 1.8 Hz, H-4), 6.89 (2 H, t, J = 1.8 Hz, H-2 and H-3), 8.11 (1 H, d, J = 8.1 Hz, H-8), 8.32 (1 H, dd, J = 8.1, 1.7 Hz, H-7), 8.69 (1 H, d, J = 1.7 Hz, H-5); MS m/e 266 (M^+).

Triad 25. To a stirred solution of the acid **16** (4.00 mg, 15 μmol), pyridine (60 μL), and anhydrous benzene (1 mL) under nitrogen was added thionyl chloride (120 μL) at room temperature. Analysis by TLC indicated comsumption of starting material in 10 min. The removal of the solvent by evaporation at reduced pressure afforded a yellowish residue which was thoroughly dried under vacuum. A solution of the carotenoporphyrin **27**[4] (15 mg, 12.6 μmol) in anhydrous dichloromethane (3 mL) was added dropwise to a stirred solution of the quinone acid chloride and pyridine (60 μL) in anhydrous dichloromethane (1 mL) under nitrogen at room temperature. The reaction progress was followed by TLC and was discontinued at the first sign of unreacted carotenoporphyrin. Distillation of solvents at

reduced pressure gave a green residue which was taken into dichloromethane and washed with water (5 x 10 mL) until a purple color was obtained in the organic layer. TLC separation (preparative plate, 1% acetone/CH_2Cl_2) afforded the desired product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 (3 H, s, CH_3-17C), 1.05 (3 H, s, CH_3-16C), 1.45-1.48 (2 H, m, CH_2-2C), 1.60-1.67 (2 H, m, CH_2-3C), 1.72 (3 H, s, CH_3-18C), 1.98 (3 H, s, CH_3-19C), 1.99 (3 H, s, CH_3-20C), 2.01 (3 H, s, CH_3-20'C), 2.04 (2 H, s, CH_2-4C), 2.10 (3 H, s, CH_3-19'C), 2.46 (1 H, d, J = 7.5 Hz, H-11 or H-11'), 2.52 (1 H, d, J = 7.5 Hz, H-11 or H-11'), 2.71 (6 H, s, CH_3, Ar (10) and CH_3, Ar (20)), 4.33-4.35 (2 H, m, H-1 and H-4), 6.13 (1 H, d, J = 17.2 Hz, H-8C), 6.16 (1 H, d, J = 7.3 Hz, H-10C), 6.19 (1 H, d, J = 17.2 Hz, H-7C), 6.27 (1 H, d, J = 10.4 Hz, H-14C), 6.33 (1 H, d, J = 9.2 Hz, H-14'C), 6.36 (1 H, d, J = 14.9 Hz, H-12C), 6.44 (1 H, d, J = 11.9 Hz, H-10'C), 6.48 (1 H, d, J = 15.7 Hz, H-12'C), 6.65 (1 H, d, J = 15.8 Hz, H-8'C), 6.66-6.68 (4 H, m, H-11C, H-11'C, H-15C and H-15'C), 6.97 (2 H, t, J = 1.4 Hz, H-2 and H-3), 7.06 (1 H, d, J = 15.8 Hz, H-7'C), 7.56 (4 H, d, J = 7.9 Hz, H-3, Ar (10,20) and H-5, Ar (10,20)), 7.62 (2 H, d, J = 8.3 Hz, H-1', ArC and H-5', ArC), 7.99 (2 H, d, J = 8.3 Hz, H-2', ArC and H-4', ArC), 8.05 (2 H, d, J = 8.4 Hz, H-3, Ar (15) and H-5, Ar (15)), 8.099 (4 H, d, J = 7.9 Hz, H-2, Ar (10,20) and H-6, Ar (10,20)), 8.10 (2 H, d, J = 8.4 Hz, H-3, Ar (5) and H-5, Ar (5)), 8.15 (1 H, s, NHCO-15), 8.23 (2 H, d, J = 8.4 Hz, H-2, Ar (15) and H-6, Ar (15)), 8.26 (2 H, d, J = 8.4 Hz, H-2, Ar (5) and H-6, Ar (5)), 8.30 (1 H, d, J = 7.7 Hz, H-8), 8.30 (1 H, s, NHCO-5), 8.44 (1 H, dd, J = 7.7, 1.8 Hz, H-7), 8.64 (1 H, d, J = 1.8 Hz, H-5) 8.86-8.89 (8 H, m, pyrrole).

6-Carbomethoxy-1,4-dihydro-1,4-methanoanthracene-9,10-dione (17). A solution of ceric ammonium nitrate (57 mg, 0.1 mmol) in water (0.1 mL) was added to ester **8** (31 mg, 0.1 mmol) dissolved in 1 mL of acetonitrile. The reaction was allowed to proceed for 1.5 h with stirring under nitrogen. The progress of the reaction was monitored by TLC and by the disappearance of the blue fluorescence which is characteristic of the starting material. Two more additions of ceric ammonium nitrate (70.6 mg, 0.13 mol) were necessary. The reaction was complete after 12 h. The workup was affected by extraction ($CHCl_3/H_2O$). Purification by flash chromatography (silica gel, $CHCl_3$) yielded pure **17** (15 mg, 57%) as a yellow powder: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (1 H, d, J = 7.7 Hz, H-11 or H-11'), 2.41 (1 H, d, J = 7.7 Hz, H-11' or H-11), 3.99 (3 H, s, CO_2CH_3-6), 4.28 (2 H, m, H-1 and H-4), 6.92 (2 H, t, J = 1.8 Hz, H-2 or H-3), 8.15 (1 H, d, J = 7.9 Hz, H-8), 8.34 (1 H, dd, J = 7.9, 1.8 Hz, H-7), 8.70 (1 H, d, J = 1.8 Hz, H-5); MS, m/e 280 (M^+).

8-Carbomethoxy-5,12-dihydro-5,12-methanonaphthacene-1,4,6,11-tetraone (18). Ester **8** (20 mg, 0.048 mmol) was suspended in 2 mL of acetonitrile. Ceric ammonium nitrate (45.8 mg, 0.084 mmol) was dissolved in 0.2 mL of a mixture of water/acetonitrile (1:1 and added to the initial suspension. The reaction was stirred under nitrogen for 12 h. An additional portion of ceric ammonium nitrate (55.3 mg, 0.1 mmol) was then added and the reaction was allowed to continue for another 12 h. The workup was done by extraction ($CHCl_3/H_2O$). A flash column (silica gel, $CHCl_3$) yielded 9.6 mg (56%) of pure **18**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.70 (2 H, t, J = 1.4 Hz, H-13 and H-13'), 3.98 (3 H, s, CO_2CH_3-8), 4.81 (1 H, d, J = 1.4 Hz, H-5 or H-12), 4.82 (1 H, d, J = 1.4 Hz, H-12 or H-5), 6.65 (2 H, s,

H-2 and H-3), 8.08 (1 H, d, J = 1.8 Hz, H-7), 8.16 (1 H, d, J = 7.9 Hz, H-10), 8.36 (1 H, dd, J = 7.9, 1.8 Hz, H-9); MS, m/e 360 (M^+).

8-Carboxy-5,12-dihydro-1,4,6,11-tetramethoxy-5,12-methanonaphthacene (19). Ester **19** (94 mg, 0.22 mmol) was dissolved in a mixture of 4 mL of methanol, 12 mL of THF (freshly distilled from LAH) and 2 mL of an aqueous solution of KOH (10%). The solution was allowed to stir under nitrogen for 24 h. The workup was done by dilution with dichloromethane and extraction with water, after acidification of the reaction mixture with aqueous HCl. Evaporation of the solvents yielded 86 mg (95%) of pure acid **19**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (1 H, dt, J = 8.3, 1.5 Hz, H-13 or H-13'), 2.48 (1 H, dt, J = 8.3, 1.5 Hz, H-13' or H-13), 3.80 (6 H, s, OCH_3-1 and OCH_3-4), 4.06 (3 H, s, OCH_3-11), 4.12 (3 H, s, OCH_3-6), 5.01 (1 H, t, J = 1.5 Hz, H-5 or H-12), 5.04 (1 H, t, J = 1.5 Hz, H-12 or H-5), 6.56 (2 H, s, H-2 and H-3), 8.01 (1 H, dd, J = 8.8, 1.8 Hz, H-9), 8.08 (1 H, d, J = 8.8 Hz, H-10), 8.83 (1 H, d, J = 1.8 Hz, H-7); MS m/e/ 406 (M^+).

Porphyrin 23. Acid **19** (48.3 mg, 0.12 mmol) was dissolved in a mixture of 2 mL of dry toluene and 0.5 mL of dry pyridine. Thionyl chloride (65 mg, 0.55 mmol) was added slowly while the mixture was stirred under nitrogen. After 5 min a small sample was taken. The complete reaction of the aliquot with methanol indicated the quantitative formation of the acid chloride. The excess thionyl chloride and solvents were eliminated by vacuum distillation and the residue was redissolved in 3 mL of dry chloroform (freshly distilled from P_2O_5). This solution was added slowly to a stirred solution of porphyrin **22**[4] (122.2 mg, 0.18 mmol) in 10 mL of dry chloroform and 2.5 mL of dry pyridine, under nitrogen. When addition was complete, the workup was done by dilution with chloroform and extraction with a saturated solution of $NaHCO_3$ followed by water. Flash column chromatography (silica gel, $CHCl_3$) yielded 57.6 mg (46%) of the desired product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (1 H, d, J = 8.3 Hz, H-13 or H-13'), 2.53 (1 H, d, J = 8.3 Hz, H-13 or H-13'), 2.71 (6 H, s, CH_3, Ar (10) and CH_3, Ar (20)), 3.83 (6 H, s, OCH_3-1 and OCH_3-4), 4.13 (3 H, s, OCH_3-11), 4.21 (3 H, s, OCH_3-6), 5.07 (1 H, d, J = 1.4 Hz, H-5 or H-12), 5.10 (1 H, d, J = 1.4 Hz, H-5 or H-12), 6.58 (2 H, s, H-2 and H-3), 7.05 (2 H, d, J = 8.3 Hz, H-3, Ar (15) and H-5, Ar (15)), 7.55 (4 H, d, J = 7.8 Hz, H-3, Ar (10,20) and H-5, Ar (10,20)), 7.99 (2 H, d, J = 8.3 Hz, H-2 Ar (15) and H-6, Ar (15)), 8.06 (1 H, dd, J = 8.4 1.8 Hz, H-9), 8.10 (2 H, d, J = 8.5 Hz, H-3 Ar (5) and H-5, Ar (5)), 8.10 (4 H, d, J = 7.8 Hz, H-2 Ar (10,20) and H-6, Ar (10,20)), 8.23 (1 H, d, J = 8.4 Hz, H-10), 8.24 (2 H, d, J = 8.5 Hz, H-2, Ar (5) and H-6, Ar (5)), 8.34 (1 H, s, NHCO-5), 8.72 (1 H, d, J = 1.7 Hz, H-7), 8.85-8.89 (6 H, m, pyrrole), 8.93 (2 H, d, J = 4.7 Hz, H-3 pyrrole and H-7 pyrrole); MS m/e 1060 (M^+).

Porphyrin 24. Porphyrin **23** (10.8 mg 0.010 mmol) was dissolved in 2 mL of dry chloroform (freshly distilled from P_2O_5), heated to reflux with an oil bath and stirred under nitrogen with an excess of iodotrimethylsilane (ca. 0.5 mL) for 48 h. The reaction was worked up by extraction with $NaHCO_3$ (2 x 50 mL) and with water (2 x 50 mL). The solvents and excess reagent were distilled under vacuum. Flash chromatography (silica gel, $CHCl_3$ and 0.5% MeOH/$CHCl_3$) yielded 3.9 mg (39%) of a non-fluorescent porphyrin more polar

than the starting material (R_f = 0.13, TLC, SiO_2, 30% EtOAc/toluene). This porphyrin was dissolved in chloroform, ca. 1 mg of PbO_2 was added, and the suspension was stirred for 5 min. Filtration through a cotton plug and evaporation of the solvent at reduced pressure produced quantitatively a less polar, non-fluorescent porphyrin (R_f = 0.32, TLC, SiO_2, 30% EtOAc-toluene). The ^1H NMR (400 MHz, $CDCl_3$) spectrum was consistent with the diquinone structure, with resonances at δ 2.70 (6 H, s, CH_3, Ar (10) and CH_3, Ar (20)), 2.75 (2 H, AB quartet, J = 8.4 Hz, H-13 and H-13'), 4.03 (2 H, br s, NH_2-15), 4.88 (2 H, t, J = 1.7 Hz, H-5 and H-12), 6.68 (2 H, s, H-2 and H-3), 7.07 (2 H, d, J = 8.3 Hz, H-3 Ar (15) and H-5, Ar (15)), 7.55 (4 H, d, J = 7.8 Hz, H-3 Ar (10,20) and H-5, Ar (10,20)), 7.99 (2 H, d, J = 8.3 Hz, H-2, Ar (15) and H-2, Ar (15)), 8.07 (2 H, d, J = 8.4 Hz, H-3, Ar (5) and H-5, Ar (5)), 8.09 (4 H, d, J = 7.8 Hz, H-2 Ar (10,20) and H-6, Ar (10,20)), 8.25 (2 H, d, J = 8.4 Hz, H-2, Ar (5) and H-6, Ar (5)), 8.28 (1 H, s, NHCO-5), 8.31 (1 H, d, J = 8.0 Hz, H-10), 8.46 (1 H, dd, J = 8.0, 1.7 Hz, H-9), 8.64 (1 H, d, J = 1.7 Hz, H-7), 8.84-8.93 (6 H, m, pyrrole), 8.92 (2 H, d, J = 4.8 Hz, H-3 pyrrole and H-7 pyrrole). Useable mass spectra data for porphyrin **24** were impossible to obtain. NMR (400 MHz, $CDCl_3$) and mass spectral analysis was performed on the acetylated form of **24**: δ 2.36 (3 H, s, $COCH_3$ Ar (15)), 2.70 (6 H, s, CH_3, Ar (10) and CH_3, Ar (20)), 2.75 (2 H, s, H-13 and H-13'), 4.87 (2 H, s, H-12 and H-5), 6.68 (2 H, s, H-2 and H-3), 7.48 (1 H, s, NHCO-15), 7.55 (4 H, d, J = 7.4 Hz, H-3, Ar (10,20) and H-5, Ar (10,20)), 7.89 (2 H, d, J = 8.0 Hz, H-3, Ar (15) and H-5, Ar (15)), 8.08 (4 H, d, J = 7.4 Hz, H-2, Ar (10,20) and H-6, Ar (10,20)), 8.08 (2 H, d, J = 8.0 Hz, H-3, Ar (5) and H-5, Ar (5)), 8.16 (2 H, d, J = 8.0 Hz, H-2, Ar (15) and H-6, Ar (15)), 8.25 (2 H, d, J = 8.0 Hz, H-2, Ar (5) and H-6, Ar (5)), 8.30 (1 H, d, J = 7.9 Hz, H-10), 8.33 (1 H, s, NHCO-5), 8.45 (1 H, d, J = 7.9 Hz, H-9) 8.64 (1 H, s, H-7), 8.84-8.87 (8 H, m, pyrrole); MS m/e 1044 (M^+, hydroquinone form).

Tetrad 1. A sample of 4-(β-apo-7'-carotenyl)benzoic acid[12] (5.9 mg, 0.01 mmol) was dissolved in 2 mL of dry toluene, and the resulting solution was kept under nitrogen and well stirred while 0.5 mL of dry pyridine and thionyl chloride (5 mg, 0.04 mmol) were added. After addition was complete, the excess of thionyl chloride and solvents were distilled under vacuum. Porphyrin **24** (4.1 mg, 0.004 mmol) was dissolved in 3 mL of dry chloroform and 0.5 mL of dry pyridine. The acid chloride prepared above was redissolved in 2 mL of dry chloroform and added to the solution of the porphyrin. The workup was done by dilution with chloroform and extraction with water (2 x 50 mL). Flash chromatography (silica gel, $CHCl_3$) yielded 3.8 mg (63%) of pure tetrad 1: ^1H NMR (400 MHz, $CDCl_3$) δ 1.04 (3 H, s, CH_3-17C[a]), 1.05 (3 H, s, CH_3-16C), 1.48 (2 H, m, CH_2-2C), 1.66 (2 H, m, CH_2-3C), 1.72 (3 H, s, CH_3-18C), 1.98 (3 H, s, CH_3-19C), 2.00 (3 H, s, CH_3-20C), 2.01 (3 H, s, CH_3-20'C), 2.07 (2 H, s, CH_2-4C), 2.11 (3 H, s, CH_3-19'C), 2.71 (6 H, s, CH_3, Ar (10) and CH_3, Ar (20)), 2.76 (2 H, s, H-13 and H-13'), 4.88 (2 H, s, H-5 and H-12), 6.14 (1 H, d,

[a] C indicates carotenoid.

J = 15.2 Hz, H-8C), 6.17 (1 H, d, J = 7.4 Hz, H-10C), 6.18 (1 H, d, J = 15.2 Hz, H-7C), 6.27 (1 H, d, J = 9.2 Hz, H-14C), 6.34 (1 H, d, J = 9.2 Hz, H-14'C), 6.41 (1 H, d, J = 14.7 Hz, H-12C), 6.45 (1 H, d, J = 13.2 Hz, H-10'C), 6.49 (1 H, d, J = 15.1 Hz, H-12'C), 6.65 (1 H, d, J = 16.0 Hz, H-8'C), 6.67-6.68 (4 H, m, H-11C, H-11'C, H-15C and H-15'C), 6.68 (2 H, s, H-2 and H-3), 7.07 (1 H, d, J = 16.0 Hz, H-7'C), 7.56 (4 H, d, J = 7.9 Hz, H-3, Ar (10,20) and H-5, Ar (10,20)), 7.63 (2 H, d, J = 8.2 Hz, H-1', ArC and H-5', ArC), 7.99 (2 H, d, J = 8.2 Hz, H-2', ArC and H-4', ArC), 8.05 (2 H, d, J = 8.0 Hz, H-3, Ar (15) and H-5, Ar (15)), 8.09 (4 H, d, J = 7.9 Hz, H-2, Ar (10,20) and H-6, Ar (10,20)), 8.09 (2 H, d, J = 8.4 Hz, H-3, Ar (5) and H-5, Ar (5)), 8.15 (1 H, s, NHCO-15), 8.23 (2 H, d, J = 8.0 Hz, H-2, Ar 15) and H-6, Ar (15)), 8.26 (2 H, d, J = 8.4 Hz, H-2, Ar (5) and H-6, Ar (5)), 8.30 (1 H, s, NHCO-5), 8.31 (1 H, d, J = 8.7 Hz, H-10), 8.46 (1 H, d, J = 8.7 Hz, H-9), 8.65 (1 H, s, H-7), 8.86-8.88 (8 H, m, pyrrole).

8-Carboxy-1,4-dihydroxy-6,11-dimethoxy-1,4,4a,5,12,12a-hexahydro-5,12-methanonaphthacene (20). Ester **9** (210 mg, 0.44 mmol) was dissolved in a mixture of 24 mL of freshly distilled (from LAH) THF, 8 mL of methanol and 4 mL of an aqueous solution of KOH (10%). The solution was allowed to stir under nitrogen for 12 h. The workup was effected by many extractions with chloroform after acidification of the reaction mixture with dilute aqueous HCl. The extraction procedure was repeated until the chloroform layer did not exhibit the typical blue fluorescence of **20**. The product, which was obtained in quantitative yield and consisted of several diastereoisomers, was used without further purification for the next step: ^{1}H NMR (400 MHz, DMSO-D6), δ 1.66 (1 H, d, J = 9.7 Hz, H-13 or H-13'), 1.71 (2 H, br s, H-12a and H-4a), 2.00 (1 H, d, J =9.7 Hz, H-13 or H-13'), 3.77 (1 H, s, H-5 or H-12), 3.80 (1 H, s, H-5 or H-12), 3.95 (3 H, s, OCH_3-11), 3.95 (2 H, s, H-1 and H-4), 4.00 (3 H, s, OCH_3-6), 5.34 (2 H, br s, OH-1 and OH-4), 5.68 (2 H, s, H-3 and H-2), 7.92 (1 H, dd, J = 8.7, 1.6 Hz, H-9), 8.05 (1 H, d, J = 8.7 Hz, H-10), 8.65 (1 H, d, J = 1.6 Hz, H-7); MS m/e 382 (M^+).

8-Carboxy-1,4-diacetoxy-6,11-dimethoxy-1,4,4a,5,12,12a-hexahydro-5,12-methanonaphthacene (21). Acid **20** (210 mg, 55 mmol) was dissolved in 1 mL of acetic anhydride and one drop of concentrated H_2SO_4 was added as a catalyst. The reaction was essentially instantaneous. The workup consisted of the addition of 50 mL of a saturated solution of $NaHCO_3$ followed by acidification with dilute aqueous HCl and extraction with many portions of chloroform. A flash column (silica gel, 2% MeOH/$CHCl_3$) provided 116 mg (45%) of **21** as a mixture of at least three stereoisomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.83-2.06 (1 H, m, H-13 or H-13'), 2.19 (3 H, s, CH_3CO_2-1 or CH_3CO_2-4), 2.24 (3 H, s, CO_2CH_3-1 or CO_2CH_3-4), 2.26-2.35 (1 H, m, H-13 or H-13'), 3.47-3.73 (2 H, m, H-5 and H-12), 3.95-4.10 (6 H, m, OCH_3-6 and OCH_3-11), 5.27-5.51 (2 H, m, H-1 and H-4), 5.75 (s, H-2 or H-3) 5.97 (s, H-2 or H-3, other stereoisomer), 8.07-8.19 (2 H, m, H-9 and H-10), 8.92-8.97 (1 H, m, H-7); MS m/e 466 (M^+).

Carotenoporphyrin 28 was prepared as described for triad **25** by using 50.4 mg (0.11 mmol) of acid **21** and 17 mg (0.014 mmol) of carotenoporphyrin **27**, to yield quantitatively carotenoporphyrin **28** (as a mixture of stereoisomers) after purification by

flash chromatography (silica gel, $CHCl_3$): ^1H NMR (400 MHz, $CDCl_3$), δ 1.04 (3 H, s, CH_3-17C), 1.05 (3 H, s, CH_3-16C), 1.46-1.49 (2 H, m, CH_2-2C), 1.60-1.63 (2 H, m, CH_2-3C), 1.72 (3 H, s, CH_3-18C), 1.98 (3 H, s, CH_3-19C), 2.00 (3 H, s, CH_3-20C), 2.01 (3 H, s, CH_3-20'C), 2.04 (2 H, m, CH_2-4C), 2.09 (3 H, s, CH_3-19'), 2.16 (1 H, d, J = 0.9 Hz, H-13 or H-13'), 2.17 (1 H, s, H-13 or H-13'), 2.20-2.25 (2 H, m, H-4a and H-12a), 2.20-2.35 (3 H, s, CH_3CO_2-1 and CH_3CO_2-4), 2.71 (6 H, s, CH_3, Ar (10) and CH_3, Ar (20)), 3.76 (1 H, s, H-5 or H-12), 3.79 (1 H, s, H-5 or H-12), 4.00-4.16 (6 H, several s, OCH_3-11 and OCH_3-6), 5.31 (2 H, dt, J = 7.9, 2.6 Hz, H-1 and H-4), 5.78 (2 H, d, J = 0.8 Hz, H-2 and H-3), 6.13 (1 H, d, J = 15.8 Hz, H-8C), 6.17 (1 H, d, J = 7.32 Hz, H-10C), 6.19 (1 H, d, J = 15.8 Hz, H-7C), 6.27 (1 H, d, J = 8.7 Hz, H-14C), 6.33 (1 H, d, J = 11.7 Hz, H-14'C), 6.37 (1 H, d, J = 15.1 Hz, H-12C), 6.44 (1 H, d, J = 12.3 Hz, H-10'C), 6.48 (1 H, d, J = 15.2 Hz, H-12C), 6.65 (1 H, d, J = 15.8 Hz, H-8'C), 6.66-6.70 (4 H, m, H-11C, H-11'C, H-15C and H-15'C), 7.06 (1 H, d, J = 15.8 Hz, H-7'C), 7.55 (4 H, d, J = 7.9 Hz, H-3 Ar (10,20) and H-5, Ar (10,20)), 7.62 (2 H, d, J = 8.4 Hz, H-1', ArC and H-5', ArC), 7.99 (2 H, d, J = 8.4 Hz, H-2', ArC and H-4' ArC), 8.05 (2 H, d, J = 8.4 Hz, H-3, Ar (15) and H-5, Ar (15), 8.10 (4 H, d, J = 7.9 Hz, H-2, Ar (10,20) and H-6, Ar (10,20)), 8.15 (1 H, s, NHCO-15), 8.21-8.24 (1 H, dd, J = 8.6, 1.7 Hz, H-9), 8.12 (2 H, d, J = 8.4 Hz, H-3, Ar (5) and H-5, Ar (5)), 8.23 (2 H, d, J = 8.4 Hz, H-2, Ar (15) and H-6, Ar (15)), 8.25 (2 H, d, J = 8.4, H-2 Ar (5) and H-6 Ar (5)), 8.28 (1 H, d, J = 8.6 Hz, H-10), 8.35 (1 H, s, NHCO-5), 8.78 (1 H, d, J = 1.7 Hz, H-7), 8.88-8.89 (8 H, m, pyrrole).

Carotenoporphyrin 29. Carotenoporphyrin **28** (24.7 mg, 0.015 mmol) was suspended in methanol and stirred vigorously under nitrogen with an excess of K_2CO_3 for 12 h. The workup was effected by evaporation of the methanol and extraction (chloroform/water 2 X). A flash column (silica gel, 2% MeOH/$CHCl_3$) yielded 15.3 mg (67%) of carotenoporphyrin **29** (mixture of stereoisomers): ^1H NMR (400 MHz, $CDCl_3$) δ 1.03 (3 H, s, CH_3-17C), 1.05 (3 H, s, CH_3-16C), 1.47-1.50 (2 H, m, CH_2-2C), 1.60-1.63 (2 H, m, CH_2-3C), 1.72 (3 H, s, CH_3-18C), 1.80-1.95 (1 H, br m, H-13 or H-13'), 1.98 (3 H, s, CH_3-19C), 1.99 (3 H, s, CH_3-20C), 2.01 (3 H, s, CH_3-20'C), 2.03 (2 H, m, CH_2-4C), 2.09 (3 H, s, CH_3-19'C), 2.05-2.15 (2 H, br m, H-4a and H-12a), 2.55-2.65 (1 H, br m, H-13 or H-13'), 2.71 (6 H, s, CH_3, Ar (10) and CH_3, Ar (20)), 3.55-3.85 (2 H, m, H-12 and H-5), 4.00-4.23 (6 H several s, OCH_3-11 and OCH_3-6), 4.50-4.65 (2 H, br m, H-1 and H-4), 5.72 (2 H, s, H-2 and H-3), 6.13 (1 H, d, J = 16.0 Hz, H-8C), 6.16 (1 H, d, J = 7.2 Hz, H-10C), 6.19 (1 H, d, J = 15.7 Hz, H-7C), 6.27 (1 H, d, J = 9.08 Hz, H-14C), 6.33 (1 H, d, J = 11.7 Hz, H-14'C), 6.36 (1 H, d, J = 15.0 Hz, H-12C), 6.44 (1 H, d, J = 12.2 Hz, H-10'C), 6.48 (1 H, d, J = 15.1 Hz, H-12'C), 6.65 (1 H, d, J = 15.8 Hz, H-8'C), 6.60-6.70 (4 H, m, H-11C, H-11'C, H-15C and H-15'C), 7.06 (1 H, d, J = 15.8 Hz, H-7'C) 7.56 (4 H, d, J = 7.7 Hz, H-3, Ar (10,20) and H-5, Ar (10,20)), 7.62 (2 H, d, J = 8.4 Hz, H-1', ArC and H-5' ArC), 7.99 (2 H, d, J = 8.4 Hz, H-2', ArC and H-4', ArC), 8.03 (1 H, dd, J = 8.6, 1.4 Hz, H-9), 8.04 (2 H, d, J = 8.4 Hz, H-3, Ar (15) and H-5, Ar (15)), 8.10 (4 H, d, J = 7.7 Hz, H-2, Ar (10,20) and H-6, Ar (10,20), 8.11 (2 H, d, J = 8.3 Hz, H-3, Ar (5) and H-5, Ar (5)), 8.15 (1 H, s, NHCO-15), 8.22 (2 H, d, J = 8.4 Hz, H-2, Ar (15) and H-6, Ar (15)), 8.24 (2 H, d, J = 8.3 Hz, H-2, Ar

(5) and H-6, Ar (5)), 8.28 (1 H, d, J = 8.6 Hz, H-10), 8.37 (1 H, s, NHCO-5), 8.76-8.77 (1 H, 3s, H-7), 8.88 (8 H, br s, pyrrole).

Carotenoporphyrin 30. Carotenoporphyrin **29** (15.3 mg, 0.01 mmol) was dissolved in 5 mL of dichloromethane and stirred vigorously under nitrogen with an excess of MnO_2 for 36 h. The suspension was filtered through a bed of celite and the solids were washed with a mixture of chloroform and methanol. Evaporation of the solvents yielded 8.9 mg of a pure porphyrin which was less polar than the starting material. This product was dissolved in 2 mL of dichloromethane and stirred under nitrogen with an excess of Al_2O_3. The reaction did not go to completion and was stopped after 48 h. The suspension was filtered through a bed of celite and the solids were washed with a mixture of chloroform and methanol. Evaporation of the solvents followed by flash chromatography (silica gel, 1% MeOH/$CHCl_3$) yielded 1.2 mg (8%) of carotenoporphyrin **30**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 (3 H, s, CH_3-17C), 1.05 (3 H, s, CH_3-16C), 1.45-1.50 (2 H, m, CH_2-2C), 1.60-1.64 (2 H, m, CH_2-3C), 1.72 (3 H, s, CH_3-18C), 1.98 (3 H, s, CH_3-19C), 1.99 (3 H, s, CH_3-20C), 2.01 (3 H, s, CH_3-20'C), 2.03 (2 H, s, CH_2-4C), 2.10 (3 H, s, CH_3-19'C), 2.51 (1 H, dd, J = 8.8, 1.6 Hz, H-13 or H-13'), 2.53 (1 H, dd, J = 8.8, 1.5 Hz, H-13 or H-13'), 2.71 (6 H, s, CH_3, Ar (10) and CH_3, Ar (20)), 4.14 (3 H, s, OCH_3-11), 4.22 (3 H, s, OCH_3-6), 5.02 (1 H, d, J = 1.6 Hz, H-5 or H-12), 5.06 (1 H, d, J = 1.5 Hz, H-5 or H-12), 6.13 (1 H, d, J = 17.6 Hz, H-8C), 6.16 (1 H, d, J = 7.3 Hz, H-10C), 6.19 (1 H, d, J = 17.6 Hz, H-7C), 6.27 (1 H, d, J = 8.7 Hz, H-14C), 6.33 (1 H, d, J = 10.1 Hz, H-14'C), 6.37 (1 H, d, J = 14.8 Hz, H-12C), 6.40 (2 H, s, H-2 and H-3), 6.45 (1 H, d, J = 12.0 Hz, H-10'C), 6.48 (1 H, d, J = 15.4 Hz, H-12'C), 6.64-6.68 (4 H, m, H-11C, H-11'C, H-15C ad H-15'C), 6.66 (1 H, d, J = 15.8 Hz, H-8'C), 7.06 (1 H, d, J = 15.8 Hz, H-7'C), 7.56 (4 H, d, J = 7.8 Hz, H-3, Ar (10,20) and H-5, Ar (10,20)), 7.63 (2 H, d, J = 8.3 Hz, H-1', ArC and H-5', ArC), 8.00 (2 H, d, J = 8.3 Hz, H-2', ArC and H-4', ArC), 8.07 (2 H, d, J = 7.7 Hz, H-3 Ar (15) and H-5, Ar (15)), 8.09 (1 H, dd, J = ca. 8.8, 1.7 Hz, H-9), 8.10 (4 H, J = 7.8 Hz, H-2, Ar (10,20) and H-6, Ar (10,20)), 8.10 (2 H, d, J = 8.1 Hz, H-3, Ar (5) and H-5, Ar (5)), 8.13 (1 H, d, J = ca. 8.8, H-10), 8.15 (1 H, s, NHCO-15), 8.23 (2 H, d, J = 7.7 Hz, H-2, Ar (15) and H-6, Ar (15)), 8.24 (2 H, d, J = 8.1 Hz, H-2, Ar (5) and H-6, Ar (5)), 8.33 (1 H, s, NHCO-5), 8.72 (1 H, d, J = 1.7 Hz, H-7), 8.86 (2 H, s, OH-1 and OH-4), 8.88 (8 H, br s, pyrrole).

Triad 26. Carotenoporphyrin **30** (1.2 mg, 0.001 mmol) was dissolved in 1 mL of chloroform and stirred under nitrogen with an excess of PbO_2. The progress of the reaction was monitored by TLC. After ca. 15 min the reaction was complete and the PbO_2 was removed by filtration through a cotton plug. The ^{1}H NMR (400 MHz, $CDCl_3$) spectrum was consistent with the benzoquinone structure, with resonances at δ 1.03 (3 H, s, CH_3-17C), 1.05 (3 H, s, CH_3-16C), 1.48-1.50 (2 H, m, CH_2-2C), 1.61-1.67 (2 H, m, CH_2-3C), 1.72 (3 H, s, CH_3-18C), 1.98 (3 H, s, CH_3-19C), 1.99 (3 H, s, CH_3-20C), 2.01 (3 H, s, CH_3-20'C), 2.03 (2 H, s, CH_2-4C), 2.10 (3 H, s, CH_3-19'C), 2.52 (1 H, dd, J = 8.4, 1.1 Hz, H-13 or H-13'), 2.61 (1 H, d, J = 8.4 Hz, H-13 or H-13'), 2.71 (6 H, s, CH_3, Ar (10) and CH_3, Ar (20)), 4.10 (3 H, s, OCH_3-11) 4.19 (3 H, s, OCH_3-6), 4.97 (1 H, d, J = 1.1 Hz, H-5 or H-12), 5.00 (1 H, s, H-5 or H-12), 6.13 (1 H, d, J = 16.2 Hz, H-8C), 6.16 (1 H, d, J = 7.4 Hz, H-10C), 6.19

(1 H, d, J = 16.2 Hz, H-7C), 6.27 (1 H, d, J = 8.28 Hz, H-14C), 6.33 (1 H, d, J = 10.2 Hz, H-14'C), 6.37 (1 H, d, J = 14.7 Hz, H-12C), 6.45 (1 H, d, J = 12.4 Hz, H-10'C), 6.48 (1 H, d, J = 15.6 Hz, H-12'C), 6.65 (2 H, s, H-2 and H-3), 6.65 (1 H, d, J = 15.8 Hz, H-8'C), 6.65-6.68 (4 H, m, H-11C, H-11'C, H-15C and H-15'C), 7.06 (1 H, d, J = 15.8 Hz, H-7'C), 7.56 (4 H, d, J = 7.9 Hz, H-3, Ar (10,20) and H-5, Ar (10,20)), 7.63 (2 H, d, J = 8.3 Hz, H-1', ArC and H-5', ArC), 8.00 (2 H, d, J = 8.3 Hz, H-2', ArC and H-4', ArC), 8.05 (2 H, d, J = 7.6 Hz, H-3, Ar (15) and H-5, Ar (15)), 8.10 (2 H, d, J = 8.4 Hz, H-3, Ar (5) and H-5, Ar (5)), 8.10 (4 H, d, J = 7.9 Hz, H-2, Ar (10,20) and H-6, Ar (10,20)), 8.14 (1 H, dd, J = ca. 8.8, 1.6 Hz, H-9), 8.15 (1 H, s, NHCO-15), 8.21 (1 H, d, J = ca. 8.8 Hz, H-10), 8.23 (2 H, d, J = 7.6 Hz, H-2, Ar (15) and H-6, Ar (15)), 8.25 (2 H, d, J = 8.4 Hz, H-2, Ar (5) and H-6, Ar (5)), 8.32 (1 H, s, NHCO-5), 8.73 (1 H, d, J = 1.6 Hz, H-7), 8.88 (8 H, br s, pyrrole).

Electrochemistry

Potentials for reduction of the quinones **12**, **17**, **18** and of 2,5-dimethylbenzoquinone (DMQ) were obtained by cyclic voltammetry on PAR instrumentation in 1,2-dichloroethane, with tetrabutylammonium hexafluorophosphate (0.10 M) as electrolyte and Pt button, wire and mesh as working, counter and reference electrodes, respectively. Ferrocene (ca. 10^{-4} M) was added to the sample and reference compartments of the electrochemical cell and served as an internal reference.

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