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ULTRAFAST PHOTOINDUCED ELECTRON TRANSFER IN RIGID DONOR-SPACER-ACCEPTOR MOLECULES: MODIFICATION OF SPACER ENERGETICS AS A PROBE FOR SUPEREXCHANGE

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ABSTRACT

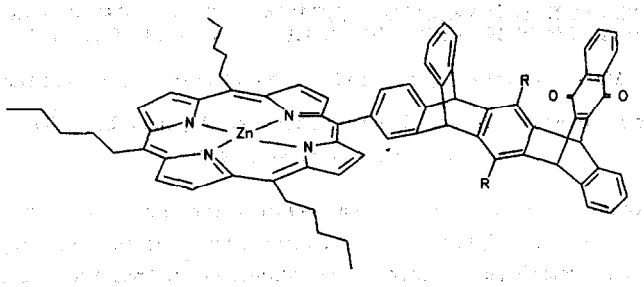
Four fixed-distance porphyrin-quinone molecules, **1-syn**, **1-anti**, **2-syn**, and **2-anti**, were synthesized. These molecules possess a zinc 5-phenyl-10,15,20-tripentylporphyrin electron donor attached to a naphthoquinone via a rigid pentiptycene spacer. The central benzene ring of the spacer is unsubstituted in **1** and possesses p-dimethoxy substituents in **2**. The naphthoquinone is oriented either **syn** or **anti** to the porphyrin across the spacer. These molecules provide information concerning the orientation dependence of electron transfer between the porphyrin and the quinone, and the dependence of this transfer on low-lying ionic states of the spacer. The rate constants for the oxidation of the porphyrin lowest excited singlet state by the naphthoquinone are **1-syn**: 8.2×10^9 s^{-1}; **1-anti**: 1.7×10^{10} s^{-1}; **2-syn**: 8.5×10^9 s^{-1}; **2-anti**: 1.9×10^{10} s^{-1}. The corresponding rate constants for the porphyrin cation - naphthoquinone anion recombination reaction are **1-syn**: 1.4×10^{10} s^{-1}; **1-anti**: 2.5×10^{10} s^{-1}; **2-syn**: 5.0×10^{10} s^{-1}; **2-anti**: 8.2×10^{10} s^{-1}. The rate constants for the **syn** isomers are uniformly a factor of about 2 slower than those of the **anti** isomers. The charge separation reaction rates for **1** and **2** are similar, while the ion pair recombination reactions are about 3-4 x faster in **2** than in **1**. The conformational effect is attributed to better overlap of the spacer wave functions in the **anti** vs the **syn** conformation, while the increase in recombination rate for **2** over **1** is attributed to a superexchange interaction involving an electronic configuration of the spacer in which the dimethoxybenzene cation contributes.

INTRODUCTION

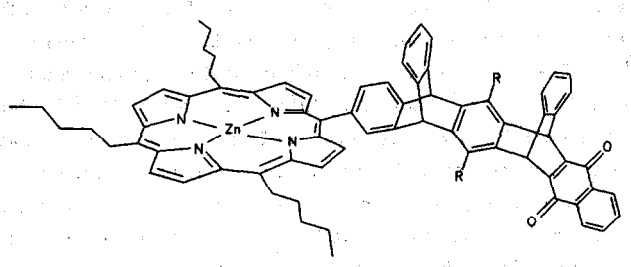
The chlorophyll and quinone electron donors and acceptors in photosynthetic reaction centers are positioned at precise distances and orientations to promote efficient charge separation and to impede charge recombination.[1] Moreover, the nature of the medium that lies between the donor and acceptor is thought to have a large influence on the observed rates of electron transfer.[2-4] Covalently-linked porphyrin-quinone molecules have been studied extensively as models for the light-initiated charge separation in photosynthesis.[5] Studies performed to date have been concerned primarily with the dependence of the electron transfer reactions on free energy, distance, and solvent.[6-9] In general, our approach to this problem is to synthesize molecules in which both the porphyrin-quinone distance and mutual orientation are restricted. This entails the use of rigid hydrocarbon spacer molecules as part of the overall molecular structure.

The role of the intervening medium that lies between a donor and an acceptor is beginning to be studied both theoretically and experimentally. In the bacterial photosynthetic reaction center a bacteriochlorophyll molecule lies between the dimeric bacteriochlorophyll donor and the bacteriopheophytin acceptor. It is thought that mixing low-lying ionic states of the intermediate bacteriochlorophyll with those of the donor and acceptor lead to a greatly increased rate of electron transfer.[10-12] This concept, known as superexchange, has its origins in the work of McConnell, which treats electron transfer between aromatic molecules across a hydrocarbon spacer.[13] This idea has been elaborated in a

number of papers regarding the dependence of electron transfer on the energies and spatial characteristics of both hydrocarbon[14-17] and protein spacer orbitals.[2,3,18-20] In general, molecules possessing low-lying π molecular orbitals can contribute strongly to a superexchange mechanism for electron transfer. It is possible that aromatic amino acids, such as tyrosine, phenylalanine, and tryptophan, which lie between an electron donor and an acceptor in proteins, can facilitate electron transfer reactions. However, there are few experimental tests of superexchange in donor-acceptor molecules, especially those involving excited state electron transfers.[21,22] The problem lies in producing a series of rigid donor-acceptor molecules in which the effects of changing the orbital energies of the intervening spacer molecule are not convolved with changes in conformation. Molecules **1-syn**, **1-anti**, **2-syn**, and **2-anti**, described in this paper, are designed to address this problem. These molecules utilize a polycyclic hydrocarbon spacer to maintain a fixed distance and restricted orientation between the porphyrin donor and the quinone acceptor. This spacer belongs to a general class of hydrocarbons that have been named "iptycenes" by Hart.[23] In particular, the hydrocarbon spacer used in **1** and **2** is a "pentiptycene" because it contains 5 aromatic rings. There are several advantages to using this ring system as a spacer.



1-anti: R = H and **2-anti**: R = OCH_3



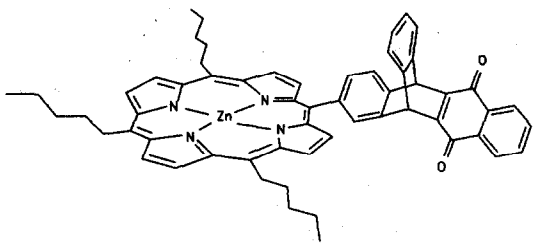
1-syn: R = H and **2-syn**: R = OCH_3

First, it is closely related to triptycene, a spacer that we have studied extensively.[5] Second, the presence of two positional isomers, in which the porphyrin and quinone are either **syn** or **anti** relative to one another, affords us the opportunity to study the orientation dependence of photoinduced electron transfer reactions at a fixed distance. Third, the presence of a central benzene ring, rigidly fixed between the two triptycene moieties, allows us to use substituents on the remaining free positions of this ring to alter the energy of the HOMO and LUMO of this intervening spacer

fragment. This alters the relative contribution of ionic states of the spacer to a superexchange description of electron transfer.

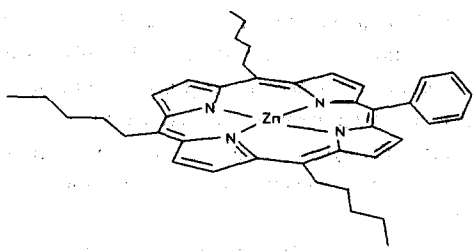
SYNTHESES

In addition to pentiptycene containing molecules, **1** and **2**, we have prepared the corresponding triptycene containing reference compound, **3**, and the appropriate porphyrin reference compound 5-phenyl-10,15,20-tripentylporphyrin, **4**.



3

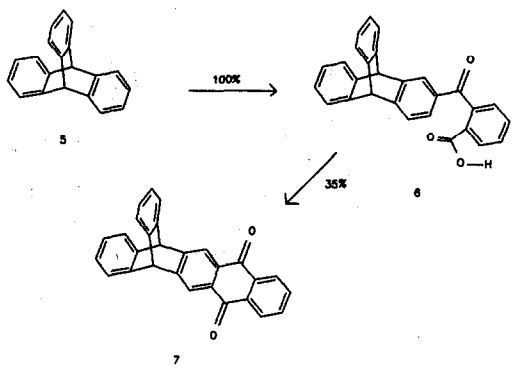
The free base of compound **3** was prepared by the Diels-Alder addition of 1,4-naphthoquinone to 5-(2-anthracenyl)-10,15,20-tripentylporphyrin, followed by *in situ* oxidation of the adduct to the desired triptycene-quinone. The anthracenyl porphyrin was prepared from 2-anthraldehyde[24], 1-hexanal, and pyrrole by Lindsey's equilibrium method.[25] The free base of compound **4** was prepared from benzaldehyde, 1-hexanal, and pyrrole using Lindsey's method. Compounds **3** and **4** were prepared from their corresponding free bases by gentle warming of the free base porphyrins with $Zn(OAc)_2$.



4

The synthesis of **1**-syn and **1**-anti proceeds as follows: Triptycene, **5**[26], is acylated with phthalic anhydride using $AlCl_3$ in 1,2-dichloroethane to yield the corresponding keto acid **6** in quantitative yield. Ring closure of the keto acid

to yield anthraquinone 7 is complicated by the presence of the additional benzene rings of the triptycene, which are activated toward electrophiles, and by the lack of solubility of the keto acid in media typically used for such closures, e.g. polyphosphoric acid. Closure in hot H_2SO_4 fails because facile sulfonation of the activated benzene rings occurs at the temperatures required to effect ring closure. We found that respectable yields of anthraquinone 7 could be obtained with good reproducibility by treating keto acid 6 with $AlCl_3$ in hot nitrobenzene. This treatment afforded a 35% conversion of 6 to anthraquinone 7.



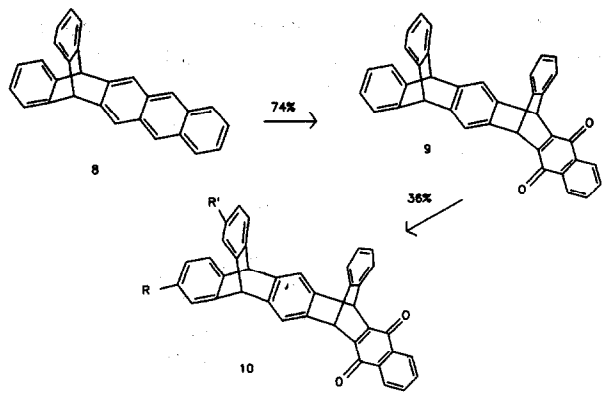
Anthraquinone 7 was reduced to the corresponding anthracene, 8, in 69% yield using Zn dust in a mixture of n-butylamine and ammonia. In this case the presence of the n-butylamine serves to dissolve the relatively insoluble quinone, 7. Hydrocarbon 8 has been prepared previously by several methods. An 8-step route, which uses the addition of the 2,3-benzyne intermediate of 9,10-anthraquinone to anthracene, results in < 1% yield of 8.[27] Hart describes 3 different routes possessing 5, 5, and 4 steps, which give 25, 30, and 69% overall yields, respectively of 8.[23] Our route involves 4 steps with an overall yield of 20% from anthracene and makes use of relatively inexpensive materials.

We find that hydrocarbon 8 is somewhat less reactive than anthracene toward Diels-Alder reactions with quinones. Naphthoquinone pentiptycene derivative 9 was prepared by a combined Diels-Alder addition, oxidation route. Heating 8 at 140° with excess naphthoquinone in nitrobenzene overnight gives 9 in 74% yield.

Formylation of 9 results in selective reaction at the benzene rings that are distal to the naphthoquinone. The benzene rings adjacent to the naphthoquinone in pentiptycene 9 are deactivated toward electrophilic substitution by a transannular effect of the naphthoquinone. Formylation of 9 was carried out with α,α-dichloromethyl methyl ether using $AlCl_3$ as the catalyst to give a 1:1 mixture of aldehydes 10-syn and 10-anti in 36% yield. The isomers were not separated, but were used in the next step.

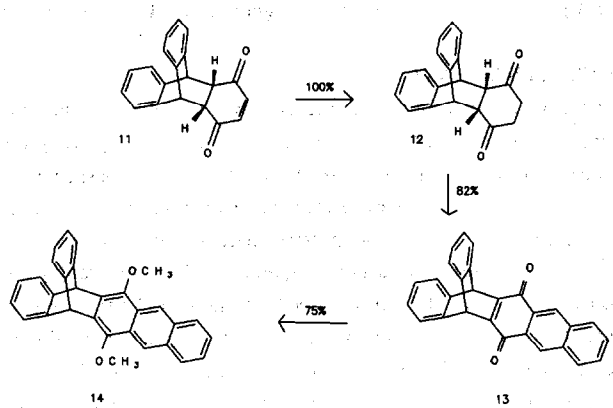
Compounds 1-syn and 1-anti were prepared from a statistical mixture of aldehydes 10-syn and 10-anti, 1-hexanal, and pyrrole using the Lindsey equilibrium method. The yield of free base 1-syn and 1-anti was 2.9%. Insertion of zinc occured readily in these compounds. The syn and anti isomers were separated by preparative TLC, and their structures were assigned by ^1H nmr spectroscopy.

In order to synthesize compounds 2-syn and 2-anti we chose to prepare a triptycenyl anthracene derivative which

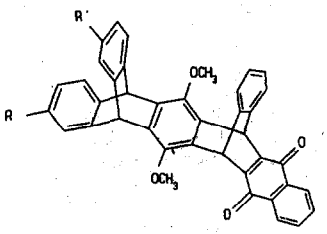


10-syn: R = CHO, R' = H; 10-anti: R = H, R'= CHO

contains two methoxy groups. Diels-Alder reaction of anthracene with p-benzoquinone gave the well-known adduct **11** in 83% yield.[28] This adduct was then hydrogenated quantitatively using H_2 on Pd/C catalyst to yield the corresponding diketone, **12**.[29] This diketone contains a useful fused cyclohexane-1,4-dione moiety, which can undergo a variety of condensation reactions. Reaction of diketone **12** with o-phthalaldehyde in the presence of OH^- results in a high yield of the double condensation, ring annelation product, which readily undergoes air oxidation to give an 82% yield of a triptycene in which one of its benzene rings has been converted to a 1,4-anthraquinone, **13**. This anthraquinone can be reduced with H_2 using a Pd/C catalyst in an aprotic solvent such as DMF to give the corresponding hydroquinone, which is not isolated. Instead, air is rigorously excluded and the hydroquinone dianion



is formed using lithium 2,6-di-tert-butyl-4-methoxyphenolate, a moderately strong, non-nucleophilic base. Nucleophilic reaction of the dianion with excess dimethyl sulfate results in a 75% yield of 1,4-dimethoxyanthracene derivative, **14**.



15: R = R' = H; **16-syn**: R = CHO, R' = H; **16-anti**: R = H, R' = CHO

The remaining synthetic pathway to produce **2-syn** and **2-anti** follows by analogy that used to produce **1-syn** and **1-anti**. Dimethoxyanthracene derivative **14** was subjected to a one-pot Diels-Alder reaction followed by *in situ* oxidation using excess 1,4-naphthoquinone in hot nitrobenzene to give naphthoquinone derivative **15** in 77% yield. Formylation of **15** was carried out in a manner analogous to that used to prepare aldehyde **10**, except that $TiCl_4$ was used as the catalyst. The formylation procedure gave aldehydes **16-syn** and **16-anti** 1:1 in 32% yield.

Preparation of the free base porphyrins of **2-syn** and **2-anti** was achieved by reacting a statistical mixture of **16**, hexanal, and pyrrole using Lindsey's procedure. The yield of the free base isomers was 4.8%. Zinc insertion into the free base porphyrins occured quantitatively to give **2-syn** and **2-anti**. These isomers were readily separated using preparative TLC on silica gel plates. The structures were assigned using ^1H nmr spectroscopy.

ABSORPTION AND FLUORESCENCE DATA

The ground state optical absorption spectrum of **1-anti** is shown in Figure 1. The spectrum is identical to that of porphyrin **4**, which indicates that the attachment of both the spacer and the naphthoquinone to the porphyrin do not strongly perturb its electronic structure. Figure 2 shows the fluorescence emission spectra of **1-anti** and **4**. The emission spectra of the two molecules are similar. The biggest difference between the emission spectra of **1-anti** and **4** are their relative intensities. The fluorescence spectra of **1-3** all possess lineshapes and maxima similar to those of **4**, but display varying intensities. The fluorescence quantum yields of compounds **1-3** are all strongly quenched relative to that of **4**, Table 1. The data in Table 1 also show that the fluorescence lifetimes of **1-3** decrease in parallel with their respective fluorescence quantum yields. This suggests that the radiative rate constants for the zinc porphyrins in compounds **1-4** remain fairly constant across this series of molecules. This further implies that the fluorescence quenching in **1-3** is due to a fast nonradiative process that depletes the lowest excited singlet state population of the porphyrin in compounds **1-3**. It is interesting to note that the fluorescence lifetimes of **1** and **2** exhibit a dependence on the orientation of the donor relative to the acceptor, i.e. **syn** or **anti**. Moreover, the fluorescence lifetimes of **1-syn** and **1-anti** are similar to

those of 2-syn and 2-anti, respectively, and therefore, are not influenced by the addition of the methoxy groups in 2.

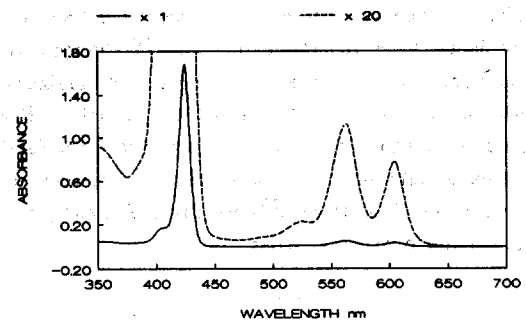


Figure 1. Ground state absorption spectrum of 1-anti in PrCN.

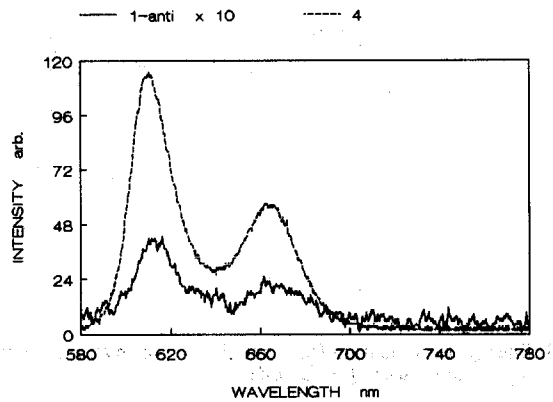


Figure 2. Fluorescence spectra of 1-anti and 4 in PrCN, excitation at 560 nm.

TABLE 1. Fluorescence data in PrCN.

Compound	ϕ_F	τ_F (ps)
1-anti	0.0012	57 ± 2
1-syn	0.0026	115 ± 2
2-anti	0.0014	52 ± 2
2-syn	0.0034	111 ± 2
3	0.00013	< 10
4	0.036	1850 ± 15

ENERGETICS

An energy level diagram for molecules 1 and 2 is shown in Figure 3. The excited singlet state energy was obtained from the maximum of the (0,0) band in the fluorescence emission spectra of 1 and 2. This maximum was the same for 1 and 2. The triplet state energy shown is that reported earlier for 4.[30] The approximate energy of $P^+ - S - Q^-$ was obtained by summing the half-wave potentials for one-electron oxidation of the zinc porphyrin donor and one-electron reduction of the naphthoquinone acceptor in 1 and 2. The redox potentials of these molecules were measured in butyronitrile containing 0.1M tetra-n-butylammonium perchlorate electrolyte and are the same for 1 and 2. The redox potentials for the tetra-alkylbenzene central rings in the pentiptycene spacers were estimated from the literature values for the analogous benzene[31,32] and p-dimethoxybenzene[33] derivatives. The energetics for 3 are the same as those for 1 and 2 excluding the availability of the ionic spacer states.

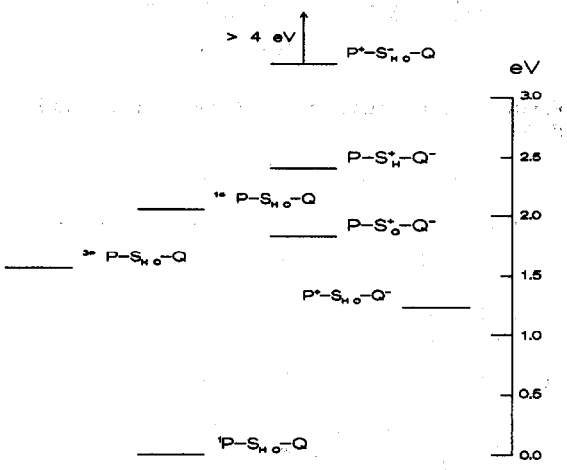


Figure 3. Energy level diagram for 1 and 2. P = porphyrin; S_H = spacer in 1; S_O = spacer in 2; Q = quinone.

Figure 3 shows that the driving force for oxidation of the porphyrin excited singlet state by the quinone is approximately -0.8 eV. Our earlier work on the dependence of charge separation rates in porphyrin-quinone molecules on free energy suggests that the energetics of 1-3 should result in near maximum rates for both charge separation and and recombination in these molecules.[6] States involving anions of the spacers will lie > 4 eV above the ground state, while states involving cations of the spacers lie at 2.4 eV for the benzene spacer and 1.8 eV for the p-dimethoxybenzene spacer. Moreover, the state $P - S_O^+ - Q^-$ is 0.6 eV lower in energy than $P - S_H^+ - Q^-$. Thus, $P - S_O^+ - Q^-$ may contribute more significantly than $P - S_H^+ - Q^-$ to a superexchange mechanism for ion pair recombination.

TRANSIENT ABSORPTION DATA

Figure 4 shows the transient absorption spectra obtained for 1-anti at 10 ps and 60 ps following excitation. The transient absorption spectra for 1-syn, 2-syn, and 2-anti are similar to those in Figure 4. The spectra for compound

3 are also similar to those in Figure 4, except that the analogous spectra for 3 occur at 1 ps and at 5 ps, respectively. The transient absorption spectrum of porphyrin 4 is shown in Figure 5. Since porphyrin 4 has no electron acceptor attached to it, the spectrum in Figure 5 is the difference between the ground state spectrum and that of the lowest excited singlet state of the porphyrin. This spectrum serves as a reference for the spectra in Figure 4. The spectra in Figure 4 are a superposition of the spectra of both $P^+ - S - Q^-$ and $^{1*}P$. The spectra in Figures 4 and 5 were obtained at similar concentrations and excitation intensities. A comparison of Figures 4 and 5 shows that the absorption feature near 460 nm of 1-anti is due to both $^{1*}P$ and $P^+ - S - Q^-$, while the absorbance in the near-infrared is dominated by $P^+ - S - Q^-$.[34] Although the spectra of 1-anti show that the mechanism of excited singlet state quenching is electron transfer from the porphyrin to the quinone, even 60 ps after excitation the spectrum of 1-anti contains significant contributions from the transient absorption of $^{1*}P$. This is supported by the presence of absorption troughs near 650 nm in both Figures 4 and 5 that are due to stimulated emission from $^{1*}P$. These spectra strongly suggest that the rate of charge separation is on same order of magnitude as that of the ion pair recombination.

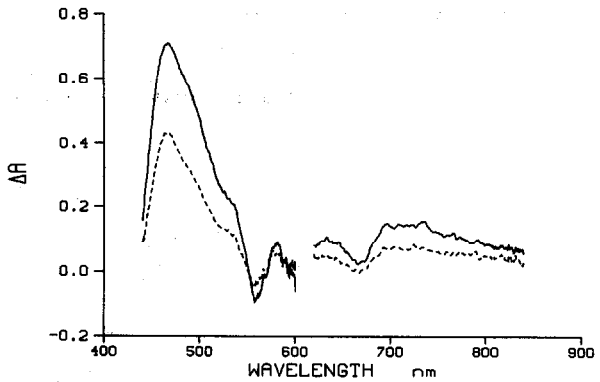


Figure 4. Transient absorption spectra of 1-anti in PrCN at 10 ps —— and 60 ps --- following a 1 ps laser flash at 610 nm.

The rate constants for charge separation, k_{cs}, and ion pair recombination, k_{cr}, are obtained from the following analysis. Constants k_{cs} in 1-3 are obtained from their respective fluorescence lifetimes given in Table 1. Assuming that the enhanced nonradiative decay route observed in 1-3 is due entirely to the charge separation process,

$$k_{cs} = 1/\tau_f - 1/\tau_4$$

where τ_f is the fluorescence lifetime of the porphyrin-quinone and τ_4 is the fluorescence lifetime of reference porphyrin 4. The relative contributions of $^{1*}P - S - Q$ and $P^+ - S - Q^-$ to the transient absorption spectra of 1-3 as a function of time are obtained by comparing the transient absorption spectra of 1-3, e.g. Figure 4, with that of 4, Figure 5. Using these two pieces of information and assuming a series A -> B -> C mechanism, where A is $^{1*}P - S - Q$, B is $P^+ - S - Q^-$, and C is P - S - Q, the kinetics for the decay of the transient absorption features for 1-3 can be fit to determine

k_{cr}. Data obtained at 460 nm and at 700 nm for 1-anti are shown in Figures 6 and 7, respectively, along with the corresponding fits. The values of k_{cs} and k_{cr} obtained in this fashion are listed in Table 2.

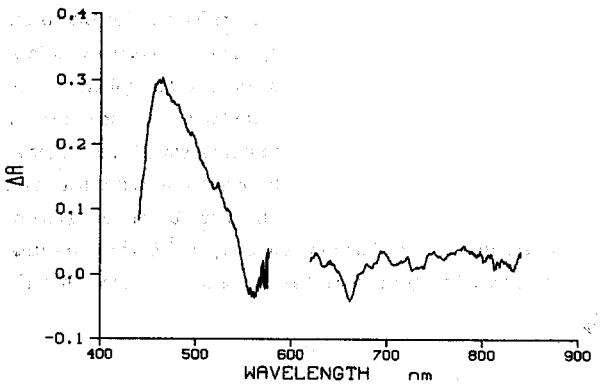


Figure 5. Transient absorption spectrum of 4 in PrCN at 60 ps following a 1 ps laser flash at 610 nm.

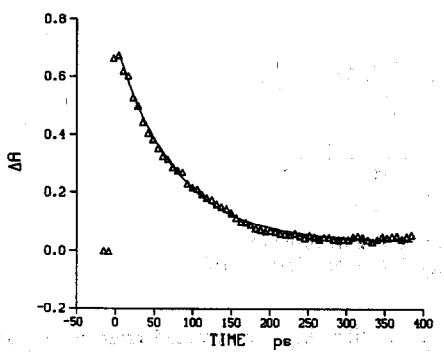


Figure 6. Transient absorption kinetics at 460 nm for 1-anti in PrCN following a 1 ps, 610 nm laser flash.

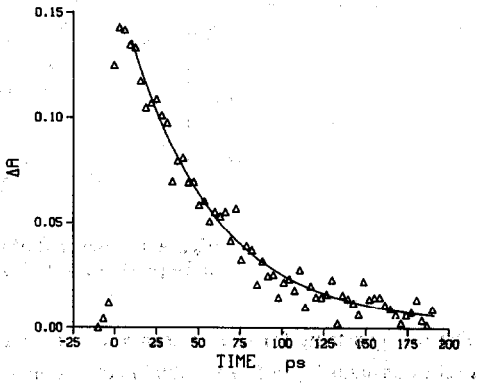


Figure 7. Transient absorption kinetics at 700 nm for 1-anti in PrCN following a 1 ps, 610 nm laser flash.

The rate constants for the ion-pair recombination reactions are all somewhat faster than those of the charge separation reactions. In addition, ion pair recombination occurs about a factor of 2 faster in the anti isomers than the syn isomers. This is similar to the observed difference between the rates of charge separation for these isomers. The recombination rates for the dimethoxy substituted compounds 2 are about 3-4 x faster than are those of the unsubstituted compounds, 1. This substituent effect is observed for both the syn and anti isomers. Both the charge

separation and recombination rates for 3 are very fast as predicted by our earlier work.[6] The rate constants for 3 are about an order of magnitude faster than those of 1 and 2.

TABLE 2. Electron Transfer Rate Constants for 1-3.

Compound	k_{cs} (s^{-1})	k_{cr} (s^{-1})
1-anti	1.7×10^{10}	2.5×10^{10}
1-syn	8.2×10^{9}	1.4×10^{10}
2-anti	1.9×10^{10}	8.2×10^{10}
2-syn	8.5×10^{9}	5.0×10^{10}
3	1.0×10^{12}	3.0×10^{11}

DISCUSSION

Introduction of the pentiptycene spacer between the porphyrin and quinone in 1 and 2 results in a decrease in the rate constants for both charge separation, k_{cs}, and charge recombination, k_{cr}, by about a factor of 10 relative to those for 3. This diminution in rate is approximately the same as we observed earlier in comparing a porphyrin - triptycene - quinone molecule to a porphyrin - trans-1,2-diphenylcyclopentane - quinone molecule.[7] The triptycene spacer possesses one saturated carbon atom between the π systems of the donor and acceptor, whereas the cyclopentane spacer possesses two saturated carbon atoms between them. At that time we determined that the difference in rate for these two molecules reflected the difference in edge-to-edge donor-acceptor distance. The rate diminished by a factor of 10 when the donor-acceptor edge-to-edge distance was increased from 2.4 Å using the triptycene spacer to 3.7 Å using the cyclopentane spacer.[7] The pentiptycene spacer in 1 and 2 possesses a central benzene ring along with two saturated carbon atoms between the donor and acceptor. The edge-to-edge distance between the π system of the porphyrin phenyl group and the naphthoquinone in 1 and 2 is 6 Å, and is similar for the syn and anti isomers, whereas the respective porphyrin-quinone distance in 3 is only 2.4 Å.[35] Even though the donor-acceptor distance has increased by 3.6 Å in going from 3 to 1 and 2, the presence of the benzene ring in the pentiptycene spacer does not appreciably slow the rates of electron transfer in 1 and 2 more than the factor of about 10 that is expected for a change from a spacer with one saturated carbon atom to one possessing two such atoms.

The data in Table 2 show that both k_{cs} and k_{cr} for 1 and 2 are slower for the syn isomer than for the anti isomer. The difference in rate constant between the two isomers is about a factor of 2. It is well-established that rate constants of electron transfer reactions most often decrease exponentially with distance.[5] The center-to-center distances between the porphyrin donor and quinone acceptor in 1 and 2 are isomer dependent: 11 Å for the syn isomers and 16 Å for the anti isomers. Even though the center-to-center porphyrin-quinone distance in the syn isomer is about 5 Å shorter than that of the anti isomer, k_{cs} and k_{cr} are actually faster for the anti isomers. This strongly suggests that the principal pathway for the electron transfer from the porphyrin to the quinone is through the bonds of the hydrocarbon spacer. Oliver et al.[36] recently observed similar behavior in molecules possessing 1,4-dimethoxynaphthalene donors attached via rigid hydrocarbon spacers to 1,1-dicyanoethylene acceptors. Their hydrocarbon spacers have either an all-trans arrangement of single bonds or a single s-cis kink in the chain. In each case the all-trans isomer gives the faster rate.

The fact that k_{cs} and k_{cr} for the anti isomers of 1 and 2 are faster than those for the syn isomers is consistent with considerations of maximum orbital interactions in hydrocarbons which have a zig-zag or all trans configuration relative to those which have cisoid segments in the chain.[14] Ohta et al.[15] recently calculated the matrix element for electron transfer between two methylene groups across a cyclohexane ring as a function of stereochemistry. They found that the equatorial-equatorial conformation of the ring, in which an all trans arrangement of the C-C bonds occurs, results in the larger matrix element, and therefore, the faster electron transfer rate. Examination of the structures of 1 and 2 show that the anti isomer maintains an effective all-trans arrangement of the C-C bonds. This phenomenon has also been demonstrated for electron transfer in radical anions of 1,4-diarylcyclohexanes.[37]

Since it is likely that electron transfer between the porphyrin and the quinone occurs through the bonds in 1 and 2, it is appropriate to ask whether the rate of electron transfer is dependent on the energies of the orbitals comprising the spacer. Placing substituents on the π system of the central benzene ring of the pentiptycene spacer provides a direct avenue for modifying the energy of the HOMO and LUMO of the spacer. These energies will determine the degree to which the states $P^+ - S^- - Q$ and $P - S^+ - Q^-$ will mix with the states $^1{}^*P - S - Q$ and $P^+ - S - Q^-$, respectively, to enhance the electronic coupling matrix element for charge separation and ion pair recombination, respectively.

The electronic matrix element, V_S for the superexchange interaction between states A, B, and C, where B is the virtual state is given by[38]

$$V_S = V_{AB}\, V_{BC} / \delta E_{AB}$$

where V_{AB} and V_{BC} are the respective electronic coupling terms between states A and B, and B and C, and δE_{AB} is the energy difference between states A and B. For the charge separation reaction in 1 and 2 $A = {}^1{}^*P - S - Q$, $B = P^+ - S^- - Q$, and $C = P^+ - S - Q^-$, while for the ion pair recombination in 1 and 2 $A = P^+ - S - Q^-$, $B = P - S^+ - Q^-$, and $C = P - S - Q$. Since the rate of the electron transfer reaction depends on V_S^2, the reaction rate will be a function of $(1/\delta E_{AB})^2$. Since the structures of 1 and 2 are esssentially the same, the terms V_{AB} and V_{BC} should remain similar for compounds 1 and 2.

Benzene and dimethoxybenzene can be reduced electrochemically at about -3.4 V and -3.6 V vs SCE, respectively. Since the zinc porphyrin in 1 and 2 oxidizes at 0.61 V vs SCE, we estimate that the energy of $P^+ - S_H^- - Q$ is about 4.0 eV, whereas that of $P^+ - S_O^- - Q$ is about 4.2 eV. Since participation of the state $P^+ - S^- - Q$ in a superexchange mechanism for charge separation depends on the square of the energy difference between that state and $^1{}^*P - S - Q$, we can estimate the ratio of the charge separation rate constants $(k_{cs})_1/(k_{cs})_2$. This ratio should be $[(1/\delta E_{AB})^2]_1/[(1/\delta E_{AB})^2]_2$, or $[1/(2.0)^2]/[1/(2.2)^2] = 1.2$. This estimate predicts that k_{cs} for both 1 and 2 should be similar. This prediction is borne out by the data for k_{cs} in Table 2. We find that substitution of two methoxy substituents on the benzene ring of the spacer does not significantly change k_{cs}.

There are two ways in which ion pair recombination in 1 and 2 can involve ionic states of the spacer. One way is via states such as $P^+ - S^- - Q$. However, these states are sufficiently high in energy relative to $P^+ - S - Q^-$ as to mix only weakly. A second route back to ground state is via states such as $P - S^+ - Q^-$. Figure 3 shows that $P - S_H^+ - Q^-$ is relatively low-lying for 1 and $P - S_O^+ - Q^-$ is especially so for 2. This suggests two things. First, a superexchange mechanism for ion pair recombination involving low-lying cationic spacer states should enhance k_{cr} for both 1 and 2. Second, since the energy of $P - S_O^+ - Q^-$ in 2 is 0.6 eV lower than that of $P - S_H^+ - Q^-$ in 1, if superexchange is

important, ion-pair recombination should be faster in 2 than in 1. The data in Table 2 show that k_{cr} is faster than k_{cs} for each isomer of 1 and 2. However, it is difficult to attribute this result solely to superexchange because the free energy of the charge separation and ion pair recombination reactions are not the same. In addition, the total reorganization energies for these two reactions are probably not equal either. Nevertheless, a much clearer case for superexchange emerges when one compares k_{cr} for 1 and 2. In this case the free energies of the ion pair recombination reactions in 1 and 2 are equal, and most likely the respective total reorganization energies for the ion pair recombination reactions in 1 and 2 are also very similar. We observe that k_{cr} is indeed 3-4 x faster for 2-syn and 2-anti than for 1-syn and 1-anti, respectively. Using the definition given above for states A and B in the ion pair recombination reaction, the data in Figure 3 show that δE_{AB} is 1.2 eV for 1 and only 0.6 eV for 2. Thus, if the superexchange mechanism is dominant for ion pair recombination in 1 and 2, the relative rates of ion pair recombination should be $[(1/\delta E_{AB})^2]_1/[(1/\delta E_{AB})^2]_2$, or $[1/(1.2)^2]/[1/(0.6)^2] = 4$. Since, our data show that the ion pair recombination rate for 2 is 3-4 x faster than that for 1, it is likely that the superexchange mechanism is responsible for the faster recombination rate in 2 relative to 1.

CONCLUSIONS

Excited state electron transfer reactions and ion pair recombination reactions in porphyrin-quinone molecules both show significant orientation dependencies. The nature of these dependencies strongly suggests that electron transfer occurs through the bonds of rigid hydrocarbon spacer molecules. Modulating the orbital energies of the spacer molecules, while maintaining conformational integrity, allows one to test the superexchange mechanism of electron transfer. The availability of a low-lying ionic spacer state that mixes with the ion pair state results in enhanced rates of electron transfer through the spacer. Since this effect occurs for simple substituted benzene spacer fragments, it is likely that similar enhancements of electron transfer reaction rates can occur when aromatic amino acids are positioned in strategic orientations between electron donors and acceptors within proteins.

EXPERIMENTAL

Physical Measurements

Solvents for all spectroscopic experiments were dried and stored over Linde 3 Å molecular sieves. HPLC grade toluene was distilled from $LiAlH_4$ (LAH). Butyronitrile (PrCN) was refluxed over $KMnO_4$ and Na_2CO_3, then twice distilled retaining the middle portion each time.

Proton NMR spectra were obtained on either a Nicolet Instruments 200 MHz or a Bruker 300 MHz spectrometer. All IR spectra were obtained on a Beckman Acculab 4 spectrometer using KBr discs. Only absorbances revealing particular structural information or very intense absorbances are reported. UV-visible absorption spectra were taken on a Shimadzu UV-160. The fluorescence spectra were obtained using a Perkin-Elmer MPF-2A fluorimeter interfaced to a PDP 11/34 computer. All samples for fluorescence were purified by prep-TLC on Merck silica gel plates. Samples for fluorescence measurements were 10^{-6} M in 1 cm cuvettes. The emission was measured 90° to the excitation beam. Fluorescence quantum yields were determined by integrating the digitized emission spectra from 580 to 780 nm and referencing the integral to that for Zn meso-tetraphenylporphyrin in benzene.[39]

The transient absorption spectra were obtained using a Rh-6G dye laser synchronously-pumped by a mode-locked, frequency-doubled CW Nd-YAG laser. The 1.0 psec pulses of 610 nm light were amplified by a 4-stage dye amplifier

(Rh-640) pumped by the frequency-doubled output of a Nd-YAG laser possessing a 10 Hz repetition rate. Saturable absorber dye jets between stages 2 and 3, and between stages 3 and 4 of the amplifier chain minimized the amplified stimulated emission generated in the amplifier. The amplification produced a 1.5 mJ/pulse at a 10 Hz repetition rate. This pulse was sent through a 60/40 beam splitter. The smaller portion was focused down to a 2 mm diameter and used as the excitation pulse. The larger portion was tightly focused into a 2 cm path length cell containing either 2/1 $CCl_4/CHCl_3$ or 1/1 H_2O/D_2O. This generated a white-light continuum probe pulse, which was used as the probe light. The arrival at the sample of the probe pulse was delayed relative to the excitation pulse by an optical delay. The probe pulse was divided into reference and sampling pulses by a 50/50 beam splitter. Both probe pulses passed through the sample. The reference pulse passed through an area that was not illuminated by the excitation pulse, while the sampling pulse passed through the same portion of the sample through which the excitation pulse passed. Both pulses were then focused onto the slit of a monochromator. The monochromator dispersed the pulses onto the face of an intensified SIT detector, which is part of an optical multichannel analyzer (PAR OMA II). Solutions of 1-4 with an absorbance of about 0.6 at 610 nm (2 mm pathlength cells) were used.

Fluorescence lifetime measurements used 1.0 psec, 1 mm diameter, 100 μJ pulses from the same source as described for the transient absorbance experiments. The samples of 1-4 were placed in 1 cm cells (optical density ca. 0.1 at 610 nm) and emission 90° to the excitation was collected and focused onto the slit of a Hamamatsu C979 streak camera. The temporally dispersed image was recorded by the intensified SIT vidicon of the PAR OMA II. The geometry of the experimental set up results in a 10 ps instrument response function.

Measurements of one-electron redox potentials vs SCE were carried out at a Pt disc electrode in butyronitrile containing 0.1 M tetra-n-butylammonium perchlorate using AC voltammetry as described previously.[40]

Synthesis

Silica gel used in chromatographic separations is Merck silica gel 60. The term "evaporate the solvent" implies the use of a rotary evaporator unless otherwise noted. All solvents were reagent grade. Solvents were generally dried by overnight treatment with Linde 3Å molecular sieves. Petroleum ether with a boiling range of 30-60° was used exclusively.

Preparation of 3

In a 5L round bottom flask is placed distilled pyrrole (1.66 g, 24.7 mmole), hexanal (1.86 g, 18.6 mmole), and 2-anthraldehyde (1.27 g, 6.16 mmol) in CH_2Cl_2 (2.48 L). N_2 is bubbled through the solution for 15 minutes. Trifluoroacetic acid (2.83 g, 24.8 mmole) is added and the solution is stirred for 2 hours at room temperature under N_2. Chloranil (4.60 g, 18.7 mmol) is added and the solution is refluxed for 1 hour. After cooling to room temperature the CH_2Cl_2 is evaporated to a volume of about 300 mL, anhydrous K_2CO_3 (50 g) is added and the mixture stirred overnight. The solution is then filtered and the solvent is evaporated. The solid is dissolved in $CHCl_3$ and chromatographed on silica gel, elution with 7/3 v/v CH_2Cl_2/CCl_4. The fractions containing the crude 5-(2-anthracenyl)-10,15,20-tripentylporphyrin are combined and the solvent is evaporated to yield 1.21 g, 7.0% of product. The porphyrin is dissolved in xylene (60 ml), 1,4-naphthoquinone (5.48 g, 34.6 mmole) is added and the solution is refluxed for 19 hours. The reaction mixture is cooled and the xylene is evaporated. The resulting solid is chromatographed on silica gel, elution with 4/1 v/v CCl_4/CH_2Cl_2. The yield of the free base of 3 is 241 mg, 4.6% based on the starting pyrrole. The

zinc porphyrin, 3, is prepared quantitatively from the free base by warming the free base in 3/1 v/v $CHCl_3/CH_3OH$ with zinc acetate dihydrate (25 mg). After a few minutes the reaction is judged complete by TLC. The reaction mixture is cooled, poured into water, and extracted with $CHCl_3$. The extract is washed twice with water, dried over anhydrous K_2CO_3, and the solvent is evaporated. Proton NMR ($CDCl_3$) δ porphyrin β hydrogens: 8.760 (d, 1H, 4.3 Hz), 8.781 (d, 1H, 4.3 Hz), 9.390 (d, 1H, 4.6 Hz), 9.397 (d, 1H, 4.6 Hz), 9.569 (s, 4H); quinone hydrogens: 6.203 (s, 1H, bridgehead), 6.345 (s, 1H, bridgehead), 7.21 (m, 2H), 7.62 (m, 1H), 7.74 (m, 3H), 7.843 (AB quartet, 2H, 7.0 Hz), 8.15 (m, 1H) 8.22 (m, 1H), 8.274(s, 1H); pentyl chains: 0.98 (m, 9H), 1.52 (m, 6H), 1.79 (m, 6H), 2.56 (m, 6H), 4.95 (m, 6H).

Preparation of 4

In a 5L round bottom flask is placed distilled pyrrole (2.01 g, 30 mmole), hexanal (2.25 g, 22.5 mmole), and benzaldehyde (0.796 g, 75 mmol) in CH_2Cl_2 (3.00 L). N_2 is bubbled through the solution for 15 minutes. Trifluoroacetic acid (3.42 g, 30 mmole) is added and the solution is stirred for 3 hours at room temperature under N_2. Chloranil (5.52 g, 22.5 mmol) is added and the solution is refluxed for 1 hour. After cooling to room temperature the CH_2Cl_2 is evaporated to a volume of about 400 mL, anhydrous K_2CO_3 (50 g) is added and the mixture stirred overnight. The solution is then filtered and the solvent is evaporated. The solid is dissolved in $CHCl_3$ and chromatographed on silica gel, elution with CH_2Cl_2. All high R_f material is collected, combined, and the solvent removed. The desired product is separated from the other pentylphenylporphyrin isomers by silica gel chromatography, elution with 19/1 v/v petroleum ether/THF. The yield of the free base of 4 is 175 mg, 3.9%. The zinc porphyrin, 4, is prepared quantitatively from the free base by warming the free base in 3/1 v/v $CHCl_3/CH_3OH$ with zinc acetate dihydrate (25 mg). After a few minutes the reaction is judged complete by TLC. The reaction mixture is cooled, poured into water, and extracted with $CHCl_3$. The extract is washed twice with water, dried over anhydrous K_2CO_3, and the solvent is evaporated. Proton NMR ($CDCl_3$) δ porphyrin β hydrogens: 8.839 (d, 2H, 4.6 Hz), 8.948 (AB quartet, 4H, 4.6 Hz), 9.315 (d, 2H, 4.6 Hz); phenyl hydrogens: 8.20 (m, 2H), 7.78 (m, 3H); pentyl chains: 4.577 (t, 4H, 7.8 Hz), 4.310 (t, 2H, 7.8 Hz), 2.40 (m, 4H), 2.24 (m, 2H), 1.76 (m, 6H), 1.51 (m, 6H), 0.998 (m, 9H).

Preparation of 6

Triptycene (10.0 g, 39.3 mmole) and phthalic anhydride (6.5 g, 43.9 mmole) are suspended in 1,2-dichloroethane (300 ml) at 0° with stirring under N_2. Aluminum chloride (15.8 g, 0.118 mole) is added in small portions over 30 minutes. The reaction mixture becomes homogeneous and stirring is continued at 0° for 2.5 hours. The reaction mixture is poured into water (500 ml), the organic layer is separated, $CHCl_3$ (100 mL) is added, and the resulting organic solution is washed with water (500 mL). The cloudy organic layer is evaporated, the solid is resuspended in toluene (200 ml) and refluxed with a Dean-Stark trap for 6 hrs. The slurry is cooled and filtered on a course frit, the solid is washed 3 times with petroleum ether, and dried in vacuo to give 6 in quantitative yield. Proton NMR ($CDCl_3$) δ 8.02 (d, 1H, 6.8 Hz), 7.831 (s, 1H), 7.56 (m, 2H), 7.384 (d of d, 4H, 3.2 and 5.2 Hz), 7.35 (m, 1H) 7.28 (m, 2H), 7.004 (d of d, 4H, 3.2 and 5.2 Hz), 5.461 (s, 2H, bridgehead).
IR (KBr disc) : 3400, 1725, 1686, 1660, 1292, 1270, 746 cm^{-1}.

Preparation of 7

Ketoacid 6 (9.06 g, 22.5 mmol) is suspended in nitrobenzene (150 mL). Aluminum chloride (10.5 g, 78.7 mmol) is

added and the mixture is stirred under N_2. The mixture turns a dark brown and the solid dissolves. The mixture is then heated at 150° for 6 hrs. After cooling the nitrobenzene is removed by evaporation on a rotary evaporator pumped by a mechanical vacuum pump. The dark, oily residue is refluxed with $CHCl_3$ (200 ml) for 1 hr. The $CHCl_3$ solution is cooled, suction filtered on a course frit and the solution is evaporated to 25 mL. The chloroform solution is then diluted with petroleum ether to yield a black solid. The solid is chromatographed on silica gel, elution with 13/7 v/v CH_2Cl_2/petroleum ether. The fractions containing the product are combined, the solvent evaporated, and the solid is redissolved in the minimum amount of CH_2Cl_2. Addition of petroleum ether results in a pale yellow precipitate, which is centrifuged, and dried in a vacuum dessicator to give anthraquinone 7: 3.0 g, 35%. Proton NMR ($CDCl_3$) δ anthraquinone protons: 8.273 (s, 2H, protons between bridgehead and carbonyl group), 8.243 (d of d, 2H, 3.2 and 5.6 Hz), 7.738 (d of d, 2H, 3.6 and 5.8 Hz); triptycene protons: 7.455 (d of d, 4H, 3.2 and 5.2 Hz), 7.058 (d of d, 4H, 3.0 and 5.2 Hz), 5.663 (s, 2H, bridgehead).
IR (KBr disc) 1666, 1590, 1458, 1350, 1322, 1295, 954, 742, 713 cm^{-1}.

Preparation of 8

Anthraquinone 7 (1.9 g, 4.9 mmole) is suspended in n-butylamine (100 mL) and conc. aqueous ammonia (40 mL). Zinc dust (5.0 g, 0.0765 mole) and anhydrous $CuSO_4$ (10 mg) are added. The mixture, which develops a deep red color, is vigorously stirred and heated to reflux. After 6 hours of heating the mixture is slate grey and exhibits a bright blue-white fluorescence under a uv light. After cooling to room temperature, the mixture is filtered through a plug of glass wool into water and extracted with CH_2Cl_2. The CH_2Cl_2 layer is washed twice with water, once with 10% HCl, once again with water, dried over anhydrous Na_2CO_3, and the solvents are evaporated. The solid is dissolved in chloroform and chromatographed on silica gel, elution with CH_2Cl_2. A small fraction of anthracene is followed by blue fluorescent 8: 1.20 g, 69%.
Proton NMR ($CDCl_3$) δ: 5.504 (S, 2H, bridgehead); 7.050 (d of d, 4H, 3.1 Hz and 5.3 Hz); 7.392 (d of d, 2H, 3.3 Hz and 6.6 Hz); 7.459 (d of d, 4H, 3.1 Hz and 5.2 Hz); 7.885 (s,2H); 7.920 (d of d, 2H, 3.2 Hz and 6.5 Hz); 8.238 (s,2H).
IR (KBr disk) 1462, 1440, 1165, 906, 743, 632 cm^{-1}.

Preparation of 9

Hydrocarbon 8 (1.00 g, 2.82 mmole) and 1,4-naphthoquinone (4.5 g, 28.5 mmole, freshly chromatographed on silica gel, elution with CH_2Cl_2) are heated for 68 hours in nitrobenzene (20 mL) at 140°C under nitrogen with stirring. The solution is then cooled, and the nitrobenzene removed on a rotary evaporator pumped by a mechanical vacuum pump. The purple-black solid is dissolved in chloroform and column chromatographed on silica gel, elution with 1/1 v/v CH_2Cl_2/CCl_4. The fractions containing the product are combined and the solvent evaporated. The resulting solid is dissolved up in a minimum of $CHCl_3$ and precipitated by addition of excess CH_3OH. The bright yellow solid is centrifuged and dried in a vacuum desiccator to yield quinone 9: 1.06 g, 73.6%.
Proton NMR ($CDCl_3$) δ: 5.34 (s, 2H, bridgehead); 5.89 (s, 2H, bridgehead); 6.96 (m,6H); 7.31 (m,4H); 7.38 (m,2H); 7.51 (s,2H); 7.64 (m,2H); 8.01 (d of d, 2H, 3.6 Hz and 6.4 Hz).
IR (KBr disk): 1656, 1454, 1296, 908, 703 cm^{-1}

Preparation of 10

Pentiptycene-naphthoquinone 9 (2.1 g, 4.1 mmole) is dissolved in dry 1,2-dichloroethane (65 mL) and cooled with stirring under nitrogen to 0°C. Aluminum chloride (1.65 g, 12.4 mmole) is added to the solution in three equal amounts over a few minutes. Stirring at 0°C is continued for 0.5 hour. α,α-Dichloromethyl methyl ether (0.47 g, 0.37 mL, 4.4 mmole) is added all at once and the solution stirred for 2.5 hours at room temperature. The reaction mixture is then poured into 10% HCl (1L) and CH_2Cl_2 (100 mL) is added. The organic layer is separated and washed once with water, dried over anhydrous Na_2CO_3, and the solvent is evaporated. The resulting oil is dissolved in $CHCl_3$ (10 mL) and chromatographed on silica gel, elution with CH_2Cl_2. Two zones are collected: starting material and quinone aldehyde 10. The fractions with 10 are combined, the solvent evaporated, the resulting solid dissolved in $CHCl_3$ and precipitated by the addition of excess petroleum ether. The solid is centrifuged and dried in a vacuum desiccator to yield pure 10: 0.794 g 36%.

Proton NMR ($CDCl_3$) δ: 5.430 (closely spaced doublet, 2H, bridgehead); 5.903 (s, 2H, bridgehead); 6.97 (m,4H); 7.37 (m,4H); 7.471 (s,1H); 7.537 (broad s,2H); 7.63 (m,2H); 7.813 (s,1H); 8.00 (m,2H); 9.835 (closely spaced doublet, 1H, 3.8 Hz).

IR (KBr disk) 2820, 2735, 1686, 1652, 1608, 1590, 1289, 1215, 750, 711 cm^{-1}.

Preparation of 1-syn and 1-anti

In a 1L round bottom flask is placed distilled pyrrole (0.416 g, 6.2 mmole), hexanal (0.465 g, 4.6 mmole), and quinone aldehyde 10 (0.77 g, 1.5 mmole) in dry CH_2Cl_2 (620 mL). N_2 is bubbled through the solution for 20 minutes. Trifluoroacetic acid (0.706 g, 6.19 mmole) is added and the solution is stirred at room temperature for 3 hours under N_2. Chloranil (1.14 g, 4.6 mmole) is added and the solution is refluxed for 1 hour. After cooling to room temperature, the CH_2Cl_2 is evaporated, the solid is dissolved in $CHCl_3$, and chromatographed on silica gel, elution with CH_2Cl_2. The fractions containing the product are combined, evaporated, and redissolved in CCl_4. Evaporation of the CCl_4 yields a mixture of the free bases of 1-syn and 1-anti: 45 mg, 2.9%. The zinc porphyrins 1-syn and 1-anti are synthesized quantitatively from the mixture of free bases by warming it in a 3/1 v/v $CHCl_3/CH_3OH$ to which zinc acetate dihydrate (25 mg) is added. After a few minutes the reaction is complete as judged by TLC. The solution is cooled and poured into water. The $CHCl_3$ layer is washed twice with water, dried over anhydrous Na_2CO_3, and the solvent is evaporated. 1-syn and 1-anti are separated by preparative thin-layer chromatography with 7/3 v/v petroleum ether/THF. The higher Rf isomer, 1-anti, gave the following data: Proton NMR ($CDCl_3$) δ porphyrin β hydrogens: 8.571 (d, 1H, 4.6 Hz), 8.756 (d, 1H, 4.6 Hz), 9.176 (d, 1H, 4.6 Hz), 9.346 (d, 1H, 4.6 Hz), 9.442 (s, 4H); quinone hydrogens: 5.583 (s, 1H, bridgehead), 5.669 (s, 1H, bridgehead), 5.898 (s, 1H, bridgehead), 5.992 (s, 1H, bridgehead), 7.07 (m, 7H), 7.53 (m, 4H), 7.66 (s, 1H), 7.70 (m, 3H), 7.72 (s, 1H), 8.182 (s, 1H); pentyl chains: 1.01 (m, 9H), 1.53 (m, 6H), 1.73 (m, 6H), 2.49 (m, 6H), 4.86 (m, 6H).

The lower R_f isomer, 1-syn, gave the following data: Proton NMR ($CDCl_3$) δ porphyrin β hydrogens: 8.684 (d, 1H, 4.6 Hz), 8.751 (d, 1H, 4.6 Hz), 9.225 (d, 1H, 4.7 Hz), 9.331 (d, 1H, 4.7 Hz), 9.434 (s, 4H); quinone hydrogens: 5.530 (s, 1H, bridgehead), 5.677 (s, 1H, bridgehead), 5.984 (s, 1H, bridgehead), 6.031 (s, 1H, bridgehead), 7.04 (m, 2H) 7.09 (m, 2H), 7.44 (m, 3H), 7.55 (m, 1H), 7.60 (m, 4H), 7.640 (s, 1H), 7.729 (s, 1H), 8.042 (m, 2H), 8.139 (s, 1H); pentyl chains: 1.00 (m, 9H), 1.54 (m, 6H), 1.73 (m, 6H), 2.47 (m, 6H), 4.83 (m, 6H).

Preparation of 11

Anthracene (20.0 g, 0.112 mole) and p-benzoquinone (12.1 g, 0.112 mole) are refluxed together in xylene (225 mL) in a round bottom flask for 5 hours with stirring under N_2. The hot solution is poured into a 600 mL beaker, the round bottom flask is rinsed with xylene, and the combined xylene solutions are cooled overnight at 5°. The solid is filtered and washed first with cold xylene, then with petroleum ether, and dried in a vacuum desiccator to yield 11: off-white crystals, 26.7 g, 83%. Proton NMR ($CDCl_3$) δ: 3.15 (s,2H); 4.85 (s,2H); 6.31 (s,2H); 7.07 (m,2H); 7.18 (m,4H); 7.39 (m,2H).

IR (KBr disk): 1667, 1458, 1277, 1130, 1096, 867, 765 cm^{-1}

Preparation of 12

A suspension of 11 (20.0g, 0.0698 mole) and 10% Pd on carbon (7.0 g) in THF (300 mL) is bubbled with N_2 for 5 minutes. The resulting suspension is hydrogenated at 3.5 atm hydrogen in a Parr shaker for 2.0 hours (loss of 7 psi). The suspension is then bubbled once again with N_2, the catalyst is removed by suction filtration on a medium glass frit, and the solvent is evaporated. Residual traces of solvent are removed in a vacuum desiccator overnight to yield 12: 20.0 g, 99%. Proton NMR ($CDCl_3$) δ: 1.68 (m,2H); 2.43 (m,2H); 3.06 (s,2H); 4.88 (s,2H); 7.13 (m,4H); 7.27 (m,2H); 7.36 (m,2H)

IR (KBr disk): 1710, 1461, 1153, 768 cm^{-1}

Preparation of 13

A solution of methanolic KOH (10.0g KOH in 200 mL CH_3OH) is added dropwise at room temperature over a period of 5 minutes to a vigorously stirred solution of diketone 12 (26.0 g, 0.0902 mole) and o-phthalaldehyde (9.4 g, 0.0701 mole) in THF (500 mL). Instantly, the mixture turns a deep brown color. Additional CH_3OH (100 mL) is then added, and the mixture is cooled in the freezer (-25°C) for 15 minutes. The cooled mixture is then stirred vigorously at room temperature again and bubbled with air for several minutes. After recooling in the freezer the yellow solid formed is filtered on a coarse glass frit and washed twice with cold CH_3OH and twice with petroleum ether to yield quinone 13: 17.8 g, 66%. $CHCl_3$ is added to the filtrate and the $CHCl_3$ solution is washed several times with H_2O. The $CHCl_3$ solution is dried over Na_2SO_4, filtered, and the solvent is evaporated. Suspension of the solid in CH_3OH and suction filtration yields an additional 4.4 grams of slightly less pure quinone. Total yield of 13: 82.4%. Proton NMR ($CDCl_3$) δ; 6.08 (s, 2H, bridgehead); 7.055 (d of d, 4H, 3.0 Hz and 5.3 Hz); 7.499 (d of d, 4H, 3.1 Hz and 5.3 Hz); 7.582 (d of d, 2H, 3.4 Hz and 6.2 Hz); 7.993 (d of d, 2H, 3.4 Hz and 6.1 Hz); 8.563 (s,2H).

IR (KBr disk): 1657, 1613, 1458, 1295, 1190, 929, 758, 699 cm^{-1}.

Preparation of 14

In a 1L 3-necked round bottom flask equipped with a gas addition frit, a rubber spectrum, and a condenser with a bubbler to monitor gas addition is placed quinone 13 (8.0 g, 0.0208 mole) in dry DMF (280 mL). Nitrogen is bubbled through the suspension with vigorous stirring for 5 minutes to purge oxygen. 10% Pd/C (2.0 g) is added and hydrogen gas is bubbled through the solution with stirring for 1 hour. Nitrogen is bubbled through the solution again for 5 minutes, additional 10% Pd/C (1.0 g) is added, and hydrogen is bubbled through the solution for 30 minutes. The solution is then flushed with N_2 for 5 minutes. The color of the suspension is yellow-green. Lithium 2,6-di-tert-butyl-

4-methoxyphenylate, prepared by the addition of n-butyllithium (52 mL of 1.6M hexane solution) to 3,5-di-tert-butyl-4-hydroxyanisole (19.7 g, 0.0833 mole) in dry DMF (100 mL), is added dropwise with vigorous stirring at room temperature over a period of three minutes. The color of the solution changes to a deep red brown. Freshly distilled dimethyl sulfate (10.6 mL, 14.2g, 0.112 mole) is added and the mixture is stirred at room temperature overnight with constant bubbling of N_2 into the solution. The mixture is poured into CH_2Cl_2 (100 mL) in a 3L Erlenmeyer flask. H_2O (1700 mL) is added and the mixture is stirred for 1 hour. The H_2O layer is decanted off through glass wool to remove the catalyst and extracted with CH_2Cl_2 (50 mL). The combined CH_2Cl_2 layers are filtered through glass wool, washed twice with H_2O (1500 mL), dried over anhydrous Na_2CO_3, and the solvent evaporated. The resulting solid is slurried in hexane (100 mL) at 50°C. The hexane slurry is cooled to 30°C and suction filtered on a coarse frit. The solid is washed twice with 30 mL hexane and dried to yield 14: 6.5 g, 75.4% Proton NMR ($CDCl_3$) δ: 4.096 (s,6H); 5.966 (s, 2H, bridgehead); 7.073 (d of d, 4H, 3.1 Hz and 5.4 Hz); 7.431 (d of d, 2H, 3.4 Hz and 6.3 Hz); 7.495 (d of d, 4H, 3.3 Hz and 5.2 Hz); 7.980 (d of d, 2H, 3.3 Hz and 6.4 Hz); 8.532 (s,2H)
IR (KBr disk): 2835, 1463, 1460, 1327, 1048, 972, 898, 757 cm^{-1}.

Preparation of 15

Dimethoxyanthracene derivative 14 (5.0 g, 0.0121 mole) and 1,4-naphthoquinone (8.0 g, 0.0506 mole, freshly chromatographed on silica gel with CH_2Cl_2) are stirred and heated under N_2 for 67 hours at 140°C in nitrobenzene (30 mL). The solution is then cooled and the nitrobenzene removed on a rotary evaporator pumped by a mechanical vacuum pump. The solid is taken up in $CHCl_3$ (10 mL) and precipitated by addition of excess CH_3OH. The yellow solid is centrifuged, washed with more CH_3OH and centrifuged again. The solid is then chromatographed on silica gel with CH_2Cl_2. The fractions containing the product are combined, the solvent evaporated, and the solid taken up in chloroform. Addition of excess CH_3OH results in precipitation of the product, which is centrifuged, washed with CH_3OH, centrifuged again, and dried in a vacuum desiccator to yield 15: 5.33 g, 77.4%. Proton NMR ($CDCl_3$) δ: 3.912 (s, 6H); 5.688 (s, 2H, bridgehead); 6.249 (s, 2H, bridgehead); 6.95 (m,6H); 7.35 (m,4H); 7.41 (m,2H); 7.637 (d of d, 2H, 3.3 Hz and 5.7 Hz); 8.012 (d of d, 2H, 3.3 Hz and 5.7 Hz).
IR (KBr disk): 2945, 1657, 1478, 1460, 1295, 1260, 1052, 910, 761, 707 cm^{-1}

Preparation of 16

Pentiptycene-naphthoquinone 15 (2.5 g, 0.0044 mole) is dissolved under N_2 with stirring at 0°C in dry 1,2-dichloroethane (100 mL). $TiCl_4$ (3.47 g, 2.01 mL, 0.0183 mole) is syringed into the solution in 4 equal portions at 0°C. The color of the solution turns from yellow-orange to deep blue immediately. After stirring 5 minutes α,α-dichloromethyl methyl ether (1.05 g, 0.83 mL, 0.00914 mole) is added, and a very fine precipitate forms. After stirring for 21 hours at room temperature, the precipitate dissolved. The reaction mixture is poured into water (700 mL) and extracted twice with CH_2Cl_2. The combined CH_2Cl_2 layers are washed once with H_2O and dried with anhydrous Na_2CO_3 and anhydrous Na_2SO_4. The solvents are evaporated, the resulting solid is redissolved in CCl_4, and the CCl_4 is evaporated. This process is repeated one more time and the resulting solid is dissolved in $CHCl_3$. Addition of excess petroleum ether precipitates the product, which is centrifuged, dried, and column chromatographed on silica gel, elution with $CHCl_3$, to yield two major zones: starting material and 16: 0.83 g, 32%. Proton NMR ($CDCl_3$) δ; 3.932 (s,6H); 5.79 (narrow doublet, 2H, bridgehead); 6.269 (s, 2H, bridgehead); 6.99 (m,4H); 7.42 (m,4H); 7.49 (s,2H); 7.62 (m,2H); 7.843

(s,1H); 7.99 (m,2H); 9.80 (narrow doublet, 1H, 3.8 Hz).
IR (KBr disk): 2935, 2825, 2720, 1693, 1619, 1477, 1292, 1258, 1050, 706 cm^{-1}

Preparation of 2-syn and 2-anti

In a 1L round bottom flask is placed distilled pyrrole (0.371 g, 5.53 mmole), hexanal (0.416 g, 4.15 mmole), and quinone aldehyde 16 (0.828 g, 1.38 mmole) in dry CH_2Cl_2 (553 mL). N_2 is bubbled through the solution for 20 minutes. Trifluoroacetic acid (0.631 g, 5.53 mmole) is added and the solution is stirred for 3 hours at room temperature under N_2. Chloranil (1.02 g, 4.19 mmole) is added and the solution is refluxed for 1 hour. After cooling to room temperature, the CH_2Cl_2 is evaporated, the solid is dissolved in $CHCl_3$ and chromatographed on silica gel, elution with CH_2Cl_2. The fractions containing the product are combined, evaporated, redissolved in CCl_4, and the CCl_4 is evaporated to yield the free bases of 2-syn and 2-anti: 72 mg, 4.8%. The zinc porphyrins, 2-syn and 2-anti, are synthesized quantitatively from the free base mixture by warming it in 3/1 v/v $CHCl_3/CH_3OH$ to which zinc acetate dihydrate (25 mg) is added. After a few minutes, the reaction is complete as judged by TLC. The solution is cooled, poured into water, and the $CHCl_3$ layer is separated, washed twice with water, dried over anhydrous Na_2CO_3, and the solvent evaporated to yield a mixture of 2-syn and 2-anti. These positional isomers are separated by preparative TLC on silica gel, elution with a 7/3 v/v mixture of petroleum ether and THF. The higher R_f isomer, 2-anti, gave the following data: Proton NMR ($CDCl_3$) δ: porphyrin β hydrogens: 8.761 (d,1H,4.7 Hz), 8.848 (d,1H,4.7 Hz), 9.342 (AB quartet,2H,5.1 Hz), 9.457 (broad s,4H); quinone hydrogens: 3.943 (s,3H,OCH_3), 4.106 (s,3H,OCH_3), 5.896 (s,1H,bridgehead), 6.028 (s,1H,bridgehead), 6.354 (s,1H,bridgehead), 6.415 (s,1H,bridgehead), 7.094 (t,2H,5.8 Hz and 6.1 Hz), 7.155 (t,2H,3.5 Hz), 7.485 (d,1H,6.1 Hz), 7.62 (m,5H), 7.705 (d,1H,7.4 Hz), 7.788 (d,1H,7.4 Hz), 800 (m,2H), 8.182 (s,1H); pentyl chains: 0.98 (m,9H), 1.55 (m,6H), 1.80 (m,6H), 2.50 (m,6H), 4.88 (m,6H).
The lower R_f isomer, 2-syn, gave the following data:
Proton NMR ($CDCl_3$) δ: porphyrin β hydrogens: 8.768 (d,1H,4.8 Hz), 8.801 (d,1H,4.6 Hz), 9.312 (d,1H,4.7 Hz), 9.382 (d,1H,4.9 Hz), 9.538 (s,4H); quinone hydrogens: 3.991 (s,3H,-OCH_3), 4.114 (s,3H,-OCH_3), 5.903 (s,1H,bridgehead), 6.031 (s,1H,bridgehead), 6.366 (s,1H,bridgehead), 6.407 (s,1H,bridgehead), 7.06 (m,2H), 7.11 (m,2H), 7.49(m,3H), 7.581 (d,1H,7.0 Hz), 7.72 (m,4H), 8.11 (m,2H), 8.199 (s,1H); pentyl chains: 4.914 (quin.,6H,~ 7.9 Hz), 2.51 (m,6H), 1.80 (m,6H), 1.57 (m,6H), 0.96 (m,9H).

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