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SYNTHESIS AND CHARACTERIZATION OF A DIRECTLY LINKED PORPHYRIN-ANTHRAQUINONE MOLECULE

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ABSTRACT

We have synthesized a porphyrin-anthraquinone molecule (PAQ) in which the AQ moiety is attached directly at a *meso*-position of tritolylporphyrin. The absorption spectrum shows pronounced perturbations in the bands of both the P and AQ groups that are independent of solvent polarity; a charge-transfer band was not observed. In contrast, the spectrum of the porphyrin fluorescence in PAQ is only moderately red-shifted, but the lifetimes and intensities depend markedly on solvent dielectric constant: the fluorescence is quenched negligibly in solvents with $\epsilon_s \leqslant 4$, moderately in solvents with $4 < \epsilon_s \leqslant 6$ and strongly in solvents with $\epsilon_s \geqslant 7$. In methylene chloride, the major emitting component has a lifetime of ~30 ps as compared to ~9.0 ns for both tetratolylporphyrin (TTP) and an ester-linked TTP-AQ molecule. An electron-transfer mechanism is implicated even though the energetics for net electron transfer do not appear to be favorable (the sum of the redox potentials being essentially isoenergetic with the porphyrin S_1 state in benzonitrile). We infer that the short distance between the P and AQ moieties (~1.4 Å edge-to-edge) compensates for the otherwise marginal energetics in accord with Marcus theory. However, calculations of the reorganization energy, based on a two-sphere dielectric continuum model, and estimates of the solvent-dependent reaction energetics, using the Weller equation, do not yield a meaningful correlation with the fluorescence data measured in 19 solvents and binary solvent mixtures. Electron transfer in this intimately linked donor-acceptor molecule may involve an inner-sphere and/or adiabatic mechanism.

INTRODUCTION

There has been a great deal of recent research on the properties of porphyrin-containing molecular assemblies in an attempt to mimic the primary light-driven step in natural photosynthetic reaction centers.[1] Many current investigations are concerned with covalently linked porphyrin-quinone (PLQ) molecules in order to understand factors such as the effects of distance, orientation, energetics, and the role of the medium on the rates of intramolecular electron transfer. The nature of the linking bridge is also a subject of much interest since light-induced intramolecular electron transfer (ET) in many linked donor-acceptor (DA) molecules is dominated by through-bond interactions.[1]

Most studies have concentrated on PLQ systems with relatively long covalent links possessing various geometries and degrees of rigidity.[1-7] In some molecules, an important factor affecting the rates of both forward ET and subsequent charge recombination appears to be the ability of the donor and acceptor moieties to assume one or more optimum configurations.[1,4,5] The distributions of rate constants that arise from this flexibility have made it difficult to unravel the relative contributions of the various factors mentioned above. There is thus a need for a variety of DA systems containing rigid linkages.[6] It should be borne in mind, however, that vibrational degrees of freedom within the link, no matter how well constructed, can give rise to distributions of ET rates,[7] and therefore complex spectroscopic profiles on the ps time scale may be unavoidable.

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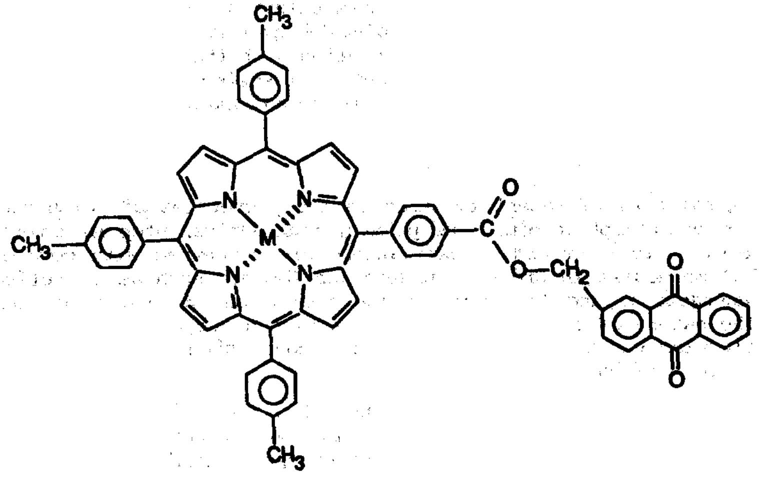
There has been only one previous report[8] on a porphyrin-quinone molecule in which conformational freedom was minimized by attaching benzoquinone (BQ) directly at a *meso*-position of the porphyrin ring. Very rapid (<6 ps) decay of the porphyrin excited singlet state (S_1) was observed. The transient absorption profiles were attributed to formation of the charge-separated radical-ion-pair state (RIP) by both singlet and triplet mechanisms; reverse ET from a vibrationally unrelaxed triplet RIP was also postulated. Some of this complex behavior may have been due to the relatively large (<-0.45 eV) driving force for forward ET, which places the energy of the RIP state very close to that of the localized porphyrin triplet state.[4]

As Bergkamp *et al.*[8b] suggested, studies of an analogous molecule containing a different quinone (*e.g.*, naphthoquinone, NQ) might yield information on the relative importance of such factors as vibrational coupling and differences in Gibbs free-energy $\Delta G^{\circ\prime}$. In such a system the detailed photophysical behavior might be simpler as well, since the driving force for photoinduced ET in a PNQ molecule should be ~0.2 eV less than in the case of the BQ analogue.[9] Anthraquinone (AQ) is in turn more difficult to reduce than NQ by an additional ~0.3 V;[9,10] hence a system containing a porphyrin coupled with AQ should have even less favorable energetics for ET and complications due to triplet mechanisms should not arise.

The fluorescence properties of the porphyrin moieties in two ester-linked PLAQ systems (H_2PEAQ and ZnPEAQ) were measured by Connolly *et al.*[11] The lifetimes of the free-base form, in nine solvents, were indistinguishable from those of an appropriate reference porphyrin, as expected if the energetics for ET are unfavorable. In ZnPEAQ, however, the charge-separated state lies ~0.4 eV below the metalloporphyrin S_1 state,[10] and significant fluorescence quenching was observed.[11] The intramolecular ET rate constant in this molecule (in *n*-butyronitrile) was found[12] to be in very good agreement with the value measured for an analogous ZnPLAQ system containing an adamantane bridge,[10] which constrains the two moieties more rigidly but at about the same average distance.[11]

The agreement of the ET rates for these two types of ZnPLAQ systems may be fortuitous since the rotational freedom of the AQ acceptor with respect to the ZnP donor is also a function of the length of the linking bridge. This could explain the much stronger distance dependence of the rate constants in this series of ZnPLAQ compounds[10] as compared to that in the so-called "Paddon-Row" molecules.[13] Alternatively, more effective superexchange in the flexible, electron-rich ester linkage relative to the more constrained, saturated hydrocarbon bridge may compensate for slower ET rates in unfavorable conformations allowed by the former.[1]



PEAQ

H_2PEAQ: M = H_2
ZnPEAQ: M = Zn

In any case, when the AQ acceptor is linked directly at a meso-position of the donor porphyrin ring, the short DA distance (~1.4 Å, edge-to-edge) should play a major role in affecting the rates of ET quenching of the donor excited singlet state.[1] Moreover, the energy of the product RIP state will be much more strongly solvent dependent than in analogous molecules with longer mean DA distances because of the work-term correction, $-e^2/\epsilon_s \cdot r_{DA}$.[14]

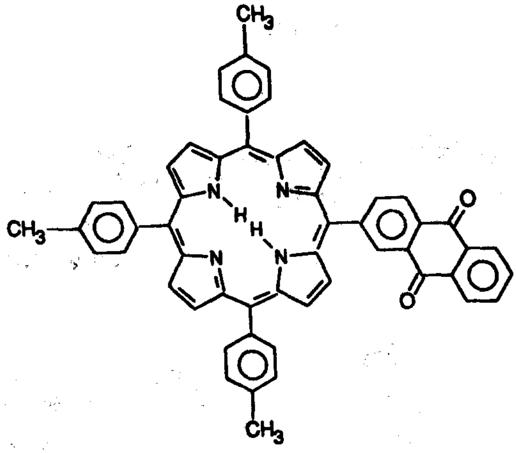
As we shall show, however, at such short distances there is a problem with quantitative interpretation of the observed ET rate constants, probably because an inner-sphere process[15] is involved. At such close DA displacements, the solvent reorganization energy is not accurately described by the two-sphere dielectric continuum model.[15a,b] Also, as predicted by Marcus theory,[16] ET rates are strongly dependent on the driving force, and it has rarely been possible to make accurate determinations of the true reaction energetics ($\Delta G^{\circ\prime}$) for ET. Even if it were possible to measure the redox potentials of both donor and acceptor in every solvent, the sum of these values does not yield the actual $\Delta G^{\circ\prime}$,[1] and the utility of the Born equation for estimating solvent effects, as proposed by Weller,[17] has been challenged on experimental grounds.[14a]

Another reason that ET rates in different solvents are not readily correlated with solvent polarity may be due to dielectric relaxation.[18] Breakdown of Marcus theory is to be expected when the rates become very fast (*e.g.*, $k_{et} \geqslant 5 \times 10^9$ s^{-1}) because of limitations imposed by solvent dynamics.[1] However, it is not clear how one should account for these effects when comparing ET rates for a given DA system in structurally dissimilar solvents.[19]

SYNTHESIS AND CHARACTERIZATION OF PAQ

Synthesis

PAQ was prepared by adapting the general method of porphyrin synthesis introduced by Lindsey and co-workers,[20] as discussed in detail below. This method involves an acid-catalyzed reaction in moderately dilute methylene chloride solution to establish an equilibrium between pyrrole and the appropriate aldehyde reactants and the porphyrinogen product. The porphyrinogen is subsequently oxidized irreversibly to the desired porphyrin. These mild reaction conditions have been demonstrated to provide porphyrin model systems cleanly and conveniently with a variety of sensitive functional groups.



PAQ

The synthetic strategy selected for preparation of PAQ is outlined in Scheme 1. The required anthraquinone-2-carboxaldehyde (AQ-2-CHO) is well known and is most conveniently prepared by oxidation of commercially available 2-(hydroxymethyl)-anthraquinone. Thus, reaction with chromium trioxide-pyridine, as described by Arjunan and Berlin[21] for preparation of the analogous 2-anthraldehyde, afforded an 81% yield of AQ-2-CHO. This material was then combined in stoichiometric proportion with *p*-tolualdehyde and pyrrole according to the Lindsey procedure. Chromatographic analysis of the crude porphyrin product, isolated in 53% yield, indicated the expected complex product distribution.

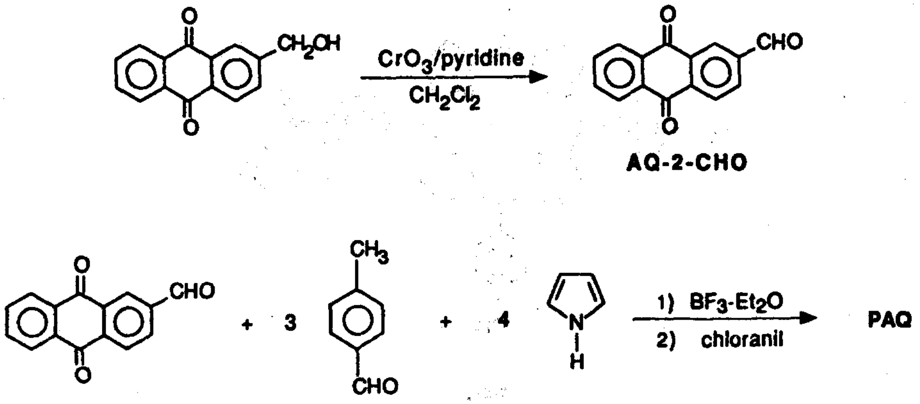
In addition to tetratolylporphyrin (TTP) and PAQ as the more mobile chromatographic components, substantial amounts of at least two other less mobile porphyrin compounds were observed. The latter are assumed to be the result of incorporation of more than one anthraquinone moiety, but no further characterization was attempted. Only incomplete resolution of the components of this complex reaction mixture could be realized with column chromatography on alumina or silica gel. Analytical samples of PAQ were most conveniently and efficiently obtained by preparative, silica-gel TLC of the isolated mixture of porphyrin products. Samples of PAQ needed for fluorescence-lifetime measurements were obtained from HPLC separation; PAQ thus obtained was demonstrated to be >99.9% pure both chromatographically and spectroscopically.

Characterization

In the ^{1}H NMR spectrum of PAQ, the highly shielded N-H protons appear at δ -2.74, while the highly deshielded protons on the β-positions of the pyrrole rings appear at ca. δ 8.8. The tolyl ring protons are readily apparent as an AA′-BB′ system at δ 7.51-8.14, while the methyl groups are clearly represented at δ 2.70. The spectrum is completed by three multiplets centered at δ 7.86, 8.40 and 8.70 and a broad singlet at δ 9.14, which are assigned to the aromatic protons of the anthraquinone substituent. These spectroscopic properties are fully consistent with those of previously reported aryl-substituted tritolylporphyrins,[22] together with consideration of the spectrum of AQ-2-CHO.

When comparing the NMR spectra of PAQ and AQ-2-CHO, it is particularly interesting to note significant perturbations in the chemical shifts of certain aromatic protons. Signals assigned to anthraquinone protons that are on the ring directly attached to the porphyrin nucleus are shifted considerably downfield relative to the same protons in AQ-2-CHO. This observation is in accord with the perturbations seen in the UV-visible absorption spectrum of PAQ, to which we now turn.

Scheme 1



RESULTS AND DISCUSSION

The electronic absorption spectrum of PAQ (Fig. 1) displays the characteristic[23] porphyrin Q-bands in the visible region and intense Soret band at 418 nm together with an absorption at 254 nm due to the AQ moiety. The intensity of the AQ band in PAQ is diminished considerably relative to the same band in the spectrum of the ester-linked PEAQ analogue.[11] In addition, the Soret band of PAQ is distinctly broadened to the red and to a lesser extent the Q-bands are as well. This broadening in the spectrum of the porphyrin moiety is independent of solvent (except for a refractive index shift[24]), and thus does not represent a charge-transfer absorption. We note also that the spectrum of tetra(2-anthracyl)porphyrin[25] manifests no such broadening, whereas the BQ analogue of PAQ does.[8a] Hence, we assign both effects (*viz.*, diminution of the AQ intensity and broadening of the porphyrin bands) to interactions between the non-bonded -C=O electrons of AQ and the π-orbitals of the porphyrin. Such interactions are consistent with a dihedral angle of ~60° between the P and AQ rings.[26]

In contrast to the absorption spectra, the fluorescence spectra of PAQ are only slightly red-shifted from those of other tetraarylporphyrins.[4] The major effect of solvent we observed on the emission spectrum of PAQ is also ascribed to refractive index. As the static dielectric constant (ϵ_s) of the solvent is increased from ~2 to ~6, the fluorescence intensities and (single-component) lifetimes decrease gradually (Table 1). However, in the moderately polar region $6 \leq \epsilon_s \leq 9$ (*i.e.*, chlorobenzene or ethyl acetate to methylene chloride), the values of both parameters decrease dramatically. To examine this effect further, we measured both the intensities and lifetimes of PAQ fluorescence in several binary mixtures of chlorobenzene and methylene chloride, with the results summarized in Table 1. The fluorescence quenching is seen to depend markedly on ϵ_s, which strongly suggests that an ET mechanism is involved.

When the lifetimes become very short (≤200 ps), the decay profiles often cannot be fit satisfactorily even with multiple (up to four) exponential components. This may be due to distributions of ET rate constants that, in turn, reflect distributions of reaction energetics due to solvent dynamics and/or hindered rotational oscillations of the AQ moiety at the site of attachment. As noted previously, solvent dielectric relaxation may also play a role.

The electrochemical data (Table 2) coupled with the fluorescence spectra indicate that, to a first approximation, the presumed RIP state ($P^{+}AQ^{-}$) is roughly isoenergetic with the porphyrin S_1 level in benzonitrile and presumably in more polar solvents as well. This assessment does not account for the Coulombic term ($-e^2/\epsilon_s \cdot r_{DA}$), which, at this center-to-center distance (~8.7 Å), would lower the RIP energy by as much as ~0.7 eV in a low-dielectric medium (*e.g.*, benzene or toluene) relative to nitrile solvents. It is likely that the sum of the redox potentials of the P and AQ groups increases with decreasing solvent polarity[14] due to less favorable solvation of both ionic species. Thus, qualitatively at least, there are two countervailing influences of solvent bulk dielectric constant, as noted previously by Weller.[17] However, as discussed below, this approach does not yield a satisfactory quantitative correlation of the observed trend of the fluorescence quenching listed in Table 1.

Correlations of ET rates for a given DA molecule with solvent properties have rarely yielded satisfactory results.[1] The major reason is that, as in the present case, it is not always possible to make accurate determinations of the true energetics. The semi-classical Marcus theory[16] of electron transfer predicts that the rate of an outer-sphere reaction is a quadratic function of the Gibbs free-energy ($\Delta G°'$):

$$k_{et} = \frac{2\pi}{\hbar} \mathcal{H}_{ps}^2 \, (4\pi\lambda kT)^{-1/2} \exp\left[- \frac{(\Delta G°' + \lambda)^2}{4\lambda kT} \right] \qquad (1)$$

Thus, the rate should increase with reaction exergonicity to a maximum that is characteristic of the total system (including solvent), and then decrease with further increases in exergonicity. The latter condition defines the Marcus "inverted" region.[16]

The electronic coupling term $\mathcal{H}_{ps}$ depends strongly on the center-to-center distance r_{DA} between D and A, whereas the reorganization energy λ should depend only weakly on r_{DA}.[1] Thus, $\mathcal{H}_{ps}$ should be the major factor in the dependence of k_{et} on distance. Since this term involves

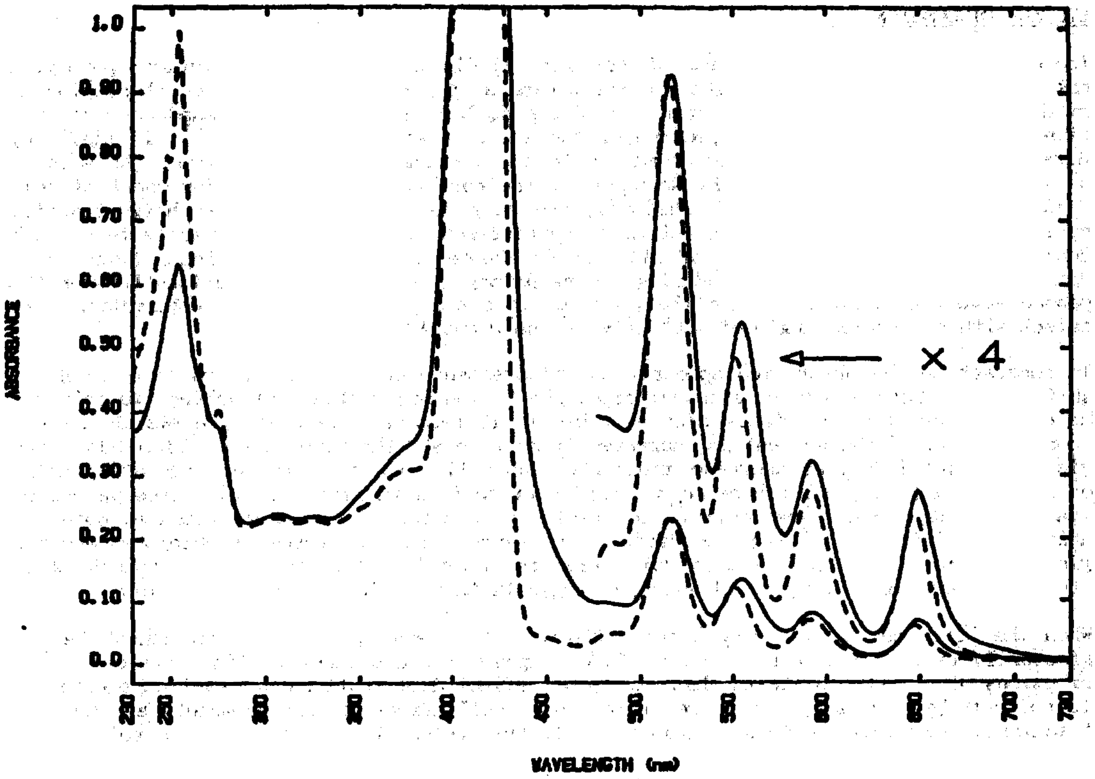


Figure 1. Absorption spectra of PAQ (———) and PEAQ (- - -) in methylene chloride at 298 K normalized at ~518 nm. Note the broadened and red-shifted absorption of PAQ relative to PEAQ in the porphyrin bands and the diminished intensity of the AQ band at ~254 nm. The spectrum of PEAQ is essentially a superposition of the spectra of equimolar concentrations of (non-linked) TTP and AQ.

Table 1. Solvent dependence of fluorescence properties of PAQ

Solvent[a]	ϵ_s[b]	Φ_{rel}[c]	τ_1/ns[d]	τ_2/ns[e]
benzene	2.27	(1.00)	11.7[f]	11.9
toluene	2.38	0.98	11.9[f]	12.1
TBME[g]	4.20	0.98	12.6[f]	12.8
EtOAc	6.02	0.72	10.1[f]	12.5
ClBz	5.62	0.64	5.9[f]	10.8
ClBz-$MeCl_2$, 8:1[h]	~6.2	0.32	1.9	--
ClBz-$MeCl_2$, 4:1	~6.6	0.20	1.1	--
ClBz-$MeCl_2$, 2:1	~7.1	0.07_9	0.5	--
ClBz-$MeCl_2$, 1:1	~7.7	0.03_9	0.2	--
ClBz-$MeCl_2$, 1:2	~8.1	0.02_4	--	--
ClBz-$MeCl_2$, 1:4	~8.5	0.02_0	--	--
$MeCl_2$	8.93	0.01_4	0.1 [0.03]	9.0
DCE	10.37	0.02_4	0.3	--
pyridine	12.91	0.01_5	0.3	--
acetone-$MeCl_2$, 1:1	~13.6	0.02_3	--	--
n-PrCN	20.3	0.04_0	0.8 [0.09]	12.1
acetone	20.56	0.03_1	0.9	--
BzCN	25.2	0.02_0	0.2 [0.15]	11.4
MeCN[i]	~36	<0.04	0.2 [0.06]	12.0

a. Abbreviations: TBME = *t*-butyl methyl ether; EtOAc = ethyl acetate; ClBz = chlorobenzene; $MeCl_2$ = methylene chloride; DCE = 1,2-dichloroethane; *n*-PrCN = *n*-butyronitrile; BzCn = benzonitrile; MeCN = acetonitrile. Measurements made on aerated solutions unless noted otherwise.

b. At 25° C from ref. 31; values for binary solvent mixtures are estimated from mole fractions. Comparisons with measurements of ϵ_s of other binary solvent mixtures[14a] show that this is a good approximation.

c. Integrated intensities relative to PAQ in benzene corrected for contributions from long-lived impurity (probably TTP) using the ns lifetime data.

d. Major component; measurements made with either ns or [ps] excitation, as indicated.

e. H_2PEAQ in deoxygenated solutions.[11]

f. Deoxygenated.

g. Solvent properties are those of diethyl ether.

h. Volume ratio, ClBz:$MeCl_2$.

i. Contains toluene (~1-5% vol).

Table 2. Electrochemical potentials[a] of PAQ and related molecules

	PAQ	PEAQ	TTP	AQ-2-CH_2OH[b]
oxidation	$+1.02_0$	$+1.00_5$	$+0.95_0$	---
reduction	-0.92_0	-0.87_5	---	-0.99_0

a. Volts vs. Ag/AgCl, measured in benzonitrile

b. 2-(hydroxymethyl)anthraquinone

integration over electronic wave functions, it is usually assumed to decrease exponentially with r_{DA}

$$\mathcal{H}_{ps}(r_{DA}) = \mathcal{H}_{ps}(r_o)\exp[-\beta(r_{DA} - r_o)/2] \qquad (2)$$

where r_o is a reference distance, and the factor of ½ in the exponent accounts for the fact that eq. 1 is expressed in terms of $\mathcal{H}_{ps}^2$. β depends on both the absolute and relative energetics of the donor, bridge and acceptor.[1] Hence, in a series of DA molecules with the same values of $\Delta G^{*\prime}$ and λ but differing r_{DA}, the rate constants should follow the relation (eq. 3)[1]

$$k_{et}(r_{DA}) = k_{et}(r_o)\exp([\beta(r_{DA} - r_o)] \qquad (3)$$

In practice, it is found that the reference distance r_o corresponds to the sum of the van der Waals radii of D and A. For a typical case with $\lambda = 1$ eV, then $\mathcal{H}_{ps}(r_o) \approx 0.025$ eV; this value represents an approximate dividing line between adiabatic and non-adiabatic ET processes.[1] It is generally considered that ET reactions become adiabatic as $r_{DA} \rightarrow r_o$.[16c]

In Eq. 1, the reorganization energy λ is composed of two parts:

$$\lambda = \lambda_{in} + \lambda_{out} \qquad (4)$$

The "inner" term, λ_{in}, is due to structural changes between the reactant and product states and is independent of the surrounding medium. For large molecules (e.g., chlorophylls and porphyrins), λ_{in} is calculated to be relatively small, *viz.*, ~0.1-0.3 eV.[15a,27]

The solvent-dependent "outer" term, λ_{out}, arises from reorganization of the surrounding medium because of differences between the orientation and polarization of solvent molecules around the neutral reactant state (DA) and ionic product state ($D^{\dagger}A^{\bar{\cdot}}$). If the medium is treated as a dielectric continuum,[16] this term can be expressed as:

$$\lambda_{out} = \frac{e^2}{4\pi\epsilon_o}\left[\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{r_{DA}}\right]\times\left[\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s}\right] \qquad (5)$$

where e is the electronic charge, r_D and r_A are the radii of the donor and acceptor molecules, respectively, and r_{DA} has been defined previously. ϵ_{op} is the optical dielectric constant (given by the square of the refractive index) and ϵ_s is the static (i.e., bulk) dielectric constant. For PLQ systems with $r_{DA} \approx 10$-15 Å, λ_{out} can be negligible in non-polar solvents or as high as ~1.5 eV in organic media that are sufficiently polar to stabilize the product RIP state.[1,14,28,29]

The lowest excited singlet state of the porphyrin moiety can relax by fluorescence, internal conversion, intersystem crossing to the triplet state, or electron transfer to the attached quinone. The first three factors are properties of the porphyrin moiety and generally do not change significantly when a quinone is attached.[30] If the shorter fluorescence lifetime of a linked PLQ molecule (relative to a reference porphyrin such as TTP) is due entirely to electron transfer, the rate constant k_{et} is given by:[1,30]

$$k_{et} \doteq 1/\tau_1 - 1/\tau_2 \qquad (6)$$

where τ_1 and τ_2 are the measured fluorescence lifetimes (defined as the reciprocals of the sums of the rate constants) of PLQ and the reference porphyrin, respectively. The ratio of these lifetimes (τ_1/τ_2) gives the extent of fluorescence quenching and should be in quantitative agreement with the measured relative quantum yields, provided that all quenching is dynamic and not static.[1,11]

We have used eq. 6 to derive values of k_{et} taking the values of τ_1 obtained with both ns and, where applicable, ps excitation (see Table 1). $\Delta G^{*\prime}$ was estimated using data available[31] for ϵ_s and the simplified form of the Weller equation:[17]

$$\Delta G^{*\prime} = -0.09 + 1.89/\epsilon_s \text{ (ev)} \qquad (7)$$

where the constants were evaluated from the energy of the excited-singlet state (fortuitously, ~1.89 eV, assumed to be essentially independent of solvent), the sum of the oxidation and reduction potentials of P and AQ, respectively (~1.94 eV in benzonitrile, Table 2), and dimensions estimated from molecular mechanics calculations.[32] λ was calculated using eqs. 4 and 5, with $\lambda_{in} = 0.2$ eV.

Substituting these calculated terms along with the values of k_{et} extracted from the fluorescence lifetimes observed for each solvent into eq. 1 yields values of $\mathcal{H}_{ps}$ that range from ~0.4 eV (in ethyl acetate and chlorobenzene) to ~0.7 eV (in methylene chloride). The fact that this approach fails to provide values of $\mathcal{H}_{ps}$ that are $\leqslant$0.025 eV and sensibly independent of solvent demonstrates that ET in this molecule does not occur *via* a non-adiabatic, outer-sphere mechanism.[15,16]

The values calculated for λ_{out} (eq. 5), $\Delta G^{*\prime}$ (eq. 7) and, therefore, $\mathcal{H}_{ps}$ are very sensitive to the choice of the molecular radii. For example, increasing the mean porphyrin and AQ radii to ~8.4 Å and ~3.9 Å, respectively (*i.e.*, the mean radii within the planes of the two rings), gives values of $\mathcal{H}_{ps} \leqslant 0.025$ eV for all solvent systems except 2:1 and 1:1 chlorobenzene-methylene chloride and neat methylene chloride. It is doubtful, however, that these dimensions are realistic.

We think that electron transfer in PAQ occurs by an inner-sphere rather than an outer-sphere mechanism,[15c] in which case calculations of λ_{out} using the two-sphere dielectric continuum model and $\Delta G^{*\prime}$ from the Weller equation are not meaningful.[14] Alternatively, since the center-to-center distance is fairly long (~8.7 Å), outer-sphere ET could indeed be the appropriate model, but eq. 1 would not apply if the reaction were adiabatic.[15,16]

Whatever the detailed explanation for this solvent dependence, PAQ appears to be a highly sensitive probe of the local dielectric environment. Further studies are currently in progress to investigate the mechanism(s) of fluorescence quenching in this molecule, including temperature and viscosity dependence and the role of solvent dielectric relaxation. Transient absorption data on the ps time scale demonstrate unambiguously that ET does in fact occur.[33] Thus, another important aspect is the solvent dependence of the lifetime of the product RIP. The energy of this state should be sufficiently high above the ground state that charge recombination is in the Marcus inverted region,[16] as is the case for virtually every linked PQ system studied to date.[1]

Our results show further that, although AQ is a poor terminal acceptor, it should be an excellent bridge to facilitate electron transfer to a secondary acceptor attached to it. We shall report on the synthesis and characterization of such a system in a future communication.

ACKNOWLEDGMENTS

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EXPERIMENTAL SECTION

Instrumentation: Absorption spectra were recorded on a Hewlett-Packard 8450A UV/visible rapid-scan spectrophotometer with samples in 1.00-cm or 2.00-mm pathlength cuvettes. A Spex Fluorolog I was used to acquire fluorescence and excitation spectra with either front-face or right-angle detection, as appropriate. Fluorescence lifetimes were measured by the technique of time-correlated single-photon-counting using a Photochemical Research Associates Model 3000 lifetime fluorimeter with ns excitation (H_2 arc lamp), usually at 355 nm. The optical system was configured for optimal detection in the red region of the spectrum,[34] and decay profiles were fit by computer deconvolution to either single- or double-exponential decay models, as required by the data. Some lifetime data were obtained at The University of Western Ontario with ps laser excitation[35] at 570 nm; these decay profiles were fit to multiple (up to four) exponential components as needed to meet the usual statistical criteria (χ^2, random residuals, autocorrelation profile).

All solvents were of the purest grade commercially available (usually Burdick and Jackson) and were used as received from freshly opened containers. The exception was methylene chloride, which was stored over anhydrous K_2CO_3 to preclude protonation of pyrrole nitrogen in the free-base porphyrins.

Oxidation and reduction potentials of PAQ, PEAQ and their non-linked constituents were measured by differential pulse polarography (PAR 174A) using a glassy carbon electrode, Ag/AgCl reference electrode and Pt counter-electrode. The carbon electrode was polished with 0.03 μm alumina and the Pt electrode was flame-cleaned prior to each sample measurement. All measurements were made on $\sim 10^{-3}$ M solutions in fresh benzonitrile (Burdick and Jackson) containing 0.1 M tetrabutylammonium hexafluorophosphate (Southwest Analytical Electrograde) as supporting electrolyte. Blank runs were made on the solvent plus supporting electrolyte before each measurement. The samples were scanned at 10 mV/s with 10 mV pulses.

^{1}H NMR spectra were obtained on a JEOL FX90Q spectrometer at an operating frequency of 89.56 MHz. Chemical shifts are expressed in ppm relative to internal tetramethylsilane.

HPLC separations were performed on a Beckman system composed of a Model 110B dual solvent delivery system and a Model 163 variable wavelength detector. Optimal separations were achieved on a normal phase silica column with methylene chloride and hexane (4:1 by volume).

Anthraquinone-2-carboxaldehyde (AQ-2-CHO): A 15.0-g (0.15 mol) portion of anhydrous chromium trioxide was added to a vigorously stirred solution of 25.0 g (0.30 mol) of anhydrous pyridine in 350 mL of methylene chloride. After the burgundy-colored solution had been stirred at ambient temperature for 15 min, a suspension of 5.0 g (0.021 mol) of 2-(hydroxymethyl)anthraquinone (Aldrich 22,652-1) in 150 mL of methylene chloride was added at once. A tarry, black deposit formed immediately, and stirring was continued for an additional 15 min. The dark solution was decanted, and the tarry deposit was washed with two 500-mL volumes of ether. The combined organic solutions were washed successively with three 500-mL portions of 5% aq NaOH, three 500-mL portions of 5% aq HCl, two 500-mL portions of 5% aq $NaHCO_3$ and one 500-mL portion of saturated aq NaCl. After drying with anhydrous Na_2SO_4, the solvent was removed on a rotary evaporator to yield 4.0 g (81%) of a pale yellow powder. This material was shown to be pure by TLC analysis (silica gel, methylene chloride). Recrystallization from benzene-heptane afforded pale yellow needles, mp 186-188° (lit.[36] mp 185-187°; lit.[37] mp 187-188°); ^{1}H NMR ($CDCl_3$) δ 7.78-7.93 (m, 2H), 8.21-8.50 (m, 4H), 8.77 (s, 1H), 10.23 (s, 1H, CHO).

5,10,15-Tri(p-tolyl)-20-(2-anthraquinonyl)porphyrin (PAQ): The following reaction was performed in a 2-L, three-necked, round-bottomed flask, which was equipped with a stirrer, reflux condenser and nitrogen inlet. The vessel was charged with a solution composed of 472 mg (2.0 mmol, 2.5×10^{-3} M) of AQ-2-CHO, 720 mg (6.0 mmol, 7.5×10^{-3} M) of *p*-tolualdehyde, and 536 mg (8.0 mmol, 1.0×10^{-2} M) of pyrrole (freshly distilled from calcium hydride) in 800 mL of methylene chloride (stored over anhydrous potassium carbonate). The atmosphere was purged with a stream of nitrogen, and 0.32 mL of a 2.5 M solution of boron trifluoride etherate in methylene chloride (0.8 mmol, 1.0×10^{-3} M) was added. The reaction vessel was wrapped with foil and stirring was continued at room temperature for 1 h. Chloranil (1.476 g, 6.0 mmol) was then added at once to the resulting red reaction mixture. The color changed immediately to purple, and the reaction mixture was refluxed with stirring for an additional 1 h. The solution was concentrated to about 50 mL on a rotary evaporator, and 15 g of Florisil (60-100 mesh, Baker) were added. The remaining solvent was removed to afford a dark purple powder, which was poured onto the top of a chromatography column (2.5-cm I.D.) dry-packed with 60 g of Florisil. The column was eluted with 800 mL of methylene chloride to remove small amounts of uncharacterized yellow, green and blue pigments. Washing with increasing amounts of diethyl ether in methylene chloride (10-33%; 1.5 L total) eluted maroon fractions containing the porphyrin products; little fractionation of these products occurred. Evaporation of the maroon solutions yielded 0.83 g (53%, assuming only PAQ) of a dark purple solid.

Analysis by TLC (silica gel, methylene chloride or chloroform-heptane, 1:1) indicated the presence of at least five components comprising the expected complex product distribution of unreacted *p*-tolualdehyde, TTP, PAQ, and other higher substituted anthraquinone porphyrins, which were not further characterized. Partial separation of the porphyrin components could be achieved by column chromatography (alumina or silica gel, methylene chloride), but analytical samples of PAQ were more conveniently isolated by preparative TLC (silica gel without fluorescent indicator, methylene chloride). Use of commercial, preparative TLC plates containing a fluorescent indicator (mainly zinc silicate) resulted in formation of considerable amounts of zinc-centered porphyrin. Samples of PAQ for fluorescence-lifetime measurements were obtained by extraction of analytical TLC plates (silica gel, methylene chloride) or by HPLC separation (silica, methylene chloride-hexane, 4:1).

PAQ was found to be quite soluble in solvents of low to moderate dielectric constant ($\epsilon_s \leqslant 10$) but less so in acetone and benzonitrile; it is virtually insoluble in simple alcohols and acetonitrile. Crystallization of PAQ together with trace amounts of a long-lived fluorescent impurity (probably TTP) readily occurred from solutions in toluene-acetonitrile mixtures.

The following data were found for PAQ: UV/Vis (CH_2Cl_2) 254, 418, 518, 556, 592, 648 nm; ^1H NMR ($CDCl_3$): δ -2.74 (br s, 2H, N-H), 2.70 (s, 9H, CH_3), 7.55 and 8.10 (AA′-BB′ d of d, J = 8 Hz, 12H, tolyl ring protons), 7.81 (m, 2H, anthraquinone ring protons), 8.38 (m, 2H, anthraquinone ring protons), 8.68-8.92 (m with s at 8.87, 10H, anthraquinone and β-pyrrole ring protons), 9.15 (br s, 1H, anthraquinone ring proton). Anal. Calcd for $C_{55}H_{38}N_4O_2$: C, 83.94; H, 4.87; N, 7.12; O, 4.07. Found: C, 84.09; H, 5.18; N, 6.64; O, 4.09 (corrected for 3.32% inert material).

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