Photoinduced Electron Transfer in a Porphyrin Dyad

Devens Gust,' Thomas A. Moore,' Ana L. Moore,' Lana Leggett, Su Lin, Janice M. DeGraziano, Roel M. Hermant, David Nicodem, Peter Craig, Gilbert R. Seely, and Ronald A. Nieman

Department of Chemistry and Biochemistry, Center for the Study of Early Events in Photosynthesis, Arizona State University, Tempe, Arizona 85287-1604

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A porphyrin dyad designed to facilitate vectorial interporphyrin electron transfer has been synthesized and studied using steady-state and time-resolved absorption and emission spectroscopies. The dyad features a zinc tetraarylporphyrin bearing electron-donating substituents linked by an amide bond to a free base porphyrin carrying electron-withdrawing groups. Excitation of the zinc porphyrin moiety in dichloromethane solution is followed by singlet energy transfer to the free base and concurrent electron transfer to the same moiety to yield a charge-separated state. The free base first excited singlet state decays by accepting an electron from the zinc porphyrin to form the same charge-separated state. Similar results are observed in butyronitrile. Transient absorption studies in butyronitrile verify the formation of a short-lived (8 ps) charge-separated state from the porphyrin first excited singlet states. The results support the suggestion that fluorescence quenching in related porphyrin dyads and carotenoid-diporphyrin triads is due to photoinduced electron transfer, rather than some other decay process.

Introduction

The initial energy conversion event of photosynthesis is photoinduced electron transfer between chlorophyll derivatives. Many of the first molecular models for photosynthesis featured photoinduced electron transfer from cyclic tetrapyrroles to quinones or other small organic acceptors.^{1,2} A variety of artificial photosynthetic species bearing two or more porphyrin moieties, some of which demonstrate interporphyrin photoinduced electron transfer, have now been prepared.³ For example, we recently reported studies of a series of amide-linked porphyrin dyad (P-P) and carotenoid-diporphyrin triad (C-P-P) molecules which exhibit quenching of the porphyrin fluorescence.⁷ This quenching was ascribed to electron transfer and produced charge-separated states of the form P*+-P*- or C-P*+-P*-. These states were not directly detected spectroscopically, although prima-facie evidence for their formation was provided by the observation of a longlived C*+-P-P*- charge-separated state in the triads via transient absorption spectroscopy on the nanosecond time scale. This longlived state was postulated to form via an intermediate C-P++-P+species. While studying a structurally different series of cyclic tetrapyrrole dyads, Wasielewski et al. observed that although fluorescence quenching led to spectroscopically detectable chargeseparated states in some circumstances such states could not be detected in others.⁶ In the latter cases, fluorescence quenching presumably occurred via virtual charge-separated states⁶ or possibly charge-separated states with ultrashort lifetimes. In light of this observation, we have investigated fluorescence quenching in one of our amide-linked porphyrin dyads with a view toward direct spectroscopic detection of any interporphyrin chargeseparated state via transient absorption spectroscopy on the picosecond time scale.

Results

The detectability of a potentially short-lived $P^{*+}-P^{*-}$ state is enhanced if its rate of formation is rapid, relative to its decay, so that its maximum concentration is relatively high. A rapid photoinduced electron-transfer rate in dyads of the type under discussion is favored by a relatively large thermodynamic driving force for the charge separation reaction. Dyad 1 was designed in order to stabilize the $P^{*+}-P^{*-}$ state. One porphyrin moiety (P_{Zn}) bears electron-donating dimethylamino groups and a zinc atom, which help stabilize the radical cation. The second porphyrin (P_F) features three electron-withdrawing pentafluorophenyl substituents at *meso* positions, which stabilize the porphyrin radical anion. The syntheses of 1 and model porphyrin monomers 2 and 3 are discussed in the Experimental Section.



Electrochemistry. Cyclic voltammetric studies of 2 and 3 were carried out in benzonitrile containing 0.1 M tetra-n-butylammonium hexafluorophosphate (see Experimental Section for details). The voltammograms were reversible in both cases. The first oxidation potential of 2 was +0.01 V relative to internal ferrocene. Thus, the zinc porphyrin moiety is a much better electron donor than zinc meso-tetraphenylporphyrin⁸ and even dimethylaniline.9 The first reduction potential of 3 was -1.33 V, and 3 is therefore a significantly better electron acceptor than meso-tetraphenylporphyrin.8 We have previously reported7 that linking porphyrin moieties through an amide bridge as in 1 does not significantly alter the first oxidation and first reduction potentials from those for model porphyrins. Based on these values, the $P_{Zn}^{*+}-P_{F}^{*-}$ state lies about 1.34 eV above the ground state. The dyad is organized to favor unidirectional electron transfer, as the P_{Zn}^{•-}-P_F^{•+} charge-separated state lies at a much higher energy.



Figure 1. Absorption spectra of dichloromethane solutions of dyad 1 (-), zinc porphyrin 2 (- -), and free base porphyrin 3 (- -) and of a linear combination of the spectra of 2 and 3 which approximates that of 1 (- $\cdot -$).



Figure 2. Corrected fluorescence emission spectra in dichloromethane with excitation at 590 nm: dyad 1 (---), zinc porphyrin 2 (---), and free base porphyrin 3 (---).

Absorption Spectra. The spectrum of zinc porphyrin 2 in dichloromethane solution exhibits a Soret absorption at 434 nm and Q-band maxima at 520, 558, and 604 nm. Fluorinated porphyrin 3 has maxima at 414 (Soret), 510, 540, 586, and 640 nm. The spectrum of dyad 1 is essentially a linear combination of the spectra of the monomers, with only minor differences in wavelength maxima and band shapes. Figure 1 shows the spectra of all three molecules in the 480–700-nm region. Also given in the figure is a linear combination of the spectra of 2 and 3 which approximates that of the dyad. The absorption spectra are consistent with only a weak interaction between the moieties; the two chromophores retain their individual identities.

Fluorescence Emission Spectra. The corrected emission spectra of 1-3, with excitation at 590 nm, are shown in Figure 2. The maximum intensities have been normalized for ease in comparison of spectral shapes. Zinc porphyrin 2 has a maximum at 625 nm, with a shoulder at about 675 nm. The free base 3 features maxima at 643 and 713 nm. The fluorescence spectrum of dyad 1 is clearly a combination of these two emissions. However, emission from both porphyrin moieties is strongly quenched in the dyad, relative to either monomer. Thus, linking the porphyrins has opened up new pathways for decay of both first excited singlet states (see the results of the time-resolved studies discussed below).

The first excited singlet-state energies of 2 and 3, calculated from the wavenumber average of the red-most absorption maximum and blue-most emission maximum for each porphyrin, were 2.02 and 1.93 eV, respectively. Figure 3 shows the energies



Figure 3. Energies of the first excited singlet and charge-separated states of dyad 1, based on results for the component monomers, and associated interconversion pathways.



Figure 4. Corrected, normalized fluorescence excitation spectrum of dyad 1 in dichloromethane ($\lambda_{em} = 719$ nm) (\odot), absorption spectra of zinc porphyrin 2 ($-\cdot$ -) and of free base porphyrin 3 ($-\cdot\cdot$ -), and the linear combination of spectra of 2 and 3 which corresponds to a singlet energy transfer quantum yield of 0.60 (—).

of the excited singlet and charge-separated states for dyad 1 based on the results for the component monomers.

Fluorescence Excitation Spectra. The fluorescence excitation spectrum of 1, corrected for the wavelength dependence of the excitation source and optics, was determined in dichloromethane solution. The emission was monitored at 719 nm where the majority of the fluorescence comes from the fluorinated free base porphyrin (Figure 4). It is clear that absorption of light by both porphyrin moieties contributes strongly to the emission. For example, the excitation spectrum contains both the 510-nm band of the fluorinated porphyrin and the 558-nm band of the zinc porphyrin. Thus, the zinc porphyrin is transferring singlet excitation to the attached free base (step 1 in Figure 3). However, the corrected excitation spectrum does not coincide with the absorption spectrum in Figure 1, and energy transfer is therefore not complete. The singlet energy-transfer efficiency was estimated by making the approximation that all of the emission at 719 nm comes from the free base porphyrin and by finding the fraction of the absorption spectrum of 2 which, when added to that of 3, best reproduces the shape of the corrected fluorescence excitation spectrum in Figure 4. The transfer efficiency calculated in this way is $60\% \pm 10\%$. Similar experiments were carried out in butyronitrile solution and gave a singlet-singlet energy-transfer efficiency of $40\% \pm 10\%$.

Time-Resolved Fluorescence Studies. Additional information concerning the singlet-state quenching processes was obtained



Figure 5. Decay-associated spectra of dyad 1 in dichloromethane obtained with 600-nm excitation. The decays at the eight indicated wavelengths were analyzed globally to yield the components shown with a χ^2 value of 1.23. The major components have lifetimes of 0.026 ns (O) and 0.216 ns (O). The minor component lifetimes are 0.83 ns (∇) and 4.9 ns (∇).

from time-resolved emission studies carried out using the single photon timing technique. Excitation of the fluorinated free base porphyrin 3 in dichloromethane solution at ambient temperatures with 590-nm laser pulses resulted in the observation of a single exponential decay with a lifetime of 8.5 ns ($\chi^2 = 1.12$). Similar experiments with zinc porphyrin 2 yielded a lifetime of 1.48 ns $(\chi^2 = 1.01)$. Decay curves at eight different wavelengths were measured for dyad 1 in dichloromethane with 600-nm excitation. These curves were analyzed globally¹⁰ to yield a fit to four exponential decay times ($\chi^2 = 1.23$, Figure 5). The two significant contributions to the decay-associated spectrum have lifetimes of 0.026 and 0.216 ns. The 0.026-ns component has the general shape of emission from the zinc porphyrin moiety, and its high amplitude is consistent with the fact that the majority of the light at 600 nm is absorbed by that chromophore. Thus, the lifetime of ${}^{1}P_{Zn}-P_{F}$ is 26 ps. The 0.216-ns component has the spectral features of the fluorinated free base porphyrin, and the lifetime of $P_{Zn}^{-1}P_F$ must therefore be 216 ps. The much shorter lifetimes observed for the porphyrin moieties in the dyad compared with the monomers 2 and 3 are consistent with the fluorescence quenching observed in the steady-state emission spectra mentioned above.

Similar time-resolved fluorescence studies were carred out in butyronitrile solution with excitation at 600 nm. Monomers 2 and 3 had lifetimes of 1.98 ($\chi^2 = 1.08$) and 9.88 ($\chi^2 = 1.06$) ns, respectively. The fluorescence decay of dyad 1 was measured at 7 wavelengths in the 640–720-nm region. Global analysis ($\chi^2 =$ 1.13) yielded lifetimes of 20 ps for ¹P_{Zn}-P_F and 58 ps for P_{Zn}-¹P_F.

Time-Resolved Absorption Studies. Transient absorption studies on the picosecond time scale were carried out in butyronitrile solution. Excitation was at 600 nm, with a \sim 200-fs pulse. The absorption spectra of 1-3 show that the absorbances of the zinc and free base porphyrin moieties are in the ratio 82:18 at this wavelength. Figure 6 reports the transient spectra for 1-3 in the 800-900-nm region recorded 10 ps after the pulse. The absorbance change for monomers 2 and 3 represents that for a solution of the monomer with an absorption at the pump wavelength identical to the contribution of the corresponding moiety to the absorption of dyad 1 used in the experiment. Free base 3 has virtually no transient absorption in this spectral region, whereas the first excited singlet state of zinc porphyrin 2 displays a broad, featureless absorption. The spectrum of dyad 1 differs from those of the monomers and in particular exhibits an absorption with a maximum at about 865 nm.

The time evolution of the 865-nm band was investigated. Figure 7a shows the time course of the transient averaged over the 850-



Figure 6. Transient absorption spectra of 1-3 in butyronitrile solution obtained 10 ps after excitation with a ~200-fs, 600-nm laser pulse. The absorbance of dyad 1 was 0.220 at the excitation wavelength in the 2-mm path length cuvette. The absorbance change for 2 represents an absorbance of 0.176 at the excitation wavelength, and that for 3 corresponds to an absorbance of 0.044.



Figure 7. Time evolution of the transient absorbance of a butyronitrile solution of 1 in the 850-870-nm region following excitation with the 200-fs, 600-nm laser pulse. The data in part a were obtained with a time resolution of 1.5 ps per point. The smooth curve shows the theoretical fit to the data based on Figure 3, with the rate constants in butyronitrile reported in the text. The absorption consists of contributions from both the P_{Zn} ⁺- P_{F} ⁺ charge-separated state and ${}^{1}P_{Zn}$ - P_{F} , which also absorbs in this spectral region. The data in part b were obtained with a time resolution of 0.5 ps per point. The smooth curve shows the theoretical fit discussed above.

870-nm region, measured with a time resolution of 1.5 ps per channel. Clearly, both a rise and a decay are present. A fitting of the data at 860 nm to three exponentials yielded a rise time of 8.3 ps, a fast decay of about 24 ps, and a slower decay component whose lifetime was not accurately determined because of the low signal-to-noise ratio. It will be noted that the 24-ps component



Figure 8. Triplet-triplet absorption spectrum $(e_T - e_G)$ of 7×10^{-5} M free base porphyrin 3 in deoxygenated butyronitrile solution obtained 1.8 μ s after excitation with a ~15-ns, 590-nm laser pulse (∇) and transient spectrum 1.8 μ s after excitation of the same solution following addition of 0.01 M tetramethylphenylenediamine (an electron donor) (\oplus). The band at 865 nm is attributed to the porphyrin radical anion.

has a lifetime similar to that of ${}^{1}P_{Zn}-P_{F}$ in the same solvent. Measurements were carried out with a time resolution of 0.5 ps per channel in order to better define the short, rising component. The time course of the transient absorption over the 850–870-nm region is shown in Figure 7b. A two-exponential fit to the data at 860 nm yielded a rising component of 8.3 ps and a decay of about 34 ps which was not well resolved on this time scale. A detailed analysis of the decay kinetics will be presented in the Discussion section.

Radical Anion of 3. The fluorescence quenching and electrochemical data reported above suggest that the 865-nm transient detected in 1 may be a porphyrin radical ion. Indeed, zinc tetraarylporphyrin radical cations¹¹ and free-base tetraarylporphyrin radical anions¹² are reported to have absorption bands in this region. Nanosecond transient absorption studies on model porphyrin 3 in butyronitrile were undertaken in order to further investigate this possibility. Excitation of a deoxygenated $7 \times$ 10⁻⁵ M solution of 3 with a 15-ns laser pulse at 590 nm led to the observation of the triplet-triplet absorption spectrum ($\epsilon_{\rm T}$ - ϵ_G). The spectrum in the 700–900-nm region, taken 1.8 μ s after excitation, is shown in Figure 8. A good electron donor, tetramethylphenylenediamine (0.01 M), was then added to the solution. At this concentration of donor, the fluorescence intensity of the porphyrin is quenched by about 80%. The steady-state absorption spectrum of the porphyrin shows no perturbation and thus no evidence for complexation with the donor. The transient absorption spectrum taken 1.8 μ s after laser excitation is shown in Figure 8. The triplet-triplet absorption spectrum has virtually disappeared, and an 865-nm band is now present. Thus, the 865-nm transient may be attributed to the radical anion of 3, formed by electron donation from the tetramethylphenylenediamine to the excited porphyrin. The 865-nm transient detected in the picosecond transient absorption spectrum of dyad 1 may likewise be assigned, at least in part, to the radical anion of the fluorinated porphyrin moiety.

Discussion

Fluorescence Results. The fluorescence lifetimes of 2 and 3 are similar to those of other tetraarylporphyrins. Thus, the *meso* substituents do not significantly affect the pathways for decay of the first excited singlet states through intramolecular electron transfer¹³ or in any other way. On the other hand, the dramatic shortening of the lifetimes of the porphyrin first excited singlet states in 1 relative to those in model monomers 2 and 3 indicates that linking the porphyrins has opened up new decay pathways for both chromophores. It is suggested that these pathways are

singlet energy and electron transfer, as shown in Figure 3. Rate constants for many of these pathways may be deduced from the steady-state and time-resolved fluorescence results.

In dichloromethane solution, the lifetime of the first excited singlet state of the zinc porphyrin moiety of 1 is 26 ps. If it is assumed that linking the two porphyrins has little effect on the intrinsic photophysics of the two chromophores,⁷ then k_3 , the rate constant for process 3 in Figure 3, will be the reciprocal of the 1.48-ns fluorescence lifetime of model porphyrin 2, or $6.8 \times 10^8 \, {\rm s}^{-1}$, and new pathways for decay of ${}^1P_{Zn}$ -P_F are clearly present in 1. Part of the quenching of the zinc porphyrin excited state is due to singlet-singlet energy transfer to the attached free base porphyrin (step 1 in the figure), which occurs with a quantum yield of about 0.60. As this process cannot account for all of the quenching of ${}^1P_{Zn}$ -P_F, the remainder is ascribed to electron transfer via step 6 in Figure 3 to yield the P_{Zn} -+P_F- chargeseparated state.

The steady-state absorption spectra of 1-3 indicate that the thermodynamic driving force for the singlet energy-transfer process is 0.090 eV. If one assumes that energy transfer between the two porphyrin moieties is an equilibrium process, then at 298 K, $k_2 = 0.030 k_1$. As will be shown below, k_2 is substantially slower than the other processes depopulating the P_{Zn} - 1P_F state, and, to a first approximation, will be ignored. This being the case, the quantum yield for singlet-singlet energy transfer, Φ_1 , will be given by eq 1.

$$\Phi_1 = \frac{k_1}{k_1 + k_3 + k_6} \tag{1}$$

In this instance, Φ_1 is 0.60 and the sum of the rate constants in the denominator is simply the reciprocal of the 26-ps lifetime of ${}^{1}P_{Zn}-P_{F}$ (eq 2), or 3.9 × 10¹⁰ s⁻¹. Thus, $k_1 = 2.3 \times 10^{10}$ s⁻¹.

$$\frac{1}{\tau_{\rm f}} = k_1 + k_3 + k_6 \tag{2}$$

Equation 2 may be used to calculate a value for k_6 of 1.4×10^{10} s⁻¹ from these values for k_1 , k_3 , and τ_f . From the spectroscopic and electrochemical data, a thermodynamic driving force of 0.68 eV may be estimated for this electron-transfer reaction.

The time-resolved fluorescence results for 3 show that the first excited singlet state decays with a lifetime of 8.5 ns. Assuming that the same photophysical processes are applicable to the free base porphyrin moiety of 1, k_4 in Figure 3 can be estimated to be $1.2 \times 10^8 \text{ s}^{-1}$. The 216-ps lifetime measured for this moiety in 1 thus represents a substantial quenching, which is ascribed to electron transfer via step 5 in Figure 3 to yield the $P_{Zn}^{*+}-P_{F}^{*-}$ state. The rate constant for this step, k_5 , is given by eq 3, and equals $4.5 \times 10^9 \text{ s}^{-1}$.

$$\frac{1}{\tau_{\rm f'}} = k_4 + k_5 \tag{3}$$

In summary, the fluorescence studies in dichloromethane show that the zinc porphyrin moiety serves as a reasonably efficient antenna for the free base porphyrin by transferring singlet excitation energy to it. In addition, both porphyrin first excited singlet states are strongly quenched by photoinduced electron transfer to yield the $P_{Zn}^{*+}-P_{F}^{*-}$ charge-separated state. Although the rate constants given above were calculated by assuming that k_2 is negligible, an exact mathematical treatment⁷ taking account of step 2 gives identical rate constants, within experimental error. It will be noted that because steps 3 and 4 in Figure 3 are slow relative to the competing pathways, the quantum yield of $P_{Zn}^{*+}-P_{F}^{*-}$ is essentially unity, regardless of the excitation wavelength.

A similar analysis of the absorption, fluorescence, and fluorescence excitation data for 1-3 in butyronitrile yields values for k_1-k_6 of 2.0 × 10¹⁰, 2.9 × 10⁹, 5.1 × 10⁸, 1.0 × 10⁸, 1.7 × 10¹⁰,

and 3.0×10^{10} s⁻¹, respectively. Again, including k_2 in the analysis has no effect on the rate constants, within the experimental error.

Transient Absorption Results. The time-resolved absorption studies of 1 on the picosecond time scale revealed a transient absorption centered at 865 nm which was not present in either of the monomers. The nanosecond studies of free base 3 in the presence of the electron donor tetramethylphenylenediamine showed the same feature, which was attributed to the porphyrin radical anion. Thus, it is reasonable to assign the 865-nm band in 1 mainly to the radical anion in the P_{Zn} ⁺⁺- P_{F} ⁻⁻ charge-separated state. The absorption in the 800-nm region (Figure 6) may be due in part to the zinc porphyrin radical cation, as such cations are known to absorb at these wavelengths.¹¹

The kinetics of the 865-nm band may appear to be unusual in that the time course of the decay of the transient absorption is comparable to the 20- and 58-ps lifetimes of the ${}^{1}P_{Zn}-P_{F}$ and P_{Z_n} - 1P_F precursor states, respectively, while the rise time (8.3 ps) is considerably shorter. However, examination of the kinetic equations for the problem shows that whenever k_3 and k_4 in Figure 3 are slow, relative to the rate constants for steps 1, 5, 6, and 7, the concentration of $P_{Zn}^{*+}-P_F^{*-}$ will rise on a time scale consistent with k_5 and k_6 and decay according to k_7 as long as k_5 and k_6 are substantially greater than k_7 . However, if k_7 is greater than k_5 and k_6 , the concentration of $P_{Zn}^{*+}-P_F^{*-}$ will quickly rise to a low maximum at a rate determined mainly by k_7 and decay on a time scale determined mainly by k_5 and k_6 . This is clearly the case for dyad 1. The kinetic behavior of the transient absorbance of 1 shown in Figure 7 may be simulated by using the rate constants determined from the time-resolved fluorescence studies in butyronitrile reported above and by assigning k_7 as 1.2×10^{11} s⁻¹. The resulting calculated absorbance as a function of time (which consists of contributions from $P_{Zn}^{+}-P_{F}^{+}$ and ${}^{1}P_{Zn}-P_{F}$) is in good agreement with the data on both time scales (Figure 7).

Conclusions

The steady-state and time-resolved fluorescence data for dyad 1 and model compounds 2 and 3 are consistent with rapid singletsinglet energy transfer from the zinc porphyrin moiety to the free base. In addition, both porphyrin first excited singlet states decay via photoinduced electron transfer to the same $P_{Zn}^{*+}-P_{F}^{*-}$ chargeseparated state. The quantum yield of this state is essentially unity. These conclusions are verified by the transient absorption results, which demonstrate that electron transfer is indeed responsible for the observed fluorescence quenching and that the resulting $P_{Zn}^{*+}-P_{F}^{*-}$ state has a very short lifetime of about 8 ps.

The results support our earlier conclusion⁷ that fluorescence quenching in a variety of other amide-linked tetraarylporphyrin dyads and carotenoid-diporphyrin triads is due to vectorial electron transfer to form an initial interporphyrin charge-separated state. In the case of the triads, this state decays in part by a second electron-transfer step which generates a C⁺⁺-P-P⁺⁻ chargeseparated state with a lifetime of several hundred nanoseconds. If the very short lifetime of the interporphyrin charge-separated state observed for dyad 1 and the resulting inverse kinetic behavior are characteristic of such states in related porphyrin dyads, then direct spectroscopic observation of these states will be difficult unless their rate of formation is also very rapid.

Experimental Section

Instrumental Measurements. The ¹H NMR spectra were obtained at 300, 400, or 500 MHz and refer to $\leq 1\%$ solutions in deuteriochloroform with tetramethylsilane as an internal reference. The numbering system for identifying the NMR resonances of the porphyrins has been previously reported.¹⁴ The UV-vis spectra were recorded on a Hewlett-Packard 8450A or Cary 5 spectrophotometer. Cyclic voltammetric measurements were carried out with either a PAR Model 173 potentiostat/galvanostat or a Pine Instrument Co. Model AFRDE4 potentiostat. All electrochemical measurements were performed in benzonitrile at ambient temperatures with a platinum button working electrode, a silver wire quasireference electrode, and a platinum wire counter electrode. The electrolyte was 0.1 M tetra-nbutylammonium hexafluorophosphate, and 0.01 M ferrocene was included as an internal reference redox system. Fluorescence decay measurements were made on ca. 1×10^{-5} M solutions in purified dichloromethane or butyronitrile using the time-correlated single photon timing method. The excitation source was a frequency-doubled, mode-locked Nd:YAG laser coupled to a synchronously pumped, cavity dumped dye laser with excitation at 590 or 600 nm. The apparatus has been described in detail elsewhere.¹⁵ Nanosecond transient absorption studies of 3 were made on deoxygenated butyronitrile solutions. Excitation was at 590 nm. The apparatus has been described elsewhere.^{14,16} Transient absorption measurements on the picosecond time scale were made using the pump-probe technique. The porphyrins were dissolved in purified butyronitrile to an absorbance of 1.0-1.8 at 600 nm in a 1-cm cell, and the resulting solution was circulated through a 2-mm path length flow cuvette in order to minimize any degradation of the sample by the laser which might occur. Excitation was at 600 nm with 200-fs, $8-\mu J$ pulses at a repetition rate of 540 Hz. The signals from the pump and continuum-generated white-light probe beam were collected by an optical spectrometric multichannel analyzer with a dual diode array detector head. Details are given elsewhere.¹⁷

Synthetic Methods. The preparation of 5-(4-carbomethoxyphenyl)-10,15,20-tris(pentafluorophenyl)porphyrin (3) has been previously reported.⁷

5-(4-Acetamidophenyl)-10,15,20-tris(4-N,N-dimethylaminophenyl)porphyrin (2). In a 3-L round-bottomed flask were placed 1.75 L of propionic acid, 50.22 g (0.337 mol) of p-N,Ndimethylaminobenzaldehyde, 18.20 g (0.112 mol) of p-acetamidobenzaldehyde, and 30.32 g (0.459 mol) of pyrrole. The mixture was refluxed for 1.0 h and cooled to room temperature. The acid solvent was removed in vacuo. The remaining tarry mixture was neutralized with aqueous sodium bicarbonate and extracted with several portions of dichloromethane. The organic extracts were combined and the solvent was removed in vacuo. The product mixture was divided into thirds, dissolved in dichloromethane, and filtered through short silica gel columns with dichloromethane eluant to remove tar. The porphyrins were extracted in a Soxhlet apparatus with chloroform, and the solvent was removed from the partially purified porphyrins in vacuo. The porphyrins were separated and purified by repeated chromatography on silica gel with gradient elution beginning with 100% dichloromethane and finishing with 3% methanol in dichloromethane. The desired porphyrin was obtained in 0.4% vield: 1H NMR (500 MHz, CDCl₃) & 8.79-8.92 (8H, m, pyrrole-H), 8.17 (2H, d, J = 8.3 Hz, 5 Ar2-H and 6-H), 8.09 (2H, d, J = 8.3 Hz, 15 Ar2-H and 6-H), 8.08 (4H, d, J = 8.3 Hz, 10,20 Ar2-H and 6-H), 7.88 (2H, d, J = 8.3 Hz, 5 Ar3-H and 5-H), 7.47 (1H, s, $-NHCO_{-}$), 7.11 (6H, overlapping doublets, J = 8.3Hz, 10,15,20 Ar3-H and 5-H), 3.24 (18H, s, 10,15,20 anilino-CH₃), 2.36 (3H, s, CH₃CO), -2.63 (2H, s, pyrrole-NH); mass spectrum (EI) m/z 800 (M+); UV-vis absorption (dichloromethane) λ_{max} (nm) = 432, 528, 572, 662; fluorescence emission $(\lambda_{ex} = 590 \text{ nm in dichloromethane}) \lambda_{max} (nm) 689, 755.$

Zinc 5-(4-Acetamidophenyl)-10,15,20-tris(4-N,N-dimethylaminophenyl)porphyrin (2) was prepared by stirring a 1:10 methanol:dichloromethane solution of 5-(4-acetamidophenyl)-10,15,20-tris(4-N,N-dimethylaminophenyl)porphyrin with an excess of zinc acetate at room temperature. After it was stirred for 24 hours, the solution was chromatographed on a short silica gel column with dichloromethane elution to remove excess zinc acetate. The solvent was evaporated at reduced pressure to yield pure (2): ¹H NMR (300 MHz, CDCl₃) δ 8.88–9.01 (8H, m, pyrrole H), 8.15 (2H, d, J = 8.0 Hz, 5 Ar2-H and 6-H), 8.07 (2H, d, J = 8.5 Hz, 15 Ar2-H and 6-H), 8.06 (4H, d, J = 8.5Hz, 10,20 Ar2-H and 6-H), 7.85 (2H, d, J = 8.0 Hz, 5 Ar3-H and 5-H), 7.08 (6H, d, J = 8.5 Hz, 10,15,20 Ar3-H and 5-H), 3.21 (18 H, s, N-CH₃), 2.35 (3H, s, CH₃CO); UV-vis absorption (dichloromethane) λ_{max} (nm) 434, 520 (sh), 558, 604; fluorescence emission ($\lambda_{ex} = 590$ nm in dichloromethane) λ_{max} (nm) 625, ~675 (sh).

Zinc 5-(4-Aminophenyl)-10,15,20-tris(4-N,N-dimethylaminophenyl) porphyrin was prepared by stirring at room temperature a 1:10 methanol: dichloromethane solution of zinc acetate in excess and 48.0 mg (0.063 mol) of 5-(4-aminophenyl)-10,15,20-tris-(4-N,N-dimethylaminophenyl)porphyrin, which was obtained by hydrochloric acid-catalyzed hydrolysis of 5-(4-acetamidophenyl)-10,15,20-tris(4-N,N-dimethylaminophenyl)porphyrin followed by neutralization with aqueous potassium carbonate and extraction with dichloromethane. The yield was 38.1 mg (73.3%): ¹HNMR (300 MHz, CDCl₃) δ 8.89-8.94 (8H, m, pyrrole H), 8.07 (6H, d, J = 8.5 Hz, 10,15,20 Ar2-H and 6-H), 7.97 (2H, d, J = 8.0Hz, 5 Ar2-H and 6-H), 7.08 (6H, d, J = 8.5 Hz, 10,15,20 Ar3-H and 5-H), 7.02 (2H, d, J = 8.0 Hz, 5 Ar3-H and 5-H), 3.21 (18H, J)s, N-CH₃); UV-vis absorption (dichloromethane) λ_{max} (nm) 436, 520 (sh), 562, 606; fluorescence emission (λ_{ex} = 590 nm in dichloromethane) λ_{max} (nm) = 625, ~675 (sh).

Dyad 1. The acid chloride of 5-(4-carboxyphenyl)-10,15,20tris(pentafluorophenyl)porphyrin was prepared as previously described⁷ starting with 79.5 mg (0.086 mmol) of the porphyrin. The acid chloride was dissolved in 8 mL of dry toluene and 3 mL of pyridine under a dry nitrogen atmosphere. Zinc 5-(4aminophenyl)-10,15,20-tris(4-N,N-dimethylaminophenyl)porphyrin (38.1 mg, 0.046 mmol) was dissolved in the same solvent and added at once to the stirred solution of the acid chloride. The reaction was essentially complete after 2 h. Purification was accomplished by chromatography on silica gel with 4% ethyl acetate in dichloromethane as the eluant and 8.4 mg of pure 1 (10.6% yield) was isolated: ¹H NMR (300 MHz, CDCl₃) δ 8.88– 9.01 (16H, m, pyrrole-H), 8.46 (4H, br s, 5' Ar2,3,5, 6-H), 8.35 (2H, d, J = 8.3 Hz, 5 Ar2-H and 6-H), 8.20 (2H, d, J = 8.3 Hz,5 Ar3-H and 5-H), 8.12 (6H, d, J = 8.3 Hz, 10,15,20 Ar2-H and 6-H), 7.12 (6H, d, J = 8.3 Hz, 10,15,20 Ar3-H and 5-H), 3.23 (18H, s, 10,15,20 anilino-CH₃), -2.83 (2H, s, pyrrole-NH); UVvis absorption (dichloromethane) λ_{max} (nm) 414, 510, 558, 604, 640; fluorescence emission ($\lambda_{ex} = 590$ nm in dichloromethane) λ_{max} (nm) 625, 646, 710.

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