Excited-State Energy Transfer and Ground-State Hole/Electron Hopping in *p*-Phenylene-Linked Porphyrin Dimers

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The ground- and excited-state properties of a series of *p*-phenylene-linked porphyrin dimers have been examined using a variety of static and time-resolved spectroscopic techniques. The dimers consist of a zinc porphyrin and a free base (Fb) porphyrin (ZnFb Φ), two zinc porphyrins (Zn₂ Φ), or two Fb porphyrins (Fb₂ Φ). In each array, the porphyrins are joined by the *p*-phenylene linker at one meso position, with the nonlinking meso positions bearing mesityl groups. Three analogous dimers in which the mesityl groups are replaced with pentafluorophenyl groups ($F_{30}ZnFb\Phi$, $F_{30}Zn_2\Phi$, and $F_{30}Fb_2\Phi$) were also synthesized and characterized. The excited-state energy-transfer rate from the photoexcited Zn porphyrin to the Fb porphyrin is $(3.5 \text{ ps})^{-1}$ for ZnFb Φ and (10 ps)⁻¹ for F₃₀ZnFb Φ . The quantum yields of excited-state energy transfer are \geq 99% for both complexes. The energy-transfer rates in the *p*-phenylene-linked dimers are considerably faster than those observed for the analogous dimers containing a diphenylethyne linker ((24 ps)⁻¹, ZnFbU; (240 ps)⁻¹, F_{30} ZnFbU). At these distances, both through bond and through space contributions to the electronic coupling are important. The faster energy-transfer rates in the *p*-phenylene- versus diarylethyne-linked dimers are attributed to enhanced electronic coupling between the porphyrins in the former dimers arising primarily from the shorter inter-porphyrin separation. The electronic coupling in the *p*-phenylene-linked dimers is sufficient to support ultrafast energy transfer in both $ZnFb\Phi$ and $F_{30}ZnFb\Phi$, but is not so large as to significantly perturb the redox or inherent lowest excited-state photophysical properties of the porphyrin constituents. Electronic perturbations resulting from fluorination have little effect on the energy-transfer rates in the *p*-phenylene-linked dimers, but the rates of room-temperature ground-state hole/electron hopping processes in the corresponding monocation radicals of the bis-Zn analogues of the p-phenylene-linked dimers ($\geq (0.05)$ $(\mu s)^{-1}$, $[Zn_2\Phi]^+$; $\leq (2.5 \ \mu s)^{-1}$, $[F_{30}Zn_2\Phi]^+$) are significantly influenced by the fluorination-induced changes in the electronic structure. Collectively, these characteristics make these constructs attractive candidates for incorporation into extended multi-porphyrin arrays for a variety of molecular photonics applications.

1. Introduction

Understanding the factors that control excited-state energy transfer is essential for the rational design of a wide variety of molecular photonic devices. We have synthesized light-harvesting arrays,¹ a molecular photonic wire,² and optoelectronic gates³ that all rely on excited-state energy transfer. Each of these devices incorporates tetraarylporphyrins joined by the semirigid⁴ p,p'-diarylethyne linker at the porphyrin meso positions. Recently, we have synthesized several series of porphyrin dimers in order to examine the factors that affect the energy-transfer process. These dimers have probed the effects of torsional constraints on the linker,^{5,6} the rotation of the porphyrins about the ethyne linker,⁷ and the nature of the metal in the metalloporphyrin.⁸ The major findings from these studies are that energy transfer predominantly involves a through-bond (TB) process mediated by the diarylethyne linker and a minor

contribution from a through-space (TS) process. The rate of energy transfer from zinc porphyrin to free base (Fb) porphyrin in the ZnFb dimer, which contains a torsionally unhindered p,p'-diphenylethyne linker (ZnFbU), is (24 ps)⁻¹, giving an energy-transfer yield of 99%.

More recently, we examined a series of dimers that revealed the effects of the nature and electron-density distributions of the frontier molecular orbitals (HOMOs and LUMOs) of the porphyrin constituents.⁹ The HOMO of each porphyrin is either $a_{1u}(\pi)$ or $a_{2u}(\pi)$, depending on factors such as the positions and electron-donating/withdrawing character of the peripheral substituents. The energy-transfer rate in F_{30} ZnFbU ((240 ps)⁻¹), which contains pentafluorophenyl groups at all nonlinking meso carbons, is an order of magnitude slower than that in ZnFbU $((24 \text{ ps})^{-1})$, which contains mesityl groups at these positions. The structures of these two dimers are shown in Figure 1. The a_{1u} HOMOs of the porphyrins in F₃₀ZnFbU have nodes at the meso positions, including those to which the linker is appended. In contrast, the a_{2µ} HOMOs of the constituents of ZnFbU have substantial electron density at these positions. This reversal of orbital ordering, together with a redistribution of electron density in the HOMOS and $e_g(\pi^*)$ LUMOS accompanying incorpora-

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Figure 1. Structures of the diarylethyne- and *p*-phenylene-linked dimers.

tion of the electron-withdrawing fluorines, substantially diminishes TB electronic coupling via the linker and reduces the rates of both excited-state energy transfer (in the neutral $F_{30}ZnFbU$ array) and ground-state hole/electron hopping (in the monocation radical of the bis-Zn analogue, $[F_{30}Zn_2U]^+$).

The diarylethyne linker used in our prototypical arrays and dimers is quite attractive both from the standpoint of modular construction¹⁰ as well as the fact that pairwise electronic interactions are relatively weak and deleterious quenching interactions are absent. However, it is desirable to construct arrays with still faster energy-transfer rates. One approach to increasing the energy-transfer rate is to shorten the distance between the porphyrins. Multi-porphyrin arrays have been constructed using several types of shorter linkers that are suitable for preparing linear or extended architectures via meso position attachment. These include porphyrins joined directly at the meso positions (no linker)¹¹ and those joined by ethene,¹² ethyne,¹³butadiyne,¹³⁻¹⁶furan,¹⁴enyne,¹⁶hexatriene,¹⁷*p*-phenylene,¹⁸⁻⁻ ⁴⁶ phenylethene,⁴⁷ naphthalene,^{35,37} biphenyl,^{19,35-37} phenanthrene,¹⁹ and ethynylphenylethyne¹⁶ groups. The attachment of porphyrins via ethyne or butadiyne units results in strong electronic coupling, as evidenced by the dramatic red-shifting of the Q bands of the porphyrin. The direct meso-meso connection results in weaker electronic coupling, as evidenced by less perturbation of the optical spectrum, presumably due to the orthogonality of the adjacent porphyrins. However, at present, the construction of this connection lacks synthetic control. Incorporation of a p-phenylene linker also results in dimers that remain in the weak coupling limit as judged by their absorption spectra.^{21,24,25,32,46} Equally important, the *p*-phenylene group is amenable to a modular synthetic approach, a key requirement for the systematic construction of molecular devices.48

Relatively few of the previous *p*-phenylene-linked dimers have been examined for their energy-transfer properties. One ZnFb dimer bearing β -pyrrole substituents has been shown to exhibit an energy-transfer rate of $(\sim 20 \text{ ps})^{-1}$.³⁵ Another ZnFb dimer bearing only meso substituents exhibits a rate estimated to be faster than $(10 \text{ ps})^{-1}$; however, the exact rate was not determined.⁴⁰ Many other architectures containing *p*-phenylene-linked porphyrins have been prepared with the goal of investigating photoinduced electron transfer to an appended acceptor.^{19,24,26,28–32,36,39–44} However, the electron-transfer process in these arrays severely complicates the precise analysis of underlying energy-transfer reactions.

In the present study, we have prepared and characterized two types of *p*-phenylene-linked dimers substituted at the meso positions, one with mesityl groups (ZnFb Φ) and the other with pentafluorophenyl groups (F₃₀ZnFb Φ). The structures of these dimers are included in Figure 1. The goals of our study were two-fold: (1) determination of how electronic communication differs in *p*-phenylene- versus diarylethyne-linked dimers and (2) the further examination of the effects of orbital characteristics (ordering and electron density distributions) on electronic communication in the arrays. Toward these objectives, we compared the excited-state energy-transfer rates in ZnFb Φ versus ZnFbU and F₃₀ZnFbU versus F₃₀ZnFb Φ , as well as the ground-state hole/electron hopping rates in the monocation radicals of the corresponding bis-Zn complexes of the respective dimers.

2. Results

a. Synthesis. Prior syntheses of meso-(*p*-phenylene)-linked multi-porphyrin architectures have employed various statistical condensations, ^{18–33} though one stepwise synthesis has recently been developed.³⁴ Most condensations require the synthesis of porphyrin carboxaldehyde or dipyrromethane precursors, ^{18–31} but the condensation of an aldehyde, terephthaldicarboxaldehyde, and pyrrole affords the *p*-phenylene-linked dimer in a one-flask process using commercially available materials.^{32,33} We have employed the latter approach in order to rapidly gain access to *p*-phenylene-linked dimers bearing various nonlinking meso substituents for spectroscopic analysis.

The *p*-phenylene-linked porphyrins were prepared using a one-flask condensation of an aldehyde, terephthaldicarboxaldehyde, and pyrrole. This reaction is performed under the standard conditions for the two-step one-flask synthesis of mesosubstituted porphyrins.^{49,50} A solution of pyrrole, mesitaldehyde, and terephthaldicarboxaldehyde (molar ratio of 8:6:1; 10 mM pyrrole) in chloroform (containing ethanol) at room temperature was treated with boron trifluoride etherate (3.3 mM). The reaction progress was monitored by the removal of aliquots and their analysis by absorption spectroscopy. The yield of porphyrin was 10% after 30 min and 15% after 60 min. After 1 h, the oxidant DDQ (7.5 mM) was added, and the mixture was stirred at room temperature for an additional 1 h. The crude reaction mixture consisted of small amounts of (uncharacterized) non-porphyrinic materials in addition to the monomeric porphyrin, desired porphyrin dimer (Fb₂ Φ), and higher molecular weight porphyrins as revealed by laser desorption mass spectrometry (LD-MS)⁵¹ and analytical size-exclusion column chromatography (SEC).9 The purification scheme involved a sequence of three consecutive chromatography procedures. Two flash silica gel columns afforded a mixture of the porphyrincontaining compounds, which were readily separated by preparative SEC in toluene, affording the desired phenylene-linked dimer $Fb_2\Phi$ in 1.4% yield.⁵² This reaction at the 3 L scale afforded 75 mg of $Fb_2\Phi$. This same approach was applied to the reaction of pentafluorobenzaldehyde, terephthaldicarboxaldehyde, and pyrrole. The *p*-phenylene-linked dimer $F_{30}Fb_2\Phi$ was obtained in 1.0% yield. Although these yields are quite low, this synthetic procedure proved straightforward and provided ready access to suitable quantities of *p*-phenylenelinked dimers with the desired substituents at the nonlinking meso positions.

The mono-Zn and bis-Zn complexes of the mesityl- and pentafluorophenyl-substituted phenylene-linked porphyrin dimers were prepared by treatment of the corresponding bis-Fb complex with methanolic zinc acetate, resulting in a mixture of mono-Zn and bis-Zn chelates that were readily separated by column chromatography. In this way, the $Fb_2\Phi$ and $F_{30}Fb_2\Phi$ complexes were converted to the mono-Zn chelates ZnFb Φ and F₃₀ZnFb Φ in 37.8% and 44.0% yields, respectively. Treatment with excess zinc acetate gave the desired bis-Zn porphyrin dimers $Zn_2\Phi$ and $F_{30}Zn_2\Phi$ in quantitative yield. The zinc insertion products were readily characterized by absorption, fluorescence, and ¹H NMR spectroscopy. The ¹H NMR spectra of the bis-Zn porphyrin dimers (Zn₂ Φ and F₃₀Zn₂ Φ) and the bis-Fb porphyrin dimers (Fb₂ Φ and F₃₀Fb₂ Φ) showed resonances that were consonant with their symmetry, while in the mono-Zn dimers (ZnFb Φ and F₃₀ZnFb Φ) resonances were observed due to the constituent Zn and Fb porphyrins.

b. Physical Properties of the Neutral Complexes. 1. Absorption Spectra. The absorption spectra of the various dimers were recorded in toluene at room temperature. The absorption maxima are given in the Experimental Section. The general spectral features of the nonfluorinated p-phenylenelinked dimers (ZnFb Φ , Zn₂ Φ , and Fb₂ Φ) and the fluorinated analogues ($F_{30}ZnFb\Phi$, $F_{30}Zn_2\Phi$, and $F_{30}Fb_2\Phi$) are as follows. (1) The visible (Q) bands of the ZnFb dimers are essentially the superposition of the spectra of the corresponding monomeric Zn and Fb reference compounds (e.g., ZnTMP + FbTMP). (2) The visible (Q) bands of the bis-Zn and bis-Fb dimers match the spectra of the respective monomeric Zn or Fb reference compounds. (3) Each of the dimers exhibits a splitting of the Soret band that can be ascribed to exciton coupling of the two porphyrin constituents, with the degree of splitting and relative intensities of the bands depending on the particular complex.

2. Fluorescence Spectra and Fluorescence Quantum Yields. The fluorescence spectra and yields of the dimers and monomeric reference compounds were recorded in toluene at room temperature. The emission yields are collected in Table 1, and the emission wavelengths are given in the Experimental Section. The fluorescence spectra and quantum yields of the bis-Fb and bis-Zn dimers closely resembled those of the corresponding Fb and Zn monomers, respectively. The emission spectrum and yield of the Fb component of $ZnFb\Phi$ obtained upon illumination at 515 nm, where the Fb porphyrin absorbs predominantly, are essentially the same as those for the Fb monomer. However, the fluorescence spectrum of $ZnFb\Phi$ obtained upon illumination at 550 nm, where the Zn porphyrin absorbs predominantly, showed emission almost exclusively from the Fb porphyrin. This observation is consistent with a high yield of excited-singletstate energy transfer from the Zn to the Fb porphyrin. Essentially identical results as those described for $ZnFb\Phi$ were obtained for $F_{30}ZnFb\Phi$.

3. Transient Absorption Spectra. The energy-transfer rate from the photoexcited Zn porphyrin to the Fb porphyrin subunit in each of the dimers (ZnFb Φ and F₃₀ZnFb Φ) was assessed using transient absorption spectroscopy.⁵⁵ For most measurements, the complexes in toluene at room temperature were excited using a 120 fs pulse at 550 nm, which predominantly pumps the Zn porphyrin component of each array. This excitation wavelength gives the best discrimination between

	$\Phi_{ m f}$		τ (ns) ^b			
compound	Zn	Fb	Zn	Fb		
Dimers						
ZnFbΦ	с	0.10	0.0035	13.1		
$F_{30}ZnFb\Phi$	с	0.063^{d}	0.010			
$Zn_2\Phi$	0.038		2.3			
$F_{30}Zn_2\Phi$	0.027		1.6			
$Fb_2\Phi$		0.10		13.0		
$F_{30}Fb_2\Phi$		0.060^{d}		11.8		
Monomers						
ZnTMP	0.039		2.5			
FbTMP		0.10		13.2		
ZnTPP	0.033 ^f		2.0			
FbTPP		0.11^{g}		13.0		
$ZnF_{15}U'^{h}$	0.022^{e}		1.6^{e}			
$FbF_{15}U'^{h}$		0.060^{e}		13.3^{e}		
ZnF ₂₀ TPP	0.019^{i}		1.4^{i}			
FbF20TPP		0.049^{i}		11.2^{i}		

^a All measurements were made at room temperature in toluene. ^b Lifetimes greater than 1 ns were determined by time-resolved emission spectroscopy ($\pm 5\%$), and lifetimes less than 1 ns were determined by time-resolved absorption spectroscopy (±10%). ^c Negligible emission was observed from the Zn porphyrin.^d The approximately 2-fold reduced fluorescence yields of the Fb porphyrin in $F_{30}ZnFb\Phi$ versus ZnFb Φ and F₃₀Fb₂ Φ versus Fb₂ Φ can be accounted for by a reduced natural radiative lifetime of the lowest excited singlet state of the fluorinated Fb porphyrin. The lower natural radiative rate for the latter components corresponds to the reduced oscillator strength of corresponding $Q_x(0,0)$ absorption band (when integrated along with the $Q_x(1,0)$ band), observed in the corresponding ground-state absorption spectra. A similar reduction in Fb emission yield has been found previously for the diarylethyne-linked dimers, namely F₃₀ZnFbU versus ZnFbU.⁹ ^e From ref 53. ^f From ref 54a. This value is used as the reference for the Zn porphyrin emission in all of the compounds studied. ^g From ref 54b. This value is used as the reference for the Fb porphyrin emission in all of the compounds studied. h These complexes contain three meso-pentafluorophenyl groups and one meso-[4-(trimethylsilylethynyl)phenyl] group.⁹ ⁱ From ref 9.

excitation of the Zn versus Fb porphyrin component. However, data were also acquired for ZnFb Φ with 580 nm excitation, which increases the fraction of the Fb porphyrin that is excited relative to the situation for 550 nm excitation. Although this results in a corresponding increase in the contribution of the Fb porphyrin spectral signatures to the transient spectra at early times after excitation, the same kinetic parameters were obtained with 580 nm excitation.

Hence, for both $ZnFb\Phi$ and $F_{30}ZnFb\Phi$, the transient absorption difference spectra observed shortly after excitation are dominated by bleaching of the Q(1,0) and Q(0,0) ground state absorption bands of the Zn porphyrin near 550 and 590 nm, respectively (1 ps spectra in Figures 2 and 3). However, the early-time spectra also contain some bleaching of the absorption bands of the Fb porphyrin, since the $Q_{\nu}(0,0)$ absorption band of this component also contributes to the absorption at the 550 nm excitation wavelength. This point is evidenced most clearly by the small dip found near 515 nm in the 1 ps spectrum for each array (Figures 2 and 3). This feature represents bleaching of the $Q_{\nu}(1,0)$ ground-state band of the Fb porphyrin in the fraction of the arrays in each sample in which this component, rather than the Zn porphyrin, was excited by the excitation pulse. (By 1 ps, the energy has also begun to flow from the photoexcited Zn porphyrin to the Fb porphyrin, as discussed below.) The Zn and Fb bleachings in these early-time spectra are imbedded on a broad featureless transient absorption that can be assigned to the respective excited states, Zn* and Fb*.



Figure 2. Time-resolved spectral data for ZnFb Φ . Note, for clarity of presentation, spectral and kinetic data at negative pump-probe delay times (t < 0) are not shown but uniformly have $\Delta A = 0$.

At increasing times after excitation for both $ZnFb\Phi$ and F_{30} -ZnFb Φ , the contribution of Zn* to the transient spectra diminishes and the contribution of Fb* increases. In particular, the 550 nm bleaching of the Zn porphyrin decays and the 515 nm bleaching of the Fb porphyrin grows (see ~ 20 ps spectra in Figures 2 and 3). These spectral changes reflect energy transfer from Zn* to the ground-state Fb component. In fact, the amplitude ratios of the bleachings in the 20 ps spectrum for $ZnFb\Phi$ match the amplitude ratios of the respective groundstate absorption bands in the spectra of Fb porphyrin reference compounds such as FbTPP and FbTMP. This observation provides evidence that by 20 ps energy transfer from Zn* to the Fb constituent of $ZnFb\Phi$ is essentially complete. Qualitatively similar results are found for $F_{30}ZnFb\Phi$, but the Zn porphyrin contributions to the spectra remain at ~ 20 ps, indicating that energy transfer is slower in this complex than in the nonfluorinated array.

The Zn* lifetimes in ZnFb Φ and F₃₀Fb Φ are obtained from the time evolution of the spectra over the 450–600 nm region investigated. Representative kinetic traces in the 550 nm region, dominated by the Zn porphyrin, and in the 515 nm region, dominated by the Fb porphyrin, are shown in Figure 2 for ZnFb Φ and Figure 3 for F₃₀ZnFb Φ . (Data for the F₃₀ZnFb Φ complex were acquired to ~500 ps, but only the first 25 ps are shown in Figure 3 to facilitate comparisons with the data for ZnFb Φ shown in Figure 2.) Both the decay of the Zn porphyrin bleaching (550 nm) and the growth of the Fb porphyrin bleaching (515 nm) for ZnFb Φ occur with a time constant of 3.5 ± 0.5 ps. Similar results were also found using 580 nm excitation. The Zn* lifetime is approximately 3-fold longer for F₃₀ZnFb Φ . In particular, the Zn bleaching decay at 550 nm and the Fb porphyrin bleaching growth at 515 nm both occur



Figure 3. Time-resolved spectra of $F_{30}ZnFb\Phi$. Data were acquired to 500 ps but are not shown to facilitate comparisons with the data for ZnFb Φ given in Figure 2. Data acquired at t < 0 are also not shown (see the legend to Figure 2).

with time constants of 10 ± 1 ps. Measurements were also carried out on ZnFb Φ in acetone/CH₂Cl₂ = 4:1, using 580 nm excitation flashes (the complex is not sufficiently soluble in a pure polar solvent to carry out transient absorption measurements). The Zn* lifetime obtained from these measurements (4 ± 1 ps) is similar to that obtained for this complex in toluene.

c. Energy-Transfer Rates. The transient absorption data and static fluorescence data all lead to the assessment that energy transfer from Zn* to the Fb porphyrin in ZnFb Φ and F₃₀ZnFb Φ is a rapid and highly efficient process. This fact can be seen from the following observations. (1) The kinetics of the decay of the Zn porphyrin bleaching matches the growth of the Fb porphyrin bleaching for both arrays. (2) The Zn* lifetime for each array is over 150-fold shorter than the lifetime of ~2 ns for the relevant Zn porphyrin monomer reference complexes (ZnTPP, ZnTMP, and ZnF₂₀TPP). (3) The emission yield for the Zn component of each ZnFb array is similarly reduced from the values for the corresponding Zn porphyrin reference compounds.

The rate and yield of energy transfer, $Zn^*Fb \rightarrow ZnFb^*$, for both $ZnFb\Phi$ and $F_{30}ZnFb\Phi$ can be obtained from either the transient absorption or static emission data. However, the former measurements give a better assessment, given the predominance of the energy-transfer channel for the decay of Zn^* in these complexes. The energy-transfer parameters are obtained from the following expressions:

$$1/\tau_{\rm D} = k_{\rm rad} + k_{\rm isc} + k_{\rm ic} \tag{1}$$

$$1/\tau_{\rm DA} = k_{\rm rad} + k_{\rm isc} + k_{\rm ic} + k_{\rm trans} \tag{2}$$

$$k_{\rm trans} = 1/\tau_{\rm DA} - 1/\tau_{\rm D} \tag{3}$$

$$\Phi_{\rm trans} = k_{\rm trans} \tau_{\rm DA} = 1 - \tau_{\rm DA} / \tau_{\rm D} \tag{4}$$

where τ_{DA} is the excited-state lifetime of the donor in the presence of the acceptor (i.e., the Zn* in the ZnFb dimer) and τ_D is the excited-state lifetime of the zinc porphyrin monomer.

These equations assume that, besides energy transfer, there are no pathways for depopulating Zn* in the arrays other than the intrinsic processes (radiative decay (rad), intersystem crossing (isc), and internal conversion (ic)) also present in the benchmark Zn porphyrin monomer. Again, the transient absorption and static emission data support this assumption. Within experimental uncertainty, we cannot exclude the possibility of a small amount of electron transfer from the Zn* state. However, the similarity of the Zn* lifetime of ZnFb Φ in toluene and in acetone/CH₂Cl₂ (4:1) indicates any such electron transfer must be $\leq 10\%$. The calculated energy-transfer rates and yields for ZnFb Φ and F₃₀ZnFb Φ are shown in Table 2. For comparison, this table also contains the results of similar measurements we carried out previously on the diarylethyne-linked analogues ZnFbU and F₃₀ZnFbU.

d. Physical Properties of the Oxidized Complexes. The oxidized arrays were investigated to gain insight into how the *p*-phenylene linker modulates the rates of ground-state hole/ electron hopping.⁵⁶ These rates are of interest because no independent assessment of the rates of ground-state charge transfer is available for the neutral arrays. Although the hole/ electron hopping rates in the ground electronic states of the cations are not expected to be equal to the charge-transfer rates in the excited states of the neutrals, they at least provide some measure of the factors that control this type of process.

1. Electrochemistry. The $E_{1/2}$ values for oxidation of the phenylene-linked dimeric arrays are summarized in Table 3. The two $E_{1/2}$ values listed in the table correspond to the first and second oxidations of the porphyrin ring.⁵⁷ In general, the values of the redox potentials and the redox characteristics of the both the fluorine-containing and non-fluorine-containing phenylene-linked dimers closely resemble those of the analogous diarylethyne-linked dimers we have previously investigated.^{5,9} The redox behavior of these latter arrays is essentially identical to that of monomeric Zn and Fb porphyrins, indicating that the ground-state interaction between the porphyrin constituents of the dimers are relatively weak. [The ground-state interaction between the π systems of the diarylethyne linker and the porphyrin rings is also quite weak.⁵⁶] Accordingly, the replacement of the diarylethyne linker with the shorter *p*-phenylene linker does not result in any clearly detectable increase in the magnitude of the ground-state interaction between the porphyrins in the dimer.

2. Absorption Spectra. The UV-vis absorption characteristics of the mono- and dications of the arrays (not shown) are typical of those of other porphyrin π -cation radicals, namely weaker, blue-shifted B bands (relative to the neutral complexes) and very weak, broad bands in the visible and near-infrared regions.^{57a} The absorption spectra of the oxidized complexes appear to be a superposition of the spectra of the neutral and cationic species of the different porphyrin units. This observation, like the results of the electrochemical studies,⁵⁸⁻⁶¹ is consistent with weak interactions between the constituent porphyrins.

3. EPR Spectra. The EPR spectra of the one-electron oxidation products of ZnFb Φ and Zn₂ Φ in CH₂Cl₂ at 295 and 100 K are shown in Figure 4. The spectra of the one-electron oxidation products of F₃₀ZnFb Φ and F₃₀Zn₂ Φ obtained under

 TABLE 2: Energy-Transfer and Hole/Electron Hopping

 Parameters

	$k_{\text{trans}}^{-1} (\text{ps})^a$	$\Phi_{ ext{trans}}{}^a$	$k_{\rm hop}^{-1} \ (\mu s)^b$
ZnFbΦ	3.5	>0.99	с
$Zn_2\Phi$			≤ 0.05
$F_{30}ZnFb\Phi$	10	0.99	с
$F_{30}Zn_2\Phi$			≥2.5
ZnFbU	24^{d}	0.99^{d}	с
Zn_2U			$\le 0.05^{e}$
F ₃₀ ZnFbU	240^{d}	0.87^{d}	с
$F_{30}Zn_2U$			$\geq 2.5^d$

^{*a*} Obtained using the transient absorption data and eqs 1–4. ^{*b*} Estimated from the 295 K EPR data (see text). ^{*c*} No hole/electron hopping occurs in the ZnFb dimers because of the large disparity in oxidation potential of the Zn and Fb constituents (Table 3). ^{*d*} From ref 9. ^{*e*} From ref 56b.

 TABLE 3: Half-Wave Potentials^a for Oxidation of the Porphyrins of the Various Arrays

	Zn porphyrin		Fb porphyrin	
	$E_{1/2}(1)$	$E_{1/2}(2)$	$\overline{E_{1/2}(1)}$	$E_{1/2}(2)$
ZnFbΦ	0.58	0.88^{b}	0.72^{b}	1.19
$Zn_2\Phi^c$	0.59	0.90		
$F_{30}ZnFb_{\Phi}$	0.99	1.23^{b}	1.18^{b}	1.41
$F_{30}Zn2_{\Phi}^{c}$	0.99	1.20		

^{*a*} Obtained in CH₂Cl₂ containing 0.1 M TBAH. $E_{1/2}$ vs Ag/Ag⁺; $E_{1/2}$ of FeCp₂/FeCp₂⁺ = 0.22 V; scan rate = 0.1 V/s. Values are ±0.01 V. ^{*b*} Values are approximated due to overlap of the Zn and Fb porphyrin waves. ^{*c*} The redox waves of the two Zn porphyrins are not resolved by cyclic voltammetry.



Figure 4. EPR spectra of $[ZnFb\Phi]^+$ and $[Zn_2\Phi]^+$ obtained at 295 and 100 K. Note that the magnetic field scales are different in the left and right panels.

the same conditions are shown in Figure 5. The EPR spectra of all of the cations were examined as a function of sample concentration. No changes in hyperfine splittings or line shape were observed for the concentrations used for the EPR studies (≤ 0.05 mM). Consequently, the differences observed in the





Figure 5. EPR spectra of $[F_{30}ZnFb\Phi]^+$ and $[F_{30}Zn_2\Phi]^+$ obtained at 295 and 100 K.

spectral features of the various complexes are intrinsic and cannot be ascribed to intermolecular interactions.

Examination of the EPR signatures of the cations of the various phenylene-linked dimeric arrays reveals the following features.

(1) The liquid- and frozen-solution EPR spectra of $[ZnFb\Phi]^+$ and $[Zn_2\Phi]^+$ are very similar to those of the analogous spectra of $[ZnFbU]^+$ and $[Zn_2U]^+$.⁵⁶ In particular, the liquid solution signal of $[ZnFb\Phi]^+$ exhibits a poorly resolved nine-line hyperfine pattern due to interaction of the unpaired electron with the four pyrrole ¹⁴N nuclei of the Zn constituent of the dimer (Figure 4, left panel). This hyperfine pattern is characteristic of a ${}^{2}A_{2u}$ porphyrin π -cation radical.⁶² The unpaired electron is localized on the Zn porphyrin due to the redox characteristics of the Zn versus Fb porphyrins.⁵⁷ In contrast, the liquid-solution signal of $[Zn_2\Phi]^+$ exhibits a much narrower line with no resolved hyperfine structure. Simulations of the EPR spectrum of $[Zn_2\Phi]^+$ indicate that the line shape is well accounted for by halving the hyperfine coupling and doubling the number of interacting nuclei (while holding the line width constant). This behavior indicates that the hole/electron of $[Zn_2\Phi]^+$ is completely delocalized on the EPR time scale,⁶³ as is also the case for $[Zn_2U]^+$.⁵⁶ This time scale is determined by the magnitude of the ¹⁴N hyperfine coupling, which is ~4.2 MHz.⁶² Thus, the hole/electron hopping rate, k_{hop} , is greater than or equal to $(0.05 \ \mu s)^{-1}$. When the solution is frozen, the EPR signal of $[Zn_2\Phi]^+$ broadens and is essentially identical to the signal observed for $[ZnFb\Phi]^+$ in frozen solution (Figure 4, right panel). This behavior indicates that the hole/electron becomes localized (on the EPR time scale) on one of the Zn constituents of $[Zn_2\Phi]^+$ $(k_{hop} \leq (1 \ \mu s)^{-1})$. This behavior again parallels that observed for $[Zn_2U]^+$, in which the hole/electron hops rapidly in liquid solution but becomes localized in frozen solution.⁵

(2) The liquid- and frozen-solution EPR spectra of $[F_{30}-ZnFb\Phi]^+$ and $[F_{30}Zn_2\Phi]^+$ are very similar to those of the

analogous spectra of [F₃₀ZnFbU]⁺ and [F₃₀Zn₂U]⁺.⁹ In particular, the liquid-solution EPR signal of $[F_{30}ZnFb\Phi]^+$ is relatively sharp and exhibits no resolved hyperfine splittings. The ¹⁴N hyperfine splittings are absent for $[F_{30}ZnFb\Phi]^+$ (and $[F_{30}ZnFbU]^+$) because the strongly electron-withdrawing pentafluorophenyl groups at the nonlinking meso positions energetically stabilize the a_{2u} molecular orbital,^{64,65} resulting in a ground state that is solely, or mostly ${}^{2}A_{1u}$ -like in character.⁹ The a_{1u} molecular orbital that contains the unpaired electron in these latter type of radicals has appreciable electron density on the β -pyrrole carbon atoms but nodal planes through the pyrrole nitrogen atoms (and meso carbon atoms).⁶⁴ Unlike the case for $[Zn_2\Phi]^+$ versus $[ZnFb\Phi]^+$ (Figure 4, left panel), the liquidsolution signal of $[F_{30}Zn_2\Phi]^+$ is essentially superimposable on the signal observed for $[F_{30}ZnFb\Phi]^+$ (Figure 5, left panel). The frozen-solution EPR signals for $[F_{30}Zn_2\Phi]^+$ and $[F_{30}ZnFb\Phi]^+$ are also essentially superimposable, although broader than the liquid solution signals (Figure 5, right panel). These spectral characteristics indicate that the hole/electron in $[F_{30}Zn_2\Phi]^+$ is localized on the EPR time scale in both liquid and frozen solution. Similar conclusions were reached for [F₃₀Zn₂U]^{+,9} Given that the largest hyperfine couplings in the ${}^{2}A_{1u}$ -like porphyrin π -cation radicals are ~ 2 MHz, 53,62 the value of k_{hop} must be $\leq (2.5 \,\mu s)^{-1}$. Accordingly, any acceleration in the hole/ electron hopping rate resulting from the replacement of the diarylethyne linker with the shorter *p*-phenylene linker is not sufficient to overcome the slower rate resulting from the effects of the fluorine atoms on the orbital characteristics of the porphyrins. For comparison, the k_{hop} values for $[Zn_2\Phi]^+$ and $[F_{30}Zn_2\Phi]^+$ are included in Table 2.

3. Discussion

In the present study, we have extended our work on the synthesis and characterization of the building blocks for porphyrin-based molecular photonic devices by exploring the rates of excited-state energy transfer and ground-state hole/ electron hopping in *p*-phenylene-linked porphyrin dimers. These studies complement our previous work on multiporphyrin architectures constructed with diarylethyne linkers.^{5-9,56} Two specific goals of the present study were as follows. (1) We wished to determine whether the incorporation of a *p*-phenylene linker would result in a significant increase in electronic communication across a porphyrin dimer without significant perturbation of the electronic properties of the constituent porphyrins or deleterious quenching reactions. The desire to minimize perturbation of the inherent photophysical and redox properties of the lowest excited states of the porphyrin constituents would thus permit incorporation of these constructs into extended arrays without compromising the properties of the individual elements. (2) We wished to further probe the effects of the characteristics of the porphyrin frontier molecular orbitals (energy ordering, electron density distributions) on electronic communication in multiporphyrin arrays. In particular, we wanted to determine whether fluorination of the nonlinking phenyl groups in a *p*-phenylene-linked porphyrin dimer (which causes specific effects on porphyrin orbital characteristic) would give rise to a decrease in the energytransfer rate, as we have previously observed for the analogous chemical modification of diarylethyne-linked dimers. The results obtained indicate that the study has been successful in all respects, as is discussed in more detail below.

a. Effects of Linker Architecture on Electronic Communication. The rate of excited-state energy transfer in the *p*-phenylene-linked array $\text{ZnFb}\Phi$ ((3.5 ps)⁻¹) is about 7-fold

faster than that for the diphenylethyne-linked analogue ZnFbU $((24 \text{ ps})^{-1})$. An even more dramatic 24-fold increase is found for $F_{30}ZnFb\Phi$ ((10 ps)⁻¹) versus $F_{30}ZnFbU$ ((240 ps)⁻¹). Likewise, the incorporation of the *p*-phenylene linker facilitates rapid ground-state hole/electron hopping (in liquid solution) in the monocation radical of the bis-Zn complex ($[Zn_2\Phi]^+$). This latter rate may well be faster than that in the diarylethyne-linked complex $[Zn_2U]^+$; however, the exact rate for either dimer cannot be determined from the existing data because the hole/ electron hopping process is in the fast-exchange limit for both. These effects, most notably the enhanced excited-state energytransfer rate, are not accompanied by significant perturbation of the inherent properties of the photophysically relevant electronic excited states (e.g., Q band absorption and emission characteristics) or the ground-state redox potentials of the porphyrin components. These findings parallel those previously identified for dimers and larger arrays incorporating the longer diarylethyne linker. Collectively, these observations indicate that the enhanced excited-state energy-transfer rates found for the *p*-phenylene-linked dimers do not arise from factors such as enhanced spectral overlap/energy matching. Rather, the enhanced rates derive principally (if not exclusively) from enhanced electronic coupling between the porphyrin constituents across the *p*-phenylene versus diarylethyne linker. This enhanced electronic coupling is attributed principally to a shorter inter-porphyrin separation in the case of the former linker. However, it should be noted that the different chemical composition/architecture (and associated electronic characteristics) of the *p*-phenylene versus diphenylethyne linker may also modulate the magnitude of electronic coupling.⁶⁶

b. Effects of Fluorination on Electronic Communication. A 3-fold reduced rate of excited-state energy transfer is found for $F_{30}ZnFb\Phi$ ((10 ps)⁻¹) versus $ZnFb\Phi$ ((3.5 ps)⁻¹). This factor is not as substantial as the 10-fold reduction found upon fluorination of the diphenylethyne-linked analogue $((240 \text{ ps})^{-1})$ for F_{30} ZnFbU versus (24 ps)⁻¹ for ZnFbU). Nevertheless, the general effect of fluorination on the energy-transfer rate in the p-phenylene-linked dimers is consistent with the fluorineinduced changes in the porphyrin orbital characteristics that we have previously discussed in detail for the diarylethyne-linked dimers.⁹ The same orbital effects underlie the observation that hole/electron hopping in $[F_{30}Zn_2\Phi]^+$ slows considerably relative to $[Zn_2\Phi]^+$, similar to the situation for $[F_{30}Zn_2U]^+$ versus $[Zn_2U]^+$. The attenuation of both the excited-state energytransfer and ground-state hole/electron hopping rates occurs in large part because fluorination of all the nonlinking phenyl groups preferentially stabilizes the a_{2u} orbital to the extent that it drops below the a_{1u} orbital in the case of the Zn porphyrins and to an energy comparable to the a_{1u} orbital in the case of the Fb porphyrins.9

The key point to be derived from the effects of fluorination is that the a_{2u} orbital has considerable electron density at the porphyrin meso carbon to which the linker is attached whereas the a_{1u} orbital has nodes at this position. Hence, fluorination increases contribution of the a_{1u} orbital to the excited-state wave function of the neutral dimers and to the ground-state wave function of the monocation radicals, which results in reduced electronic coupling between the two porphyrin constituents. This in turn gives rise to a slowing of both photoinduced energy transfer and ground-state hole/electron hopping. It should be emphasized, however, that the reduced electronic coupling in the fluorinated versus nonfluorinated dimers most likely does not derive exclusively from the change in the relative energies of the a_{1u} and a_{2u} orbitals. In particular, the general effect of the electron-withdrawing fluorine groups, which shift electron density in both the HOMOs and LUMOs away from the linking position in each porphyrin, must augment the HOMO ordering effect on the reduction in electronic coupling. The reader is referred to our previous work for a more detailed discussion of these issues.^{6,9,53}

The observation that the fluorination-induced reduction in the excited-state energy-transfer rate in the *p*-phenylene-linked dimers (ZnFb Φ , (3.5 ps)⁻¹; F₃₀ZnFb Φ , (10 ps)⁻¹) is not as substantial as that for the arylethyne-linked analogues (ZnFbU, $(24 \text{ ps})^{-1}$; F_{30} ZnFbU, $(240 \text{ ps})^{-1}$) warrants further comment. From an empirical point of view, this result is advantageous for the use of the *p*-phenylene-linked dimer motif in extended architectures. In particular, the less substantial effect of fluorination leads to an excited-state energy-transfer rate ((10 $ps)^{-1}$) that remains 2-fold faster (and slightly more efficient, see Table 2) than in the nonfluorinated diphenylethyne dimer ZnFbU. Hence, F_{30} ZnFb Φ has the advantage of an ultrafast photoinduced energy-transfer rate coupled with the porphyrin redox properties that disfavor competing charge-transfer reactions that are deleterious when energy transfer is the desired function.^{6,9,53} In general, the ability to use halogenation (or other types of functionalization) to tune both the characteristic properties of the chromophores and the energy-transfer and hole/ electron hopping rates is highly desirable. The combination of favorable properties associated with $F_{30}ZnFb\Phi$ is an unexpected result of the present study and should find utility in future applications.

c. Mechanism(s) of Electronic Communication. The final issue concerns the mechanism(s) of electronic communication, particularly the mechanism of energy transfer, in the *p*-phenylene-linked versus diarylethyne-linked dimers. The observation that fluorination has a lesser impact on the energy-transfer rate in the former class of dimers (a factor of 3 versus 10) has direct bearing on this issue and suggests that the energy-transfer mechanism is different for the *p*-phenylene-linked versus diarylethyne-linked dimers. This view is explained in more detail below.

In both types of dimers, the observed energy-transfer rate is assumed to be due to the additive effects of TB and TS processes.

$$k_{\rm trans} = k_{\rm TB} + k_{\rm TS} \tag{5}$$

All of our previous work on the diarylethyne-linked porphyrins indicates that excited-state energy transfer occurs predominantly via an exchange-mediated TB mechanism with a much lesser contribution from the TS mechanism.⁵⁻⁹ In particular, the TS energy-transfer rate for ZnFbU is calculated to be on the order of $(1 \text{ ns})^{-1}$, which is approximately 2 orders of magnitude slower than the observed rate of $(24 \text{ ps})^{-1.9}$ [These rates were calculated using the Förster theory of resonance energy transfer assuming a dipole-dipole approximation, which is reasonable because of the large center-to-center distance (~ 20 Å) between the Zn and Fb constituents).] The TS energy-transfer rate calculated for ZnFbU thus supports the empirical evidence^{5-9,56,57} that the TB mechanism dominates the excited-state energy process for the diarylethyne-linked arrays. On the other hand, Förster calculations (dipole approximation) for the TS energytransfer rate for the *p*-phenylene-linked dimers give a value on the order of $(50-100 \text{ ps})^{-1}$ (see Supporting Information). These values are relatively close to the observed rates (ZnFb Φ , (3.5 ps)⁻¹; $F_{30}ZnFb\Phi$, (10 ps)⁻¹). Furthermore, previous studies have shown that the 13 Å center-to-center distance between the Zn and Fb porphyrins in these *p*-phenylene-linked dimers is

sufficiently short that multipole corrections to the dipole-dipole approximation could increase the energy-transfer rate by a factor of 5 or more.⁶⁷ These considerations indicate that the TS contribution to excited-state energy transfer in the *p*-phenylenelinked dimers is much more substantial than that in the diarylethyne-linked dimers. In fact, the TS mechanism may make a dominant contribution to the energy-transfer process in the former arrays. This view is further consistent with the less substantial effect of fluorination on the excited-state energytransfer rate in the *p*-phenylene-linked versus diarylethyne-linked dimers. This effect may derive from two sources as the TS mechanism becomes increasingly important. (1) The effect of fluorination on the orbital characteristics and thus electronic coupling for the TB transfer becomes less significant. (2) The spectral overlap integral in the Förster TS mechanism is approximately 2-fold less for the fluorinated versus nonfluorinated dimers (Supporting Information).⁹ The difference in spectral overlap is inconsequential when the TB transfer process is dominant but becomes increasingly significant as the TS process becomes a larger contributor to the overall energytransfer rate.68

Finally, it should be noted that the characteristics of the ground-state hole/electron hopping in the fluorinated versus nonfluorinated dimers provides indirect evidence that the TS mechanism plays an important role in the excited-state energytransfer process in the *p*-phenylene-linked dimers. In particular, the hole/electron hopping rate in the *p*-phenylene-linked dimers is diminished at least 50-fold by fluorination ($[Zn_2\Phi]^+$, $\geq (0.05)$ $\mu s)^{-1}$; $[F_{30}Zn_2\Phi]^+$, $\geq (2.5 \text{ ps})^{-1})$. The magnitude of this attenuation is qualitatively in the same range as that which occurs upon fluorination of the diarylethyne-linked dimers $([Zn_2U]^+, \geq (0.05 \ \mu s)^{-1}, [F_{30}Zn_2U]^+, \geq (2.5 \ ps)^{-1}).$ This behavior is quite different from the effect of fluorination on the energy-transfer rate on the two classes of dimers (vide supra). The ground-state hole/electron hopping process is most certainly governed by TB electronic coupling over the large separation distances in the diarylethyne-linked dimers. Although the *p*-phenylene linker is shorter, the porphyrin–porphyrin separation is still sufficiently large that the TB process should dominate. Thus, the fluorination-induced changes in HOMO characteristics have a significant impact on the hole/electron hopping rates in the *p*-phenylene-linked dimers. Accordingly, the significantly smaller effect of fluorination on the excitedstate energy-transfer rate points to the increasing importance of a new channel (i.e., the TS mechanism) for this process.

4. Conclusions

In previous studies, we have found that the rates and yields of excited-state energy transfer and ground-state hole/electron hopping in diarylethyne-linked porphyrin dimers can be modulated in predictable ways through manipulation of the porphyrin constituents (types of metal ion and substituents on the nonlinking aryl rings) and the aryl rings of the linker. The manipulation of these structural features affords control of the electronic and steric factors that mediate the dynamic processes (as well as other important features, such as solubility, chemical stability, and redox properties) and permits tuning for specific applications. Here, we have found that the desirable goal of even faster rates of photoinduced energy transfer can be achieved through the use of a simple *p*-phenylene linker. Furthermore, the enhanced dynamic properties are obtained without perturbing the desirable and well characterized electronic properties of the porphyrin subunits. In particular, the inherent excited-state photophysical and ground-state redox properties of the porphyrin

constituents are maintained in both ZnFb Φ and F₃₀ZnFb Φ , both of which exhibit ultrafast photoinduced energy-transfer rates (~(10 ps)⁻¹ or faster). The fluorinated complex should be particularly useful for applications where fast energy transfer is required, charge transfer must be minimized, and chemical stability must be enhanced. Overall, the results of this study provide new architectures for the design of porphyrin-based arrays for a variety of molecular photonics applications.

5. Experimental Section

a. Synthesis. 1. General. ¹H NMR spectra were recorded on either a Varian Gemini 300 MHz or General Electric GN-300 MHz (IBM FT-300) spectrometers. Chemical shifts for the ¹H NMR spectra are reported in ppm using the deuterated solvent resonances as the internal reference (CDCl₃, $\delta = 7.26$ ppm; toluene- d_8 , $\delta = 2.09$ ppm; THF- d_8 , $\delta = 3.58$ ppm). Porphyrins were analyzed by fast atom bombardment (FAB-MS) on a JEOL, HX 110 HF or by laser desorption mass spectrometry (LD-MS) using a Bruker Proflex II equipped with a linear (1.2 m) flight tube. Absorption and emission spectra were routinely obtained (as described below) to monitor purity. The spectral characteristics of the purified products are summarized in Table 1. Unless otherwise indicated, all reagents were obtained from Aldrich Chemical Co., Milwaukee, WI, and all solvents were obtained from Fisher Scientific.

2. Solvents. All solvents were dried by standard methods prior to use. Toluene (Fisher, certified ACS or HPLC), triethylamine (Fluka, puriss), and pyridine (Acros) were distilled from CaH₂. CHCl₃ (Fisher, certified ACS) and CH₂Cl₂ (Fisher, reagent grade) were subjected to simple distillation from K₂CO₃. Pyrrole (Acros) was distilled under reduced pressure from CaH₂. Other solvents were used as received.

3. Chromatography. Adsorption column chromatography was performed using flash silica gel (Baker, 60-200 mesh) or alumina (Fisher A540-3, 80-200 mesh). Preparative scale size-exclusion chromatography (SEC) was performed using BioRad Bio-Beads SX-1. A preparative scale glass column (4.8 \times 60 cm) was packed using BioRad Bio-Beads SX-1 in toluene and eluted with gravity flow (~1.2 mL/min). Following purification, the SEC column was washed with 2 volume equiv of toluene. Analytical scale SEC was performed to monitor the dimer-forming reactions and assess the purity of the dimers. Analytical SEC columns (styrene-divinylbenzene copolymer) were purchased from Hewlett-Packard and Phenomonex. Analytical SEC was performed with a Hewlett-Packard 1090 HPLC using 500 Å (300×7.8 mm), 500 Å (300×7.5 mm), and 100 Å (300 \times 7.5 mm) columns (5 μ m) in series eluting with THF (flow rate = 0.8 mL/min; void volume $\approx 15.0 \text{ min}$).

4. Compounds. 1,4-Bis(10,15,20-trimesitylporphin-5-yl)benzene (Fb₂ Φ). A 5 L, three-necked, round-bottom flask was charged with 3 L of distilled CHCl₃, pyrrole (2.08 mL, 30.0 mmol), mesitaldehyde (3.32 mL, 22.5 mmol), and terephthaldicarboxaldehyde (503 mg, 3.75 mmol). The resulting solution was magnetically stirred at room temperature, and BF₃•OEt₂ (1.25 mL, 9.90 mmol) was added dropwise via syringe. The reaction vessel was shielded from ambient lighting. The reaction was monitored by treating 25 μ L aliquots with excess 2,3dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in toluene (150 μ L) followed by absorption spectroscopy (418 nm, assuming ϵ = 5 × 10⁵ M⁻¹ cm⁻¹ for all porphyrin species).⁴⁹ The yield of porphyrin was found to level off after 1 h, at which point DDQ (5.11 g, 22.5 mmol, 3 equiv per porphyrinogen, 3/4 equiv per pyrrole) was added. After the mixture was stirred at room temperature for 1 h, triethylamine (1.38 mL, 9.90 mmol) was added to neutralize the acid and the solvent was removed under reduced pressure. The resultant black solid from the reaction mixture was dissolved in 100 mL of CH₂Cl₂, diluted with an equal volume of hexanes, and loaded onto a silica gel column (10 cm diameter \times 28 cm) with CH₂Cl₂/hexanes (1:1) as the eluent. The porphyrins as well as other pigments (uncharacterized) were eluted as a single fast-moving dark-red band. The fractions were collected, combined, and concentrated to afford a crude purple solid containing three major components: monomeric porphyrin, desired dimeric porphyrin, and putative trimeric porphyrin. The crude porphyrin mixture was further purified by column chromatography (10 cm diameter \times 20 cm) over flash silica gel with CH₂Cl₂/hexanes (1:1) to remove small amounts of slow moving pigments (uncharacterized). The three porphyrin products were slightly visible on the column as the separation proceeded. The porphyrin-containing fractions were combined and concentrated to dryness. LD-MS and analytical SEC data of this solid were consistent with the presence of monomeric, dimeric, and trimeric porphyrins. The mixture of porphyrins was then dissolved in 60 mL of toluene and placed on top of a preparative SEC column. Gravity elution afforded four major bands with the desired dimeric porphyrins as the third band. The dimer-containing fractions were collected and concentrated to dryness, affording 75.1 mg (1.42%) of a purple solid. ¹H NMR (CDCl₃) δ -2.42 (s, 4H), 1.89 (s, 12H), 1.92 (s, 24H), 2.64 (s, 6H), 2.66 (s, 12H), 7.29 (s, 4H), 7.33 (s, 8H), 8.59 (s, 4H), 8.67 (s, 8H), 8.86 (d, 4H, J = 5.1 Hz), 9.22 (d, 4H, J = 5.1 Hz). C₁₀₀H₉₀N₈: calcd mass 1402.7288, obsd m/z1402.7196 (FAB-MS); calcd av mass 1402.9, obsd m/z 1402.6 (LDI-MS). λ_{abs} (toluene) 419, 428, 482, 516, 550, 592, 650 nm; λ_{em} (toluene, $\lambda_{ex} = 514$ m) 650, 717 nm. Anal. Calcd for $Fb_2\Phi \cdot 2H_2O$ (C₁₀₀H₉₄N₈O₂): C, 83.42; H, 6.58; N, 7.78. Found: C, 83.61; H, 6.36; N, 7.73.

1,4-Bis[10,15,20-tris(pentafluorophenyl)porphin-5-yl]benzene $(F_{30}Fb_2\Phi)$. In a 5 L, three-necked, round-bottom flask containing 3 L of distilled CH₂Cl₂, pyrrole (2.08 mL, 30.0 mmol), pentafluorobenzaldehyde (2.77 mL, 22.5 mmol), and terephthaldicarboxaldehyde (503 mg, 3.75 mmol) were condensed following the procedure outlined above. Workup included chromatography by flash silica gel (CH2Cl2/hexanes (1:1), 10 cm diameter \times 28 cm), flash silica gel (CH₂Cl₂/hexanes (1:1), 2 cm diameter \times 20 cm), and preparative SEC (toluene), affording a purple solid, 64.7 mg (1.0%). ¹H NMR (THF- d_8) δ -2.64 (s, 4H), 8.80 (s, 4H), 9.18 (dd, 8H, J = 4.4 and 4.4 Hz), 9.23 (d, 4H, J = 4.4 Hz), 9.53 (d, 4H, J = 4.4 Hz). ¹⁹F NMR (CD₂Cl₂, CFCl₃) δ -137.46 (m, 12F), -152.66 (t, 6F, J = 22.3 Hz), -162.31 (m, 12F). $C_{82}F_{30}H_{24}N_8$: calcd mass 1690.1645, obsd m/z 1690.0620 (FAB-MS); calcd av mass 1691.1, obsd m/z 1691.3 (LD-MS). λ_{abs} (toluene) 413, 426, 512, 542, 587, 643 nm; λ_{em} (toluene, $\lambda_{ex} = 511$ m) 646, 713 nm.

1-(Zinc 10,15,20-Trimesitylporphin-5-yl)-4-(10,15,20-trimesitylporphin-5-yl)benzene (ZnFbΦ). A sample of dimeric porphyrin Fb₂Φ (20.0 mg, 14.2 µmol) was dissolved in 8 mL of CHCl₃, and then a methanolic solution of Zn(OAc)₂·2H₂O (2.5 mg, 11.4 µmol, 0.9 mL of methanol) was added. The reaction mixture was heated at reflux and was monitored by fluorescence excitation spectroscopy. After 90 min, the reaction mixture was cooled to room temperature, washed with 10% NaHCO₃, dried (Na₂SO₄), and filtered and the solvent was removed under reduced pressure. Column chromatography on alumina (CHCl₃/ hexanes (1:1), 7 cm diameter × 12 cm) gave Fb₂Φ as the first band and ZnFbΦ as the second porphyrin band. Final elution with CHCl₃ afforded the bis-zinc porphyrin (Zn₂Φ). The fractions containing the desired mono-zinc dimer ZnFb Φ were combined and concentrated to give 7.92 mg (37.8%) of a red solid. ¹H NMR (toluene- d_8) δ – 1.70 (s, 2H), 1.89 (s, 6H), 2.01 (s, 6H), 2.02 (s, 12H), 2.10 (s, 12H), 2.48 (s, 3H), 2.52 (s, 3H), 2.53 (s, 6H), 2.56 (s, 6H), 7.16 (s, 2H), 7.22 (s, 2H), 7.24 (s, 4H), 7.28 (s, 4H), 8.38 (d, 2H, J = 8.1 Hz), 8.48 (d, 2H, J = 8.1 Hz), 8.80 (dd, 4H, J = 4.8 and 11.3 Hz), 8.93 (dd, 4H, J = 5.5 and 7.0 Hz), 8.94 (d, 2H, J = 3.9 Hz), 9.05 (d, 2H, J = 4.4 Hz), 9.31 (d, 2H, J = 5.1 Hz), 9.39 (d, 2H, J = 4.4 Hz). C₁₀₀H₈₈N₈Zn: calcd mass 1464.6423, obsd *m*/*z* 1464.6416 (FAB-MS); calcd av mass 1467.2, obsd *m*/*z* 1470.1, 1468.1 (LD-MS). λ_{abs} (toluene) 420, 430, 480, 514, 550, 592, 650 nm; λ_{em} (toluene, λ_{ex} = 551 m) 651, 720 nm.

1,4-Bis(zinc 10,15,20-Trimesitylporphin-5-yl)benzene (Zn2- Φ). A sample of Fb₂ Φ (30.0 mg, 21.4 μ mol) was dissolved in 12 mL of CHCl₃, and then a methanolic solution of Zn(OAc)₂. $2H_2O$ (14.1 mg, 64.2 μ mol, 1.3 mL of methanol) was added. The reaction mixture was stirred at room temperature for 20 h then heated at reflux for 2 h. The progress of the reaction was monitored by fluorescence excitation spectroscopy. When complete, the reaction mixture was allowed to cool to room temperature and washed with 10% NaHCO₃, and the solvent was removed under reduced pressure. Column chromatography on silica gel (toluene, 1.5 cm diameter \times 12 cm) gave 32.8 mg (100%) of a red solid. ¹H NMR (toluene- d_8) δ 2.01 (s, 12H), 2.10 (s, 24H), 2.52 (s, 6H), 2.56 (s, 12H), 7.22 (s, 4H), 7.28 (s, 8H), 8.56 (s, 4H), 8.93 (dd, 8H, J = 4.4 and 6.6 Hz), 9.06 (d, 4H, J = 5.1 Hz), 9.44 (d, 4H, J = 4.4 Hz). C₁₀₀H₈₆N₈Zn₂: calcd mass 1526.5558, obsd 1526.5508 (FAB-MS); calcd av mass 1530.6, obsd m/z 1530.3, 1531.5 (LD-MS). λ_{abs} (toluene) 420, 431, 513, 550, 590 nm; λ_{em} (toluene, $\lambda_{ex} = 550$ m) 597, 645 nm.

1-(Zinc 10,15,20-Tris(pentafluorophenyl)porphin-5-yl)-4-(10,-15,20-tris(pentafluorophenyl)porphin-5-yl)benzene (F_{30} ZnFb Φ). A sample of $F_{30}Fb_2\Phi$ (33.5 mg, 19.8 μ mol) in CHCl₃ (35 mL) was treated with a methanolic solution of Zn(OAc)2+2H2O (13.0 mg, 59.4 µmol, 3.9 mL of methanol). The reaction mixture was heated at reflux for 18 h, and workup proceeded as previously described. Purification by column chromatography on alumina (CHCl₃/hexanes (1:1), 2 cm diameter \times 20 cm) afforded 15.3 mg (44.0%) of a red solid. ¹H NMR (THF- d_8) δ -2.63 (s, 2H), 8.78 (s, 4H), 9.11 (dd, 2H, J = 4.4 and 4.4 Hz), 9.18 (d, 2H, J = 4.4 Hz), 9.19 (dd, 2H, J = 4.4 and 4.4 Hz), 9.24 (d, 2H, J = 4.4 Hz), 9.50 (d, 2H, J = 4.4 Hz), 9.54 (d, 2H, J = 4.4 Hz). C₈₂F₃₀H₂₂N₈Zn: calcd mass 1752.0780, obsd 1752.0031 (FAB-MS); calcd avg mass 1754.5, obsd m/z 1754.3 (LD-MS). λ_{abs} (toluene) 413, 426, 508, 552, 584, 643 nm; λ_{em} (toluene, $\lambda_{ex} = 508$ m) 646, 711 nm.

1,4-Bis(zinc 10,15,20-Tris(pentafluorophenyl)porphin-5-yl)benzene ($F_{30}Zn_2\Phi$). A sample of $F_{30}Fb_2\Phi$ (23.2 mg, 13.7 μmol) in CHCl₃ (54 mL) was treated with a methanolic solution of Zn(OAc)₂·2H₂O (15.1 mg, 68.6 μmol, 6.0 mL of methanol). The reaction mixture was heated at reflux for 18 h, and workup proceeded as previously described. Purification by column chromatography on silica (CH₂Cl₂/hexanes (1:1), 2 cm diameter × 20 cm) afforded 24.8 mg (100%) of a red solid. ¹H NMR (THF- d_8) δ 8.75 (s, 4H), 9.11 (d, 8H, J = 4.4 Hz), 9.18 (d, 4H, J = 4.4 Hz), 9.51 (d, 4H, J = 4.4 Hz). C₈₂F₃₀H₂₀N₈Zn₂: calcd mass 1813.9915, obsd 1813.9969 (FAB-MS); calcd avg mass 1817.8, obsd m/z 1817.4 (LDI-MS). λ_{abs} (toluene) 421, 430, 508, 549, 581 nm; λ_{em} (toluene, $\lambda_{ex} = 550$ m) 587, 643 nm.

b. Physical Methods. The static and time-resolved absorption and fluorescence studies were performed on samples

prepared in toluene at room temperature. Toluene (EMI, Omnisolve) was distilled from sodium. The samples for timeresolved fluorescence measurements were degassed by several freeze–pump–thaw cycles on a high-vacuum line. The samples for static fluorescence and time-resolved absorption measurements were not degassed. The electrochemical and EPR studies were performed on samples prepared in CH₂Cl₂. CH₂Cl₂ (Aldrich, HPLC Grade) was purified by vacuum distillation from P₂O₅, followed by another distillation from CaH₂. For the electrochemical studies, tetrabutylammonium hexafluorophosphate (TBAH; Aldrich, recrystallized 3 times from methanol and dried under vacuum at 110 °C) was used as the supporting electrolyte. The solvents were degassed thoroughly by several freeze–pump–thaw cycles prior to use.

1. Static Absorption and Fluorescence Spectroscopy. Static absorption (HP8451A, Cary 3, Perkin-Elmer Lamba 3B) and fluorescence (Spex Fluoromax or Fluorolog II) measurements were performed as described previously.^{5–9}

2. Time-Resolved Absorption Spectroscopy. Transient absorption data were acquired as described elsewhere.^{8,9,55} Samples (~0.2 mM in toluene) in 2 mm path length cuvettes at room temperature were excited at 10 Hz with a 120 fs, 550 nm or 580 nm, 2–4 μ J flash from an optical parametric amplifier (OPA) pumped by an amplified Ti:sapphire laser system (Spectra Physics). Absorption changes were monitored using a white-light probe flash generated in water with the residual 800 nm light (~0.4 mJ per pulse) from the Ti:sapphire/OPA system. On each laser flash, spectral data across the 450-600 nm region were obtained, and data from 300 flashes were averaged to achieve a ΔA resolution of ± 0.005 . Spectra at different pump-probe delay times were acquired by changing the path length over which the probe light traveled with respect to the pump pulse. The kinetic data shown in Figures 2 and 3 were generated by averaging the ΔA values in the range 520-525 nm (for the Fb porphyrin bleaching) or in the range 550-555 nm (for the Zn porphyrin bleaching) at each delay time (-10 to 200 ps) and then plotting these values as a function of time. The kinetic traces were then fit to a function consisting of a single exponential plus a constant using a nonlinear leastsquares algorithm.

3. Electrochemistry. The oxidized complexes were prepared and manipulated in a glovebox as described previously.⁹ The integrity of the samples was checked by cyclic voltammetry after each successive oxidation. In all cases, the cyclic voltammograms were reproducible upon repeated scans and exhibited no scan rate dependence in the 20-100 mV/s range. Studies were performed immediately after oxidation and transfer of the samples to an optical cuvette (absorption) or quartz capillary (EPR).

4. *EPR Spectroscopy*. The EPR spectra were recorded as described previously.⁹ The sample concentration for all the experiments was typically 0.05 mM. The microwave power and magnetic field modulation amplitude were typically 5.7 mW and 0.32 G, respectively.

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Supporting Information Available: A table showing the results of the Förster energy-transfer calculations for several dimers is provided (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) Prathapan, S.; Johnson, T. E.; Lindsey, J. S. J. Am. Chem. Soc. 1993, 115, 7519-7520.

(2) Wagner, R. W.; Lindsey, J. S. J. Am. Chem. Soc. 1994, 116, 9759–9760.

(3) Wagner, R. W.; Lindsey, J. S.; Seth, J.; Palaniappan, V.; Bocian, D. F. J. Am. Chem. Soc. **1996**, 118, 3996–3997.

(4) Bothner-By, A. A.; Dadok, J.; Johnson, T. E.; Lindsey, J. S. J. Phys. Chem. **1996**, 100, 17551–17557.

(5) Hsiao, J.-S.; Krueger, B. P.; Wagner, R. W.; Delaney, J. K.; Mauzerall, D. C.; Fleming, G. R.; Lindsey, J. S.; Bocian, D. F.; Donohoe, R. J. J. Am. Chem. Soc. **1996**, *118*, 11181–11193.

(6) Strachan, J.-P.; Genteman, S.; Seth, J.; Kalsbeck, W. A.; Lindsey, J. S.; Holten, D.; Bocian, D. F. *Inorg. Chem.* **1998**, *37*, 1191–1201.

(7) Wagner, R. W.; Seth, J.; Yang, S. I.; Kim, D.; Bocian, D. F.; Holten, D.; Lindsey, J. S. J. Org. Chem. **1998**, 63, 5042–5049.

(8) Li, F.; Gentemann, S.; Kalsbeck, W. A.; Seth, J.; Lindsey, J. S.; Holten, D.; Bocian, D. F. *J. Mater. Chem.* **1997**, *7*, 1245–1262.

(9) Strachan, J. P.; Gentemann, S.; Seth, J.; Kalsbeck, W. A.; Lindsey, J. S.; Holten, D.; Bocian, D. F. J. Am. Chem. Soc. **1997**, 119, 11191–11201.

(10) Wagner, R. W.; Johnson, T. E.; Lindsey, J. S. J. Am. Chem. Soc. 1996, 118, 11166-11180.

(11) (a) Osuka, A.; Shimidzu, H. Angew. Chem., Int. Ed. Engl. 1997, 36, 135–137.
(b) Khoury, R. G.; Jaquinod, L.; Smith, K. M. Chem. Commun. 1997, 1057–1058.
(c) Ogawa, T.; Nishimoto, Y.; Yoshida, N.; Ono, N.; Osuka, A. Chem. Commun. 1998, 337–338.

(12) (a) Ponomarev, G. V.; Borovkov, V.; Sugiura, K.-I.; Sakata, Y.; Shul'ga, A. *Tetrahedron Lett.* **1993**, *34*, 2153–2156. (b) Senge, M.; Gerzevske, K.; Vicente, M.; Forsyth, T.; Smith, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 750–753. (c) Ponomarev, G.; Borovkov, V.; Shul'ga, A.; Sakata, Y. J. Chem. Soc., Chem. Commun. **1994**, 1927–1928. (d) Senge, M.; Vicente, M.; Gerzevske, K.; Forsyth, T.; Smith, K. *Inorg. Chem.* **1994**, *33*, 5625–5638. (e) Higuchi, H.; Takeuchi, M.; Ojima, J. Chem. Lett. **1996**, 593–594.

(13) (a) Lin, V. S.-Y.; DiMagno, S. G.; Therien, M. J. Science **1994**, 264, 1105–1111. (b) Lin, V. S.-Y.; Therien, M. J. Chem.–Eur. J. **1995**, 1, 645–651.

(14) Arnold, D.; Nitschinsk, L. Tetrahedron 1992, 48, 8781-8792.

(15) Anderson, H. L. Inorg. Chem. 1994, 33, 972-981.

(16) Arnold, D.; Nitschinsk, L. Tetrahedron Lett. 1993, 34, 693-696.

(17) Vicente, M. G. H.; Smith, K. J. Org. Chem. 1991, 56, 4407-4418.

(18) Osuka, A.; Liu, B.-L.; Maruyama, K. *Chem. Lett.* 1993, 949–952.
(19) Heiler, D.; McLendon, G.; Rogalskyj, P. J. Am. Chem. Soc. 1987,

109, 604–606.
(20) Wennerström, O.; Ericsson, H.; Raston, I.; Svensson, S.; Pimlott, W. *Tetrahedron Lett.* 1989, *30*, 1129–1132.

(21) (a) Sessler, J.; Johnson, M. R.; Lin, T.-Y. *Tetrahedron* 1989, 45, 4767–4784. (b) Sessler, J.; Johnson, M.; Creager, S.; Fettinger, J.; Ibers,

J. J. Am. Chem. Soc. **1990**, 112, 9310–9329.

(22) Nagata, T.; Osuka, A.; Maruyama, K. J. Am. Chem. Soc. 1990, 112, 3054–3059.

(23) Osuka, A.; Tanabe, N.; Zhang, R.-P.; Maruyama, K. Chem. Lett. **1993**, 1505–1508.

(24) Sessler, J.; Capuano, V.; Harriman, A. J. Am. Chem. Soc. 1993, 115, 4618-4628.

(25) Osuka, A.; Tanabe, N.; Nakajima, S.; Maruyama, K. J. Chem. Soc., Perkin Trans. 2 **1996**, 199–203.

(26) Osuka, A.; Nagata, T.; Maruyama, K. Chem. Lett. 1991, 481–484.

(27) Osuka, A.; Nagata, T.; Maruyama, K. Chem. Lett. 1991, 1687–1690.

(28) Osuka, A.; Zhang, R.-P.; Maruyama, K.; Ohno, T.; Nozaki, K. Chem. Lett. 1993, 1727-1730.

(29) Osuka, A.; Nakajima, S.; Maruyama, K.; Mataga, N.; Asahi, T.; Yamazaki, I.; Nishimura, Y.; Ohno, T.; Nozaki, K. *J. Am. Chem. Soc.* **1993**, *115*, 4577–4589.

(30) Osuka, A.; Zhang, R.-P.; Maruyama, K.; Ohno, T.; Nozaki, K. Bull. Chem. Soc. Jpn. 1993, 66, 3773–3782.

(31) Osuka, A.; Nakajima, S.; Okada, T.; Taniguchi, S.; Nozaki, K.; Ohno, T.; Yamazaki, I.; Nishimura, Y.; Mataga, N. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 92–95.

(32) Rempel, U.; von Maltzan, B.; von Borczyskowski, C. Chem. Phys. Lett. 1995, 245, 253-261.

- (33) Chernook, A.; Shulga, A.; Zenkevich, E.; Rempel, U.; von Borczyskowski, C. J. Phys. Chem. **1996**, 100, 1918–1926.
 - (34) Zhou, X.; Chan, K. S. J. Org. Chem. 1998, 63, 99-104.
- (35) Osuka, A.; Maruyama, K.; Yamazaki, I.; Tamai, N. Chem. Phys. Lett. 1990, 165, 392–396.
- (36) (a) Osuka, A.; Nakajima, S.; Maruyama, K.; Mataga, N.; Asahi,
- T. Chem. Lett. 1991, 1003–1006. (b) Osuka, A.; Maruyama, K.; Mataga,
- N.; Asahi, T.; Yamazaki, I.; Tamai, N.; Nishimura, Y. Chem. Phys. Lett.
- **1991**, 181, 413–418. (c) Osuka, A.; Nagata, T.; Maruyama, K.; Mataga,
- N.; Asahi, T.; Yamazaki, I.; Nishimura, Y. *Chem. Phys. Lett.* **1991**, *185*, 88–94. (d) Osuka, A.; Zhang, R.-P.; Maruyama, K.; Mataga, N.; Tanaka,
- Y.; Okada, T. Chem. Phys. Lett. 1993, 215, 179–184.
- (37) Osuka, A.; Maruyama, K.; Mataga, N.; Asahi, T.; Yamazaki, I.; Tamai, N. J. Am. Chem. Soc. **1990**, 112, 4958–4959.
- (38) Greiner, S.; Winzenburg, J.; von Maltzan, B.; Winscom, C.; Möbius, K. *Chem. Phys. Lett.* **1989**, *155*, 93–98.
- (39) Rempel, U.; von Maltzan, B.; von Borczyskowski, C. Chem. Phys. Lett. 1990, 169, 347-354.
- (40) Rempel, U.; von Maltzan, B.; von Borczyskowski, C. J. Lumin. 1991, 48/49, 415-418.
- (41) Rempel, U.; von Maltzan, B.; von Borczyskowski, C. J. Lumin. **1992**, *53*, 175–178.
- (42) (a) Jaegermann, P.; Plato, M.; von Maltzan, B.; Möbius, K. Mol.
 Phys. 1993, 78, 1057–1074. (b) Rempel, U.; Meyer, S.; von Maltzan, B.; von Borczyskowski, C. J. Lumin. 1998, 78, 97–110.
- (43) Sessler, J.; Johnson, M.; Lin, T.-Y.; Creager, S. J. Am. Chem. Soc.
- 1988, 110, 3659–3661.
 (44) Rodriguez, J.; Kirmaier, C.; Johnson, M.; Friesner, R.; Holten, D.;
 Sessler, J. J. Am. Chem. Soc. 1991, 113, 1652–1659.
- (45) Sessler, J.; Capuano, V. *Tetrahedron Lett.* 1993, 34, 2287–2290.
 (46) Eriksson, S.; Källebring, B.; Larsson, S.; Mårtensson, J.; Wennerström, O. *Chem. Phys.* 1990, 146, 165–177.
- (47) Burrell, A.; Officer, D.; Reid, D. Angew. Chem., Int. Ed. Engl. 1995, 34, 900-902.
- (48) Lindsey, J. S. In *Modular Chemistry*; Michl, J., Ed.; NATO ASI Series C, Mathematical and Physical Sciences, Vol. 499; Kluwer Academic Publishers: Dordrecht, 1997; pp 517–528.
- (49) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. J. Org. Chem. **1987**, *52*, 827–836.
- (50) Lindsey, J. S.; Wagner, R. W. J. Org. Chem. 1989, 54, 828–836.
 (51) Fenyo, D.; Chait, B. T.; Johnson, T. E.; Lindsey, J. S. J. Porphyrins Phthalocyanines 1997, 1, 93–99.

(52) When the same reaction was performed at $10 \times$ the concentration (100 mM pyrrole), the isolated yield of Fb₂ Φ varied significantly with the BF₃·OEt₂ concentration: 0.15% (3.3 mM), 0.72% (10 mM), 0.84% (33 mM), and 0.01% (100 mM).

(53) Yang, S. I.; Seth, J.; Strachan, J. P.; Genteman, S.; Kim, D.; Holten, D.; Lindsey, J. S.; Bocian, D. F. J. Porphyrins Phthalocyanines, in press.

(55) (a) Kirmaier, C.; Holten, D. *Biochemistry* 1991, *30*, 609–613. (b)
Drain, C. M.; Kirmaier, C.; Medforth, C. J.; Nurco, D. J.; Smith, K. M.;
Holten, D. *J. Phys. Chem.* 1996, *100*, 11984–11993.

(56) (a) Seth, J.; Palaniappan, V.; Johnson, T. E.; Prathapan, S.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1994**, *116*, 10578–10592. (b) Seth, J.; Palaniappan, V.; Wagner, R. W.; Johnson, T. E.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1996**, *118*, 11194–11207.

(57) (a) Felton, R. H. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. V, pp 53–126. (b) Davis, D. G. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. V, pp 127–152.

⁽⁵⁸⁾ Heath, G. A.; Yellowlees, L. J.; Braterman, P. S. J. Chem. Soc., Chem. Commun. **1981**, 287–289.

(59) Elliot, C. M.; Hershenhart, E. J. Am. Chem. Soc. 1982, 104, 7519–7526.

(60) Edwards, W. D.; Zerner, M. C. Can. J. Chem. 1985, 63, 1763-1772.

(61) (a) Angel, S. M.; DeArmond, M. K.; Donohoe, R. J.; Wertz, D. W. J. Phys. Chem. 1985, 89, 282–285. (b) Donohoe, R. J.; Tait, C. D.; DeArmond, M. K.; Wertz, D. W. Spectrochim. Acta 1986, 42A, 233–240. (c) Tait, C. D.; MacQueen, D. B.; Donohoe, R. J.; DeArmond, M. K.; Hanck, K. W.; Wertz, D. W. J. Phys. Chem. 1986, 90, 1766–1771. (d) Donohoe, R. R.; Tait, C. D.; DeArmond, M. K.; Wertz, D. W. J. Phys. Chem. 1986, 90, 3923–3926. (e) Donohoe, R. J.; Tait, C. D.; DeArmond, M. K.; Wertz, D. W. J. Phys. Chem. 1986, 90, 3927–3930.

(62) Fajer, J.; Davis, M. S. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, pp 197-256.

(63) Huber, M.; Kurreck, H.; von Maltzan, B.; Plato, M.; Möbius, K. J. Chem. Soc., Faraday Trans. **1990**, 86, 1087–1094.

(64) Spellane, J. P.; Gouterman, M.; Antipas, A.; Kim, S.; Liu, Y. C. Inorg. Chem. **1980**, 19, 386-391.

(65) Ghosh, A. J. Am. Chem. Soc. 1995, 117, 4691-4699.

(66) Davis, W. B.; Svec, W. A.; Ratner, M. A.; Wasielewski, M. R. *Nature*, in press.

(67) Chang, J. J. Chem. Phys. 1977, 76, 3901-3909.

(68) The assumptions inherent in the Forster calculation for the phenylene-linked dimers preclude a precise analysis of the TB and TS rates. However, the observed rate for $F_{30}ZnFb\Phi$ is likely dominated by a TS process, as seen in the following comparison. Assume that the TS energy transfer is the sole contributor to the observed (10 ps)⁻¹ rate in $F_{30}ZnFb\Phi$. The TS rate in ZnFb Φ would then be about (5 ps)⁻¹ based on the larger spectral overlap for ZnFb Φ than for $F_{30}ZnFb\Phi$ (Table 1 of Supporting Information).⁹ Accordingly, the measured (3.5 ps)⁻¹ rate in $F_{30}ZnFb\Phi$ would be about 120 ps (based on previous finding of a 10-fold greater measured rate for $F_{30}ZnFbU$ versus ZnFbU, both of which are dominated by a TB mechanism).