# Synthesis and Excited-State Photodynamics of Perylene–Porphyrin Dyads. 1. Parallel Energy and Charge Transfer via a Diphenylethyne Linker

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The photophysical properties of a perylene-porphyrin dyad have been examined with the aim of using this construct for molecular photonics applications. The dyad consists of a perylene-bis(imide) dye (PDI) connected to a zinc porphyrin (Zn) via a diphenylethyne linker (pep). In both polar and nonpolar solvents, the photoexcited perylene unit (PDI\*) decays very rapidly (lifetimes of 2.5 (toluene) and 2.4 ps (acetonitrile)) by energy transfer to the porphyrin, forming PDI-pep- $Zn^*$  in high yield (80%, toluene; 70% acetonitrile), and hole transfer to the porphyrin, forming  $PDI^-$  pep $-Zn^+$  in lesser yield (20%, toluene; 30% acetonitrile). In both toluene and acetonitrile, the  $Zn^*$  excited state subsequently decays with a lifetime of 0.4 ns primarily (80%) by electron transfer to the perylene (forming  $PDI^-pep-Zn^+$ ). In the nonpolar solvent (toluene), the  $PDI^-pep-Zn^+$ charge-transfer product has a lifetime of > 10 ns and decays by charge recombination primarily to the ground state but also by thermal repopulation of the Zn\* excited state. The occurrence of the latter process provides a direct experimental measure of the energy of the charge-separated state. In the polar solvent (acetonitrile), the PDI<sup>-</sup> pep $-Zn^+$  charge-separated state decays much more rapidly ( $\leq 0.5$  ns) and exclusively to the ground state. In general, the complementary perylene and porphyrin absorption properties together with very fast and efficient PDI\* $-pep-Zn \rightarrow PDI-pep-Zn^*$  energy transfer suggest that perylenes have significant potential as accessory pigments in porphyrin-based arrays for light-harvesting and energy-transport applications. Furthermore, the finding of fast energy transfer initiated in PDI\*, charge-transfer reactions that can be elicited either in PDI\* or Zn\*, and a charge-separated state (PDI<sup>-</sup>-pep-Zn<sup>+</sup>) that can be long- or short-lived depending on solvent polarity, indicates the versatility of the perylene-porphyrin motif for a variety of applications in molecular photonics.

#### Introduction

The development of molecular photonic devices requires the creation of molecular arrays that absorb light of specific wavelengths and undergo excited-state energy- and/or chargetransfer reactions. The versatile optical, redox, and photochemical properties of porphyrins makes them ideally suited as components of molecular devices. The ability to introduce photo excitation at a specific site in a multiporphyrin array requires the use of accessory pigments. The ideal accessory pigment for use with porphyrins would exhibit the following features: (1) absorb strongly in the trough between the B and Q bands, (2) exhibit a singlet-excited-state lifetime (preferably monophasic) this is sufficiently long to support highly efficient energy transfer, (3) undergo energy transfer without deleterious excitedstate quenching reactions, (4) exhibit a high level of stability, (5) provide compatibility with the synthetic building block approach, and (6) exhibit sufficient solubility for chemical processing. In considering the advantages and disadvantages of various pigments for use with porphyrins, including carotenoids, coumarins, cyanines, and xanthenes, we originally turned to the boron-dipyrrin dyes as the most suitable accessory pigment.<sup>1</sup>

Thus, our first-generation molecular photonic wire<sup>2</sup> and optoelectronic gates<sup>3</sup> employed a boron–dipyrrin dye input unit, and several light-harvesting arrays were constructed that employed from one to eight boron–dipyrrin accessory pigments.<sup>4</sup>

The boron-dipyrrin dyes were found to exhibit a modest fluorescence yield as well as two excited-state conformers. The existence of the latter caused the analysis of the excited-state dynamics of extended arrays to be unduly complicated. We subsequently considered the use of perylene dyes as accessory pigments in conjunction with porphyrins. The N,N'-bis(2,5-ditert-butylphenyl)-3,4,9,10-perylenedicarboximide dye, for example, has strong absorption between the porphyrin Soret (B) and Q bands ( $\epsilon = 58\ 000\ M^{-1}cm^{-1}$  at 490 nm in CHCl<sub>3</sub>),<sup>5</sup> a high fluorescence quantum yield ( $\Phi_{\rm f}$  ~1),<sup>5,6</sup> a long fluorescence lifetime ( $\sim 4 \text{ ns}$ ),<sup>7</sup> and very high photostability.<sup>6</sup> Though many perylene bis(imide) derivatives have poor solubility in common organic solvents, their solubility is considerably enhanced by the introduction of bulky substituents.<sup>5-9</sup> The absorption and emission characteristics of perylene-imide dyes are not affected significantly by the presence of bulky substituents at the imide nitrogen.10

The perylene dyes have been employed in diverse applications ranging from paint pigments to use in solar cells.<sup>11</sup> In solar cells, perylene bis(imide) dyes have served multiple functions in addition to light absorber, including energy-transfer participant<sup>12,13</sup> and charge carrier.<sup>14</sup> Despite the wide use of perylene

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PDI-pep-Mg (M = Mg)PDI-pep-Zn (M = Zn)

dyes as intense absorbers and energy-transfer donors, perylene has rarely been employed as an energy-transfer donor in covalently linked arrays with porphyrins. There is only one study we are aware of in which a perylene bis(imide) dye and a porphyrin are linked: Wasielewski's group prepared a molecular optical switch comprised of a pervlene bis(imide) dye attached to two free base porphyrins via N-phenyl linkers.<sup>15</sup> Excitation of the porphyrin resulted in electron transfer from the porphyrin to the perylene. These results showed that a perylene bis(imide) would participate as an electron acceptor with a porphyrin joined via a short linker. Perylene bis(imide) derivatives have also been used in arrays with energy donors,<sup>13</sup> other perylenes,<sup>16-18</sup> phthalocyanines,<sup>19</sup> or carotenoids.<sup>20</sup> The only examples of energy transfer in any type of perylene-porphyrin array that we are aware of involved a perylene monoimide in a molecular switch<sup>21</sup> devised by Wasielewski's group and a molecular wire<sup>22</sup> that we developed upon extension of the work reported herein. The molecular switch is comprised of a dialkylamino-bis-(alkoxy)perylene monoimide derivative attached to a zinc porphyrin; the perylene has extensive charge-transfer character and serves primarily as an electrochromic sensor but also can transfer excited-state energy ( $\sim$ 370 ps) to the zinc porphyrin.

We sought to investigate the use of perylene-imide dyes as accessory pigments (i.e., energy-transfer donors) with porphyrins, using a longer linker than in Wasielewski's phenyl-linked system<sup>15</sup> in an attempt to suppress electron-transfer quenching while maintaining energy transfer. The perylene-porphyrin dyads are comprised of a perylene-diimide joined at an N-imide position to the porphyrin (magnesium, zinc, or free base) via a diphenylethyne (designated pep) linker (Chart 1). As anticipated, a variety of excited-state processes are indeed observed for the pervlene-porphyrin dyads. However, the diversity in the behavior exceeded our expectations and includes (1) energy transfer from the photoexcited perylene to the porphyrin, (2) competing hole transfer from the photoexcited perylene to the porphyrin, (3) electron transfer from the excited porphyrin to the perylene, (4) charge recombination of transient products derived from the perylene excited state forming the porphyrin excited state, and (5) charge recombination of products derived from the porphyrin excited state either reforming the excited state or deactivating to the ground state.

The results of our studies are divided into four articles. In this first paper, the photoinduced energy- and charge-transfer processes that occur in either the excited perylene or porphyrin are discussed for the dyad containing the zinc porphyrin (PDI– pep–Zn). The second, companion paper extends the studies to two dyads that incorporate a magnesium or free base (Fb) porphyrin in place of the zinc porphyrin.<sup>23</sup> The differences in excited-state and redox properties of these three porphyrins afford considerable latitude in manipulating the energy- versus charge-transfer processes for specific applications. The third and fourth articles describe even greater tunability in the rates and yields of the various excited-state processes upon replacing the





perylene-diimide component with a monoimide, changing the linker to the phenylethyne unit and altering the site of linker attachment to the perylene.<sup>24</sup> Collectively, these studies along with Wasielewski's work<sup>15,21,25</sup> lay a foundation for utilizing tunable perylene-porphyrin units in multichromophore arrays for a variety of applications in molecular photonics.

#### Results

Synthesis. A monoethynyl porphyrin (ZnU') was selected as the porphyrin building block.<sup>26</sup> We have previously employed the diarylethyne unit to bridge chromophores in various molecular devices.<sup>27</sup> These linkages are semirigid and maintain a relatively fixed center-to-center distance between chromophores.<sup>28</sup> The perylene dye building block was prepared building on the foundation established by Langhals and co-workers. 5,6,8,10,16,17,29 The 2,5-di-tert-butylphenyl group was selected as one N-aryl substituent to enhance the solubility, chemical stability, and light fastness.<sup>5-8</sup> The N,N'-bis(2,5-di-tert-butylphenyl)-3,4,9,10perylenedicarboximide dye (PDI-m)<sup>5</sup> was partially hydrolyzed to give 1 (Scheme 1). Subsequent condensation with 4-iodoaniline gave the desired iodo-substituted perylene 2. This route is superior to the earlier route to this class of compounds which required successive imidation of perylene-3,4,9,10-tetracarboxylic dianhydride.<sup>30,31</sup> The diphenylethyne-linked perylene-porphyrin dyad PDI-pep-Zn was prepared by the Pd(0)-mediated coupling of the iodo- and ethynyl-substituted pigments, using the conditions developed initially for porphyrin-porphyrin coupling reactions.<sup>26</sup> Thus, reaction of ethynyl porphyrin ZnU' and the iodo-perylene 2 afforded PDI-pep-Zn in 34% yield following chromatographic purification (Scheme 2). The <sup>1</sup>H NMR, IR, and mass spectral data were consistent with the expected structure.

**Redox Potentials.** The electrochemical data for PDI-pep-Zn and its monomeric component parts are summarized in Table

## **SCHEME 2**



PDI-pep-Zn

TABLE 1: Half-Wave Potentials  $(E_{1/2})$  for the Perylene-Containing Compounds<sup>*a*</sup>

|                     | oxidat      | ion pote                | ntials       | reduction potentials    |              |                         |              |  |
|---------------------|-------------|-------------------------|--------------|-------------------------|--------------|-------------------------|--------------|--|
|                     |             | porp                    | hyrin        | pery                    | lene         | porphyrin               |              |  |
|                     | perylene    | $\overline{E_{1/2}(1)}$ | $E_{1/2}(2)$ | $\overline{E_{1/2}(1)}$ | $E_{1/2}(2)$ | $\overline{E_{1/2}(1)}$ | $E_{1/2}(2)$ |  |
| PDI-pep-Zn<br>PDI-m | +1.40 +1.36 | +0.52                   | +0.90        | -0.77<br>-0.81          | -1.06 -1.07  | -1.71                   | -2.12        |  |

<sup>*a*</sup> Obtained in butyronitrile containing 0.1 M TBAH.  $E_{1/2}$  vs Ag/Ag<sup>+</sup>;  $E_{1/2}$  of FeCp<sub>2</sub>/FeCp<sub>2</sub><sup>+</sup> = 0.19 V. The  $E_{1/2}$  values are obtained from square wave voltammetry (frequency = 10 Hz). Values are  $\pm$  0.01 V.

1. The  $E_{1/2}$  values were obtained with square wave voltammetry (frequency 10 Hz). The isolated perylene—diimide dyes exhibit one oxidation wave and two reduction waves in the +1.5 to -2.0 V range. The  $E_{1/2}$  values of the perylene unit in the PDI—pep—Zn dyad are quite similar to those of the benchmark PDI-m monomer and to those found previously for the isolated dye and related perylene—imide molecules.<sup>32,33</sup> The zinc porphyrin unit in the dyad exhibits two oxidation and two reduction waves in the +1.5 to -2.0 V range with  $E_{1/2}$  values that are similar to those of other tetraarylporphyrins.<sup>34</sup> These data are indicative of relatively weak ground-state electronic interactions between the perylene and porphyrin constituents of the dyad.

Absorption Spectra. The electronic ground-state absorption spectrum of PDI-pep-Zn in toluene at room temperature is shown in Figure 1 (panel A, solid spectrum). This figure also gives the spectra of the ZnU' and PDI-m reference compounds. The spectrum of the dyad closely matches the sum of the spectra of the component parts. In particular, the porphyrin Soret (B) band of PDI-pep-Zn is essentially unchanged in position or width (424 nm, fwhm 12 nm) from that of ZnU', and the same is true of the weaker porphyrin Q(1,0) and Q(0,0) bands at 550 and 590 nm, respectively. Likewise, the perylene absorption bands of PDI-pep-Zn are, except for ~1 nm shifts, superimposable on those of PDI-m (consisting of a progression of four features at 528, 491, 460, and 434 nm of decreasing intensity that will be denoted the (0,0), (1,0), (2,0), and (3,0) bands, respectively). The essentially identical spectral features of the dyad and its component chromophores indicates that the perylene-porphyrin ground-state electronic interactions are weak (but not necessarily insignificant), in agreement with the



**Figure 1.** Electronic absorption spectra (solid) and fluorescence spectra (dashed and dotted) for the dyad PDI–pep–Zn (A) and the monomers ZnU' (B) and PDI-m (C) in toluene at room temperature. The porphyrin absorption in the 450–650 nm region in panels A and B have been multiplied by the factors shown. The porphyrin emission in the dyad in panel A was obtained using perylene excitation at 490 nm (dashed) or porphyrin excitation at 420 nm (dotted). All spectra have been normalized to the same amplitude in the respective regions. The extinction coefficient of the porphyrin Soret band at 424 nm is 468 000 M<sup>-1</sup> cm<sup>-1</sup> and that for the perylene at the Q(1,0) band at 490 nm is 43 900 M<sup>-1</sup> cm<sup>-1</sup>. Fluorescence yields are given in Table 2.

conclusion drawn from the redox data. A very attractive feature of the PDI-pep-Zn dyad is that the perylene unit absorbs strongly in the region between the porphyrin Soret and Q bands



**Figure 2.** Room temperature fluorescence spectra. Panel A shows the spectra in toluene obtained using perylene excitation at 420 nm for the PDI–pep–Zn dyad (solid), the PDI-m monomer (dashed) normalized at the (0,0) emission maximum near 530 nm, and the spectrum for the dyad minus that of the monomer (dotted). The difference spectrum is virtually identical to the spectrum of ZnU' (Figure 1B). These data afford one estimate of the fluorescence yield of the perylene component of the dyad (see text and Table 2). Panel B compares the fluorescence spectra of PDI–pep–Zn in toluene (solid) and acetonitrile using excitation of the porphyrin at 420 nm.

(allowing preferential excitation of the dye) but has minimal absorption in the Soret region (allowing preferential excitation of the porphyrin). For example, at 490 nm, the perylene ( $\epsilon = 43\ 900\ M^{-1}cm^{-1}$ ) absorbs 125 times that of the zinc porphyrin, whereas at 423 nm, the zinc porphyrin ( $\epsilon = 468\ 000\ M^{-1}cm^{-1}$ ) absorbs 140 times that of the perylene dye (based on PDI-m and ZnU' in toluene).

Fluorescence Spectra and Quantum Yields. The fluorescence spectra of PDI-pep-Zn and the ZnU' and PDI-m reference compounds in toluene are shown in Figure 1 (dashed and dotted spectra). Some of these data are reproduced in Figure 2 along with the emission spectrum of the dyad in acetonitrile. In the following, emphasis is given to the results in toluene. For both monomers, the emission features are in approximate mirror symmetry to the corresponding absorption features. The fluorescence spectrum of ZnU' consists principally of the Q(0,0)and Q(0,1) bands at 595 and 645 nm, respectively (Figure 1B).<sup>35</sup> The fluorescence spectrum of PDI-m consists of a progression extending from the (0,0) band near 530 nm through the (0,3)band at 700 nm (Figure 1C). The fluorescence quantum yield of PDI-m in toluene is found to be  $\Phi_{\rm f} = 0.97$ , in excellent agreement with the literature value of 0.96.6 The fluorescence yield of ZnU' in toluene is 0.035.35 These values are listed in Table 2.

The emission of PDI-pep-Zn was monitored using excitation at several wavelengths where either the perylene or the porphyrin primarily absorbs. Upon illumination of PDI-pep-Zn in toluene at 490 nm, where the perylene absorption is > 100fold that of the porphyrin, the emission spectrum is dominated by porphyrin fluorescence (Figure 1A, dashed spectrum). Only a small amount of PDI\* fluorescence is observed (e.g., the (0,0) emission at 530 nm). Comparison of optically matched solutions of PDI-pep-Zn and PDI-m (at 490 nm) reveals that the perylene emission is diminished by ~1000-fold in the dyad to  $\Phi_f \sim 0.001$ . Collectively, these results are consistent with substantial energy transfer from the photoexcited perylene (PDI\*) to the ground-state zinc porphyrin to produce the porphyrin excited-state Zn\*. This process is illustrated in Figure 3.

The PDI-pep-Zn dyad was also illuminated at 420 nm where the zinc porphyrin absorption is >100-fold that of the perylene. As expected, emission occurs essentially exclusively from the porphyrin with only a trace of perylene fluorescence (Figure 1A, dotted spectrum). However, the yield of Zn\* emission in the dyad is reduced considerably from that in the reference compound. In particular, comparison of optically matched solutions of PDI-pep-Zn and ZnU' in toluene (at  $\lambda_{exc}$ at 420, 550, or 585 nm) shows that the Zn\* fluorescence yield in the dyad in toluene is decreased to 0.010 compared with 0.035 in the monomer (Table 2). The most likely process by which Zn\* is guenched in the dyad relative to the monomer is electron transfer to the perylene unit to form the PDI<sup>-</sup>-pep-Zn<sup>+</sup> state (Figure 3). The alternative charge-transfer product PDI<sup>+</sup>-pep- $Zn^{-}$  (formed by hole transfer from  $Zn^{*}$  to the perylene) lies at significantly higher energy based on the redox data (Table 1). Direct support for the PDI-pep-Zn\*  $\rightarrow$  PDI-pep-Zn<sup>+</sup> process is provided by the transient absorption data (vide infra).

The electron-transfer quenching of Zn\* to form PDI-pep-Zn<sup>+</sup> will also necessarily occur when Zn\* is formed from PDI\* via energy transfer rather than by direct excitation. In particular, this Zn\* quenching process will diminish the observed Zn\* fluorescence yield obtained upon excitation of the perylene or upon excitation of the porphyrin. Thus, comparison of the Zn\* emission intensity with perylene versus porphyrin excitation will give a measure of the yield of PDI\*-pep-Zn  $\rightarrow$  PDI-pep-Zn\* energy transfer. (The intensity of the Zn emission using perylene excitation is the product of the quantum yield of energy transfer from the perylene to the porphyrin and the quantum yield of emission from the porphyrin.) Predominant excitation of the perylene at 515 nm gives an apparent emission quantum yield from Zn\* of 0.008, which is 20% lower than the value of 0.010 found with porphyrin excitation (Table 1). These results indicate that energy transfer from PDI\* to the porphyrin has a quantum yield of  $\sim$ 80% in the PDI-pep-Zn dyad in toluene. This value together with the low (<0.1%) PDI\* fluorescence yield in the dyad (and the fact that PDI fluorescence dominates the inherent decay pathways in this dye) indicate that the other  $\sim$ 20% of the PDI\* decay in the dyad must reflect a pathway not present in the monomer. The most likely such process is hole transfer from PDI\* to the porphyrin to form PDI-pep-Zn<sup>+</sup> (Figure 3; vide infra).

Very similar fluorescence behavior is found for PDI-pep-Zn in acetonitrile or dimethyl sulfoxide (Table 2). The major difference compared to toluene is that the positions and intensity ratio of the porphyrin fluorescence bands are changed in the polar solvents (Figure 2B). These effects are attributable to coordination of a solvent molecule to the central zinc ion of the porphyrin.

**Fluorescence Lifetimes.** The lifetime of the Zn\* excited state of PDI-pep-Zn was measured by fluorescence modulation (phase shift) spectroscopy. The dyad in toluene exhibits a dual-exponential fluorescence decay ( $\lambda_{exc} = 420$  or 550 nm). The lifetime components are  $0.4 \pm 0.1$  and  $10 \pm 2$  ns with a 80/20 amplitude ratio. Only the shorter lifetime component is observed

TABLE 2: Photophysical Properties of PDI-pep-Zn and Reference Monomers<sup>a</sup>

|                  |                               | perylene<br>excited-state decay |                           |                        | porphyrin<br>excited-state decay |                          |                            | CSS decay <sup>h</sup>                       |             |
|------------------|-------------------------------|---------------------------------|---------------------------|------------------------|----------------------------------|--------------------------|----------------------------|--|-------------|
| compound         | solvent                       | τ (ps)                          | $\Phi_{\mathrm{f}}{}^{b}$ | $\Phi_{	ext{ENT}}{}^c$ | $\Phi_{ m HT}{}^{d}$             | $\tau$ (ns) <sup>e</sup> | $\Phi_{\mathrm{f}}{}^{f}$  | $\Phi_{\mathrm{ET}^g}$                       | $\tau(ns)$  |
| Monomers<br>ZnU' | toluene<br>CH3CN              |                                 |                           |                        |                                  | 2.4<br>$2.2^{i}$         | $0.035 \\ 0.05^{i}$        |  |             |
| PDI-m            | toluene                       | 3600                            | $0.97^{j}$                |                        |                                  |                          |                            |  |             |
| Dyad             |                               |                                 |                           |                        |                                  |                          |                            |  |             |
| PDI-pep-Zn       | toluene<br>CH <sub>3</sub> CN | 2.5<br>2.4                      | $0.001^k$<br>0.001        | $0.8^{l}$<br>0.7       | $0.2^m$ 0.3                      | $0.4^{n}$<br>$0.5^{n}$   | $0.008^{o}$<br>$0.007^{q}$ | $\begin{array}{c} 0.8^p \ 0.8^p \end{array}$ | >10<br><0.5 |

<sup>a</sup> All data were taken at room temperature. The errors in the lifetimes are  $\pm 10\%$  as are those for the fluorescence yields except for values <0.01, which have errors  $\pm 0.001$ . <sup>b</sup> Perylene fluorescence yield. The value for PDI was measured as in footnote f and those for the dyads relative to PDI-m, using perylene excitation at 490 nm. <sup>c</sup> Yield of energy transfer to the porphyrin. <sup>d</sup> Yield of hole transfer to the porphyrin. <sup>e</sup> The lifetime for ZnU' is  $\pm 0.2$  ns (determined by fluorescence decay), and those in the dyads are  $\pm 0.1$  ns (average of fluorescence lifetime and transient absorption measurements). <sup>f</sup> Porphyrin fluorescence yield referenced to a value of 0.033 for zinc tetraphenylporphyrin (ZnTPP),<sup>44</sup> obtained using porphyrin Soret excitation. <sup>8</sup> Yield of electron transfer to the perylene. <sup>h</sup> Decay of the charge-separated species PDI<sup>-</sup>-pep-Zn<sup>+</sup>. <sup>i</sup> We have obtained a range of values for the lifetime and fluorescence yield for ZnU' and related molecules such as zinc tetraphenylporphyrin in acetonitrile and other coordinating solvents, affording average values of  $\tau = 2.2 \pm 0.6$  ns and  $\Phi_f = 0.05 \pm 0.01$ . These values imply that the radiative rate  $k_f$  is somewhat greater in these solvents than in toluene, as is inferred also from the stronger Q(0,0) band in the absorption and emission spectra in the coordinating solvents. <sup>j</sup> Essentially the same value was measured previously in a variety of solvents. <sup>k</sup> Composite value from measurements using reduction in perylene emission in dyad versus the PDI-m monomer, integrated PDI versus porphyrin emission in the dyad, and reduction in the PDI\* lifetime in the dyad versus the monomer. <sup>1</sup> The same value was deduced from the energy-transfer yield obtained from the yield of porphyrin fluorescence with perylene versus porphyrin excitation and  $1 - \Phi_{HT}$  in the following column.<sup>m</sup> The same value is obtained from the amplitude of the transient absorption features and from  $1 - \Phi_{ENT}$  in the previous column. "Composite value from transient absorption and fluorescence lifetime measurements, with the latter also containing a slower, delayed component. <sup>o</sup> The measured emission yield determined relative to the ZnTPP monomer using porphyrin excitation is 0.010. However, this value contains a 20% contribution of delayed fluorescence, so the actual yield of prompt fluorescence is 0.008. A yield of 0.008 was also determined using perylene excitation, and this value similarly must be corrected down by 20% to  $\sim$ 0.006. The value with perylene excitation is lower than that obtained from porphyrin excitation because of hole transfer (20%) competing with energy transfer (80%) to the porphyrin. <sup>p</sup> Similar values were obtained from the reduction in porphyrin fluorescence yield in the dyad versus monomer, the porphyrin lifetime in the dyad versus the monomer, and the amplitudes of the features in the transient absorption spectra. <sup>q</sup> The same result is found in dimethyl sulfoxide.



Figure 3. State diagram and kinetic scheme for the photoinduced processes for the PDI-pep-Zn dyad in toluene and acetonitrile. The excited-state energies were obtained from the static absorption and emission spectra and the energy of the charge-separated state from the delayed fluorescence data (see text). The lifetimes and yields are given in Table 2 and the rate constants in Table 3. Note the scale break on the energy (eV) axis.

 TABLE 3: Summary of Kinetic Data for the PMI-pep-Zn Dyad<sup>a</sup>

| solvent            | $(k_0)^{-1}$<br>(ns) | $(k_1)^{-1}$ (ps) | $(k_2)^{-1}$ (ps) | $(k_3)^{-1}$ (ns) | $(k_{-3})^{-1}$ (ns) | $(k_4)^{-1}$ (ns) | $(k_5)^{-1}$<br>(ns) |
|--------------------|----------------------|-------------------|-------------------|-------------------|----------------------|-------------------|----------------------|
| toluene            | 3.6                  | 3.1               | 12.5              | 0.5               | ~1.5                 | 2.4               | >10                  |
| CH <sub>3</sub> CN | 3.6                  | 3.4               | 8.0               | 0.5               | NA                   | 2.2               | <0.5                 |

<sup>a</sup> The rate constants refer to the processes shown in Figure 3.

for PDI-pep-Zn in acetonitrile or dimethyl sulfoxide. Three points regarding these observations are noteworthy. (1) The shortening of the Zn\* lifetime to 0.4 ns for the PDI-pep-Zn dyad from 2.4 ns for the ZnU' monomer, like the corresponding diminution in the fluorescence yield, is indicative of a process (such as electron transfer from Zn\* to the perylene) that is not present in the monomer. (2) The 10 ns component to the Zn\*

emission decay in the dyad in toluene can be ascribed to delayed fluorescence resulting from thermal repopulation of  $Zn^*$  via charge recombination of PDI<sup>-</sup>-pep-Zn<sup>+</sup> (Figure 3). The repopulation process and thus the magnitude of the slow fluorescence component is greatly diminished as the chargeseparated species is energetically stabilized below that of Zn<sup>\*</sup> in the more polar media. (3) The yield of prompt fluorescence from Zn<sup>\*</sup> in PDI-pep-Zn in toluene is 0.008 (with porphyrin excitation) because the measured value of 0.010 contains a 20% contribution from the delayed component (Table 2). This low fluorescence yield is essentially the same as that found in acetonitrile or dimethylsolfoxide, validating this analysis and giving consistency to the results.

Time-Resolved Absorption Spectra. Transient absorption spectra were acquired for PDI-pep-Zn in toluene and in acetonitrile. The spectral changes were measured at time delays extending to about 3.5 ns following excitation of either the perylene or the porphyrin with a 130 fs flash. The assignments of the absorption difference spectra ( $A_{\text{transient-state}} - A_{\text{ground-state}}$ ) are aided by comparison of the features with those in the static absorption and fluorescence spectra given in Figure 1. Consider first the spectra observed using excitation of PDI-pep-Zn in toluene at 550 nm, which primarily excites the porphyrin component (Figure 4B). The spectrum at 0.2 ps after the flash can be ascribed predominantly to the photoexcited porphyrin Zn\*. The spectrum contains bleaching of the zinc porphyrin Q(1,0) ground-state absorption band at 550 nm and of the weaker Q(0,0) band at 590 nm. The feature at 590 nm in the transient spectrum is  $\sim$ 50% Q(0,0) stimulated emission from Zn\* (emission stimulated by the white-light probe pulse that occurs at approximately the position of the corresponding static-fluorescence band). The trough at 650 nm is the corresponding Q(0,1) stimulated emission band. The ratios of all of these features are those expected based on the static optical



**Figure 4.** Time-resolved absorption difference spectra for PDI-pep-Zn in toluene at room temperature obtained using predominant excitation of the perylene unit at 490 nm (A) or the porphyrin at 550 nm (B) with a 130 fs flash.

spectra in Figure 1B. The 0.2 ps transient spectrum also contains small features at 530 and 490 nm that can be assigned to bleaching in the perylene (0,0) and (1,0) ground-state absorption bands, respectively (see Figure 1C). The latter features are present because of minor direct excitation of the perylene component.

As time progresses, the Zn\* spectral features give way to the absorbance changes shown at 1 ns in Figure 4B. This spectrum retains bleaching of the porphyrin ground-state bands at 550 and 590 nm, but the stimulated emission features are no longer present (evident by the ratio of the features). These findings indicate that the zinc porphyrin has not returned to the ground state but is no longer in the emissive Zn\* excited state. The nature of the species present at 1 ns is revealed by the presence of substantial bleaching in the perylene (0,0) and (1,0)ground-state absorption bands at 530 and 490 nm, respectively. Because the corresponding perylene stimulated emission features are absent (see the 0.2 ps spectrum in Figure 4A where these features contribute at 530 and 580 nm), the perylene component of the dyad is not in the PDI\* excited state at 1 ns. Instead, the broad transient absorption with a distinct maximum near 710 nm indicates that the perylene unit is in the anionic form PDI<sup>-.33</sup> Thus, the 1 ns spectrum in Figure 4B can be assigned as the PDI<sup>-</sup>-pep-Zn<sup>+</sup> species formed by electron transfer from Zn\* to the ground-state perylene unit (Figure 3). A yield of 80% for the latter process is estimated from the amplitude of the PDI bleachings at 490 and 530 nm in the 1 ns spectrum relative to the amplitude of the bleachings in the 0.2 ps Zn\* spectrum. The time evolution of the spectral features gives a Zn\* lifetime of 400  $\pm$  50 ps for PDI-pep-Zn in toluene (Table 2; vide infra).

Consider next the transient absorption data for PDI-pep-Zn in toluene obtained upon excitation of the perylene component (Figure 4A). In this case, we expect to see the behavior just described for Zn\* but preceded by behavior associated with PDI\*. The spectrum at 0.2 ps (solid) is due predominantly to the photoexcited perylene PDI\*. This assignment is made on the following basis. The spectrum contains bleaching of the perylene (0,0) and (1,0) ground-state absorption bands near 530 and 490 nm (see Figure 1C). About one-half of the negative-going feature near 530 nm also derives from PDI\* (0,0) stimulated emission, and the troughs at 580 and 635 nm correspond to (0,1) and (0,2) stimulated emission (compare with monomer fluorescence spectra in Figure 1C). The positive absorption at ~690 nm derives from PDI\*.

As time proceeds, the PDI\* spectrum decays into the transient difference spectrum shown at 20 ps in Figure 4A. This spectrum is due predominantly to Zn\* formed via energy transfer from PDI\*. This assignment is based on the spectral characteristics expected for Zn\* and also found, as discussed above, upon direct excitation of the porphyrin component of the dyad (see the 0.2 ps spectrum in Figure 4B). However, the 20 ps spectrum produced by decay of PDI\* also contains features associated with the perylene component. The latter features include the same characteristics (bleaching in the regions of the groundstate bands at 530 and 490 nm, no PDI\* stimulated emission, and a broad absorption band at 710 nm) that were assigned above to the PDI<sup>-</sup>-pep-Zn<sup>+</sup> species formed (with  $\tau \sim 400$ ps) from Zn\* upon direct porphyrin excitation (see the 1 ns spectrum in Figure 4B). Thus, the perylene-associated spectral features in the 20 ps spectrum in Figure 4A must represent a small amount of PDI<sup>-</sup>-pep-Zn<sup>+</sup>. In this case, the PDI<sup>-</sup>-pep- $Zn^+$  species forms in <20 ps by hole transfer from PDI\* to the porphyrin, in parallel with energy transfer from PDI\* to the porphyrin to form Zn\* (Figure 3). On the basis of characteristics such as the magnitude of the 530 nm perylene bleaching (referenced to the broad background transient absorption) at 20 ps versus 0.2 ps, the PDI\* $-pep-Zn \rightarrow PDI^{-}-pep-Zn^{+}$  holetransfer process in toluene has a yield of 20%. Thus, the predominant (80%) decay pathway of the photoexcited perylene is the PDI\*-pep-Zn  $\rightarrow$  PDI-pep-Zn\* energy-transfer process. Subsequently, the spectral features at 20 ps associated with Zn\* evolve into those shown at 1 ns (Figure 4A). This evolution includes a dramatic increase in the perylene-associated characteristics that can be assigned to the PDI<sup>-</sup>-pep-Zn<sup>+</sup> species, as described above for the spectrum taken 1 ns after direct porphyrin excitation (Figure 4B). Subsequently, the PDI<sup>-</sup>-pep-Zn<sup>+</sup> spectrum does not change appreciably over the 3.5 ns time scale of the transient absorption measurements.

Representative kinetic data for PDI-pep-Zn in toluene associated with the spectra in Figure 4a are shown in Figure 5. A PDI\* lifetime of 2.5 ps is found from the average time constant determined from the evolution of the spectral features associated with either the perylene or the porphyrin. These features include the formation of the Zn\* absorption at 465 nm, substantial decay of bleaching in the perylene (1,0) groundstate absorption band at 490 nm (together with formation of  $Zn^*$  absorption), and decay of the perylene (0,1) stimulated emission at 570 nm. The subsequent evolution of the absorbance changes are associated with the decay of Zn\*, which has an average time constant of  $370 \pm 70$  ps (insets to Figure 5). These features include decay of the Zn\* excited-state absorption at 465 nm and formation of perylene bleachings (because of PDI<sup>-</sup>-pep-Zn<sup>+</sup>) at 490 and 530 nm. The reason the associated time constants appear somewhat wavelength dependent may derive from the equilibrium involving the Zn\* and PDI<sup>-</sup>-pep-Zn<sup>+</sup> species depicted in Figure 3 (which is also reflected in the



**Figure 5.** Kinetic profiles at selected wavelengths for PDI-pep-Zn in toluene using predominant excitation of the perylene component at 490 nm. For the insets, which emphasize the longer-time behavior, data before and during the excitation flash are not shown for clarity; the  $\Delta A = 0$  line is the horizontal axis in panel A and the horizontal line in panels B and C. The solid lines through the data are fits using a dual-exponential function giving the time constants shown. (Average values for the time constants at these and other wavelengths are given in Table 2.)

slow component to the Zn\* fluorescence decay noted above). Similar results are found when the porphyrin is excited directly (Zn\* lifetime of 400  $\pm$  50 ps). Note that a Zn\* lifetime of ~400 ps derived from the transient absorption data is in good agreement with the value of 400  $\pm$  100 ps for the fast, primary component to the Zn\* fluorescence decay. Following the decay of Zn\*, the absorbance changes associated with PDI<sup>-</sup>-pep-Zn<sup>+</sup> do not decay on the time scale of these measurements, indicating a lifetime for the charge-transfer product of >10 ns (Figure 5, insets).

Transient absorption measurements were also performed on PDI-pep-Zn in acetonitrile. The spectra at 0.2 and 20 ps after excitation of the perylene at 490 nm (Figure 6A) are very similar to those obtained under similar conditions in toluene (Figure 4A) and can be similarly assigned. The 0.2 ps spectrum in acetonitrile can be ascribed to PDI\*, which is found to decay with a lifetime of 2.4  $\pm$  0.2 ps (similar to the 2.5 ps value in toluene) from the average of measurements at several wavelengths (see Figure 6B). Following PDI\* decay, the spectrum at 20 ps has features that can be assigned to a combination of Zn\* (decreased slightly to 70% from 80% in toluene) and PDI<sup>-</sup>-pep-Zn<sup>+</sup> (increased to 30% from 20% in toluene). However, the subsequent behavior has both similarities and differences from that found in toluene. The main difference is that the 20 ps spectrum in acetonitrile decays uniformly to zero with a time constant of 400  $\pm$  100 ps (Figure 6), whereas in toluene the spectrum assigned to PDI<sup>-</sup>-pep-Zn<sup>+</sup> increased in magnitude over this time frame and then remained unchanged to the 3.5 ns limit of the measurements. The 0.4 ns decay time



**Figure 6.** (A) Time-resolved absorption difference for PDI-pep-Zn in acetonitrile at room temperature obtained using predominant excitation of the perylene unit at 490 nm. The inset gives an expanded view of the data at 20 ps and 2.8 ns on the same wavelength scale as the main panel. (B) Kinetic data for the growth of the Zn\* transient absorption at 460 nm and its subsequent decay. The dual exponential fit (solid line) gives time constants of  $2.6 \pm 0.2$  and  $390 \pm 30$  ps for the two components. The inset shows data at 530 nm and a single-exponential fit with a time constant of  $2.3 \pm 0.2$  ps. (These values and those obtained at other wavelengths afford the average values given in Table 2.)

in acetonitrile is similar to the Zn\* lifetime of  $0.5 \pm 0.1$  ns determined from fluorescence decay in this solvent (and to the Zn\* lifetime of 0.4 ns found in toluene). Again, these values are much shorter than the excited-state lifetime of monomeric zinc porphyrins (Table 2). Collectively, these results suggest the following: (1) The Zn\* lifetime in the dyad is dominated by electron transfer to form PDI<sup>-</sup>-pep-Zn<sup>+</sup> in both solvents (80% yield as described above in toluene). (2) PDI<sup>-</sup>-pep-Zn<sup>+</sup> decays by charge recombination to the ground state in <0.5 ns in acetonitrile, compared to the >10 ns lifetime of this species in toluene.

#### Discussion

The state diagram and kinetic model in Figure 3 summarizes the primary photophysical processes observed for PDI-pep-Zn in toluene and acetonitrile. The microscopic rate constants for the various processes can be obtained in terms of this model using the corresponding yields and the lifetimes of the transient states derived from the time-resolved and static optical measurements (Tables 2 and 3). In the following, we draw together the various results to (1) verify their consistency, (2) derive the kinetic parameters, and (3) allow insights into the mechanisms of photoinduced processes in this dyad. These considerations and the resulting conclusions not only give a comprehensive description of the excited-state pathways operable in the PDIpep-Zn array but also form a benchmark for the varied behavior observed for the other perylene-porphyrin dyads described in subsequent articles, including the following paper. The lowest excited singlet state of an isolated chromophore such as the perylene-diimide (PDI\*) or the zinc porphyrin (Zn\*) decays by fluorescence and internal conversion to give the ground electronic state, as well as intersystem crossing to form the excited triplet state. The rate constants for these three processes are  $k_f$ ,  $k_{ic}$ , and  $k_{isc}$ , respectively. Thus, the isolated perylene and porphyrin chromophores have a lifetime of their respective lowest excited singlet state,  $\tau^m$ , and a fluorescence yield,  $\Phi_f^m$ , given by eqs 1 and 2:

$$\tau^{\rm m} = (k_{\rm f} + k_{\rm ic} + k_{\rm isc})^{-1} \tag{1}$$

$$\Phi_{\rm f}^{\rm m} = k_{\rm f} / (k_{\rm f} + k_{\rm ic} + k_{\rm isc}) \tag{2}$$

It is reasonable to assume that the rate constants for the inherent decay pathways of PDI\* and Zn\* in the PDI-pep-Zn dyad are well approximated by those for the isolated monomers. This view is supported by the findings that the redox potentials and static optical spectra of the dyad are essentially given by (the sum of) those of the isolated reference compounds, indicating essentially no perturbation of the pervlene because of the presence of the porphyrin (and linker) and vice versa. However, in the dyad, there are additional decay channels for the excited states not possible in the monomer. The fluorescence and transient absorption data indicate that these channels for the PDI-pep-Zn dyad are energy transfer, hole transfer, and electron transfer (rate constants  $k_{\text{ENT}}$ ,  $k_{\text{HT}}$ , and  $k_{\text{ET}}$ , respectively). The rate constant by which either the PDI\* or Zn\* excited state in the dyad decays by one or a combination of these quenching processes can be denoted  $k_{q}$ . Thus, in analogy with eqs 1 and 2 for the isolated pigments, the lifetime of the lowest excited singlet state,  $\tau$ , and the fluorescence yield,  $\Phi_{\rm f}$ , of either PDI\* or Zn\* in the dyad are given by eqs 3 and 4:

$$\tau = (k_{\rm f} + k_{\rm ic} + k_{\rm isc} + k_{\rm o})^{-1} \tag{3}$$

$$\Phi_{\rm f} = k_{\rm f} / (k_{\rm f} + k_{\rm ic} + k_{\rm isc} + k_{\rm q}) \tag{4}$$

The yield of the energy-transfer pathway, for example, is

$$\Phi_{\rm ENT} = k_{\rm ENT} / (k_{\rm f} + k_{\rm ic} + k_{\rm isc} + k_{\rm q})$$
(5)

where again  $k_q$  is the rate constant for the energy-transfer channel plus that for any other process (hole or electron transfer) not operable in the monomer that contributes to the dynamics of the associated excited state in the dyad.

Photodynamics of the Excited Perylene in PDI-pep-Zn. The excited state of the isolated perylene dye (PDI\*) has a lifetime  $\tau^{\rm m} = 3.6$  ns. Thus,  $k_0 = (3.6 \text{ ns})^{-1}$  in the kinetic model in Figure 3 for PDI-pep-Zn, following the considerations given above concerning minimal perturbation of the inherent properties of the perylene in the array. The isolated perylene dye decays almost exclusively by fluorescence ( $\Phi_f^m = 0.97$ ). Although fluorescence remains the major contributor to  $k_0$  in the dyad, the yield is reduced dramatically to  $\Phi_{\rm f} = 0.001$ , as determined by direct measurement of this quantity. The same value ( $\Phi_{\rm f} =$ 0.001) is calculated from the corresponding reduction in the PDI\* lifetime in the dyad ( $\tau = 2.5$  ps in toluene) versus the monomer via the expression  $\Phi_{\rm f} = \Phi_{\rm f}^{\rm m} \tau / \tau^{\rm m}$  (obtained by manipulation of eqs 1–4). A similar value ( $\Phi_f = 0.0015$ ) is obtained from the product of the following three factors: (a) the ratio of integrated perylene versus porphyrin fluorescence spectra measured with perylene excitation, 0.26, (b) the measured yield of perylene-to-porphyrin energy transfer, 0.8, and (c) the yield of porphyrin prompt fluorescence measured with direct porphyrin excitation, 0.008. These considerations demonstrate the consistency of the various measurements and combine to show that the fate of the photoexcited perylene unit in the PDI-pep-Zn dyad is overwhelmingly dictated (>99%) by processes involving the porphyrin that are not operable in the isolated perylene dye.

The fluorescence and transient absorption data further indicate that the primary processes of the perylene excited state in the dyad are energy transfer (PDI\*-pep-Zn  $\rightarrow$  PDI-pep-Zn\*) and hole transfer (PDI\*-pep-Zn  $\rightarrow$  PDI<sup>-</sup>-pep-Zn<sup>+</sup>). These processes have rate constants  $k_1$  and  $k_2$ , respectively (Figure 3). Thus,  $k_1 + k_2 \gg k_0$ . Furthermore, energy-transfer from PDI\* to the porphyrin dominates over hole transfer  $(k_1 > k_2)$ . In particular, a yield of 80% for the PDI\* $-pep-Zn \rightarrow PDI-pep-$ Zn\* energy-transfer process is estimated from the Zn\* fluorescence yield in the dyad obtained using predominantly perylene excitation versus that with porphyrin excitation (Table 2). This finding implies a corresponding yield of 20% for the PDI\* $pep-Zn \rightarrow PDI^--pep-Zn^+$  hole-transfer process. The same 20% yield of hole transfer is estimated from the amplitudes of the features in the transient absorption spectra, again indicating an 80% energy-transfer yield. Using the model in Figure 3, these yields and the measured PDI\* lifetime of 2.5 ps for PDI-pep-Zn in toluene give  $k_1/(k_1 + k_2) = 0.8$ ,  $k_2/(k_1 + k_2) = 0.2$ , and  $k_1 + k_2 = (2.5 \text{ ps})^{-1}$ . Thus, the rate constants of the parallel energy- and hole-transfer pathways of PDI\* are  $k_1 = (3.1 \text{ ps})^{-1}$ and  $k_2 = (12.5 \text{ ps})^{-1}$  (Table 3). Generally similar values are obtained from the analysis of the measurements on PDI-pep-Zn in acetonitrile, except for a slightly faster hole-transfer rate for PDI\* than in toluene. These rate constants again reflect the fact that energy transfer to the porphyrin is the primary fate of the photoexcited perylene dye in the PDI-pep-Zn dyad.

Photodynamics of the Excited Porphyrin. The Zn\* excited state of PDI-pep-Zn can be formed via energy transfer from the excited perylene (in 80% yield) or via direct excitation. As expected, the course of decay of Zn\* is identical in the two cases. The Zn\* lifetime in the isolated zinc porphyrin ZnU' is  $\tau^{\rm m} = 2.4$  ns. Following the logic given above (negligible change in the inherent decay rates of the porphyrin),  $k_4 = (2.4 \text{ ns})^{-1}$ for the PDI-pep-Zn dyad (Figure 3 and Table 3). The primary fate of the Zn\* in the isolated chromophore is intersystem crossing ( $\Phi^m_{isc}\sim 0.9)$  with only a small fluorescence contribution ( $\Phi_{\rm f}^{\rm m} = 0.035$ ). The yield of prompt fluorescence yield is reduced in the dyad ( $\Phi_f = 0.008$ ). This reduction occurs not because of energy transfer to the perylene (which is energetically uphill) but rather because of PDI-pep-Zn\*  $\rightarrow$  PDI-pep-Zn<sup>+</sup> electron transfer. A yield of 77% for this latter process is calculated using the expression  $\Phi_{\rm ET} = 1 - \Phi_{\rm f} / \Phi_{\rm f}^{\rm m}$  (derived from manipulation of eqs 2, 4, and 5). The yield of this electrontransfer process is also measured to be 80% from the amplitudes of the features in the transient absorption spectra (Figure 3B). A yield of 83% also can be calculated using the Zn\* lifetime  $\tau$ = 0.4 ns in the dyad (composite value from fluorescence and transient absorption) and the lifetime  $\tau^{\rm m} = 2.4$  ns in the monomer using the expression  $\Phi_{\rm ET} = 1 - \tau/\tau^{\rm m}$  (derived from manipulation of eqs 1, 3, and 5). Thus, there is consistency in the various results regarding the yield of the electron-transfer pathway of Zn\* in the dyad (80%), which dominates the excitedstate dynamics.

The rate constant  $(k_3)$  for the PDI-pep-Zn\*  $\rightarrow$  PDI-pep-Zn<sup>+</sup> electron-transfer reaction can be obtained by several means. The most rigorous is to utilize the expressions for the timeevolving populations of Zn\* and PDI-pep-Zn<sup>+</sup> derived for the kinetic model in Figure 3, which includes thermal repopu-

CHART 2



lation of the former species from the latter (see Appendix A). This close equilibrium is indicated by the finding of a 10 ns (delayed) component to the Zn\* fluorescence decay in toluene, in addition to the dominant 0.4 ns faster (prompt) component. In order for the kinetic model to reproduce the data, a rate constant  $k_3 \sim (0.5 \text{ ns})^{-1}$  for the PDI-pep-Zn\*  $\rightarrow$  PDI-pep- $Zn^+$  electron-transfer process is required. (Similar values of  $k_3$ are obtained in a more straightforward manner from the lifetime or fluorescence data and expressions obtained by manipulation of eqs 1-5 that ignore the thermal repopulation process in Figure 3.<sup>36</sup>) This modeling also returns a rate constant of the reverse process of  $k_{-3} \sim (1.5 \text{ ns})^{-1}$ . This value implies that PDI<sup>-</sup>-pep-Zn<sup>+</sup> lies only  $\sim kT$  below Zn<sup>\*</sup>, which must be the case to observe the delayed component to the Zn\* decay. The modeling also indicates that charge recombination of PDI- $pep-Zn^+$  to directly give the ground state (and perhaps the triplet excited state of the perylene) may have a rate constant  $k_5 \sim (50 \text{ ns})^{-1}$ . However, given the observed lack of decay of the charge-transfer product over the 3.5 ns span of the transient absorption measurements, a more conservatively estimate of  $k_5$ < (10 ns)<sup>-1</sup> is more appropriate. For PDI-pep-Zn in acetonitrile, the same primary decay processes of Zn\* are operable, although the rates and yields differ. The most notable of these is that the decay of PDI<sup>-</sup>-pep-Zn<sup>+</sup> is measured to be much faster than in toluene (Table 3). Additionally, thermal repopulation of Zn\* from PDI<sup>-</sup>-pep-Zn<sup>+</sup> is negligible ( $k_{-3} \ll k_3$ ), and  $k_3$  is estimated simply from the lifetime and fluorescence data (Table 3).

Collectively, these results and considerations lead to a selfconsistent description of the primary excited-state processes in the PDI-pep-Zn dyad, as summarized in Figure 3 and Tables 2 and 3. The dynamics are dominated by energy transfer from the photoexcited perylene diimide to the zinc porphyrin (80% yield) on the time scale of a few picoseconds and subsequent electron-transfer back from the excited porphyrin to the perylene (80% yield) on the time scale of several hundred picoseconds.

**Mechanisms of Energy and Electron Transfer.** We have carried out extensive studies of excited-state energy transfer between porphyrins joined by the same diphenylethyne linker used in the perylene–porphyrin dyad PDI–pep–Zn.<sup>37–40</sup> One example is Zn–pep–Fb (previously denoted ZnFbU), which contains zinc and free base porphyrins (Chart 2). We found that porphyrin–porphyrin energy transfer in this architecture is dominated by a through-bond (TB) mechanism, with only a

minimal contribution of the Förster through-space (TS) process. The empirical evidence for this assessment includes the dependence of the rate on factors such as porphyrin orbital characteristics and porphyrin-linker torsional constraints that primarily modulate the linker-mediated inter-porphyrin electronic coupling. Additionally, the calculated Förster rates are far slower than the measured values. For example, the measured rate of energy transfer from Zn\* to Fb in the Zn-pep-Fb dyad is  $(24 \text{ ps})^{-1}$ , which is ~30-fold faster than the calculated Förster rate of  $\sim$ (750 ps)<sup>-1</sup> (Table 4).<sup>37</sup> The measured rate is even faster for energy transfer from Zn\* to Mg in the analogous dyad Zn $pep-Mg (9 ps)^{-1}$  even though the calculated Förster rate is slower than for Zn-pep-Fb because of poorer spectral overlap (Table 4). Indeed, faster energy transfer in Zn-pep-Mg versus Zn-pep-Fb can be traced largely to enhanced TB coupling derived from the differences in the electron density in the molecular orbitals at the site of linker attachment in the Mg versus Fb porphyrin acceptor.<sup>40</sup> A Förster calculation for PDIpep-Zn using the same formalism (Appendix B) gives a TS rate of  $(17 \text{ ps})^{-1}$ , which is 5.5-fold slower than the experimental value of  $(3.1 \text{ ps})^{-1}$  (Tables 3 and 4). This comparison suggests that the TS mechanism makes a modest contribution to the energy transfer from the photoexcited perylene to the porphyrin in PDI-pep-Zn but that the TB mechanism again plays the principal role. This behavior is consistent with that in a related dyad BDPY-pep-Zn, in which energy transfer occurs from a boron-dipyrrin pigment to a zinc porphyrin via a diphenylethyne linker (Chart 2).<sup>4</sup> In the latter dyad, energy transfer occurs with rate constants of  $\sim (20 \text{ ps})^{-1}$  and  $\sim (2 \text{ ps})^{-1}$  (70:30 amplitude ratio) that are associated with two excited states produced by a photoinduced conformational change in the BDPY chromophore, a process that also exists in the isolated dye.<sup>4</sup>

Implications for Use of the PDI-pep-Zn Dyad in Molecular Photonic Devices. Comparison of the results described above for the PDI-pep-Zn and BDPY-pep-Zn dyads delineates several advantages of the perylene-diimide dye versus boron-dipyrrin pigment as a light-input unit in porphyrin-based arrays. These favorable characteristics include faster rates of energy transfer, single-exponential excited-state behavior, and enhanced absorption in the spectral window between the porphyrin Soret and Q bands. A drawback of the PDI-pep-Zn unit is that the yield of energy transfer from PDI\* to the porphyrin is not quite as high (80%) as that which occurs from BDPY\* to the porphyrin in BDPY-pep-Zn (>99%).<sup>4</sup> The ultrafast rate of  $\sim (3 \text{ ps})^{-1}$  for PDI\*-pep-Zn  $\rightarrow$  PDI-pep-Zn\* energy transfer would clearly support the same nearquantitative yield were it not for the competing PDI\*-pep- $Zn \rightarrow PDI^-pep-Zn^+$  hole transfer process, which has a rate of  $\sim (13 \text{ ps})^{-1}$ . Thus, one means of improving the energy-transfer efficiency in this dyad is to decrease the rate of hole-transfer by making the energetics of the latter process less favorable. This can be achieved by altering the redox potentials of the porphyrin as described in the companion paper.

The substantial electron-transfer quenching of Zn\* that occurs once the energy has arrived from PDI\* presents a limitation of PDI-pep-Zn as a light-input element in light-harvesting arrays. This PDI-pep-Zn\*  $\rightarrow$  PDI<sup>-</sup>-pep-Zn<sup>+</sup> quenching process has a yield of 80% and a rate of ~(0.5 ns)<sup>-1</sup>. Thus, for use as a light-input element, the energy-transfer rate from Zn\* to the next constituent in an array would have to be rapid compared with ~(0.5 ns)<sup>-1</sup>. However, as noted above, we have previously found that energy transfer from Zn\* to the Fb porphyrin in Znpep-Fb has a rate of (24 ps)<sup>-1</sup>.<sup>37</sup> Thus, in a hypothetical PDIpep-Zn-pep-Fb triad, energy transfer would be the preferable

TABLE 4: Calculated Förster Energy-Transfer Rate for Several Porphyrin-Containing Dyads<sup>a</sup>

| dyad                   | R (Å) <sup>b</sup> | $\kappa^2$ | $\Phi_{\mathrm{f}}{}^{c}$ | $\tau$ (ns) <sup>c</sup> | $J (\mathrm{cm}^6\mathrm{mmol}^{-1})^d$ | $(k_{\rm ENT}^{\rm calc})^{-1}  ({\rm ps})^e$ | $(k_{ENT})^{-1} (ps)^f$ | $\Phi_{	ext{ENT}}{}^{g}$ |
|------------------------|--------------------|------------|---------------------------|--------------------------|---|---|-------------------------|--------------------------|
| PDI-pep-Zn             | 21.1               | 2          | 0.96                      | 3.7                      | $5.8 \times 10^{-14}$                   | 17  | 3.1                     | $0.80^{h}$               |
| BDPY-pep-Zn            | 18                 | 0.25       | 0.058                     | 0.52                     | $1.3 \times 10^{-13}$                   | 53  | 20/2*                   | 0.98                     |
| BDPY-pep-Fb            | 18                 | 0.25       | 0.058                     | 0.52                     | $7.0 \times 10^{-14}$                   | 99  | 20/2*                   | 0.95                     |
| Zn-pep-Fb <sup>i</sup> | 20.1               | 1.125      | 0.033                     | 2.4                      | $2.9 \times 10^{-14}$                   | 745   | 24                      | 0.99                     |
| $Zn-pep-Mg^k$          | 20.1               | 1.125      | 0.033                     | 2.4                      | $1.6 \times 10^{-14}$                   |   | 9                       | 0.99                     |

<sup>*a*</sup> All data were obtained in toluene at room temperature. <sup>*b*</sup> Center-to-center distance. The distance in PDI-pep–Zn was estimated at 21.1 Å using Discover 3 in INSIGHT II from Molecular Simulations, Inc. <sup>*c*</sup> Fluorescence yield and excited-state lifetime for the energy-transfer donor in the absence of the acceptor (e.g., Figure 1). <sup>*d*</sup> The Förster spectral overlap term (*J*) was computed using selected monomers which best approximate those units in the dyad. The extinction coefficients used for PDI-pep–Zn are as follows: ZnU', 490 nm (350 M<sup>-1</sup> cm<sup>-1</sup>), 423 nm (468 000 M<sup>-1</sup> cm<sup>-1</sup>); PDI-m, 490 nm (43 900 M<sup>-1</sup> cm<sup>-1</sup>), 423 nm (3300 M<sup>-1</sup> cm<sup>-1</sup>). <sup>*e*</sup> Calculated Förster rate. <sup>*f*</sup> Measured rate. <sup>*g*</sup> Measured yield. <sup>*h*</sup> The energy-transfer yield for PDI-pep–Zn is reduced from >0.99 to 0.80 because of competition with ultrafast hole transfer to the porphyrin (see Figure 3 and text). <sup>*i*</sup> These complexes exhibit dual-exponential behavior with time constants of ~20 and ~2 ps with 70:30 relative amplitudes (see text). <sup>*i*</sup> Complex was previously denoted ZnFbU.<sup>37</sup> <sup>*k*</sup> Complex was previously denoted MgZnU.<sup>40</sup>

pathway (99.5% yield) if it were in competition with electron transfer (rate  $\sim (0.5 \text{ ns})^{-1}$ ). The yield of energy transfer would be even higher (than in PDI–pep–Zn–pep–Fb) if the Fb porphyrin output element were replaced with a magnesium porphyrin or a phthalocyanine, which exhibit energy-transfer rates from the neighboring Zn\* of  $\sim$ (9 ps)<sup>-1</sup> and  $\sim$ (3 ps)<sup>-1</sup>, respectively.<sup>40,41</sup> Thus, the electron-transfer quenching that occurs following formation of Zn\* from PDI\* could be circumvented by appropriate molecular design. We have recently utilized these ideas, together with the insights gained from the results given in the two other papers in this series on perylene–porphyrin dyads,<sup>23,24</sup> to prepare a perylene-bis(porphyrin)– phthalocyanine wire that exhibits enhanced energy-transfer properties relative to our first-generation wires.<sup>22</sup>

For applications such as molecular switching, the high yield of electron transfer that occurs from Zn\* to the perylene component of PDI-pep-Zn can be exploited. The use of perylene-based dyes as electron acceptors when attached to porphyrins has been explored previously but with different linkers connected to the N-imide position of the perylene unit than the diphenylethyne linker used in PDI-pep-Zn.<sup>15,21,25</sup> One example is the phenyl-linked dyad PDI-p-Fb in which electron transfer from Fb\* to the perylene occurs with a rate constant of  $\sim (10 \text{ ps})^{-1}$  in pyridine, followed by charge recombination to the ground state with a time constant of  $\sim (120 \text{ ps})^{-1.15}$  It is noteworthy that the forward electron-transfer and chargerecombination rates initiated in Fb\* in PDI-p-Fb are both faster than the values of  $\sim (500 \text{ ps})^{-1}$  and  $< (10 \text{ ns})^{-1}$  observed for PDI-pep-Zn in toluene. This difference can be ascribed predominantly to greater perylene-porphyrin electronic coupling via the phenyl (p) versus diphenylethyne (pep) linker. (Along the same lines, we have found that excited-state energy transfer from Zn to Fb porphyrins is also faster across a phenyl versus diphenylethyne linker:  $(3.5 \text{ ps})^{-1}$  versus  $(24 \text{ ps})^{-1}$ , respectively.42) We have also found that the charge recombination in PDI<sup>-</sup>-pep-Zn<sup>+</sup> is enhanced in polar solvents such as acetonitrile; this effect no doubt reflects a more favorable balance between the free-energy change for the process (smaller) and the reorganization energy (larger) than in toluene, as is discussed in more detail in the companion paper that follows. The availability of perylene-porphyrin dyads with tunable rates of formation and decay of the electron-transfer product is potentially useful for applications involving molecular switching.

Finally, we note that in order to design molecular devices for applications in which it is desirable to either optimize or minimize charge-transfer processes, it is essential to have a firm understanding of the rate versus free-energy relationship for the charge-transfer processes. It is also highly desirable to have direct experimental information on the absolute energies of all of the species involved, including the charge-separated products. The observation of delayed fluorescence from Zn\* in PDI– pep–Zn (in toluene), which occurs via thermal repopulation of the excited state from the PDI–pep–Zn<sup>+</sup> charge-transfer product, indicates that the energy of this latter species lies  $\sim kT$ (0.026 eV at 298 K) below Zn\* (Figure 3, vide supra). This information along with the absolute energies of the PDI\* and Zn\* excited states (as indicated by the static absorption and emission properties of these constituents) provides a starting point for a detailed analysis of the charge-transfer behavior of the perylene-porphyrin dyads. In the accompanying paper,<sup>23</sup> the data for the benchmark PDI–pep–Zn dyad are used along with those for analogous arrays containing Mg and Fb porphyrins to construct a complete and fully self-consistent picture of the excited-state properties of this class of dyads.

## **Experimental Section**

**General.** <sup>1</sup>H NMR spectra were collected at 300 MHz. Products were analyzed by fast-atom bombardment (FAB) or by laser desorption mass spectrometry (LD-MS) in the absence of a matrix.<sup>43</sup> All reagents were obtained from Aldrich Chemical Co., and all solvents were obtained from Fisher Scientific.

N-(2,5-Di-tert-butylphenyl)-3,4,9,10-pervlenetetracarboxylic-3,4-anhydride-9,10-imide (1). Following a slight modification of method II described by Kaiser et al.,16 N,N'-bis(2,5di-tert-butylphenyl)-3,4,9,10-perylenebis(dicarboximide)<sup>5</sup> (4.0 g, 5.2 mmol) was suspended in 100 mL of tert-butyl alcohol. Powdered KOH (80%, 1 g) was added, and the mixture was refluxed with vigorous stirring for 2 h. After cooling to room temperature, the reaction mixture was treated with a mixture of HCl (50 mL, 2 M) and glacial acetic acid (100 mL) with vigorous stirring. The resulting mixture was refluxed for 1 h, cooled, and filtered. The residue obtained was suspended in 100 mL of 10% K<sub>2</sub>CO<sub>3</sub> and refluxed for 0.5 h and then filtered using a frittered-glass funnel under vacuum to separate the soluble monopotassium salt of 3,4,9,10-perylenetetracarboxylic acid. (Note: The residue should not be washed with water). The residue obtained was washed twice with 10% K<sub>2</sub>CO<sub>3</sub> solution. The funnel was then filled with 2% HCl, kept for 0.5 h and filtered. This process was repeated twice. The residue was then washed with distilled water until the washings were neutral and then suspended in 10% triethylamine in water (50 mL) and refluxed for 0.5 h. The mixture was filtered to separate the insoluble residue of unreacted starting material. The filtrate was acidified with a minimum amount of 10% HCl, and the product was separated by filtration (0.45 g, 15%).

*N*-(4-Iodophenyl)-*N*'-(2,5-di-*tert*-butylphenyl)-3,4,9,10perylenebis(dicarboximide) (2). A mixture of 1 (0.45 g, 0.78 mmol), *p*-iodoaniline (0.42 g, 2.0 mmol), imidazole (2.5 g), and anhydrous zinc acetate (0.15 g) was stirred in an oil bath at

130 °C for 1 h. The mixture was allowed to cool to room temperature, and 25 mL of 60% ethanol was added, stirred at room temperature for 2 h, and filtered. The residue was treated with 25 mL of 10% aqueous triethylamine, and the resulting mixture was refluxed. After cooling, the suspension was filtered and the residue was washed several times with 60% ethanol, then with ethanol, and finally with hexanes. The solid product obtained was dried in an oven and chromatographed over silica gel (CH<sub>2</sub>Cl<sub>2</sub>) to yield 0.45 g (84%) of the pure product: mp >270 °C; IR (KBr) 1708, 1670 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.30 (s, 9 H), 1.334 (s, 9 H), 7.084 (d, J = 2 Hz, 1H), 7.137 (d, J =8 Hz, 2 H), 7.488 (dd,  $J_{AX} = 2$  Hz,  $J_{AM} = 8$  Hz, 1 H, AMX), 7.615 (d, J = 8 Hz, 1 H, AMX), 7.915 (d, J = 8 Hz, 2 H), 8.644-8.790 (m, 8 H); FAB-MS obsd 781.1587, calcd exact mass 781.1563 (C<sub>44</sub>H<sub>33</sub>N<sub>2</sub>O<sub>4</sub>I);  $\lambda_{abs}$  (toluene) 432, 460, 491, 528 nm. Alternatively, a mixture of perylene-3,4,9,10-tetracarboxylic dianhydride (1 equiv), 2,5-di-tert-butylaniline (3 equiv), piodoaniline (2 equiv), zinc acetate, and imidazole was heated under nitrogen at 180-190 °C for 2 h. The reaction mixture was cooled to room temperature, diluted with 60% ethanol and allowed to stand for 2 h. The resulting precipitate was collected by filtration and washed with ethanol and then suspended in 10% KOH solution, refluxed, and filtered. The residue was taken up in CH<sub>2</sub>Cl<sub>2</sub>, and the insoluble diimide was separated by filtration. The filtrate was concentrated and chromatographed over silica gel. The product was collected as the second fraction (2% overall yield).

Perylenediimide-Diphenylethyne-Zinc Porphyrin Dyad (PDI-pep-Zn). Following a method for porphyrin-porphyrin coupling reactions,<sup>26</sup> samples of 2 (0.021 g, 0.031 mmol, 2.5 mM), ZnU' (0.028 g, 0.03 mmol, 2.5 mM), 26 Pd2dba3 (0.004 g, 4.4  $\mu$ mol, 15 mol %), and tri-o-tolylphosphine (0.011 g, 0.036 mmol, 4:1 per mol Pd) were weighed into a 50 mL Schlenk flask. The reaction vessel was purged with Ar and then 13 mL of distilled and degassed toluene/triethylamine (5:1) was added under inert conditions. The reaction mixture was heated to 35 °C and stirred for 1 h. The crude reaction mixture was filtered through Celite, rotary evaporated to dryness, chromatographed on silica (CH<sub>2</sub>Cl<sub>2</sub>/hexanes, 3:1), chromatographed by SEC (THF), and recrystallized (ethanol) to afford a purple solid (0.025 g, 57%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.32 (s, 9 H), 1.36 (s, 9 H), 1.56 (s, 18 H), 2.65 (s, 9 H), 7.05 (d, 1 H), 7.28-7.29 (6 H), 7.46 (d, J = 8 Hz, 2 H), 7.50 (dd, 1 H), 7.63 (d, J = 8 Hz, 1 H), 7.90 (d, J = 8 Hz, 2 H), 7.97 (d, J = 8 Hz, 2 H), 8.26 (d, J = 8 Hz, 2 H), 8.77-8.91 (m, 8 H); FAB-MS obsd 1480.8, calcd exact mass 1478.5 (C<sub>99</sub>H<sub>78</sub>N<sub>6</sub>O<sub>4</sub>Zn);  $\lambda_{abs}$  (toluene) 424, 460, 492, 528, 548 (s), 589 nm.

**Electrochemistry.** The electrochemical studies were performed in butyronitrile (Burdick and Jackson) using previously described instrumentation.<sup>38</sup> The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate (Aldrich; recrystallized three times from methanol and dried at 110 °C in vacuo). The electrochemical cell was housed in a Vacuum Atmospheres glovebox (Model HE-93) equipped with a Dri-Train (Model 493).

Static Absorption and Emission. Static absorption (HP8451A, Cary 3 and 219) and fluorescence (Spex Fluoromax or Fluorolog II) measurements were performed as described previously.<sup>41,42</sup> Nondeaerated samples with an absorbance  $\leq 0.15$  at  $\lambda_{exc}$  (0.3–0.8  $\mu$ M) were used for the key emission measurements, although more concentrated samples were investigated; the detection band pass was 4–5 nm, and the spectra were corrected for the detection-system spectral response. Emission quantum yields

were measured relative to the appropriate reference monomer (ZnTPP and  $H_{2}TPP).^{44}$ 

**Time-Resolved Fluorescence.** Fluorescence lifetimes were obtained on samples that had concentrations of  $0.5-10 \,\mu$ M and were deaerated by bubbling with N<sub>2</sub>. Lifetimes were determined by fluorescence modulation (phase shift) techniques using a Spex  $\tau$ 2 spectrometer. Samples were excited at various wavelengths and detected through using the appropriate colored glass filters. Modulation frequencies from 20 to 300 MHz were utilized, and both the fluorescence phase shift and modulation amplitude were analyzed.

**Time-Resolved Absorption.** Transient absorption data were acquired as follows.<sup>41,42</sup> Samples ( $\sim 10 \,\mu$ M in toluene) in 2 mm path length cuvettes at room temperature were excited at 10 Hz with  $\sim 130$  fs,  $4-7 \,\mu$ J pulses at the appropriate wavelength and probed with white-light probe pulses of comparable duration.

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# Appendix A. Kinetic Model for Equilibrium Involving the Zn\* Excited State

The following expression describes the time evolution of the concentration of the photoexcited zinc porphyrin ( $Zn^*$ ) in the equilibrium kinetic model of Figure 3:

$$[Zn^*](t) = A \exp\left[-\frac{1}{2}(a+b)t\right] + B \exp\left[-\frac{1}{2}(a-b)t\right]$$
(1)

$$A = \frac{1}{2b}(-2b_{0}k_{-3} + a_{0}k_{3} - k_{-3} - k_{5} + k_{4} + b) \quad (2a)$$

$$B = \frac{1}{2b}(2b_{0}k_{-3} - a_{0}k_{3} + k_{-3} + k_{5} - k_{4} + b)$$
 (2b)

$$a = k_3 + k_{-3} + k_4 + k_5 \tag{3a}$$

$$b = \sqrt{(k_3 + k_{-3} + k_4 + k_5)^2 - 4[k_3k_5 + (k_{-3} + k_5)k_4]}$$
(3b)

$$a_{o} = [Zn^*](0) \tag{4a}$$

$$b_{o} = [PDI^{-}-pep-Zn^{+}](0)$$
 (4b)

The observed dual exponential fluorescence Zn\* decay with components having time constants of 0.4 and 10 ns comprising 80 and 20% of the decay, respectively, gives

$$[\text{Zn}^*](t) = 0.8 \exp[-(0.4 \text{ ns})^{-1}t] + 0.2 \exp[-(10 \text{ ns})^{-1}t]$$
(5)

Equating eqs A1 and A2 affords  $(a + b) = (0.2 \text{ ns})^{-1}$ ,  $(a - b) = (5 \text{ ns})^{-1}$ , A = 0.8, and B = 0.2. The relative yields of Zn<sup>\*</sup> and PDI<sup>-</sup>-pep-Zn<sup>+</sup> from PDI<sup>\*</sup> determined from the transient absorption data gives  $a_0 = 0.8$  and  $b_0 = 0.2$ . The Zn<sup>\*</sup> lifetime in the ZnU' monomer affords  $k_4 = (2.4 \text{ ns})^{-1}$ .

A consistent set of results is given by  $k_3 \sim (0.5 \text{ ns})^{-1}$ ,  $k_{-3} \sim (1.6 \text{ ns})^{-1}$ , and  $k_5 \sim (50 \text{ ns})^{-1}$ . The value of  $k_3$  is slightly longer than the measured 0.4 ns Zn\* fluorescence-decay component, as expected from the equilibrium involved. The values of  $k_{-3}$ 

and  $k_3$  together suggest that PDI<sup>-</sup>-pep-Zn<sup>+</sup> lies ~1.2kT below Zn\*, which is consistent with the finding of a measurable delayed fluorescence component. The value of  $k_5$  is consistent with the finding of essentially no decay of PDI<sup>-</sup>-pep-Zn<sup>+</sup> over the 3.5 ns time scale of the experiments. However, given the time span of the measurements, it is more appropriate to use an upper limit  $k_5 < (10 \text{ ns})^{-1}$ .

#### **Appendix B. Förster Calculations**

The Förster rate is calculated using the standard formulation based on the point dipole-dipole approximation (eq B1), using the program PhotochemCAD.45

$$k_{\text{Förster}} = (8.8 \times 10^{23}) \kappa^2 \Phi_{\text{f}}^{\text{m}} J n^{-4} R^{-6} (\tau^{\text{m}})^{-1} \qquad (B1)$$

Here,  $\kappa^2$  is the orientation factor (obtained by dynamic averaging about the pigment-linker bonds),  $\Phi_f^m$  is the fluorescence yield of the donor in the absence of the acceptor, J is the spectral overlap term (in cm<sup>6</sup> mmol<sup>-1</sup>) obtained from the optical spectra of the monomers, n is the refractive index (1.496 for toluene),  $R^6$  is the donor-acceptor center-to-center distance (in Å) obtained from molecular modeling, and  $\tau^{m}$  is the lifetime of the donor in the absence of the acceptor. For other Förster calculations of perylene-bis(imide) dyes, see ref 46.

#### **References and Notes**

(1) Wagner, R. W.; Lindsey, J. S. Pure Appl. Chem. 1996, 68, 1373-1380.

(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) Li, F.; Yang, S. I.; Ciringh, Y.; Seth, J.; Martin, C. H., III; Singh, D. L.; Kim, D.; Birge, R. R.; Bocian, D. F.; Holten, D.; Lindsey, J. S. J. Am. Chem. Soc. 1998, 120, 10001-10017.

(5) Langhals, H. Chem. Ber. 1985, 118, 4641-4645.

(6) (a) Rademacher, A.; Märkle, S.; Langhals, H. Chem. Ber. 1982, 115, 2927-2934. (b) Ebeid, E. M.; El-Daly, S. A.; Langhals, H. J. Phys. Chem. 1988, 92, 4565-4568.

(7) Ford, W. E.; Kamat, P. V. J. Phys. Chem. 1987, 91, 6373-6380. (8) (a) Demmig, S.; Langhals, H. Chem. Ber. 1988, 121, 225-230.

(b) Feiler, L.; Langhals, H.; Polborn, K. Liebigs. Ann. 1995, 1229-1244. (9) Cormier, R. A.; Gregg, B. A. Chem. Mater. 1998, 10, 1309-1319.

(10) Langhals, H.; Demmig, S.; Huber, H. Spectrochim. Acta 1988, 44A, 1189 - 1193

(11) Zollinger, H. Color Chemistry: Syntheses, Properties, and Applications of Organic Dyes and Pigments; VCH: Weinheim, Germany, 1991.

(12) Kerp, H. R.; Donker, H.; Koehorst, R. B. M.; Schaafsma, T. J.; van Faassen, E. E. Chem. Phys. Lett. 1998, 298, 302-308.

(13) Tian, H.; Liu, P.-H.; Zhu, W.; Gao, E.; Wu, D.-J.; Cai, S. J. Mater. Chem. 2000, 10, 2708–2715.

(14) (a) Gregg, B. A. Chem. Phys. Lett. 1996, 258, 376-380. (b) Petritsch, K.; Dittmer, J. J.; Marseglia, E. A.; Friend, R. H.; Lux, A.; Rozenberg, G. G.; Moratti, S. C.; Holmes, A. B. Sol. Energy Mater. Sol. Cells 2000, 61, 63-72.

(15) O'Neil, M. P.; Niemczyk, M. P.; Svec, W. A.; Gosztola, D.; Gaines, G. L., III; Wasielewski, M. R. Science 1992, 257, 63-65.

(16) Kaiser, H.; Lindner, J.; Langhals, H. Chem. Ber. 1991, 124, 529-535

(17) (a) Langhals, H.; Gold, J. J. Prakt. Chem. 1996, 338, 654-659. (b) Langhals, H.; Gold, J. Liebigs Ann. 1997, 1151-1153. (c) Langhals,

H.; Jona, W. Angew. Chem. 1998, 37, 952-955.

(18) Würthner, F.; Sautter, A. Chem. Commun. 2000, 445-446.

(19) Liu, S.-G.; Liu, Y.-Q.; Xu, Y.; Jiang, X.-Z.; Zhu, D.-B. Tetrahedron Lett. 1998, 39, 4271-4274.

(20) Wasielewski, M. R.; Gosztola, D.; Svec, W. A. Mol. Cryst. Liq. Cryst. 1994, 253, 289-296.

(21) Just, E. M.; Wasielewski, M. R. Superlattices Microstr. 2000, 28, 317 - 328.

(22) Miller, M. A.; Lammi, R. K.; Prathapan, S.; Holten, D.; Lindsey, J. S. J. Org. Chem. 2000, 65, 6634-6649.

(23) Yang, S. I.; Prathapan, S.; Miller, M. A.; Seth, J.; Bocian, D. F.; Lindsey, J. S.; Holten, D. J. Phys. Chem. B 2001, 105, 8249.

(24) (a) Yang, S. I.; Lammi, R. K.; Prathapan, S.; Miller, M. A.; Seth,

J.; Diers, J. R.; Bocian, D. F.; Lindsey, J. S.; Holten, D. J. Mater. Chem.,

in press. (b) Yang, S. I.; Prathapan, S.; Miller, M. A.; Seth, J.; Diers, J. R.; Bocian, D. F.; Lindsey, J. S.; Holten, D. Manuscript in preparation.

(25) Gosztola, D.; Niemczyk, M. P.; Wasielewski, M. R. J. Am. Chem. Soc. 1998, 120, 5118-5119.

(26) Wagner, R. W.; Johnson, T. E.; Li, F.; Lindsey, J. S. J. Org. Chem. 1995. 60. 5266-5273

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

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

(29) Langhals, H. Heterocycles 1995, 40, 477-500.

(30) Nagao, Y.; Misono, T. Bull. Chem. Soc. Jpn. 1981, 54, 1191-1194.

(31) Nagao, Y.; Misono, T. Dye Pigments 1984, 5, 171-188.

(32) Salbeck, J.; Kunkely, H.; Langhals, H.; Saalfrank, R. W.; Daub, J. Chimia 1989, 43, 6-9.

(33) Ford, W. E.; Hiratsuka, H.; Kamat, P. V. J. Phys. Chem. 1989, 93, 6692-6696.

(34) Felton, R. H. In The Porphyrins; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. V, pp 53-126.

(35) Yang, S. I.; Seth, J.; Strachan, J.-P.; Gentemann, S.; Kim, D.; Holten, D.; Lindsey, J. S.; Bocian, D. F. J. Porphyrins Phthalocyanines 1999, 3, 117-147.

(36) One calculation of  $k_3$  in Figure 3 based on the Zn\* lifetime in the dyad and the yield of PDI<sup>-</sup>-pep- $Zn^+$  gives 0.8/(0.4 ns) ~ (0.5 ns)<sup>-1</sup>. The same value is obtained solely from the Zn\* lifetime in the dyad versus the monomer of  $k_3 = (\tau)^{-1} - (\tau^m)^{-1} = (0.4 \text{ ns})^{-1} - (2.4 \text{ ns})^{-1} \sim (0.5 \text{ ns})^{-1}$ Last, a value of  $\sim (0.7 \text{ ns})^{-1}$  is estimated from the fluorescence yield and lifetime data via the expression  $k_3 = [(\Phi_f^m/\Phi_f) - 1]/\tau^m$ , using values of  $\Phi_{\rm f}^{\rm m} = 0.033$  and  $\Phi_{\rm f} = 0.008$ . (The latter value is used instead of the measured value of 0.010 because only the prompt component of the fluorescence is relevant to the calculation.) These estimates for  $k_3$  are in good agreement with the value of  $k_3 \sim (0.5 \text{ ns})^{-1}$  obtained from the equilibrium kinetic model for the decay of Zn\* in Figure 3 using the lifetime and yield data (see Appendix A).

(37) Hsiao, J.-S.; Krueger, B. P.; Wagner, R. W.; Johnson, T. E.; 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.

(38) 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. (39) Yang, S. I.; Seth, J.; Balasubramanian, T.; Kim, D.; Lindsey, J. S.;

Holten, D.; Bocian, D. F. J. Am. Chem. Soc. 1999, 121, 4008-4018. (40) Hascoat, P.; Yang, S. I.; Lammi, R. K.; Alley, J.; Bocian, D. F.;

Lindsey, J. S.; Holten, D. Inorg. Chem. 1999, 38, 4849-4853. (41) Yang, S. I.; Li, J.; Cho, H. S.; Kim, D.; Bocian, D. F.; Holten, D.;

Lindsey, J. S. J. Mater. Chem. 2000, 10, 283-296. (42) Yang, S. I.; Lammi, R. K.; Seth, J.; Riggs, J. A.; Arai, T.; Kim,

D.; Bocian, D. F.; Holten, D.; Lindsey, J. S. J. Phys. Chem. 1998, 102, 2, 9426-9436.

(43) (a) Fenyo, D.; Chait, B. T.; Johnson, T. E.; Lindsey, J. S. J. Porphyrins Phthalocyanines 1997, 1, 93-99. (b) Srinivasan, N.; Haney, C. A.; Lindsey, J. S.; Zhang, W.; Chait, B. T. J. Porphyrins Phthalocyanines **1999**, 3, 283-291.

(44) Seybold, P. G.; Gouterman, M. P. J. Mol. Spectrosc. 1969, 31, 1 - 13.

(45) Du, H.; Fuh, R.-C. A.; Li, J.; Corkan, L. A.; Lindsey, J. S. Photochem. Photobiol. 1998, 68, 141-142.

(46) Johansson, L. B.-Å.; Langhals, H. Spectrochim. Acta 1991, 47A, 857-861.