

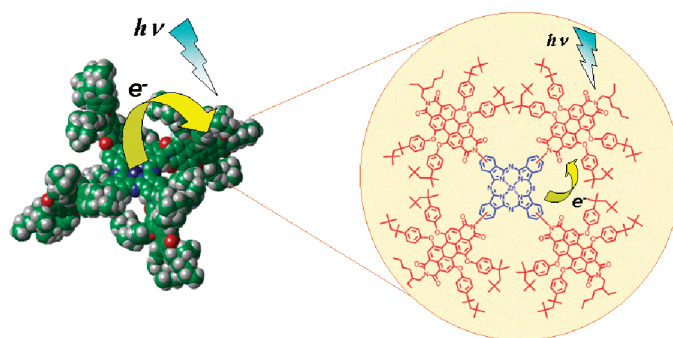
## Synthesis and Photoinduced Electron Transfer of Phthalocyanine–Perylenebisimide Pentameric Arrays

F. Javier Céspedes-Guirao,<sup>†</sup> Kei Ohkubo,<sup>‡</sup> Shunichi Fukuzumi,<sup>\*,‡</sup> Ángela Sastre-Santos,<sup>\*,†</sup> and Fernando Fernández-Lázaro<sup>\*,‡</sup>

<sup>†</sup>División de Química Orgánica, Instituto de Bioingeniería, Universidad Miguel Hernández, Elche 03202, Spain, and <sup>‡</sup>Department of Material and Life Science, Graduate School of Engineering, Osaka University and SORST (JST), 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan

fukuzumi@chem.eng.osaka-u.ac.jp; asastre@umh.es; fdofdez@umh.es

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Zinc phthalocyanine–perylenebisimide pentameric arrays, ZnPc(PDI)<sub>4</sub> **1** and **2**, have been synthesized. ZnPc(PDI)<sub>4</sub> **1** has no substituents in the PDI bay positions, while ZnPc(PDI)<sub>4</sub> **2** presents four phenoxy groups in the bay positions of each perylene. In both cases, the PDI moieties are directly connected to the ZnPc. As a consequence of aggregation, photoexcitation of **1** affords the intermolecular exciplex rather than the charge-separated state. In contrast to **1**, photoexcitation of **2**, which contains sterically demanding substituents in the PDI moieties, affords the charge-separated (CS) state, which was clearly detected by its transient absorption spectrum in femtosecond laser flash photolysis measurements. The CS lifetime was determined to be 26 ps. The addition of Mg(ClO<sub>4</sub>)<sub>2</sub> to a benzonitrile solution of **2** and the photoexcitation affords the long-lived CS state with the lifetime of 480 μs, whereas no such long-lived CS state was formed in the case of **1** under such conditions. The remarkable elongation of the CS lifetime results from the strong binding of Mg<sup>2+</sup> to the PDI<sup>•-</sup> moiety in the CS state.

### Introduction

Photoinduced electron transfer is a key process in photosynthesis<sup>1–3</sup> and has attracted great scientific attention in order to prepare artificial photosynthetic systems, wires for

photonic systems, photovoltaic devices, etc.<sup>4–7</sup> The presence of porphyrins in natural photosynthetic systems has determined their prevalence in the artificial model as electron donors.<sup>6–9</sup> However, phthalocyanines<sup>10</sup> (Pcs) are increasing their presence in such systems due to some special features they display, such as the more enhanced absorptive cross sections at those wavelengths corresponding to maxima of emission in the solar spectrum as compared with porphyrins,

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or the possibility of intense absorption almost in the near-infrared. Moreover, as it has been so many times stated, they are versatile building blocks, which depending on the nature of the central atom can undergo covalent functionalization both in the peripheral and in the axial positions, or even coordinative linkage in the axial positions. Thus, in recent years, Pcs bearing interesting electro- or photoactive species have been reported as light-harvesting systems and charge-transfer complexes.<sup>11</sup> However, few reports described the occurrence of a long-lived charge-separated state based in phthalocyanines, as opposed to porphyrins, due to the presence of a low-lying triplet excited state.<sup>12</sup>

On the other hand, perylenebisimides<sup>13</sup> (PDIs) exhibit a number of unique properties that make them of great interest in many different scientific and technological areas. These compounds, which normally behave as electron acceptors, are therefore interesting chromophores to be covalently

linked to electron-rich systems as porphyrins or phthalocyanines to study their possible electronic interactions. Although much effort has been paid to the study of linked porphyrin–PDI and phthalocyanine–PDI systems,<sup>14–16</sup> there have been only a few systems that afforded long-lived charge-separated states.<sup>16</sup> Phthalocyanine–PDI systems containing multiple PDI units to enhance the light-harvesting efficiency, which afford long-lived charge-separated states, have yet to be reported.

Here we describe the synthesis and photophysics of two different phthalocyanine–PDI pentameric arrays, namely, **1** and **2** (see Figure 1), in which the perylenebisimide moieties are directly connected to the phthalocyanine core. To the best of our knowledge, there is only one example about another Pc–(PDI)<sub>4</sub> system reported by Wasielewski et al. showing fast energy transfer.<sup>15d</sup> In this case, the phthalocyanine moiety bears also imide substituents, which contribute to enhance its electron affinity. This means that all of the subunits of the array are electron acceptors, thus making the electron-transfer process thermodynamically unfavorable, as experimentally observed. Perylene chromophores possess two differentiated sites for easy covalent linking, the nitrogen atoms at the imido functions and the so-called bay positions (locations 1, 6, 7, and 12 of the skeleton). With the aim to achieve long-lived charge-separated states, we have gambled for the substitution at the imido positions. In fact, a recent work compared the photophysics of *N,N'*-(porphyrin)<sub>2</sub>–PDI and 1,7-(porphyrin)<sub>2</sub>–PDI ensembles, showing that both systems have a similar charge separation rate constant, with the charge recombination being much slower in the *N,N'*-disubstituted system, which yields the longer-living charge-separated state.<sup>17</sup>

## Results and Discussion

### Synthesis of Phthalocyanine–Perylenebisimide Arrays.

The synthesis of phthalocyanine–perylenebisimide arrays ZnPc(PDI)<sub>4</sub> **1** and ZnPc(PDI)<sub>4</sub> **2** was accomplished using different strategies. The first approach consisted of the synthesis of a perylene-substituted phthalonitrile derivative, followed by its direct cyclotetramerization using the usual procedures for Pc synthesis.<sup>10</sup> Thus, the new phthalonitrile **3**, bearing a perylenebisimide moiety, was synthesized by condensation of the monoanhydride monoimide perylene derivative **4** with 4-aminophthalonitrile<sup>18</sup> (see Scheme 1). Unfortunately, attempts of cyclization of **3** to obtain ZnPc–(PDI)<sub>4</sub> pentad **1** were unsuccessful, despite of the different conditions investigated. Only decomposition products were obtained, as previously reported by Lindsey,<sup>15b</sup> for a different phthalonitrile–perylenebisimide derivative.

Then, taking into consideration the work previously reported by Hu,<sup>15c</sup> we devised an alternative strategy. This author synthesized different MgPcs bearing four PDI units, which were

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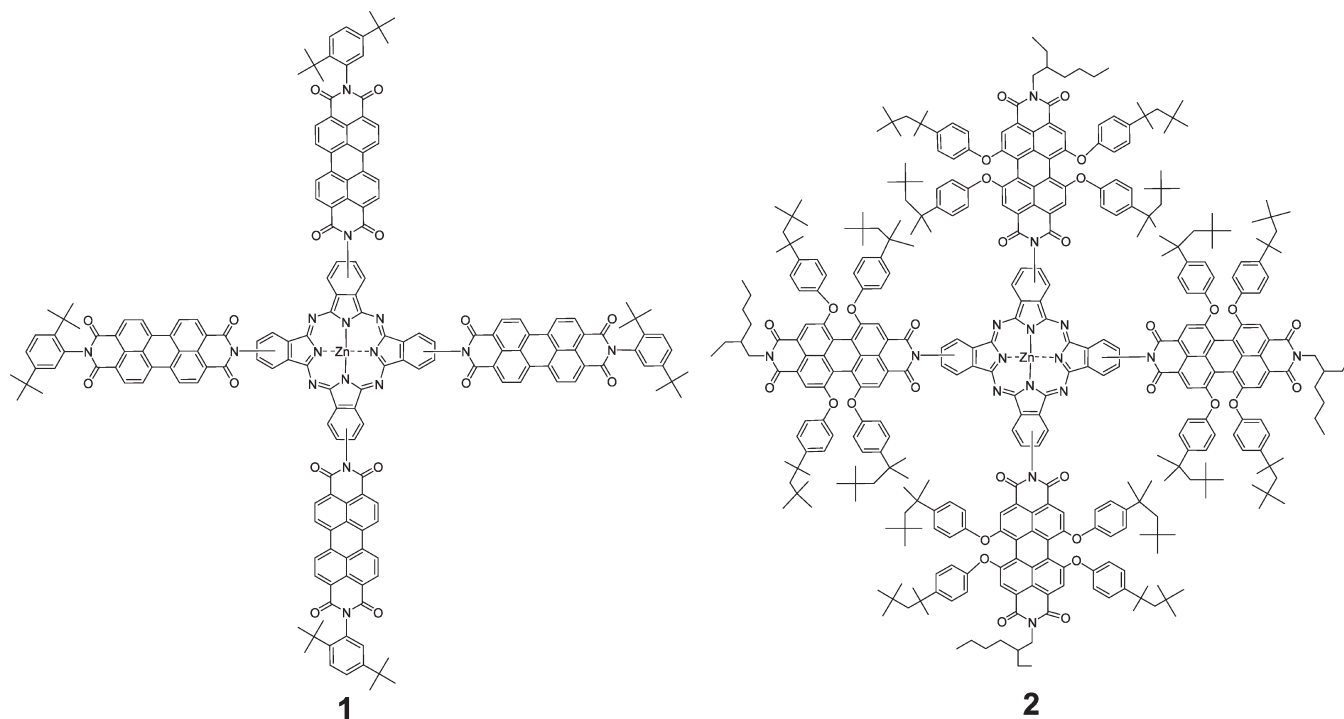
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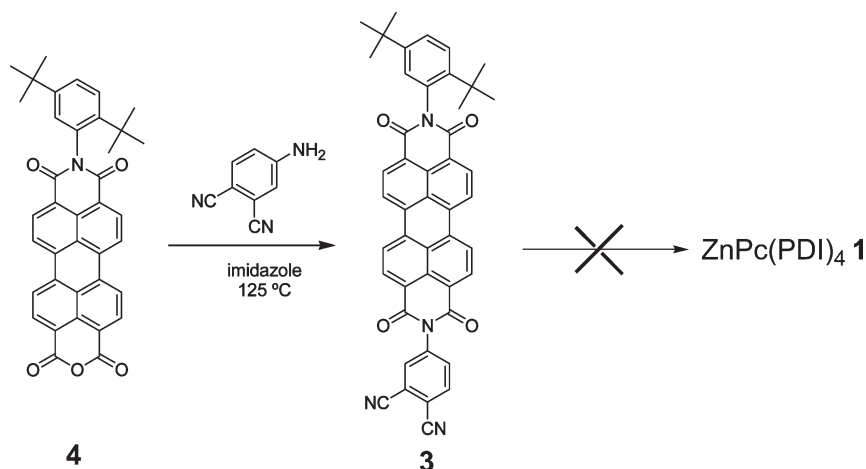
**FIGURE 1.** Chemical structures of ZnPc(PDI)<sub>4</sub> **1** and ZnPc(PDI)<sub>4</sub> **2**.

connected through the imide nitrogen by a flexible linker. So, we decided to synthesize a bisperylenebisimide-substituted phthalonitrile **5** (Scheme 2) where the PDI moieties would be spatially disconnected from the Pc core, in order to avoid electronic interactions in the cyclotetramerization step. Moreover, using a 3,4-disubstituted phthalonitrile, we would obtain an octakisperylenebisimide-substituted phthalocyanine, avoiding the presence of the four regioisomers obtained in the tetrasubstituted ones. The new bisperylenebisimide phthalonitrile **5** was prepared in 50% yield by esterification of the previously reported phthalonitrile **6**<sup>19</sup> with *N*-(2-ethylhexyl)-*N'*-(hydroxyethyl)-1,6,7,12-tetrabromoperylenebisimide **7** (Scheme 2). There are several reasons for the selection of a 1,6,7,12-tetrabromoperylenebisimide. In addition to prevent aggregation, thus improving solubility of the phthalocyanine system, the presence of four bromo atoms in the so-called *bay* position of the PDI makes this system more electron acceptor than the unsubstituted one.

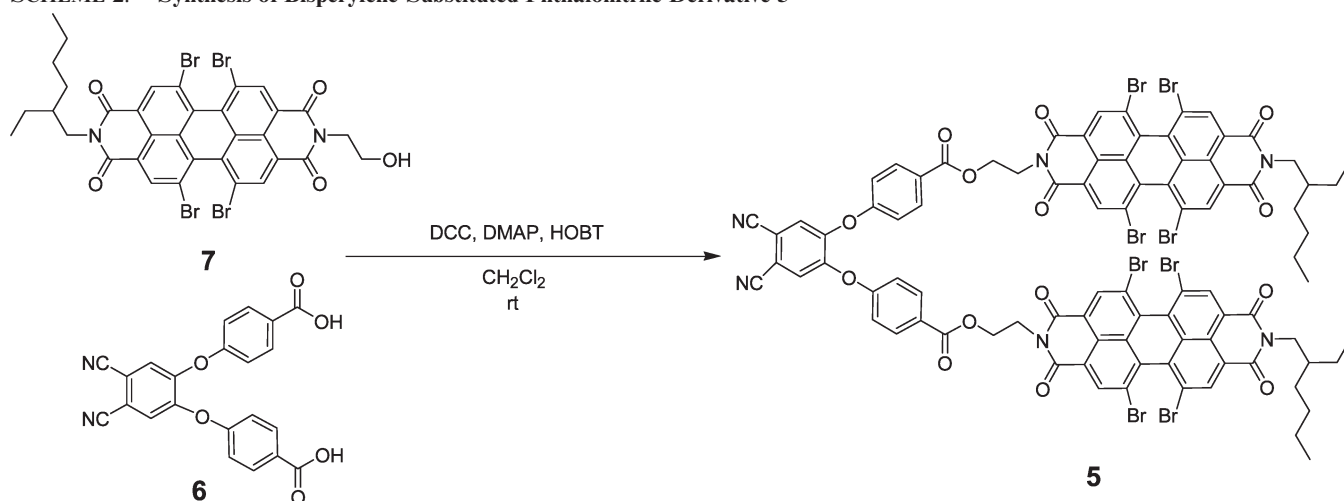
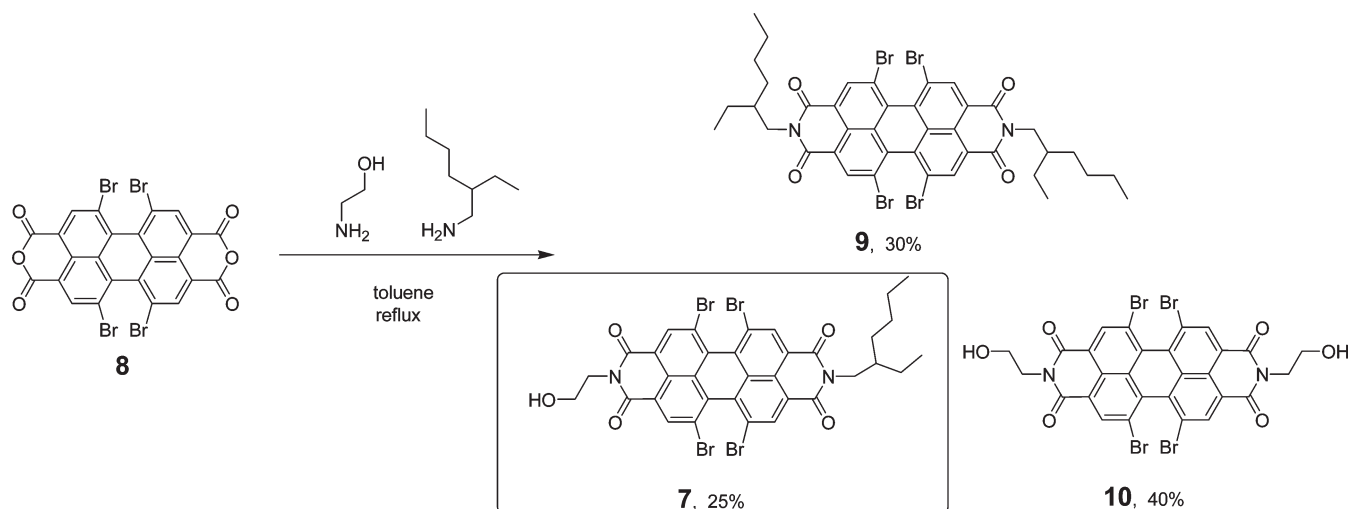
Asymmetric substituted PDI **7** was easily synthesized in 25% yield, in an analogous way to that described for related PDI systems,<sup>20</sup> by the one-step statistical condensation of 2-ethylhexylamine and ethanolamine with 1,6,7,12-tetrabromoperylenebisimide (**8**).<sup>21</sup> The two other condensation products, namely, bisethylhexylperylenebisimide **9** and bishydroxyethylperylenebisimide **10**, were separated from the desired one by column chromatography (Scheme 3). Unfortunately, we were not able to achieve the cyclotetramerization of phthalonitrile **5**, although different reported synthetic procedures for the preparation of Pcs were tried.

We also tried to prepare octakisperylenebisimide-substituted phthalocyanines [ZnPc(PDI)<sub>8</sub>] by esterification of the already known phthalocyanineoctakis-carboxylic acid<sup>22</sup> and *N*-(2-ethylhexyl)-*N'*-(hydroxyethyl)-1,6,7,12-tetrabromoperylenebisimide **7** using different activating agents such

#### SCHEME 1. Synthesis of Perylene-Substituted Phthalonitrile Derivative 3



SCHEME 2. Synthesis of Bisperylene-Substituted Phthalonitrile Derivative 5

SCHEME 3. Synthesis of *N*-(2-Ethylhexyl)-*N'*-(hydroxyethyl)-1,6,7,12-tetrabromoperylenebisimide 7

as thionyl chloride or carbonyldiimidazole. However, this approach was ineffective for the synthesis of ZnPc(PDI)<sub>8</sub> due to the isolation of complex mixtures of phthalocyanine derivatives with different degrees of esterification, which were impossible to separate by column chromatography.

Finally, taking advantage of the high effectivity of the condensation reaction between amino derivatives and perylene-carboxyanhydrides,<sup>16a,16c</sup> we were able to synthesize ZnPc-(PDI)<sub>4</sub> pentads **1** and **2** in 41 and 30% yield, respectively, by reaction of the tetraamino-substituted phthalocyanine **11**<sup>23</sup>

with the corresponding perylene derivatives **4**<sup>24</sup> and **12**<sup>25</sup> (Scheme 4). It is worth mentioning that perylene monoimide **12** with four *tert*-octylphenoxy groups in the so-called bay positions of the perylene moiety precludes  $\pi$ - $\pi$  stacking,<sup>25</sup> giving rise to a much higher solubility in organic solvents of ZnPc(PDI)<sub>4</sub> **2** than ZnPc(PDI)<sub>4</sub> **1**.

All new compounds were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, UV/vis, and IR spectroscopies, mass spectrometry, and elemental analysis (see Experimental Section). The MS spectra (MALDI-TOF) display clusters at  $m/z = 2881$ – $2890$  (ZnPc(PDI)<sub>4</sub> **1**) and  $5844$ – $5854$  (ZnPc(PDI)<sub>4</sub> **2**), which correspond to the theoretically calculated patterns for [M]<sup>+</sup> (see Supporting Information). The FT-IR spectra of compounds **1** and **2** show the typical imido carbonyl bands at  $1705$  and  $1668$  cm<sup>-1</sup>.

It is important to mention that compound **2**, being a mixture of four regioisomers, shows broad signals all over the NMR spectrum, although these are easily assigned (see Supporting Information). This situation is even more complicated for compound **1**, due to its tendency to aggregate, thus precluding the obtention of a useful NMR spectrum.

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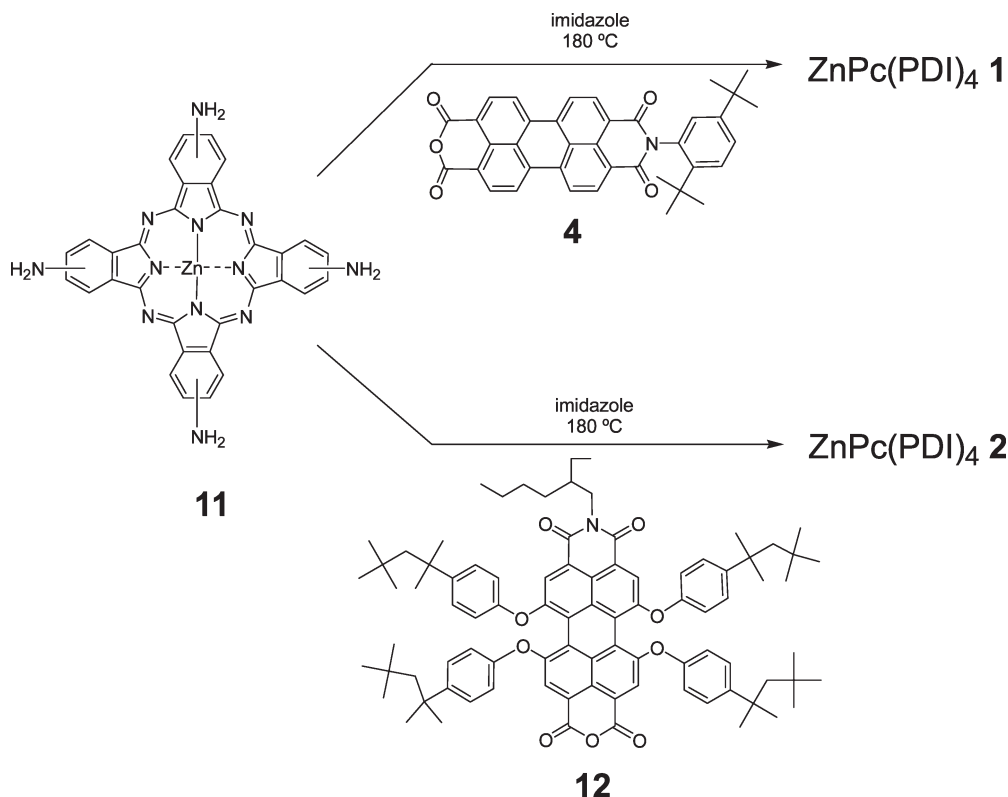
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SCHEME 4. Synthesis of ZnPc(PDI)<sub>4</sub> **1** and ZnPc(PDI)<sub>4</sub> **2**

**Spectroscopic and Redox Properties.** The UV/vis spectra of compounds **1** and **2** show a high absorption in the entire UV/vis region from 300 to 700 nm, or even longer wavelengths for **1** (see Figure 2). In both cases, splitting of the phthalocyanine Q-band at *ca.* 636 and 671 nm (in compound **1**, the latter appears as a shoulder) is observed. The blue shift of the maxima of the Q-bands in **1** and **2**, when compared with that of the tetra-*tert*-butylphthalocyaninato zinc(II) (ZnPc,  $\lambda_{\text{max}} = 680$  nm) (Figure 2), is noteworthy. The broad absorption in the longer wavelength region for the Q-band in **1**, which is absent in **2**, suggests the existence of intermolecular charge-transfer interaction between the ZnPc and PDI moieties in **1**, probably due to aggregation phenomena.<sup>26</sup> Such intermolecular charge-transfer interaction may be absent because of bulky substituents of the PDI moiety in **2**.

It is also interesting to mention that the bands between 400 and 600 nm in compound **2**, which correspond to the perylene chromophore, are red-shifted when compared with the corresponding ones in **1** (see Figure 2). This behavior can be explained in terms of the influence of the four phenoxy groups present in the perylene bay positions (see the spectra for PDI reference compounds **13**<sup>24</sup> and **14**<sup>27</sup> in Figure 3). Moreover, a dramatic change is observed in the ratio of the relative intensities of the PDI absorptions in the 450–550 nm region (0–0/0–1/0–2 peaks) of **1** compared with the corresponding ones of the PDI reference compound, which is

typical of H-type aggregation,<sup>28</sup> the same behavior also noted for compound **2**. From the above-mentioned facts, it is clear that UV/vis spectra for **1** and **2** do not correspond with the simple superimposition of the spectra of a Pc and a PDI, thus strengthening the hypothesis of a ground-state interaction between the moieties.

Cyclic and differential pulse voltammograms of ZnPc(PDI)<sub>4</sub> **1** and ZnPc(PDI)<sub>4</sub> **2** are shown in the Supporting Information. The energies of the charge-separated state, ZnPc<sup>•+</sup>–PDI<sup>•-</sup>, for pentads **1** and **2** are quite similar and are estimated as 1.36 and 1.32 eV, respectively, from the  $E_{\text{ox}}$  value of the ZnPc moiety and the  $E_{\text{red}}$  value of the PDI moiety. It is worth mentioning the cathodic shift of  $E_{\text{ox}}$  (0.55 V vs SCE) and  $E_{\text{red}}$  (–0.77 V vs SCE) values of the ZnPc(PDI)<sub>4</sub> **2** versus  $E_{\text{ox}}$  (0.73 V vs SCE) and  $E_{\text{red}}$  (–0.63 V vs SCE) values of the ZnPc(PDI)<sub>4</sub> **1**, as a consequence of the lower acceptor character of the tetraphenoxy-substituted perylene derivative compared to the unsubstituted one,<sup>13</sup> thus making the ZnPc moiety easier to be oxidized and the PDI moiety more difficult to be reduced in ZnPc(PDI)<sub>4</sub> **2**.

**Calculated Structures.** HOMO and LUMO orbitals of ZnPc(PDI)<sub>4</sub> **1** have been calculated with the optimized structure using a semiempirical method (AM1).<sup>29</sup> The results are shown in Figure 4, indicating that the HOMO orbital is localized on the ZnPc moiety and the LUMO orbital is placed on the PDI moiety. The spin distributions of LUMO+1, LUMO+2, and LUMO+3 are localized on each

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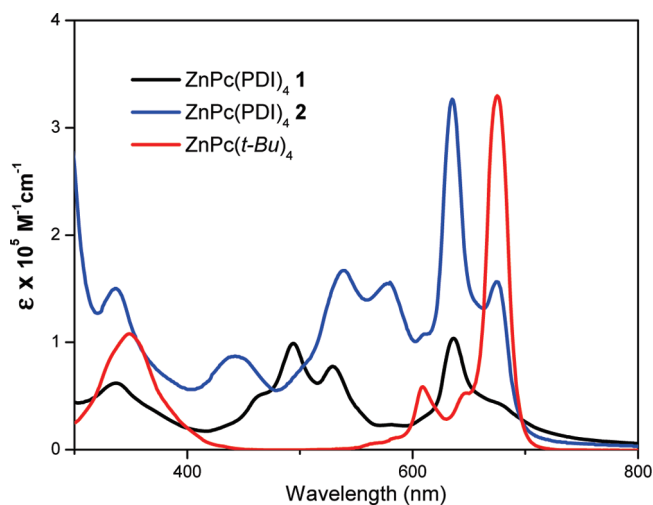


FIGURE 2. UV-vis spectra of **1**, **2**, and ZnPc(*t*-Bu)<sub>4</sub> in DMF.

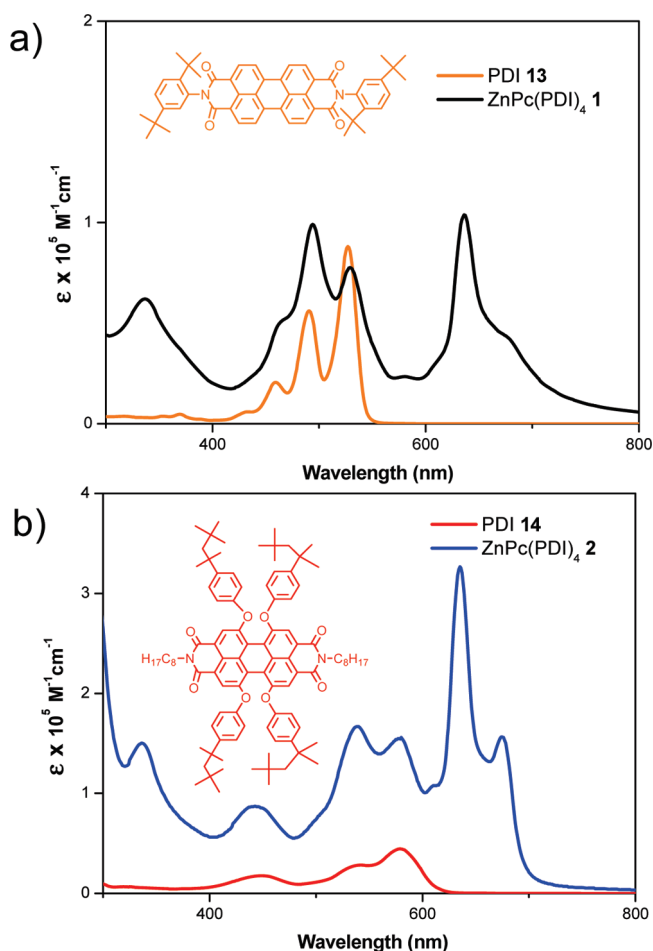


FIGURE 3. (a) UV/vis spectra of ZnPc(PDI)<sub>4</sub> **1** and reference PDI **13** in DMF. (b) UV/vis spectra of ZnPc(PDI)<sub>4</sub> **2** and reference PDI **14** in DMF.

other's PDI moiety. The energy difference between LUMO and LUMO+3 is small (0.26 eV).

The optimized structures of **1** and **2** are compared in Figure 5. In the case of ZnPc(PDI)<sub>4</sub> **1**, the intermolecular charge-transfer interaction may be possible because of the

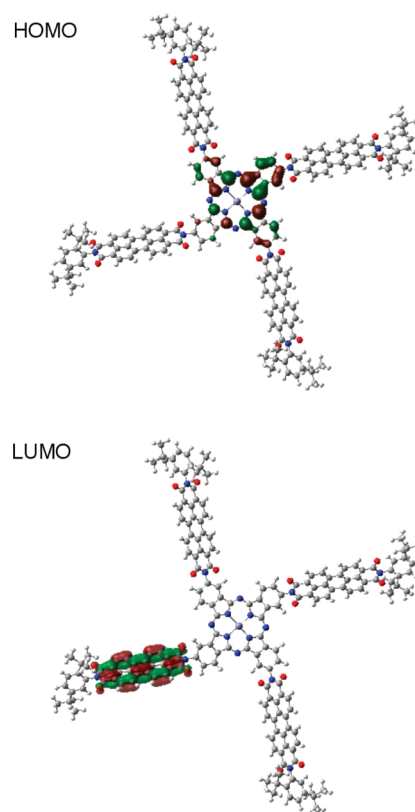


FIGURE 4. HOMO and LUMO orbitals of ZnPc(PDI)<sub>4</sub> **1**, calculated by the AM1 method.

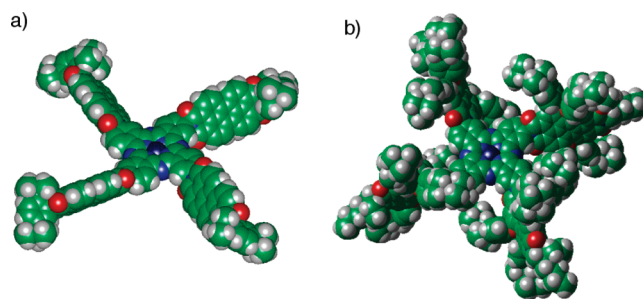
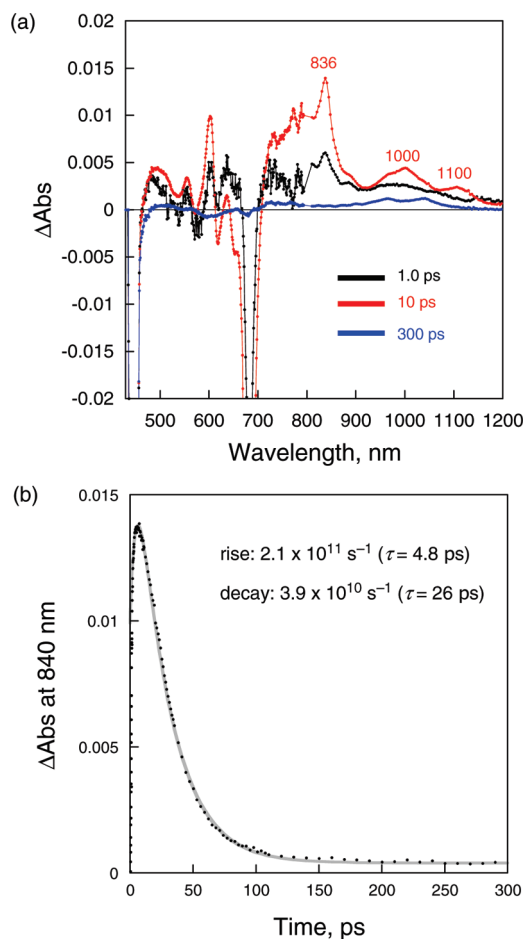


FIGURE 5. Optimized structures of (a) ZnPc(PDI)<sub>4</sub> **1** and (b) ZnPc(PDI)<sub>4</sub> **2**, calculated by the AM1 method.

lack of steric hindrance. In contrast, the bulky substituents of the PDI moiety in ZnPc(PDI)<sub>4</sub> **2** preclude such intermolecular charge-transfer interaction between the ZnPc and the PDI moieties.

**Photoinduced Charge Separation.** The occurrence of photoinduced electron transfer was examined by femtosecond laser flash photolysis measurements. A deaerated PhCN solution containing ZnPc(PDI)<sub>4</sub> **2** gave rise upon a 450 nm femtosecond laser pulse to transient absorption bands at 836, 1000, and 1100 nm with strong bleaching at 690 nm, as shown in Figure 6a. The strong bleaching at 690 nm is ascribed to the fluorescence and absorption of the ZnPc moiety. The absorption band at 836 nm is assigned to ZnPc<sup>•+</sup> by comparison with those of ZnPc<sup>•+</sup> produced by the electron-transfer oxidation of ZnPc(PDI)<sub>4</sub> **2** with [Fe(bpy)<sub>3</sub>]<sup>3+</sup> ( $\lambda_{\max} = 834$  nm) (see Figure 7). The absorption bands in the NIR region between 1000 and 1100 nm are

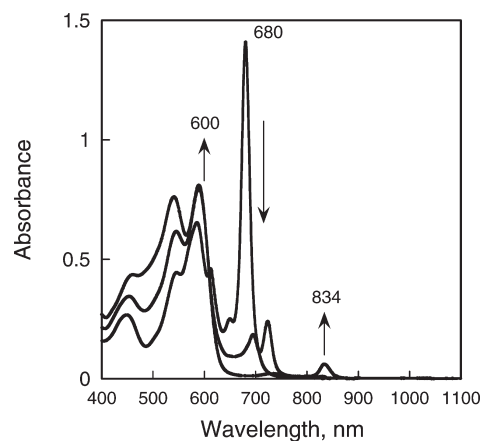


**FIGURE 6.** (a) Transient absorption spectra of  $\text{ZnPc(PDI)}_4 \mathbf{2}$  ( $1.0 \times 10^{-5}$  M) in deaerated PhCN at 298 K after laser excitation at 450 nm. (b) Time profile at 840 nm. Gray curve represents the best fit to the two-exponential rise and decay.

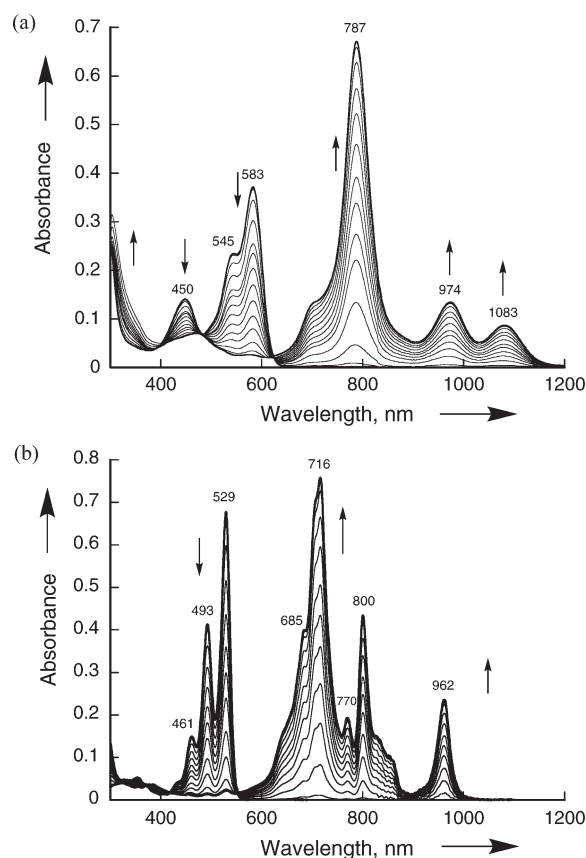
assigned to  $\text{PDI}^{\bullet-}$  by comparison with those due to  $\text{PDI}^{\bullet-}$  produced by the electrochemical reduction of the reference compound **PDI 14** (Figure 8a;  $\lambda_{\text{max}} = 974$  and 1083 nm).<sup>30</sup> Although the transient absorption maxima observed in Figure 6a are slightly red-shifted as compared to those of  $\text{PDI}^{\bullet-}$  reference, the absorption bands due to  $\text{PDI}^{\bullet-}$  and  $\text{ZnPc}^{\bullet+}$  in Figure 6a are quite distinct and well-separated. This clearly indicates formation of the charge-separated (CS) state.

From the rise in absorbance at 840 nm in Figure 6b, the CS rate constant in  $\text{ZnPc(PDI)}_4 \mathbf{2}$  is determined to be  $2.1 \times 10^{11} \text{ s}^{-1}$ . The photoexcitation of **2** at 450 nm affords initially the singlet excited state of the PDI moiety because there is no absorption at 450 nm due to the  $\text{ZnPc}$  moiety (see Figure 2). The observation of the fluorescence of the  $^1\text{ZnPc}^*$  moiety indicates the occurrence of efficient energy transfer from the  $^1\text{PDI}^*$  moiety to the  $\text{ZnPc}$  moiety. Then, intramolecular electron transfer from  $^1\text{ZnPc}^*$  to PDI occurs to produce the CS state,  $\text{ZnPc}^{\bullet+}-\text{PDI}^{\bullet-}(\text{PDI})_3$ . The lifetime of the CS state in PhCN is determined to be 26 ps from the decay of absorbance at 840 nm in Figure 6b.

**Formation of Intermolecular Exciplex.** In contrast to the case of  $\text{ZnPc-PDI}_4 \mathbf{2}$  in Figure 6a, transient absorption



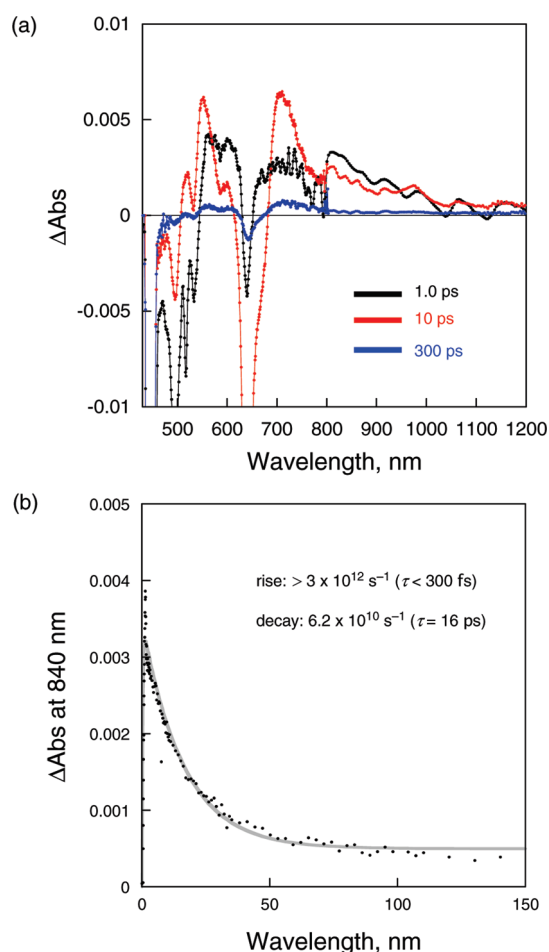
**FIGURE 7.** Spectral change in the electron-transfer oxidation of  $\text{ZnPc(PDI)}_4 \mathbf{2}$  with  $\text{Fe(bpy)}_3(\text{PF}_6)_3$  in deaerated PhCN at 298 K.



**FIGURE 8.** Spectral changes in the electrochemical reduction of PDI (a) **14** and (b) **13** in deaerated PhCN containing  $\text{TBAPF}_6$  (0.10 M) with an applied potential at  $-0.9$  V vs SCE for **15** and  $-0.7$  V for **14** at 298 K.

spectra of  $\text{ZnPc-PDI}_4 \mathbf{1}$  ( $1.0 \times 10^{-5}$  M) obtained after femtosecond laser excitation at 450 nm exhibit no clear absorption bands due to  $\text{ZnPc}^{\bullet+}$  and  $\text{PDI}^{\bullet-}$ , as shown in Figure 9a. The featureless broad transient absorption observed in Figure 9a, which is quite different from distinctive transient absorption bands due to the CS state in Figure 6a, results from aggregation of **1** as indicated by the broader absorption band of **1** in Figure 3a and also by the  $^1\text{H}$  NMR data (vide supra). Thus, the broad absorption bands in the

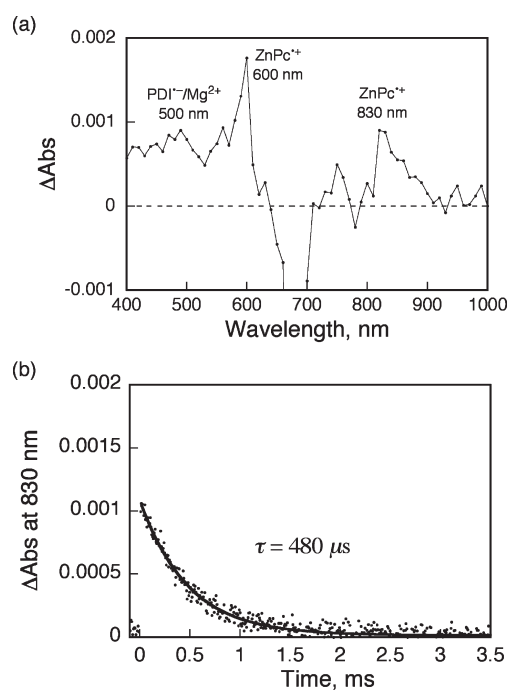
(30) Gosztola, D.; Niemczyk, M. P.; Svec, W.; Lukas, A. S.; Wasielewski, M. R. *J. Phys. Chem. A* **2000**, *104*, 6545–6551.



**FIGURE 9.** (a) Transient absorption spectra of ZnPc(PDI)<sub>4</sub> **1** ( $1.0 \times 10^{-5}$  M) in deaerated PhCN at 298 K after laser excitation at 450 nm. (b) Time profile at 840 nm. Gray curve represents the best fit to the two-exponential rise and decay.

region of 700–1200 nm may be ascribed to formation of the intermolecular exciplex due to the aggregation. Such a strong interaction results from less steric hindrance of the PDI moiety in **1** as compared with **2**. The rate of formation of the exciplex is too fast to be determined with our equipment ( $> 3 \times 10^{12} \text{ s}^{-1}$ ), and this is much faster than the CS rate constant in **2** ( $2.1 \times 10^{11} \text{ s}^{-1}$ ). The decay rate constant of the exciplex of **1**, determined from the decay of absorbance at 840 nm ( $6.2 \times 10^{10} \text{ s}^{-1}$ ), is also faster than that of the CS state in **2** ( $3.9 \times 10^{10} \text{ s}^{-1}$ ). No transient absorption spectrum of **1** was observed after nanosecond laser excitation, suggesting that the strong aggregation of **1** gave no formation of the triplet excited state of ZnPc, PDI, or any long-lived component. On the other hand, nanosecond transient absorption spectrum of **2** revealed the characteristic absorption band due to the triplet excited state of PDI. The triplet PDI is formed via energy transfer from the triplet excited state of ZnPc to PDI (see Supporting Information S14).<sup>16</sup>

**Formation of a Long-Lived CS State with Mg(ClO<sub>4</sub>)<sub>2</sub>.** Addition of Mg(ClO<sub>4</sub>)<sub>2</sub> (10 mM) to a PhCN solution of ZnPc(PDI)<sub>4</sub> **2** results in drastic change in the photodynamics to generate the long-lived CS state (vide infra). Nanosecond laser excitation ( $\lambda = 430 \text{ nm}$ ) of ZnPc(PDI)<sub>4</sub> **2** in deaerated PhCN gave formation of the CS state, as shown in



**FIGURE 10.** (a) Transient absorption spectrum of **2** ( $1.0 \times 10^{-5}$  M) in deaerated PhCN containing Mg(ClO<sub>4</sub>)<sub>2</sub> (10 mM) at 298 K taken at 1  $\mu$ s after nanosecond laser excitation at 450 nm. (b) Time profile at 830 nm. Gray curve represents the best fit to the single-exponential decay.

Figure 10a. The transient absorption bands at 600 and 830 nm are assigned to ZnPc<sup>•+</sup>, as shown in Figure 7. On the other hand, with regard to PDI<sup>•-</sup>, no transient absorption band around 1000 nm was observed in the presence of Mg<sup>2+</sup>. The absorption band of PDI<sup>•-</sup> in the presence of Mg<sup>2+</sup> is significantly shifted from that of PDI<sup>•-</sup> since it has been reported that PDI<sup>•-</sup> forms a strong complex with Mg<sup>2+</sup>.<sup>16c</sup> The broad absorption at 500 nm agrees with that due to PDI<sup>•-}/Mg<sup>2+</sup> complex.<sup>16c</sup></sup>

The decay of the CS state in the presence of Mg<sup>2+</sup> (10 mM) was monitored at 830 nm due to ZnPc<sup>•+</sup> (see Figure 10b). The decay curve obeys first-order kinetics. The decay rate constant was determined to be  $2.1 \times 10^3 \text{ s}^{-1}$ . The lifetime of the CS state is determined to be 480  $\mu$ s.

## Conclusion

Photoexcitation of the zinc phthalocyanine–perylenebisimide pentameric array **1** affords the intermolecular exciplex in which strong interaction between the ZnPc and the PDI moieties is recognized because of the aggregation. In contrast, photoexcitation of the zinc phthalocyanine–perylenebisimide pentameric array **2**, with bulky substituents on the PDI moieties, results in formation of the CS state. The lifetime of the CS state of **2** is remarkably elongated by the binding of Mg<sup>2+</sup> to the CS state to attain a lifetime of 480  $\mu$ s, which is one of the longest CS lifetimes ever reported in electron donor–acceptor ensembles.

## Experimental Section

**2,9,16,23-Tetrakis-[N'-(2'',5''-di-*tert*-butylphenyl)perylene-3',4':9',10'-bis(dicarboximide)-N(-yl)]phthalocyaninato zinc(II) (1).** Perylene **4** (145 mg, 0.25 mmol),<sup>24</sup> tetraaminophthalocyanine



**11** (20 mg, 0.031 mmol),<sup>23</sup> and imidazole (2 g) were stirred under argon for 60 h at 180 °C. After being cooled to room temperature, the reaction mixture was treated with 100 mL of MeOH and 70 mL of glacial acetic acid and stirred for 4 h. The purple precipitate obtained was centrifuged and washed twice with MeOH/glacial acetic acid and MeOH, respectively. Flash chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH 9.5:0.5) yielded ZnPc-PDI<sub>4</sub> **1** (37 mg, 41%) as a dark purple powder: mp > 300 °C; <sup>1</sup>H NMR (300 MHz, TFA-*d*<sub>1</sub>, 25 °C, TMS) δ = 10.30–9.40 (4H, broad), 9.26–8.70 (36H, broad), 8.70–8.00 (4H, broad), 7.85–7.40 (12H, broad), 1.38–1.19 (72H, broad); FT-IR (KBr) ν = 2957, 1705 (C=O imide), 1668 (C=O imide), 1594, 1578, 1432, 1402, 1345, 1253, 1176, 1148, 1097 cm<sup>-1</sup>; UV/vis (DMF) λ<sub>max</sub>/nm (log ε) = 266 (4.87), 337 (4.80), 494 (5.00), 529 (4.90), 580 (4.38), 636 (5.02); MS (MALDI-TOF-dithranol) *m/z* 2881 [M<sup>+</sup>], 2882 [M<sup>+</sup> + 1], 2883 [M<sup>+</sup> + 2], 2304 [M<sup>+</sup> - perylene]. Anal. Calcd for C<sub>184</sub>H<sub>128</sub>N<sub>16</sub>O<sub>16</sub>Zn·10H<sub>2</sub>O: C, 72.11; H, 4.87; N, 7.31. Found: C, 72.20; H, 5.10; N, 7.01.

**2,9,16,23-Tetrakis**-(*N'*-(2''-ethylhexyl)-1',6',7',12'-tetrakis-[4''(1''',1''',3''',3'''-tetramethylbutyl)phenoxy]perylene-3',4',9',10'-bis(dicarboximide)-*N*-yl))-phthalocyaninato zinc(II) (**2**). Perylene **12** (300 mg, 0.23 mmol),<sup>25</sup> tetraaminophthalocyanine **11** (20 mg, 0.031 mmol),<sup>23</sup> and imidazole (2 g) were stirred under argon for 60 h at 180 °C. After being cooled to room temperature, the reaction mixture was repeatedly washed with MeOH. Flash chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether 1:1) afforded ZnPc(PDI<sub>4</sub>) **2** (55 mg, 30%) as a dark purple powder: mp > 300 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 10.15–8.39 (8H, broad), 8.39–7.87 (16H, broad), 7.73 (4H, broad), 7.17 (32H, broad), 6.90 (16H, broad), 6.49 (16H, broad), 4.04 (8H, broad), 1.81 (4H, broad), 1.66 (32H, broad), 1.46–1.15 (128H, broad), 1.02–0.58 (168H, broad); FT-IR (KBr) ν = 2955, 1704 (C=O imide), 1666 (C=O imide), 1591, 1503, 1432, 1408, 1365, 1339, 1284, 1214, 1173, 1095, 1015 cm<sup>-1</sup>; UV/vis (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub>/nm (log ε) = 266 (5.37), 286 (5.34), 335 (5.15), 448 (4.89), 542 (5.17), 582 (5.12), 638 (5.51), 671 (5.05); MS (MALDI-TOF-dithranol) *m/z* 5843 [M<sup>+</sup>], 5844 [M<sup>+</sup> + 1], 5845 [M<sup>+</sup> + 2], 5779 [M<sup>+</sup> - Zn]. Anal. Calcd for C<sub>384</sub>H<sub>432</sub>N<sub>16</sub>O<sub>32</sub>·10H<sub>2</sub>O: C, 76.50; H, 7.56; N, 3.72. Found: C, 76.73; H, 7.60; N, 3.55.

***N*-(2',5'-Di-*tert*-butylphenyl)-*N'*-(3',4'-dicianophenyl)perylene-3,4,9,10-bis(carboximide) (**3**)**. Perylene **4** (100 mg, 0.17 mmol),<sup>24</sup> 4-aminophthalonitrile (49.3 mg, 0.34 mmol),<sup>18</sup> and imidazole (1 g) were stirred under argon for 24 h at 125 °C. After being cooled to room temperature, the reaction mixture was dissolved with CH<sub>2</sub>Cl<sub>2</sub>, washed with 2 N HCl, water, and a saturated solution of NaHCO<sub>3</sub> sequentially, and dried with anhydrous MgSO<sub>4</sub>. Purification by column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/AcOEt 40:1) gave 16 mg (15%) of **3** as a red powder: mp 280–285 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 8.73 (2H, d, *J* = 7.9 Hz), 8.69 (2H, d, *J* = 7.9 Hz), 8.59 (2H, d, *J* = 8.1 Hz), 8.57 (2H, d, *J* = 8.1 Hz), 8.01 (1H, d, *J* = 8.1 Hz), 7.88 (1H, s), 7.87 (1H, d, *J* = 8.1 Hz), 7.60 (1H, d, *J* = 8.6 Hz), 7.48 (1H, dd, *J* = 8.6 and 1.5 Hz), 7.14 (1H, d, *J* = 1.5 Hz), 1.31 (9H, s), 1.26 (9H, s); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 164.1, 162.6, 150.3, 143.5, 141.8, 141.0, 139.5, 135.6, 134.5, 134.4, 134.1, 133.7, 132.3, 132.1, 131.6, 129.5, 129.5, 128.8, 127.9, 126.5, 126.4, 125.0, 124.1, 123.7, 123.2, 122.2, 117.0, 116.0, 114.9, 114.6, 35.5, 34.3, 31.7, 31.1; FT-IR (KBr) ν = 3076, 2962, 2237 (C≡N), 1707 (C=O imide), 1668 (C=O imide), 1594, 1578, 1403, 1356, 1345, 1254, 1175, 972, 811, 748 cm<sup>-1</sup>; UV/vis (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub>/nm (log ε) = 229 (4.68), 259 (4.58), 460 (4.14), 491 (4.57), 528 (4.77); MS (MALDI-TOF-dithranol) *m/z* 704 [M<sup>+</sup>], 705 [M<sup>+</sup> + 1]. Anal. Calcd for C<sub>46</sub>H<sub>32</sub>N<sub>4</sub>O<sub>4</sub>·H<sub>2</sub>O: C, 76.44; H, 4.74; N, 7.75. Found: C, 76.08; H, 4.86; N, 7.59.

**4,5-Bis**[*p*-[2'-(*N'*-2''-ethylhexyl)-1',6',7',12'-tetrabromoperylene-3,4,9,10-tetracarboxydimide-*N*-yl]ethoxycarbonyl]phenoxy]phthalonitrile (**5**). 1-Hydroxybenzotriazole (HOBt) (23.5 mg, 0.17 mmol), 4-dimethylaminopyridine (DMAP) (21.26 mg, 0.17 mmol), and CH<sub>2</sub>Cl<sub>2</sub> (8 mL) were stirred at 0 °C. Then

34.8 mg (0.087 mmol) of 4,5-di-(*p*-carboxyphenoxy)phthalonitrile **6**<sup>19</sup> and 150 mg (0.17 mmol) of perylene **7** were added to the mixture and stirred at 0 °C for 5 min. After that, 45.4 mg (0.22 mmol) of dicyclohexylcarbodiimide (DCC) was added, and the mixture was stirred under argon for 3 days at rt. After solvent distillation, purification by chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/AcOEt 40:1) gave 91 mg (50%) of **5** as a red powder: mp 237–240 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 8.80 (8H, s), 8.04 (4H, d, *J* = 7.6 Hz), 7.35 (2H, s), 7.00 (4H, d, *J* = 7.6 Hz), 4.67 (8H, m), 4.12 (4H, m), 1.92 (2H, m), 1.39–1.25 (16H, m), 0.94–0.89 (12H, m); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 165.2, 162.4, 162.3, 158.2, 150.7, 136.2, 136.1, 132.3, 132.0, 131.4, 131.4, 131.4, 127.0, 124.4, 124.1, 124.0, 123.9, 123.8, 122.8, 122.2, 118.4, 114.3, 112.1, 62.6, 44.6, 39.6, 38.0, 30.6, 28.6, 23.9, 23.0, 14.1, 10.5; FT-IR (KBr) ν = 3067, 2954, 2925, 2857, 2232 (C≡N), 1705 (C=O imida), 1667 (C=O imida), 1585, 1499, 1433, 1381, 1339, 1271, 1233, 1155, 1111, 804, 744, 528 cm<sup>-1</sup>; UV/vis (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub>/nm (log ε) 251 (4.90), 441 (4.43), 499 (4.65), 531 (4.79); MS (MALDI-TOF-dithranol) *m/z* 2080 [M<sup>+</sup>], 2081 [M<sup>+</sup> + 1], 2000 [M<sup>+</sup> - Br]. Anal. Calcd for C<sub>90</sub>H<sub>60</sub>Br<sub>8</sub>N<sub>6</sub>O<sub>14</sub>·H<sub>2</sub>O: C, 51.31; H, 2.97; N, 3.99. Found: C, 51.17; H, 2.98; N, 4.07.

***N*-(2'-Ethylhexyl)-*N'*-(2'-hydroxyethyl)-1,6,7,12-tetrabromoperylene-3,4,9,10-tetracarboxydimide (**7**)**. 2-Ethylhexylamine (388 mg, 3 mmol), ethanolamine (183 mg, 3 mmol), 1,6,7,12-tetrabromoperylene-3,4,9,10-tetracarboxyanhydride **8** (2 g, 2.8 mmol),<sup>21</sup> and toluene (15 mL) were stirred under argon for 24 h at reflux. After being cooled to room temperature, 50 mL of CH<sub>2</sub>Cl<sub>2</sub> was added, obtaining a red precipitate. This solid was washed with water and dried, yielding diol **10** (869 mg, 40%). Purification by chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH 9:1) was used to characterize compound **10**: <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, 40 °C, TMS) δ = 8.70 (4H, s), 4.83 (2H, t, *J* = 5.9 Hz), 4.17 (4H, t, *J* = 5.3 Hz), 3.65 (4H, dt, *J* = 5.9 and 5.3 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>/MeOD 5:1, 25 °C, TMS) δ 162.6, 136.0, 131.6, 131.2, 123.8, 122.3, 59.4, 42.4; FT-IR (KBr) ν = 3418 (OH), 3053, 2952, 1700 (C=O imide), 1663 (C=O imide), 1584, 1432, 1385, 1340, 1284, 1234, 1171, 1054, 804, 744, 647, 529 cm<sup>-1</sup>; UV/vis (DMSO) λ<sub>max</sub>/nm (log ε) = 259 (4.50), 441 (4.07), 500 (4.34), 531 (4.46); MS (MALDI-TOF-dithranol) *m/z* 790 [M<sup>+</sup>], 791 [M<sup>+</sup> + 1], 711 [M<sup>+</sup> - Br]. Anal. Calcd for C<sub>28</sub>H<sub>14</sub>Br<sub>4</sub>N<sub>2</sub>O<sub>6</sub>: C, 42.35; H, 1.78; N, 3.53. Found: C, 42.26; H, 2.03; N, 3.49.

The organic phase (with CH<sub>2</sub>Cl<sub>2</sub>) was recovered, and solvent was evaporated. Purification by chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>) gave 789 mg (30%) of symmetrical perylene **9** (first fraction) as a red powder: mp 290–294 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 8.80 (4H, s), 4.13 (4H, m), 1.93 (2H, m), 1.40–1.25 (16H, m), 0.95 (6H, m), 0.90 (6H, m); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ 162.4, 136.1, 131.5, 131.3, 123.9, 122.6, 44.5, 37.9, 30.6, 28.6, 23.9, 23.0, 14.1, 10.5, 10.5; FT-IR (KBr) ν = 2956, 2927, 2857, 1704 (C=O imide), 1666 (C=O imide), 1583, 1434, 1411, 1386, 1365, 1279, 1232, 1180, 1155, 805, 646, 529 cm<sup>-1</sup>; UV/vis (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub>/nm (log ε) = 231 (4.85), 272 (4.39), 439 (4.11), 497 (4.36), 529 (4.51); MS (MALDI-TOF-dithranol) *m/z* 926 [M<sup>+</sup>], 927 [M<sup>+</sup> + 1], 847 [M<sup>+</sup> - Br]. Anal. Calcd for C<sub>40</sub>H<sub>38</sub>Br<sub>4</sub>N<sub>2</sub>O<sub>4</sub>: C, 51.64; H, 4.12; N, 3.01. Found: C, 51.41; H, 4.12; N, 3.12.

Finally, perylene **7** was collected from chromatography as the second fraction using CH<sub>2</sub>Cl<sub>2</sub>/AcOEt 9:1. This purification gave 608 mg (25%) of unsymmetrical substituted perylene **7** as a red powder: mp 290–294 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 8.82 (2H, s), 8.81 (2H, s), 4.47 (2H, m), 4.13 (2H, m), 3.99 (2H, t, *J* = 4.65 Hz), 2.15 (1H, broad s), 1.93 (1H, m), 1.47–1.31 (8H, m), 0.94 (3H, m), 0.89 (3H, m); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 162.9, 162.5, 136.3, 136.1, 131.9, 131.5, 131.4, 131.3, 124.1, 124.0, 123.9, 123.8, 122.7, 122.3, 61.2, 44.6, 42.9, 38.0, 30.7, 28.6, 24.0, 23.9, 23.0, 23.0,

14.1, 10.5; FT-IR (KBr)  $\nu$  = 3446 (OH), 2956, 2928, 1704 (C=O imide), 1665 (C=O imide), 1585, 1434, 1386, 1282, 1233, 804, 529  $\text{cm}^{-1}$ ; UV/vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}/\text{nm}$  ( $\log \epsilon$ ) = 238 (4.90), 276 (4.40), 440 (4.13), 497 (4.37), 529 (4.51); MS (MALDI-TOF-dithranol)  $m/z$  858 [ $\text{M}^+$ ], 859 [ $\text{M}^+ + 1$ ], 778 [ $\text{M}^+ - \text{Br}$ ]. Anal. Calcd for  $\text{C}_{34}\text{H}_{26}\text{Br}_4\text{N}_2\text{O}_5$ : C, 47.36; H, 3.04; N, 3.25. Found: C, 47.38; H, 3.09; N, 3.35.

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**Supporting Information Available:** Text describing the Experimental Section (chemical information, laser flash photolysis, theoretical calculations, and cyclic voltammetry),  $^1\text{H}$  spectra of **1** and **2**,  $^1\text{H}$  and  $^{13}\text{C}$  spectra of **3**, **5**, **7**, **9**, and **10**, MALDI-TOF spectra of **1** and **2**, voltammograms of **1** and **2**, and transient absorption spectra of **2** and **14** (obtained by nanosecond laser flash photolysis). This material is available free of charge via the Internet at <http://pubs.acs.org>.