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Supramolecular Zinc Phthalocyanine–Imidazolyl Perylenediimide Dyad and Triad: Synthesis, Complexation, and Photophysical Studies

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Dedicated to Prof. Dr. Dr. h.c. Tomás Torres on the occasion of his 60th birthday

Abstract: Two new supramolecular architectures based on zinc phthalocyanine (Pc) and imidazolyl-substituted perylenediimide (PDI), ZnPc/DImPDI/ ZnPc 1 and ZnPc/ImPDI 2, have been prepared. A strong electron-donor, ZnPc-8, which contained eight tert-octylphenoxy groups was synthesized to ensure high solubility, thereby reducing aggregation in solution and providing σ-donor features while avoiding regioisomeric mixtures. Also, PDI units were functionalized with tert-octylphenoxy groups at the bay positions, which provide solubility to avoid aggregation in solution, together with one and two imidazole moieties in the amide position, PDI-6 and PDI-4, respectively, to be able to strongly coordinate with the ZnPc complex. Supramolecular complexation studies by ¹H NMR spectroscopy and ESI-MS demonstrate a high coordinative binding constant between imidazole-substituted **PDI-4** or **PDI-6** and **ZnPc-8**. The same results were confirmed by UV/Vis and fluorescence titration studies. UV/Vis titration studies revealed the formation of a 1:1 complex ZnPc/ImPDI **2** for the systems **ZnPc-8** and **PDI-6** and a 2:1 complex ZnPc/DImPDI/ZnPc **1** for the interaction of **ZnPc-8** and **PDI-4**. The

Keywords: electron transfer • perylenediimide • photophysics • supramolecular chemistry • zinc pthalocyanine binding constant in both cases was determined to be on the order of $10^5 \,\mathrm{M}^{-1}$. Femtosecond laser flash photolysis measurements provided a direct proof of the charge-separated state within both supramolecular assemblies by observing the transient absorption band at 820 nm due to the zinc phthalocyanine radical cation. The lifetimes of charge-separated states are (9.8 ± 3) ns for triad **1** and (3 ± 1) ns for dyad **2**. As far as we know, this is the first time that a radical ion pair has been detected in a supramolecular assembled ZnPc-PDI system and has obtained the longest lifetime of a charge-separated state published for ZnPc-PDI assemblies.

Introduction

Photoinduced electron transfer in donor–acceptor molecules has been extensively studied in solution as model systems of natural photosynthesis to efficiently harvest solar energy.^[1-7] The controlled organization of functional molecules into highly ordered self-assembled arrays is expected to yield supramolecular architectures with unique properties, and offers an interesting way to design new donor–acceptor systems.^[8] Supramolecular systems of multifunctional donor–acceptor hybrids in which the complementary electroactive constituents are phthalocyanines (Pcs) and perylenediimides (PDIs) can be interesting targets due to the outstanding

Pcs have emerged as promising molecular components for artificial photosynthetic systems because they contain large conjugated π systems suitable for efficient electron-transfer

processes, they possess reducing or oxidizing characteristics

properties displayed by each moiety.

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determined by the nature of the peripheral groups, they are very robust, and they exhibit very high extinction coefficients around 700 nm (at which point the maximum solar photon flux occurs) for efficient photon harvesting.^[9-12] In particular, we want to emphasize the importance of ZnPcs in electron-transfer processes^[13,14] and in the development of dye-sensitized solar cells.^[15] The UV/Vis properties of Pcs have a limitation owing to the lack of absorption between 400 and 600 nm. Therefore, it might be interesting to use Pcs in combination with an appropriate dye to achieve panchromatic sensitization.

On the other hand, PDIs are highly thermostable n-type semiconductors, with both relatively high electron affinity and facile electrochemical reduction. They also possess an extremely efficient fluorescent emission.^[16] Because of this, PDI dyes have been used extensively as light absorbers, energy-transfer agents, and charge carriers.^[17-20] Moreover, PDIs exhibit high extinction coefficients in the 400–600 nm

Abstract in Spanish: Se han preparado dos nuevos sistemas supramoleculares basados en ftalocianina de zinc y en perilenobisimida sustituida con grupos imidazolilo, ZnPc/ DImPDI/ZnPc 1 y ZnPc/ImPDI 2. Se ha sintetizado la ftalocianina ZnPc-8 con ocho grupos terc-octilfenoxilo con objeto de aumentar la solubilidad, reducir la agregación en disolución, introducir grupos dadores de electrones y, por último, evitar mezclas de regioisómeros. Además, las PDI-6 y PDI-4 también se han funcionalizado con grupos terc-octilfenoxilo en las posiciones bahía, los cuales les confieren solubilidad e impiden la agregación en disolución, y con una o dos unidades de imidazol en la posición imida, respectivamente, con objeto de coordinar fuertemente la ZnPc. Los estudios de complejación supramolecular llevados a cabo por ¹H-RMN y MS-ESI han demostrado una constante de complejación muy alta entre las PDI-4 o PDI-6 sustituidas con imidazol y la ZnPc-8. Los mismos resultados han sido confirmados mediante estudios de valoración realizados por UV-vis y fluorescencia. Los estudios de valoración realizados mediante UV-vis indican la formación de un complejo 1:1 ZnPc/ImPDI 2 para los sistemas ZnPc-8 y PDI-6, y un complejo 2:1 ZnPc/DImPDI/ZnPc 1 para los sistemas ZnPc-8 y PDI-4. Las constantes de complejación en los dos son del orden de 10⁵ M⁻¹. En ambos sistemas supramoleculares también ha sido posible determinar el estado de separación de cargas mediante medidas de fotólisis por destello láser, observando la banda de absorción transiente a 820 nm debida al catión radical de la ftalocianina de zinc. Los tiempos de vida de los estados de separación de carga son (9.8 \pm 3) ns para la tríada 1 y (3 ± 1) ns para la díada 2. Según nuestros datos, esta es la primera vez que ha sido detectada la existencia de un par ión radical en un sistema de ZnPc-PDI ensamblado de manera supramolecular, obteniendo el tiempo de vida más largo, conocido hasta la fecha, de un estado de separación de cargas en un sistema ZnPc-PDI.

region, thus matching the UV/Vis optical window of Pcs. Therefore, the coupling of Pcs and PDIs could be a promising strategy to build light-harvesting antennae. Previous reports on the linked Pc–PDI motif are scarce, and include covalent hybrids of the two chromophores connected through either the PDI imido or the bay positions,^[13,14,21–25] or supramolecular hybrids through axial coordination of the perylene moiety.^[26,27]

To achieve this supramolecular system, the chromophores need to have the capability of self-organizing into higher-ordered and stable structures. Metal-ligand interactions have been used as an appropriate strategy to construct supramolecular entities. Several investigation groups have been particularly interested in the implementation of an assembling strategy exploiting the coordination ability of peripheral pyridyl groups of different photoactive dyes (porphyrins, perylenes, fullerenes, and so on) to the metal center of porphyrins^[28-36] or Pcs.^[27,37,38] The key to the stability of axially ligated dyes is the strength of the coordinative bond between the ligand and metal ion. For example, ligation of a pyridyl ring to zinc porphyrin and ZnPc is intrinsically weak (binding constant of $K = 1 \times 10^3 \text{ M}^{-1}$).^[27,29] Thus, in solution, coordination oligomers are generally in equilibrium with the monomers.[28]

A well-established method in the field of porphyrin chemistry, developed by Kobuke et al., is the preparation of imidazolyl-substituted porphyrins that can coordinate through the imidazolyl moiety to the central zinc(II) ion of a different porphyrin^[39–41] or phthalocyanine^[42,43] unit, with large association constants. D'Souza et al. also used the better coordinating ability of imidazole moieties to form dyes by means of axial coordination of zinc porphyrins and phthalocyanines with fullerenes and carbon nanotubes.^[35,44–47]

The objective of the current work was to prepare two electron donor-acceptor hybrids that bear PDI chromophores as the acceptor unit and two (ZnPc/DImPDI/ZnPc, 1) or one (ZnPc/ImPDI, 2) units of ZnPc as the donor counterparts by means of strong imidazolyl-mediated metal coordination. The complexation studies and the photophysics of these constructs are examined in detail. We observed for the first time the presence of a radical ion pair in a supramolecular ZnPc-PDI system.

Results and Discussion

Synthesis

Unsubstituted Pc and PDI are very insoluble in organic solvents. Therefore, functionalization of both molecular precursors is necessary. Hereby the choice of the substituent is decisive for processing and characterization. In the context of the ZnPc unit, *tert*-octylphenoxy groups were selected, as eight units of this bulky substituent are expected to ensure high solubility, reduce aggregation in solution, and provide o-donor features, while avoiding regioisomer mixtures typical of the commonly used tetra(*tert*-butyl)ZnPc. As a conse-



commercially available 4-(1Himidazol-1-yl)aniline in Nmethyl-2-pyrrolidone (NMP) to give the corresponding PDI-3 with two imidazole groups at the peri positions. This compound is not very soluble in chloroform or dichloromethane, but this problem was overcome when PDI-3 was treated with tert-octylphenol and K₂CO₃ in NMP to yield PDI-4 (Scheme 1).

Synthesis of PDI-6 started from N-(2'-ethylhexyl)-1,6,7,12tetrakis-[4'(1",1",3",3"-tetramethylbutyl)phenoxy]perylene-9,10-dicarboximide-3,4-dicarboxyanhydride (5),^[20] which was treated with 4-(1H-imidazol-1-yl)aniline in molten imidazole (Scheme 2).

As depicted in Scheme 3, phthalonitrile 7 was prepared by ipso substitution on 4,5-dichlorophthalonitrile with tertoctylphenol in dry dimethyl sulfoxide by using K₂CO₃. ZnPc-8 was obtained by cyclotetramerization of 7 with ZnCl₂ (0.5 M in THF) in the presence of dimethylaminoethanol (DMAE).

All new compounds were characterized by UV/Vis, FTIR, ¹H NMR, and ¹³C NMR spectroscopy, and mass spectrometry, whereas purity was checked

bay positions of the PDI with the same tert-octylphenoxy substituents would provide solubility (despite the existence of two imidazole polar groups at the

imide positions of the PDI) and would avoid aggregation.^[48] The synthetic routes for the preparation of the imidazolyl-PDI derivatives 4 and 6 are indicated in Schemes 1 and 2, respectively.

Our synthesis of PDI-4 started from commercial 1,6,7,12tetrachloropervlene-3,4:9,10tetracarboxylic acid bisanhydride, which was treated with

quence, the corresponding ZnPc would bear a strong electron-donor character.^[13,14,26] Equally, functionalization at the by elemental analysis. The UV/Vis spectrum of ZnPc-8 (Figure 1) shows the Q-band and B-band absorptions char-



Scheme 1. Synthetic route to PDI-4.

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Scheme 2. Synthetic route to PDI-6.



Figure 1. UV/Vis spectra of ZnPc-8 (\bigtriangledown), PDI-4 (\odot), and PDI-6 (—) in CH_2Cl_2

acteristic of nonaggregated compounds, which may arise from the steric hindrance of the bulky *tert*-octylphenoxy groups. On the other hand, there are few, if any, differences between UV/Vis spectra of **PDI-4** and **PDI-6**. The ¹H NMR

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spectrum of **ZnPc-8** shows only one singlet for the nonperipheral protons of the phthalocyanine core (for a total of eight protons) at $\delta = 8.96$ ppm. The signals are so well-resolved, as shown in Figure 2, because the eight *t*-octylphenoxy groups preclude aggregation, thus increasing the solubility of the compound and the resolution of the spectrum.



Figure 2. ¹H NMR spectrum (300 MHz, $[D_8]$ THF, 25 °C) of **ZnPc-8** (enlargement of the aromatic region).

Supramolecular Complexation

Figure 3 (top) represents a comparison of the ¹H NMR spectra of **PDI-4** and complex **1** when all PDI are assembled with two ZnPcs ([**ZnPc-8**]/[**PDI-4**]=2). In this complex, **PDI-4** is located between two **ZnPc-8** rings; thus it experiences the influence of the diamagnetic ring currents of two



Scheme 3. Synthetic route to ZnPc-8

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Figure 3. a) Comparison of ¹H NMR spectra in CDCl₃ for **PDI-4** and **1** (ZnPc/DImPDI/ZnPc). b) Partial ¹H NMR spectra (CDCl₃, 300 MHz, 25 °C) showing the shift of the protons in **PDI-4** upon the addition of increasing quantities of **ZnPc-8** (number of equiv indicated to the right) to a solution of **PDI-4** (concentration of PDI was fixed at 0.44 mM).

ZnPc-8. As a result, all **PDI-4** signals are shifted upfield; the magnitude of this effect depends on the distance between a given proton and the Pc core. The effect is particularly pronounced for the imidazole moiety, which displays a strong upfield shift: H-6, H-7, and H-8 protons of imidazole substituents go from $\delta = 7.89$, 7.32, and 7.23 ppm to $\delta = 5.72$, 3.99, and 3.06 ppm, respectively. Analogous changes in the chemical shifts of protons in zinc porphyrin–perylene^[28,29,49] and ZnPc–perylene^[27] supramolecular systems had been reported, but using pyridyl moieties.

A ¹H NMR spectroscopic titration experiment was carried out in deuterated chloroform at 25 °C to evaluate the coordination of PDI-4 to ZnPc-8. The addition of increasing amounts of ZnPc-8 to a solution of PDI-4 produced a significant upfield shift of the proof PDI-4 (discussed tons above). This shift can only be observed when [PDI-4]/[ZnPc-[8] < 0.5 (Figure 3, lower part). As the mole fraction of the coordinated partner increases, the signals for PDI-4 were broadened (in the case of H-1 protons of PDI-4) or missing (in the case of H-4, H-5, H-6, H-7, and H-8). Concomitantly, a new set of signals appears that can be attributed to the 2:1 heterotriad 1 (ZnPc/DImPDI/ZnPc). This behavior indicates that the host-guest complexation equilibrium has a similar exchange rate compared to the NMR spectroscopic timescale, so by using this technique it is impossible to study the complexation,^[50] which may be attributed to the generally strong binding between imidazole ligands and ZnPcs.^[42] Because of this, it was not possible to assess the stoichiometry of the supramolecular complex and to determine binding constant its with ¹H NMR spectroscopy experiments. We obtained the same results by using PDI-6 and ZnPc-8 in a ¹H NMR spectroscopic titration experiment.

Moreover, the strong interaction in this type of complex was confirmed by electrospray ionization (ESI) mass spectrometry (see the Supporting Information; m/z 3670 $[M]^+$ of complex

2). The expected peak of complex **1** was not observed with this method, probably due to poor transmission around the expected high mass $(m/z 5909 [M]^+)$.

The complexation of the imidazolyl perylenes and **ZnPc-8** was also studied by UV/Vis spectroscopy. **PDI-6** was first studied to know the changes in the UV/Vis when only one ZnPc interacts with one PDI (1:1 stoichiometry) and to extrapolate the data to 2:1 stoichiometry with **PDI-4**. The absorption spectrum of **ZnPc-8** displays a Soret band at 348 nm and an intense Q band at 681 nm (Figure 1). The addition of increasing amounts of **PDI-6** to a constant concentration of **ZnPc-8** induced spectral changes (Figure 4).



Figure 4. Absorption spectral changes of **ZnPc-8** on addition of increasing concentrations of **PDI-6** in CH₂Cl₂. The concentration for **ZnPc-8** was kept constant at 0.11×10^{-3} mM. The inset shows the enlarged UV/ Vis spectrum between 325 and 400 nm (region in which complex 2 absorbs).

The Q band of **ZnPc-8** was gradually increased, as the Soret band also does but with a major change in the maximum (from 348 to 365 nm; Figure 4, inset). Previous UV/Vis titration experiments^[27] with ZnPc and a pyridyl-bearing PDI found no change in the Soret band, and this may be due to the strong interaction between ZnPc and the imidazole moiety of PDI. This new maximum can be attributed to the formation of the complex, so the absorbance at 365 nm was used to evaluate a titration experiment. The "background absorbance" method^[51,52] was used to calculate the absorbance that corresponds to complex **2** (ZnPc/ImPDI), because both PDI and ZnPc absorb at this wavelength [Eq. (1)]:

$A_{\rm obs(365nm)} = A_{\rm PDI(365nm)} + A_{\rm ZnPc(365nm)} + A_{\rm complex(365nm)}$

in which $A_{obs(365nm)}$ is the total absorption of mixture at 365 nm, $A_{PDI(365nm)}$ is the absorption that corresponds to **PDI-6** at 365 nm, $A_{ZnPc(365nm)}$ is the absorption that corresponds to **ZnPc-8** at 365 nm, and $A_{complex(365nm)}$ is the absorption that corresponds to complex 2 (ZnPc/ImPDI) at 365 nm. Then, substituting the Beer–Lambert law in Equation (1) affords Equation (2):

$$A_{\text{complex}(365\text{nm})} = A_{\text{obsd}(365\text{nm})} - [\text{PDI}]_0 \cdot \varepsilon_{\text{PDI}(365\text{nm})}$$
$$- [\text{ZnPc}]_0 \cdot \varepsilon_{\text{ZnPc}(365\text{nm})}$$

in which $[PDI]_0$ is the gradually increased concentration of **PDI-6**, $\varepsilon_{PDI(365nm)}$ is the molar extinction coefficient of **PDI-6** at 365 nm, $[ZnPc]_0$ is the constant concentration of **ZnPc-8**, and $\varepsilon_{ZnPc(365nm)}$ is the molar extinction coefficient of **ZnPc-8** at 365 nm.

A continuous variation UV/Vis spectroscopic experiment was carried out in dichloromethane to determine the stoichi-



Figure 5. UV/Vis titration curve (CH_2Cl_2) showing the changes in the absorbance at 365 nm (due to formation of 2 (ZnPc/ImPDI) complex) when increasing amounts of **PDI-6** were added to **ZnPc-8** solution ([**ZnPc-8**] = 0.0056 mM); the regression coefficient for the nonlinear least-squares curve-fitting analysis is $r^2 = 0.99497$. Inset: UV/Vis Job plot of **ZnPc-8** versus **PDI-6**. [**PDI-6**]+[**ZnPc-8**] ≈ 0.023 mM.

ometry of the binding between PDI-6 and ZnPc-8. The Job plot^[52,53] obtained in this way (Figure 5, inset) exhibited a maximum at a mole ratio of 0.48, consistent with a 1:1 interaction. Titration experiments were carried out in dichloromethane at 25 °C to determine the binding constant for the coordination of PDI-6 to ZnPc-8. The concentration of ZnPc-8 was kept constant, and the changes in the absorbance at 365 nm of the Soret band [see the previous "background absorbance" method using Eq. (2)] were plotted as a function of the increasing concentration of PDI-6, these data being subjected to a nonlinear least-squares curve-fitting analysis^[52] (Figure 5). The binding constant for the 1:1 complex 2 (ZnPc/ImPDI) was determined to be $K=3.42\times$ $10^{5}(\pm 0.15)$ M⁻¹. This value is on the same order of magnitude as others described in the literature,^[42,43] for imidazolyl-ZnPc complexes.

The complexation study to evaluate complex 1 (ZnPc/ DImPDI/ZnPc) was carried out using the same approach. A continuous variation UV/Vis spectroscopic experiment was carried out in dichloromethane to determine the stoichiometry of the binding between PDI-4 and ZnPc-8. The Job plot^[52,53] obtained in this way (Figure 6, inset) exhibited a maximum at a mole ratio of 0.34, consistent with a 2:1 interaction. Titration experiments were carried out in dichloromethane at room temperature to determine the binding constants for the coordination of PDI-4 to ZnPc-8. In this case, the mathematical treatment to evaluate the binding constants K_1 and K_2 using a 2:1 stoichiometry, is very complicated. Normally, in this type of study an analysis with a 1:2 model (host/guest) is used, which is simpler.^[54,55] But we needed to evaluate the changes in the absorbance at 365 nm, so we could not use PDI-4 as a host. Because of this, we were forced to make an approach in which K_1 of **1** (ZnPc/DImPDI/ZnPc) = K of 2 $(ZnPc/ImPDI) = 3.42 \times 10^{5}$ (± 0.1) M⁻¹. We believe this approach is correct because both



Figure 6. UV/Vis titration curve (CH₂Cl₂) showing the changes in the absorbance at 365 nm (due to the formation of 1 (ZnPc/DImPDI/ZnPc) complex) when increasing amounts of PDI-4 were added to ZnPc-8 solution ([ZnPc-8]=0.01 mM); the regression coefficient for the nonlinear least-squares curve-fitting analysis is r^2 = 0.99774. Inset: UV/Vis Job plot of ZnPc-8 versus PDI-4. [PDI-4]+[ZnPc-8] ≈ 0.012 mM.

molecules are very similar; they differ only in an imidazole group at the *peri* position of **PDI-4**.

The data obtained were plotted as a function of increasing concentration of **PDI-4**, these data being subjected to a nonlinear least-squares curve-fitting analysis^[54] (Figure 6). The second binding constant for the 2:1 complex **1** (ZnPc/ DImPDI/ZnPc) was determined to be $K_2=1.5 \times 10^5$ - $(\pm 0.3) \text{ M}^{-1}$. This value is on the same order of magnitude as K_1 .

The complexation of **PDI-6** and **ZnPc-8** was also studied by fluorescence spectroscopy to evaluate the relationship between UV/Vis and fluorescence binding constants. Figure 7 shows the change in the fluorescence spectrum of **PDI-6** (0.25 μ M) in dichloromethane (after excitation at



Figure 7. Change in the fluorescence spectrum of **PDI-6** (0.25 μ M) upon titration with **ZnPc-8** in CH₂Cl₂ (excited at 584 nm). The inset shows the corresponding Benesi–Hildebrand plot for the determination of the binding constant; the regression coefficient for the nonlinear least-squares curve-fitting analysis is r^2 =0.99843.

584 nm, at which ZnPc-8 is relatively transparent) upon titration with ZnPc-8. The fluorescence emission due to PDI-6 at 611 nm diminishes gradually, whereas a very weak emission band at 687 nm emerges, which is due to the added ZnPc-8. From the functional point of view, it is noteworthy that the fluorescence of **PDI-6** is quenched upon complexation of ZnPc-8, which is probably a result of a photoinduced electron-transfer process.^[29,56,57] The binding constant K for complex 2 [ZnPc-ImPDI] was determined by the Benesi-Hildebrand equation $I_0/(I_0-I) =$ 1/A+1/AK [**ZnPc-8**], for which I_0 and I represent the fluorescence intensities of PDI-6 with

and without the addition of **ZnPc-8**, respectively, and *A* is a constant related to the difference in the emission quantum yield of the complexed and uncomplexed **PDI-6**.^[58] When $I_0/(I_0-I)$ versus 1/[**ZnPc-8**] (inset of Figure 7) was plotted, a straight line was obtained from which the value of *k* was determined to be $1 \times 10^6 (\pm 0.1) \text{ M}^{-1}$. This value is in good agreement with that obtained from the absorption-based studies discussed above. UV/Vis and fluorescence techniques have demonstrated the high binding constants of these imidazolyl PDI–ZnPc complexes.

Electrochemical Studies and Theoretical Calculations

Cyclic voltammograms of **1** and **2** are shown in Figure 8. The comparison with the uncomplexed compounds shows that the cyclic voltammograms consist of two-electron re-



Figure 8. Cyclic voltammograms of a) $\mathbf{2}$ (1.0 mM) and b) $\mathbf{1}$ (1.0 mM) in deaerated CH₂Cl₂ containing TBAPF₆ (0.1 M); sweep rate: 0.1 V s⁻¹.



Figure 9. HOMO and LUMO orbitals of ZnPc-PDI dyad 2. The structural optimization was carried out by DFT B3LYP/3-21G(d) basis set.

duction processes of imidazolyl–PDI and the one-electron oxidation process of ZnPc. The HOMO and LUMO orbitals of dyad **2** (Figure 9) are localized separately on each moiety. The energy of the charge-separated states determined from the one-electron reduction and oxidation potentials are 1.38 eV for **2** and 1.36 eV for **1**, respectively. These values are smaller than those of the energies of singlet excited states of ZnPc (1.80 eV) and PDI (2.31 eV), so the freeenergy changes of photoinduced electron transfer are negative. Thus, photoinduced electron transfer from the singlet excited state of ZnPc to PDI as well as from ZnPc to the singlet excited state of PDI is possible in the supramolecular complexes to form the charge-separated states.

Femtosecond Transient Absorption Spectral Investigations

The confirmation of the charge-separated state and evaluation of the charge-recombination rate were performed by the femtosecond transient absorption spectral technique using dearated dichloromethane as a solvent to avoid decomplexation due to the solvent competition effect. A deaerated solution of **ZnPc-8** in dichloromethane gave rise upon a 410 nm femtosecond laser pulse to a transient absorption band at 480 nm due to the singlet–singlet transition band of ZnPc with strong bleaching at 680 nm, as shown in Figure 10. The strong bleaching at 680 nm is ascribed to the fluorescence and absorption of the ZnPc moiety. The decay obeyed first-order kinetics, and the rate constant could be determined as 9.0×10^8 s⁻¹(Figure 10).

The transient absorption spectra of supramolecular triad ZnPc/DImPDI/ZnPc **1** and dyad ZnPc/ImPDI **2** upon irradiation at 410 nm revealed the characteristic bands at 955 and 1030 nm of the perylenediimide singlet excited state^[59] followed by the apparition of the band at 820 nm that corresponded to the zinc phthalocyanine radical cation; this served as a direct proof of the charge-separated state (CS) within both supramolecular assemblies (Figures 11 and 12). The bands of the perylene radical anion, expected at approximately 970 and 1080 nm, are masked under the bands of the PDI singlet excited state. From the decay of the absorbance of the band at 955 nm, the lifetime of the ¹PDI*



Figure 10. a) Femtosecond transient absorption spectra of **ZnPc-8** in deaerated PhCN taken at 2 and 3000 ps after laser excitation at 410 nm. b) Time profile of absorbance at 480 nm. The gray line was drawn by single-exponential fitting.

excited state in dichloromethane was determined to be 5.5 and 4.3 ps for the ZnPc/DImPDI/ZnPc triad **1** (Figure 12b) and for the ZnPc/ImPDI dyad **2** (Figure 11b), respectively.

The transient absorption band observed at 3000 ps is the charge-separated state. The slower decay process shown in Figures 11c and 12c can be assigned to the charge recombination. The lifetimes of charge-separated states are (9.8 ± 3) ns for triad **1** and (3 ± 1) ns for dyad **2**. To our knowledge, this is the first time that a radical ion pair has been detected in a supramolecularly assembled ZnPc–PDI system. Moreover, the supramolecular approach clearly avoids the fast recombination process observed in covalently bonded electrochemically decoupled^[13,14a] and electrochemically coupled^[24] ZnPc–PDI structures, thus obtaining the longest lifetime of a charge-separated state published for ZnPc–PDI assemblies.

Conclusions

We have applied the very strong coordination between zinc complexes with imidazole ligands to synthesize a supramolecular ZnPc-PDI dyad and ZnP-PDI-ZnPc triad. We



Figure 11. a) Femtosecond transient absorption spectra of ZnPc/ImPDI 2 in deaerated CH_2Cl_2 taken at 1, 10, 500, and 3000 ps after laser excitation at 410 nm. b) and c) Time profiles of absorbance at 955 nm in the time range of 50 and 3000 ps. The gray lines were drawn by double-exponential fitting.



have demonstrated the association between ZnPc and PDI moieties by ¹H NMR spectroscopy, ESI, UV/Vis, and fluorescence measurements. Moreover, for the first time the existence of a charge-separated state in a supramolecular complex between a ZnPc and a perylenediimide has been confirmed by femtosecond laser flash photolysis. This supramolecular approach delays the back-electron transfer to obtain a charge-separated state with a longer lifetime than those of the covalentbond approximation between a ZnPc and a PDI system. The application of these types of supramolecular phthalocyanineacceptor systems in photovoltaic applications has been recently reviewed, thus making them promising candidates for highly efficient solar cells.[60]

Experimental Section

Synthetic Procedures

All chemicals were reagent-grade, purchased from commercial sources, and used as received unless otherwise specified. Column chromatography: silica (40-63 µm) TLC plates coated with silica 60F254 were visualized by UV light. NMR spectra were measured with a Bruker AC 300 instrument. UV/Vis spectra were recorded with a Helios Gamma spectrophotometer. Fluorescence spectra were recorded with a Perkin-Elmer LS 55 luminescence spectrometer and IR spectra with a Nicolet Impact 400D spectrophotometer. Mass spectra were obtained with a Bruker Reflex III matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) instrument and from a VG AutoSpec instrument (FAB). Mass spectra of the complex 2 was obtained with a QSTAR-Applied Biosystems (ESI) QTOF hybrid analyzer. Elemental analyses were performed with a LECO CHNS-932 elemental analyzer.

Compound 3

1,6,7,12-Tetrachloroperylene-3,4:9,10tetracarboxylic acid bisanhydride (0.5 g, 0.94 mmol), acetic acid (0.37 g, 6.25 mmol), 4-(1H-imidazol-1-yl)aniline (0.41 g, 2.6 mmol), and dry NMP

Figure 12. a) Femtosecond transient absorption spectra of ZnPc/DImPDI/ZnPc 1 in deaerated CH_2Cl_2 taken at 1, 10, 500, and 3000 ps after laser excitation at 410 nm. b) and c) Time profiles of absorbance at 955 nm in the time ranges of 50 and 3000 ps. The gray lines were drawn by double-exponential fitting.

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(15 mL) were stirred under argon for 6 h at 85 °C. After being cooled to room temperature, the resulting orange precipitate was filtered and washed with MeOH (100 mL). At this point, CH₂Cl₂ was added to the precipitate and filtered (unreacted perylene bisanhydride remained in the filter). The solvent was evaporated under reduced pressure, and the orange solid was washed and centrifuged twice with MeOH to give pervlene 3 as a red-orange solid (651 mg, 85%). ¹H NMR (300 MHz, CDCl₃/ MeOD 5:1): $\delta = 7.63$ (d, J = 8.8 Hz, 4H; phenyl), 7.65 (br, 2H; imidazole), 7.75 (br, 2H; imidazole), 7.84 (d, J=8.8 Hz, 4H; phenyl), 8.78 (s, 4H; perylene), 9.20 ppm (br, 2H; imidazole); ¹³C NMR (75 MHz, CDCl₃/MeOD 4:1): δ =118.26, 122.21, 122.92, 128.80, 129.54, 130.11, 131.33, 133.06, 133.51, 135.23, 135.41, 162.21 ppm; UV/Vis (CDCl₃/ MeOD 5:1): λ (log ε) = 429 (4.04), 489 (4.49), 522 nm (4.65); FTIR (KBr): v=1710 (C=O imide), 1674 (C=O imide), 1558, 1521, 1384, 1299, 1244, 1196, 1057 cm⁻¹; MS (MALDI-TOF, dithranol): m/z: 811 [M^++1]; elemental analysis calcd (%) for $C_{42}H_{18}Cl_4N_6O_4{\mbox{\cdot}}H_2O{\mbox{\cdot}}C$ 60.74, H 2.43, N 10.12; found: C 60.99, H 2.50, N 10.13.

Compound 4

Perylene 3 (0.4 g, 0.49 mmol), tert-octylphenol (1 g, 4.92 mmol), K₂CO₃ (0.34 g, (2.46 mmol), and dry NMP (15 mL) were stirred under argon for 16 h at 90 °C. During the course of the reaction, the color changed from the red of the initial mixture to dark purple. After being cooled to room temperature, the reaction mixture was treated with HCl (2n) and stirred for 2 h. The purple precipitate was collected by vacuum filtration and washed several times with water. The crude product was dissolved in CH₂Cl₂ and this organic phase was washed with a saturated dissolution of NaHCO₃, water, and then dried with anhydrous MgSO₄. Purification by chromatography (silica, EtOAc) afforded 4 (367 mg, 50%) as a redpurple powder. ¹H NMR (300 MHz, CDCl₃): $\delta = 0.74$ (s, 36 H; *tert*-butyl), 1.33 (s, 24H; $-CH_3$), 1.71 (s, 8H, $-CH_2$ -), 6.88 (d, J=8.2 Hz, 8H; phenol), 7.23 (br, 2H; imidazole), 7.27 (d, J=8.2 Hz, 8H; phenol), 7.32 (br, 2H; imidazole), 7.38 (d, J=8.4 Hz, 4H; phenyl), 7.53 (d, J=8.4 Hz, 4H; phenyl), 7.89 (br, 2H; imidazole), 8.20 ppm (s, 4H; perylene); 13 C NMR (75 MHz, CDCl₃): δ = 31.52, 31.82, 32.39, 38.33, 56.97, 118.28, 119.51, 119.54, 119.73, 120.52, 122.30, 122.34, 127.72, 130.35, 130.60, 133.02, 134.35, 135.63, 137.44, 146.98, 152.37, 156.39, 163.43 ppm; UV/Vis (CH_2Cl_2) : λ $(\log \varepsilon) = 454$ (4.23), 547 (4.47), 586 nm (4.69); FTIR (KBr): v=2953, 2902, 1708 (C=O imide), 1675 (C=O imide), 1586, 1520, 1503, 1407, 1364, 1340, 1319, 1286, 1210, 1174, 837 cm⁻¹; MS (MALDI-TOF, dithranol): m/z: 1492 $[M^++1]$; elemental analysis calcd (%) for C₉₈H₁₀₂N₆O₈: C 78.90, H 6.89, N 5.63; found: C 78.48, H 6.96, N 5.63.

Compound 6

N-(2'-Ethylhexyl)-1,6,7,12-tetrakis-[4'(1",1",3",3"-tetramethylbutyl)phenoxy]perylene-9,10-dicarboximide-3,4-dicarboxyanhydride (5; 95 mg, 0.072 mmol), 4-(1H-imidazol-1-yl)aniline (114 mg, 0.72 mmol), and imidazole (1 g) were stirred under argon for 24 h at 160 °C. After being cooled to room temperature, the reaction mixture was treated with ethanol and this suspension was added into HCl (2 N) and stirred for 24 h. The product was extracted twice with CH2Cl2, and the organic phase was washed with a saturated dissolution of NaHCO3, water, and then dried with anhydrous MgSO₄. Purification by chromatography (silica, CH₂Cl₂/acetone 20:3) afforded 6 (52.5 mg, 50%) as a red-purple powder. ¹H NMR (300 MHz, CDCl₃): $\delta = 0.75$ (s, 18H; tert-butyl), 0.79 (s, 18H; tert-butyl), 0.86 (t, J=7.2 Hz, 3H; -CH₃), 0.88 (t, J=7.2 Hz, 3H; -CH₃), 1.33-1.19 (m, 8H; -CH₂-), 1.33 (s, 12H; -CH₃), 1.37 (s, 12H; -CH₃), 1.71 (s, 4H, -CH₂-), 1.73 (s, 4H; -CH₂-), 1.87 (m, 1H; -CH-), 4.04 (m, 2H; -CH₂-N) 6.86 (d, J=8.7 Hz, 4H; phenol), 6.87 (d, J=8.7 Hz, 4H; phenol), 7.22 (br, 1H; imidazole), 7.26 (d, J=8.7 Hz, 4H; phenol), 7.28 (d, J=8.7 Hz, 4H; phenol), 7.30 (br, 1H; imidazole), 7.37 (d, J=8.7 Hz, 2H; phenyl), 7.52 (d, J=8.7 Hz, 2H; phenyl), 7.89 (br, 1H; imidazole), 8.17 (s, 2H; perylene), 8.18 ppm (s, 2H; perylene); 13 C NMR (75 MHz, CDCl₃): $\delta =$ 10.63, 14.09, 23.04, 24.13, 28.71, 29.29, 30.74, 31.52, 31.82, 31.88, 32.40, 32.44, 37.99, 38.32, 38.37, 44.24, 57.00, 57.07, 119.23, 119.43, 119.59, 119.78, 120.80, 122.00, 122.34, 122.82, 127.69, 127.72, 130.36, 132.81, 132.92, 134.43, 146.83, 146.85, 152.47, 156.14, 156.47, 163.49, 163.71 ppm; UV/Vis (CH₂Cl₂): λ (log ε) = 288 (4.68), 452 (4.27), 544 (4.49), 585 nm (4.71); FTIR (KBr): $\tilde{v} = 2955$, 1703 (C=O imide), 1666 (C=O imide),

1589, 1503, 1409, 1341, 1286, 1214, 1174 cm⁻¹; MS (MALDI-TOF, dithranol): m/z: 1461 [M^+], 1462 [M^+ +1]; MS (MALDI-TOF, dithranol): m/z: 1461 [M^+], 1462 [M^+ +1]; elemental analysis calcd (%) for C₉₇H₁₁₂N₄O₈·0.5H₂O: C 79.20, H 7.74, N 3.81; found: C 79.09, H 7.74, N 3.85.

Compound 7

4,5-Dichlorophthalonitrile (2 g, 10.14 mmol), 4-(2,4,4-trimethylpentan-2yl)phenol (t-octylphenol; 6.3 g, 30.42 mmol) and dry DMSO (30 mL) were heated while stirring at 90°C under argon. Powdered K₂CO₃ $(22.1 \text{ g}, 0.16 \text{ mol}; 8 \times 20 \text{ mmol every 5 min})$ was added. The mixture was stirred for 3 h, cooled to room temperature, and treated with water. The white precipitate obtained was filtered, washed several times with water, and dried. Purification by chromatography (silica, CH2Cl2) afforded 7 (3.2 g, 60%) as a white powder. ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3)$: $\delta = 0.73$ (s, 18H; tert-butyl), 1.40 (s, 12H; $-CH_3$), 1.75 (s, 4H; $-CH_2$ -), 6.99 (d, J =8.8 Hz, 4H; phenol), 7.11 (s, 2H; Ar-H), 7.45 ppm (d, J=8.8 Hz, 4H; phenol); ¹³C NMR (75 MHz, CDCl₃): δ=31.51, 31.71, 32.38, 38.46, 57.09, 109.83, 115.16, 119.33, 121.25, 128.25, 148.13, 151.39, 152.16 ppm; UV/Vis (CH₂Cl₂): λ (log ε) = 231 (4.49), 286 nm (4.18); FTIR (KBr): $\tilde{\nu}$ = 3046, 2952, 2898, 2238 ($C \equiv N$), 1588, 1559, 1496, 1390, 1365, 1311, 1219, 1170, 911, 883 cm⁻¹; MS (MALDI-TOF, dithranol): *m*/*z* : 537 [*M*⁺+1]; elemental analysis calcd (%) for C₃₆H₄₄N₂O₂: C 80.56, H 8.26, N 5.22; found: C 80.60, H 8.28, N 5.25.

Compound 8

Anhydrous ZnCl₂ (1.86 mL, 0.93 mmol; in THF, 0.5 M) was added to dimethylaminoethanol (DMAE; 4 mL) and heated to 90 °C under a continuous argon flow. After all the THF was evaporated, the mixture was cooled to 60°C. At this point, phthalonitrile 7 (0.5 g, 0.93 mmol) was added and the reaction mixture was stirred under argon for 24 h at 140°C. During the course of the reaction, the color changed from white of the initial mixture to dark green of the phthalocyanine. After being cooled to room temperature, the resulting dark green mass was poured into MeOH (50 mL), and the precipitate was filtered and washed twice with MeOH. Purification by chromatography (silica, toluene/acetone 100:1) afforded 8 (335 mg, 65 %) as a green powder. ¹H NMR (300 MHz, CDCl₃): $\delta = 0.72$ (s, 72 H; *tert*-butyl), 1.36 (s, 48 H; -CH₃), 1.72 (s, 16 H; $-CH_2$ -), 6.98 (d, J=9 Hz, 16H; phenol), 7.29 (d, J=9 Hz, 16H; phenol), 8.46 ppm (s, 8H; Pc); ¹³C NMR (75 MHz, CDCl₃): δ = 31.55, 31.81, 32.36, 38.18, 57.13, 117.38, 119.12, 127.28, 127.93, 144.90, 147.19, 150.17, 154.99 ppm; UV/Vis (CH₂Cl₂): λ (log ε) = 286 (4.89), 348 (4.95), 614 (4.60), 681 nm (5.39); FTIR (KBr): $\tilde{\nu} = 2954$, 2903, 1506, 1486, 1451, 1400, 1365, 1271, 1218, 1180, 1087, 1029, 892 cm⁻¹; MS (MALDI-TOF, dithranol): m/z: 2209 $[M^+]$; elemental analysis calcd (%) for C144H176N8O8Zn•2H2O: C 76.92, H 8.07, N 4.98; found: C 76.65, H 8.15, N 4.78.

¹H NMR Spectroscopic Experiments

NMR spectroscopic titrations of **ZnPc-8** with **PDI-4** were performed as follows. An initial volume of 600 μ L of a 0.44 mM solution of **PDI-4** in CDCl₃ was placed in an NMR tube. Aliquots of a solution of **ZnPc-8** (8 mM) and **PDI-4** (0.44 mM) in CDCl₃ were subsequently added, and a spectrum was recorded after each addition (300 MHz, 298 K). **PDI-4** was added to avoid dilution effects. The same procedure was used to perform the NMR spectroscopic titrations of **ZnPc-8** with **PDI-6**.

UV/Vis Titration Experiments

Job plots to determine the stoichiometry of the binding between **PDI-6** and **ZnPc-8** were carried out using a continuous variation of the UV/Vis absorption that corresponded to complex **2** (ZnPc/ImPDI) at 365 nm [see the previous "background absorbance" method using Eq. (2)]. An initial volume of 1.6 mL of a 10 μ M solution of **ZnPc-8** in CH₂Cl₂ was placed in a sealed quartz cuvette. Aliquots (100 μ L) of a solution of **PDI-6** in CH₂Cl₂ (10 μ M) were subsequently added, and a UV/Vis spectrum was recorded after each addition.

Job plots to determine the stoichiometry of the binding between PDI-4 and ZnPc-8 were carried out using a continuous variation of the UV/Vis

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absorption that corresponded to complex 1 (ZnPc/ImPDI) at 365 nm [see the previous "background absorbance" method using Eq. (2)]. An initial volume of 1.5 mL of a 5.5 μ M solution of **ZnPc-8** in CH₂Cl₂ was placed in a sealed quartz cuvette. Aliquots (100 μ L) of a solution of **PDI-4** in CH₂Cl₂ (5.5 μ M) were subsequently added, and a UV/Vis spectrum was recorded after each addition.

Analyses of the interactions between receptor **ZnPc-8** and guests **PDI-6** and **PDI-4** were also carried out using UV/Vis spectroscopy. UV/Vis titrations of **PDI-6** with **ZnPc-8** were performed as follows. An initial volume of 1.6 mL of a 5.6 μ M solution of **ZnPc-8** in CH₂Cl₂ was placed in a sealed quartz cuvette. Aliquots of a solution of **PDI-6** (111.5 μ M) and **ZnPc-8** (5.6 mM) in CH₂Cl₂ were subsequently added, and a UV/Vis spectrum was recorded after each addition (298 K). **PDI-6** was added to avoid dilution effects. The data were analyzed using standard curve-fitting methods,^[52] and the binding constants were evaluated by nonlinear least-squares regression analysis from the changes in the absorbance at 365 nm of the Soret band [see the previous "background absorbance" method using Eq. (2)].

UV/Vis titrations of **PDI-4** with **ZnPc-8** were performed as follows. An initial volume of 1.6 mL of a 7.5 μ M solution of **ZnPc-8** in CH₂Cl₂ was placed in a sealed quartz cuvette. Aliquots of a solution of **PDI-4** (74 μ M) and **ZnPc-8** (7.5 mM) in CH₂Cl₂ were subsequently added, and a UV/Vis spectrum was recorded after each addition (298 K). **PDI-4** was added to avoid dilution effects. The data were analyzed using standard curve-fitting methods,^[54] and the binding constants (K_1 and K_2) were evaluated by nonlinear least-squares regression analysis (we made an approach in which $K_1 = K$ of complex $2 = 3.42 \times 10^5 (\pm 0.1) M^{-1}$) from the changes in the absorbance at 365 nm of the Soret band [see the previous "background absorbance" method using Eq. (2)].

Fluorescence Titration Experiments

The fluorescence binding constant was obtained as follows. An initial volume of 1.7 mL of a 0.25 μ M solution of **PDI-6** in CH₂Cl₂ (spectrosol quality) was placed in a sealed quartz cuvette. Aliquots of a solution of **ZnPc-8** (5.1 μ M) and **PDI-6** (0.25 mM) in CH₂Cl₂ (spectrosol quality) were subsequently added, and a fluorescence spectrum was recorded after each addition (after excitation of **PDI-6** at 584 nm, 298 K). **PDI-6** was added to avoid dilution effects. The binding constant *k* was determined by the Benesi–Hildebrand equation [Eq. (3)] from the changes in the fluorescence of **PDI-6**.

Laser Flash Photolysis

Femtosecond transient absorption spectroscopy experiments were conducted with an ultrafast source (Integra-C, Quantronix Corp.), an optical parametric amplifier (TOPAS, Light Conversion Ltd.), and a commercially available optical detection system (Helios, provided by Ultrafast Systems LLC). The source for the pump and probe pulses was derived from the fundamental output of Integra-C (780 nm, 2 mJ per pulse, and full width at half-maximum = 130 fs) at a repetition rate of 1 kHz. The fundamental output of the laser (75%) was introduced into TOPAS, which has optical frequency mixers that result in a tunable range from 285 to 1660 nm, whereas the rest of the output was used for white-light generation. Typically, 2500 excitation pulses were averaged for 5 s to obtain the transient spectrum at a set delay time. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. All measurements were conducted at 298 K. The transient spectra were recorded by using fresh solutions in each laser excitation.

Theoretical Calculations

Density functional theory (DFT) calculations were performed with a COMPAQ DS20E computer. Geometry optimizations of supramolecular systems were carried out with the Becke 3LYP functional and 3-21G* basis set,^[31-33] with the restricted Hartree–Fock (RHF) formalism and as implemented in the Gaussian 03 program.^[61] Graphical outputs of the computational results were generated with the GaussView software program.^[62]

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- [1] D. Gust, T. A. Moore, A. L. Moore, Acc. Chem. Res. 2001, 34, 40.
- [2] M. R. Wasielewski, Chem. Rev. 1992, 92, 435.
- [3] D. M. Guldi, Chem. Soc. Rev. 2002, 31, 22.
- [4] M. N. Paddon-Row, Acc. Chem. Res. 1994, 27, 18.
- [5] M. J. Blanco, M. C. Jiménez, J.-C. Chambron, V. Heitz, M. Linke, J.-P. Sauvage, *Chem. Soc. Rev.* **1999**, 28, 293.
- [6] S. Fukuzumi, D. M. Guldi, *Electron Transfer in Chemistry, Vol. 2* (Ed.: V. Balzani), Wiley-VCH, Weinheim, **2001**, pp. 270–337.
- [7] S. Fukuzumi, Org. Biomol. Chem. 2003, 1, 609.
- [8] F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, *Chem. Rev.* 2005, 105, 1491.
- [9] G. de la Torre, M. Nicolau, T. Torres, *Phthalocyanines: Synthesis Supramolecular Organization and Physical Properties (Supramolecular Photosensitive and Electroactive Materials)* 2001, Academic Press, New York.
- [10] C. C. Leznoff, A. B. P. Lever, *Phthalocyanines: Properties and Appli*cations, Vols. 1–4, 1989, 1993, 1996, VCH, Weinheim, Germany.
- [11] G. de la Torre, P. Vazquez, F. Agulló-López, T. Torres, Chem. Rev. 2004, 104, 3723.
- [12] G. de la Torre, C. G. Claessens, T. Torres, Chem. Commun. 2007, 2000.
- [13] a) S. Fukuzumi, K. Ohkubo, J. Ortiz, A. M. Gutiérrez, F. Fernández-Lázaro, Á. Sastre-Santos, *Chem. Commun.* 2005, 3814; b) S. Fukuzumi, K. Ohkubo, J. Ortiz, A. M. Gutiérrez, F. Fernández-Lázaro, Á. Sastre-Santos, *J. Phys. Chem. A* 2008, *112*, 10744.
- [14] a) F. J. Céspedes-Guirao, K. Ohkubo, S. Fukuzumi, Á. Sastre-Santos, F. Fernández-Lázaro, J. Org. Chem. 2009, 74, 5871; b) F. J. Céspedes-Guirao, L. Martín-Gomis, K. Ohkubo, S. Fukuzumi, F. Fernández-Lázaro, Á. Sastre-Santos, Chem. Eur. J. 2011, DOI: 10.1002/chem.201100320.
- [15] J. J. Cid, J. H. Yum, S. R. Jang, M. K. Nazeeruddin, E. Martínez-Ferrero, E. Palomares, J. Ko, M. Grätzel, T. Torres, *Angew. Chem.* 2007, 119, 8510; *Angew. Chem. Int. Ed.* 2007, 46, 8358.
- [16] F. Würthner, Chem. Commun. 2004, 1564.
- [17] T. van der Boom, R. T. Hayes, Y. Zhao, P. J. Bushard, E. A. Weiss, M. R. Wasielewski, J. Am. Chem. Soc. 2002, 124, 9582.
- [18] B. Rybtchinski, L. E. Sinks, M. R. Wasielewski, J. Am. Chem. Soc. 2004, 126, 12268.
- [19] A. Herrmann, K. Müllen, Chem. Lett. 2006, 35, 978.
- [20] a) M. Planells, F. J. Céspedes-Guirao, A. Forneli, Á. Sastre-Santos, F. Fernández-Lázaro, E. Palomares, J. Mater. Chem. 2008, 18, 5802;
 b) M. Planells, F. J. Céspedes-Guirao, L. Gonçalves, Á. Sastre-Santos, F. Fernández-Lázaro, E. Palomares, J. Mater. Chem. 2009, 19, 5818.
- [21] S.-G. Liu, Y.-Q. Liu, Y. Xu, X.-Z. Jiang, D.-B. Zhu, *Tetrahedron Lett.* 1998, 39, 4271.
- [22] X. Li, L. E. Sinks, B. Rybtchinski, M. R. Wasielewski, J. Am. Chem. Soc. 2004, 126, 10810.
- [23] Y. Chen, Y. Lin, M. E. El-Khouly, X. Zhuang, Y. Araki, O. Ito, W. Zhang, J. Phys. Chem. C 2007, 111, 16096.
- [24] A. J. Jiménez, F. Spänig, M. S. Rodríguez-Morgade, K. Ohkubo, S. Fukuzumi, D. M. Guldi, T. Torres, Org. Lett. 2007, 9, 2481.
- [25] M. O. Liu, C.-H. Tai, A. T. Hu, J. Photochem. Photobiol. A 2004, 165, 193.
- [26] M. S. Rodríguez-Morgade, T. Torres, C. Atienza-Castellanos, D. M. Guldi, J. Am. Chem. Soc. 2006, 128, 15145.
- [27] B. Gao, Y. Li, J. Su, H. Tian, Supramol. Chem. 2007, 19, 207.

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- [28] A. Prodi, C. Chiorboli, F. Scandola, E. Iengo, E. Alessio, R. Dobrawa, F. Würthner, J. Am. Chem. Soc. 2005, 127, 1454.
- [29] C.-C. You, F. Würthner, Org. Lett. 2004, 6, 2401.
- [30] E. B. Fleischer, A. M. Shachter, *Inorg. Chem.* **1991**, *30*, 3763.
- [31] C. A. Hunter, R. K. Hyde, Angew. Chem. 1996, 108, 2064; Angew. Chem. Int. Ed. Engl. 1996, 35, 1936.
- [32] F. Würthner, A. Sautter, C. Thalacker, Angew. Chem. 2000, 112, 1298; Angew. Chem. Int. Ed. 2000, 39, 1243.
- [33] C. A. Hunter, R. Tregonning, Tetrahedron 2002, 58, 691.
- [34] T. S. Balaban, R. Goddard, M. Linke-Schaetzel, J.-M. Lehn, J. Am. Chem. Soc. 2003, 125, 4233.
- [35] A. L. Schumacher, A. S. D. Sandanayaka, J. P. Hill, K. Ariga, P. A. Karr, Y. Araki, O. Ito, F. D'Souza, *Chem. Eur. J.* 2007, 13, 4628.
- [36] F. D'Souza, M. E. El-Khouly, S. Gadde, M. E. Zandler, A. L. McCarty, Y. Araki, O. Ito, *Tetrahedron* 2006, *62*, 1967.
- [37] F. D'Souza, S. Gadde, M. E. El-Khouly, M. E. Zandler, Y. Araki, O. Ito, J. Porphyrins Phthalocyanines 2005, 9, 698.
- [38] a) D. M. Guldi, J. Ramey, M. V. Martínez-Díaz, A. de la Escosura, T. Torres, T. D. Ros, M. Prato, *Chem. Commun.* 2002, 2774; b) F. J. Céspedes-Guirao, F. Fernández-Lázaro, L. Martín-Gomis, Á. Sastre-Santos, *J. Porphyrins Phthalocyanines* 2009, 13, 266.
- [39] K. Ogawa, Y. Kobuke, Angew. Chem. 2000, 112, 4236; Angew. Chem. Int. Ed. 2000, 39, 4070.
- [40] R. Takahashi, Y. Kobuke, J. Am. Chem. Soc. 2003, 125, 2372.
- [41] H. Ozeki, A. Nomoto, K. Ogawa, Y. Kobuke, M. Murakami, K. Hosoda, M. Ohtani, S. Nakashima, H. Miyasaka, T. Okada, *Chem. Eur. J.* 2004, 10, 6393.
- [42] K. Kameyama, M. Morisue, A. Satake, Y. Kobuke, Angew. Chem. 2005, 117, 4841; Angew. Chem. Int. Ed. 2005, 44, 4763.
- [43] M. Morisue, Y. Kobuke, Chem. Eur. J. 2008, 14, 4993.
- [44] R. Chitta, A. S. D. Sandanayaka, A. L. Schumacher, L. D'Souza, Y. Araki, O. Ito, F. D'Souza, J. Phys. Chem. C 2007, 111, 6947.
- [45] F. D'Souza, P. M. Smith, M. E. Zandler, A. L. McCarty, M. Itou, Y. Araki, O. Ito, J. Am. Chem. Soc. 2004, 126, 7898.
- [46] F. D'Souza, O. Ito, Coord. Chem. Rev. 2005, 249, 1410.
- [47] M. E. El-Khouly, L. M. Rogers, M. E. Zandler, G. Suresh, M. Fujitsuka, O. Ito, F. D'Souza, *ChemPhysChem* 2003, 4, 474.
- [48] F. Würthner, C. Thalacker, A. Sautter, W. Schärtl, W. Ibach, O. Hollricher, *Chem. Eur. J.* 2000, 6, 3871.
- [49] F. Würthner, A. Sautter, J. Schilling, J. Org. Chem. 2002, 67, 3037.
- [50] H. Xu, D. K. P. Ng, Inorg. Chem. 2008, 47, 7921.

- [51] S. Nygaard, C. N. Hansen, J. O. Jeppesen, J. Org. Chem. 2007, 72, 1617.
- [52] K. Hirose, J. Inclusion Phenom. Macrocyclic Chem. 2001, 39, 193.
- [53] P. Job, Annal. Chim. France 1928, 9, 113.
- [54] K. A. Connors, The Measurement of Molecular Complex Stability, Wiley, New Work, 1987.
- [55] K. A. Nielsen, G. H. Sarova, L. Martín-Gomis, P. C. Stein, L. Sanguinet, E. Levillain, J. L. Sessler, D. M. Guldi, F. Fernández-Lázaro, Á. Sastre-Santos, J. O. Jeppesen, J. Am. Chem. Soc. 2008, 130, 460.
- [56] A. Berg, Z. Shuali, M. Asano-Someda, H. Levanon, M. Fuhs, K. Mobius, R. Wang, C. Brown, J. L. Sessler, *J. Am. Chem. Soc.* **1999**, *121*, 7433.
- [57] A. J. Myles, N. R. Branda, J. Am. Chem. Soc. 2001, 123, 177.
- [58] H. A. Benesi, J. H. Hildebrand, J. Am. Chem. Soc. 1949, 71, 2703.
- [59] W. Seitz, A. J. Jiménez, E. Carbonell, B. Grimm, M. S. Rodríguez-Morgade, D. M. Guldi, T. Torres, *Chem. Commun.* 2010, 46, 137.
- [60] G. Bottari, G. de la Torre, D. M. Guldi, T. Torres, Chem. Rev. 2010, 110, 6768–6816.
- [61] Gaussian 03 (Revision C.02), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
- [62] GaussView, Version 3.09, Semichem, Inc., Shawnee Mission, KS, 2003.

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