

# A Tightly Coupled Bis(zinc(II) phthalocyanine)–Perylenediimide Ensemble To Yield Long-Lived Radical Ion Pair States<sup>†</sup>

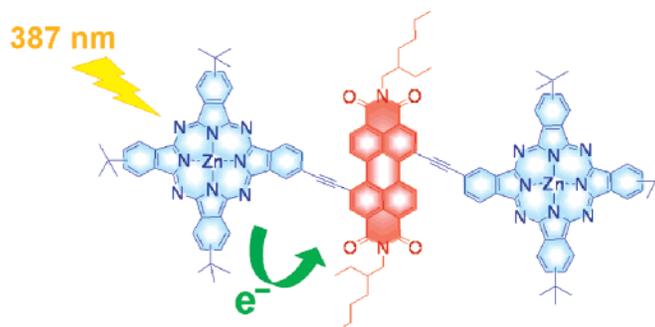
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## ABSTRACT



A conjugated donor–acceptor array composed of two phthalocyanines connected to the bay region of a perylenediimide is assembled by using palladium chemistry. Excitation of the phthalocyanine produces a nanosecond lived charge-separated state.

The quest for artificial photosynthetic reaction centers, as a part of “the modular strategy”,<sup>1</sup> constitutes an expanding trend in the field of solar photochemistry and solar energy conversion.<sup>2</sup> In particular, there is considerable interest in the design of systems composed of electron donor and acceptor entities displaying energy and/or electron-transfer events.<sup>3</sup> The efficiency of those processes is governed by

the selected building block functionalities, linkers, and geometrical arrangements.<sup>4</sup> The benefits of phthalocyanines (Pc’s)<sup>5</sup> as components for such systems is beyond question.

<sup>†</sup> Dedicated to Professor Miguel Yus on the occasion of his 60th birthday.

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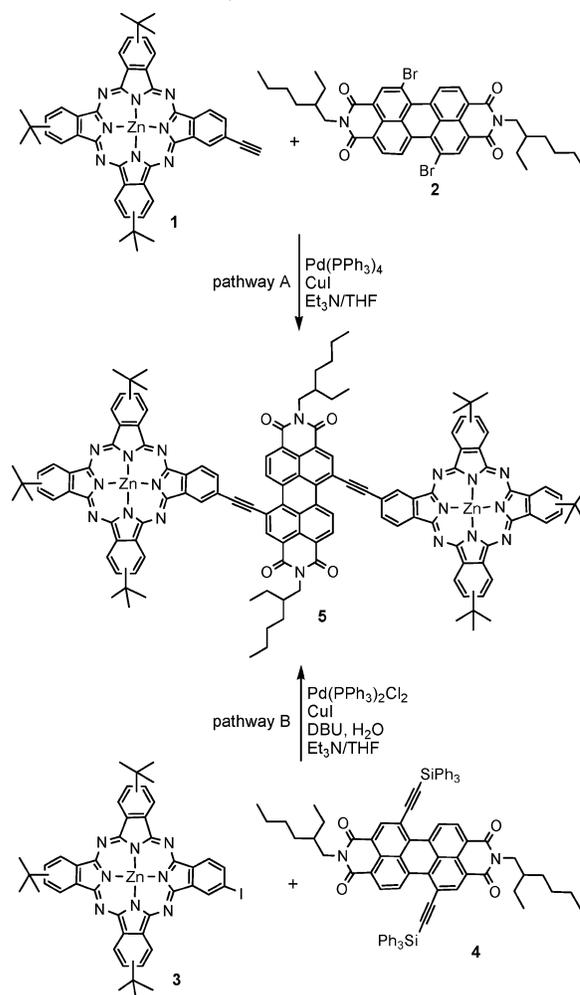
Thus, their extended  $\pi$ -conjugated structure provides them with strong absorption in the visible and redox features that make them specially suitable for photoinduced charge separation.<sup>6</sup> In the past few years we have directed our attention to construct Pc-based multinuclear systems with additional  $\pi$ -extended conjugation, as well as multifunctional donor–acceptor hybrids in which the complementary electroactive constituents (i.e., C<sub>60</sub>) are connected through a variety of junctions.<sup>7,8</sup> Remarkably, ZnPc–C<sub>60</sub> systems tend to yield shorter radical ion pair state lifetimes, when compared with analogous ZnP–C<sub>60</sub> systems.<sup>9</sup>

Recently, perylene-3,4,9,10-tetracarboxylic diimides (PDI's) have attracted our attention as the complementary oxidizing moieties,<sup>10</sup> and hence, we have reported a supramolecular RuPc–PDI–RuPc that forms upon photoexcitation a long-lived radical ion pair state.<sup>11</sup> Herein, we wish to describe a novel, covalently linked, conjugated array **5** (Scheme 1) composed of two Zn(II)-phthalocyanines attached through ethynyl functions to the 1,7-positions of a perylene-3,4,9,10-tetracarboxylic diimide moiety.

Previous reports on the Pc–PDI motif are very scarce, and include organization of the two dyes in thin films,<sup>12</sup> or covalent hybrids of the two chromophores connected through the PDI imido positions.<sup>13</sup> In the triad **5** the two phthalocyanines are bound to the PDI-bay region so that the system was expected to be electronically coupled,<sup>14</sup> with the PDI component profoundly influenced by the presence of the two phthalocyanines.<sup>15</sup>

The ZnPc–PDI–ZnPc triad **5** can be assembled by Sonogashira coupling of suitable Pc and PDI derivatives. In a first approach (Scheme 1, pathway A) the intermediate **2**

**Scheme 1.** Synthesis of ZnPc–PDI–ZnPc **5**



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(14) The presence of nodes at the imido nitrogens in the HOMO and LUMO of the PDI molecule prevents electronic coupling between subunits, when such subunits are attached through the PDI imido positions.

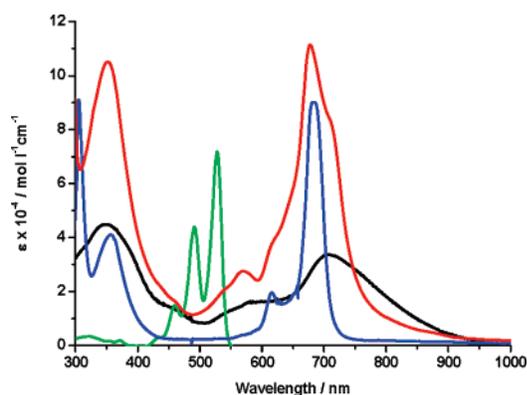
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was attained by bromination of perylene bisanhydride, followed by imidation in propionic acid.<sup>16</sup> Under these conditions, the 1,7-dibrominated compound **2** was obtained as the major product, even though it was accompanied by the corresponding 1,6-regioisomer and 1,6,7-tribrominated product, arising from the bromination step.<sup>17</sup> We could easily remove the minor tribrominated component (4% of the mixture)<sup>17</sup> by standard column chromatography. However, the 1,7-derivative **2** (76% of the mixture)<sup>17</sup> could only be separated from its 1,6-regioisomer by repetitive recrystallization from a 3:1 mixture of methanol and dichloromethane. Once isolated, the two subunits **1** and **2** were assembled in 16% yield by using palladium chemistry to afford **5**. Alternatively, the array **5** can be prepared by the palladium cross-coupling reaction of an iodo-substituted phthalocyanine **3** and a PDI derivative **4** endowed with two ethynyl rests (Scheme 1, pathway B). The strategy relies on the premise that functionalization of PDI's at the bay region with bulky

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groups prevents aggregation and makes separation by chromatography easier. The alkyne linkers were introduced via reaction of triphenylsilylacetylene and **2**, as a 1,6- and 1,7-regioisomeric mixture. Here, the choice of the large triphenylsilane as the protecting group for the alkyne function is critical, since this allowed the straightforward separation of the 1,7- from the 1,6-PDI regioisomer by column chromatography. Subsequent one-pot deprotection and Sonogashira coupling with phthalocyanine **3**, following a protocol reported by Grieco and co-workers,<sup>18</sup> afforded the hybrid **5** in quite good yield (33%), taking into account that this yield is referred to four chemical reactions, namely two alkyne deprotections and two Sonogashira couplings.



**Figure 1.** UV/vis spectra of phthalocyanine **1** (ZnPc, blue), *N,N'*-di-(2-ethylhexyl)perylene-3,4,9,10-tetracarboxylic acid bisimide (PDI, green), and ZnPc-PDI-ZnPc (**5**) (black) in chloroform. The red spectrum shows **5** in a THF solution containing 1% pyridine.

Figure 1 shows the electronic spectra of the hybrid **5** together with those corresponding to its Pc and PDI fragments. Compound **5** strongly aggregates in solution of noncoordinating solvents such as chloroform, as is clearly evidenced by its broad, abnormally low intense Q-band. The use of coordinating solvents such as THF or pyridine produces stable coordinative complexes with the phthalocyanine metal ion, thus reducing aggregation in diluted solutions ( $c < 10^{-5}$  M).<sup>19</sup> Under these conditions the broadening still lingers, although to a much lesser extent. This speaks for a significant redistribution of charge density in the ground state, that is, from the electron donating ZnPc to the electron accepting PDI. Moreover, the characteristic Q- and B-absorption bands, corresponding to the  $S_1$  and  $S_2$  states, split in ZnPc-PDI-ZnPc (**5**) with 330/351 nm and 678/710 nm components respectively in THF/pyridine. Compare those to maxima at 361 and 686 nm for the phthalocyanine fragment **1**.

The spectral changes are rationalized by referring to the simple point-dipole exciton coupling theory developed by

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(19) However, the <sup>1</sup>H NMR spectrum (see the Supporting Information) shows that **5** is still aggregated at higher concentrations (3 mM).

Kasha. The phthalocyanine B-band has two perpendicular components of  $B_x$  and  $B_y$ . In **1**, they are degenerate, but in ZnPc-PDI-ZnPc (**5**) they couple differently with the adjacent perylene, so that only the  $B_x$  transitions couple and, in turn, shift to the blue. The other dipole interactions (i.e.,  $B_y$ ) should be zero leaving the corresponding transitions unchanged.

Importantly, the large splitting of the B-bands (0.36 eV) is mainly due to exciton-coupling between neighboring ZnPc and PDI moieties. Much weaker splitting (0.1 eV), as well as smaller red shifts, indicating a weak coupling of transition dipoles, is seen for the Q-bands. Moreover, the PDI transitions, which occur in the reference at 464, 495, and 529 nm, are red shifted to 540 and 570 nm. Part of these changes arise from the substitution by conjugated ethynyl groups at the PDI bay (see the Supporting Information). In addition, the presence of two bulky phthalocyanines in **5** must necessarily have a strong influence on the planarity of the red chromophore. Still, all this evidence speaks for strong electronic communication between the two redox-active components. It is likely that a partial redistribution of charge density—transfer from ZnPc (i.e., electron donor) to PDI (i.e., acceptor)—is active.

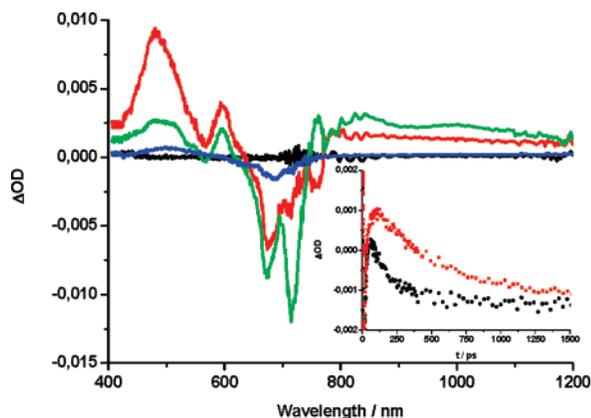
Steady-state fluorescence helped to shed light onto the excited state interactions. Taking the photo- and redox-activity of both ZnPc and PDI units into account, their high fluorescence quantum yields of 0.3 and 0.75 are particularly helpful. In this context, we compared PDI with ZnPc-PDI-ZnPc (**5**) and ZnPc with **5** by exciting them in the 450–525 and 600–675 nm ranges, respectively. In both cases, although seeing a similar ZnPc and PDI fluorescence pattern, strong fluorescence quenching is noted: For the PDI unit a quenching of 200 evolves around the emission in the visible (i.e., shifted from 540 nm at 2.3 eV to 590 nm at 2.1 eV), while for the ZnPc component, emission in the near-infrared (i.e., shifted from 690 nm at 1.79 eV to 700 nm at 1.77 eV), the quenching is 250-fold.

Prior to conducting photolytic tests with ZnPc, PDI, and ZnPc-PDI-ZnPc (**5**), the possible redox products, namely, one-electron oxidized ZnPc radical cation and one-electron reduced PDI radical anion, were generated pulse radiolytically. The corresponding spectra are gathered in Figure S-20 (Supporting Information). For PDI, we see in the visible a set of minima at 460, 490 and 530 nm, followed in the near-infrared by a broad maximum at 625 nm, as features of the one-electron reduced radical anion. For ZnPc, maxima at 530 and 840 nm are well-known attributes of the one-electron oxidized radical cation. We also tested the PDI triplet excited state features via triplet–triplet energy transfer from the radiolytically generated anthracene triplet excited state.

Next, the excited state properties of ZnPc shall be discussed, since they emerge as important reference points for the interpretation of the features expected in the triad **5**. The differential spectrum, recorded immediately after the laser pulse for the ZnPc reference, is characterized by bleaching of the Q-band absorption at 686 nm and broad absorption between 400 and 600 nm (Figure S-21, Supporting Information). These spectral attributes are indicative of the ZnPc singlet excited state and are formed with a rate constant

of  $> 1 \times 10^{12} \text{ s}^{-1}$ . The singlet excited state features decay slowly (i.e., 3.0 ns;  $3.3 \times 10^8 \text{ s}^{-1}$ ) to the energetically lower-lying triplet excited state, predominantly via intersystem crossing (ZnPc triplet quantum yield,  $\Phi_{\text{Triplet}} = 0.7$ ).

When turning to the assembly **5**, photoexcitation at 387 nm, seeing the ZnPc singlet excited state features right after the laser pulse confirms the nearly exclusive excitation of the ZnPc moiety—see Figure 2.



**Figure 2.** Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (387 nm) of ZnPc-PDI-ZnPc (**5**) in nitrogen saturated THF/pyridine with several time delays (i.e., 0 ps, black; 1 ps, red; 15 ps, green; 3000 ps, blue) at room temperature. Inset: Time-absorption profiles of the spectra shown above at 620 nm, monitoring the charge separation and charge recombination in toluene/pyridine (red) and THF/pyridine (black).

We rule out an excitation of PDI due to the low extinctions in this range of wavelength (i.e., less than 5%). In line with this assumption, the differential spectra lack any measurable PDI singlet excited state contributions. The ZnPc singlet excited state features decay rapidly (i.e., 7.2 ps;  $1.4 \times 10^{11} \text{ s}^{-1}$ ) to yield a transient product that looks distinctly different from any possible excited states (i.e., ZnPc triplet, PDI singlet, or PDI triplet). First, let us look at the visible range, where minima at 540 and 565 nm and maxima at 600 and 760 nm are discernible. Notably, the minima mirror image the ground state absorption maxima of PDI and resemble equally that part of the radical anion spectrum. The maxima, on the other hand, are only the blue and red flanks of what would be the 625 nm maximum of the radical anion band. However, the strong bleaching of the ZnPc radical cation affects the net changes in this part of the differential absorption spectrum. In the NIR part we note maxima at

840 and 1000 nm, which correspond to the ZnPc radical cation. In other words, we have accomplished a full spectral characterization of the radical ion pair state, namely,  $\text{ZnPc}^{\bullet+}\text{-PDI}^{\bullet-}\text{-ZnPc}$  (1.2 eV), as it has evolved from a thermodynamically allowed (0.52 eV) electron transfer. A deceleration of the charge separation is seen when looking at toluene/pyridine, due to a lower driving force.

By following the temporal changes of the aforementioned radical ion pair features—throughout the visible and near-infrared regions—a lifetime of 224 ps ( $4.4 \times 10^9 \text{ s}^{-1}$ ) was derived. In toluene/pyridine, the lifetime increases to 517 ps ( $1.9 \times 10^9 \text{ s}^{-1}$ ). Some time absorption profiles are illustrated in Figure 2. With the conclusion of this charge recombination process the triplet excited state spectrum of ZnPc evolves in, however, minute yields (i.e., 7% and 2% in toluene/pyridine and THF/pyridine, respectively—relative to ZnPc). This decay pathway helps to explain the unusually long lifetime of the radical ion pair states, when compared to analogous, but electronically decoupled ZnP-PDI-ZnP conjugate (i.e., 77 ps;  $1.3 \times 10^{10} \text{ s}^{-1}$ ). A markedly higher lying radical ion pair state (1.61 eV) affords, however, the triplet excited states to be formed quantitatively.<sup>20</sup> It should be noted that photoexcitation of a different ZnPc-PDI conjugate (i.e., linked at the imido positions) affords only triplet excited states.<sup>13c</sup>

In summary, we have reported the synthesis and physico-chemical characterization of a ZnPc-PDI-ZnPc ensemble, which yields long-lived radical ion pair states. Key to this success is a charge recombination that leads mainly to the recovery of the singlet ground state. We are currently investigating related multinuclear Pc-PDI-based systems in which both covalent and supramolecular motifs<sup>11</sup> are involved.

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**Supporting Information Available:** Synthetic procedures for the preparation of unreported compounds, as well as NMR, IR, UV/vis and MS, radiolytic transient absorption, femtosecond transient absorption, and fluorescence spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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