Chemical Science

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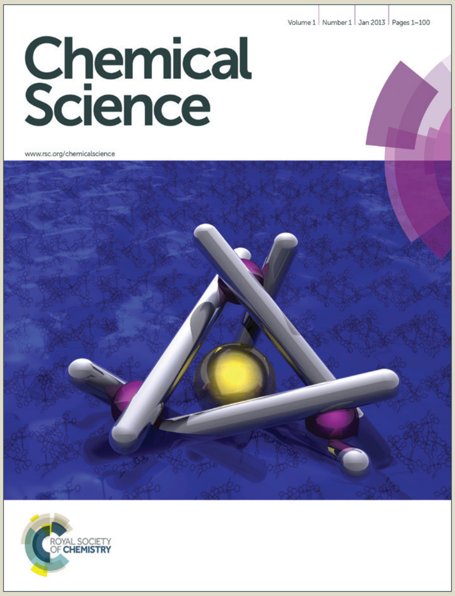

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Submillisecond-lived photoinduced charge separation in a fully conjugated phthalocyanine-perylenebenzimidazole dyad

Vicente M. Blas-Ferrando,[a] Javier Ortiz[a], Kei Ohkubo,[b] Shunichi Fukuzumi,*[,b] Fernando Fernández-Lázaro[a] and Ángela Sastre-Santos*[,a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

A fully electronically conjugated phthalocyanine-perylenemonoimidebenzimidazole system **ZnPc-PMIBI 2**, where the conjugation goes through the imide position of the perylene has been synthesized. The preparation was possible by condensation of a new unsymmetrically substituted diaminophthalocyaniane, ZnPc(NH_2)$_2$, with a perylene monoanhidride monoimide. Both the experimental and the computational (DFT) results indicate that ZnPc-PMIBI exhibits significant intramolecular electronic interactions. The lifetime of the charge-separated (CS) state was expanded to 0.26 ms, corresponding to the longest values ever reported for a covalent phthalocyanine-peryleneimide system in solution and is attributed to the synergy of an extremely low CS energy, lower than the triplet energy of each chromophore, together with the coupling between both units, that allows a fast charge separation.

Introduction

The design and synthesis of arrays formed by electron donor and acceptor units undergoing photoinduced electron transfer processes represents a very important issue in the development of organic optoelectronics.[1] For this purpose is crucial to study their photophysical behaviour to find out whether they are able to generate long-lived charge-separated excited states that allow the efficient generation of charge carriers.[2]

Well-defined molecular model systems typically comprise a donor (D) and an acceptor (A) covalently linked by a bridge (B). In the resulting D–B–A structures, the role of the bridge is ideally to facilitate the desired initial photoinduced charge separation, while slowing down the undesired charge recombination. Quite often, D-σ-A ensembles show redox and photophysical properties that are just given by the sum of the properties of the corresponding building blocks due to the lack of strong electronic interactions between D and A moieties. In contrast, sterically controlled and compactly fused D-π-A systems exhibit significant intramolecular interactions potentially giving rise to efficient photoinduced charge-separation processes.[3] Moreover, such π-bridged systems allow the combination of a high-lying HOMO localized on D with a low-lying LUMO on A, resulting in conjugated systems bearing small HOMO-LUMO gaps which allow efficient injection of both holes and electrons.[4] Among the many combinations of donors and acceptors that have been explored, those consisting of phthalocyanines and perylenediimide derivatives have shown outstanding results.[5]

Electron rich phthalocyanines (Pcs)[6] have been widely used in devices[7] for their thermal and photochemical stabilities, their high absorption in the red-near IR region and the possibility to tune their properties through the introduction of suitable substituents (metal ion, α and β positions and even axial positions depending on the metal ion).

Perylenediimides (PDIs)[8] are thermally, chemically and photochemically stable electron acceptors absorbing in the visible area, just in a region complementary to that of Pc absorption. Their acceptor properties can be increased by introducing electron-withdrawing groups which may also provide solubility. They have been used in organic optoelectronic devices[9] and biological applications.[10] Thus Pcs and PDI are ideal components to form very stable D-π-A arrays that absorb strongly in the visible spectrum.[11] The photophysical properties of various Pc–PDI conjugates featuring different molecular bridges have been investigated. However, these systems have triplet excited states of lower energy than the charge-separated ones, so they are the finally detected long-lived excited species , while the charge-separated states display short lifetimes ranging from pico to nanoseconds.[12] Nevertheless, in the presence of magnesium ions, which coordinate with the oxygen of the imides stabilizing the radical anions, the charge-separated states $Pc^{\cdot+}$-$PDI^{\cdot-}$ become the more stable, and hence long-lived, excited states, with lifetimes in the range of hundreds of microseconds.[5b,12b-d] Of particular interest is our previous work on ZnPc-PDI dyad **1** (Chart 1), composed of a ZnPc substituted with electron-donating *tert*-octylphenoxy groups and a PDI whose acceptor properties have been exacerbated by the presence of two *p*-tolylsulfonyl moieties.[13] These modifications pushed down the energy of the charge separated-state, so it turned to be, by far, the most stable excited state, displaying a lifetime of 72 µs, without the presence of any Mg^{2+} ions. This Pc–σ–PDI dyad used a flexible 2-aminoetoxy chain as bridge. However, this architecture contains an inherent drawback as, even with optimized substituents in the ZnPc and s in the PDI, the bridge avoids the coupling between D and A, thus hindering the initial charge separation. From a synthetic point of view, the linkage of a strong donor ZnPc to a strong acceptor PDI in a D-π-A system is a synthetic challenge not yet achieved. Moreover, if the bridge were part of a rigid and planar structure, the molecule would exhibit a well-defined symmetry, thus providing full geometric control over the relative positions and orientations of the subunits. Additionally, besides the amphoteric ground-state properties, photoinduced intramolecular charge-transfer (CT) processes might result in interesting photophysical phenomena such as long-lived charge-separated states.

As a continuation of our ongoing project, we describe herein the synthesis of a compactly fused, π-conjugated zinc phthalocyanine-perylenemonoimidebenzimidazole (ZnPc-PMIBI **2**, Chart 1), which is the first example of a heteroarene annulated assembly incorporating ZnPc and PDI. Moreover, we also describe its fast adiabatic electron-transfer process. ZnPc-PMIBI **2** incorporates an electron rich phthalocyanine subunit, bearing 6 electron-donating phenoxy groups, linked to a strongly electron-demanding perylenebenzimidazole substituted at the bay positions with two electron-accepting sulfone groups. Moreover, we show with this ZnPc-PMIBI architecture that the lifetime of the charge-separated state can be significantly prolonged by increasing the coupling between both units, which allows a fast charge separation, together with a rational design of the system, which lowers the CS energy below the energy of the triplet states of each chromophore.

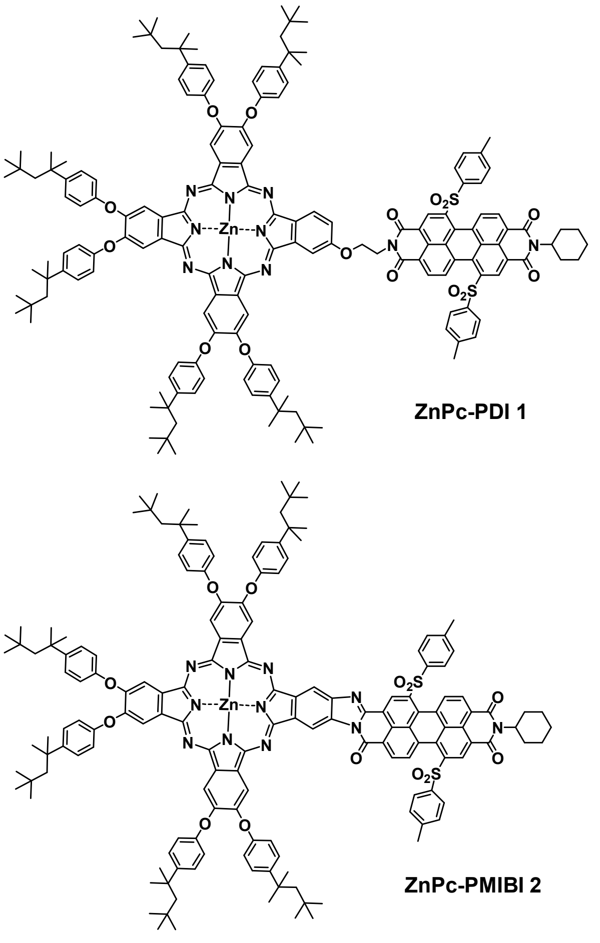


Chart 1.Chemical structure of **ZnPc–PDI 1** and **ZnPc-PMIBI 2**.

Results and discussion

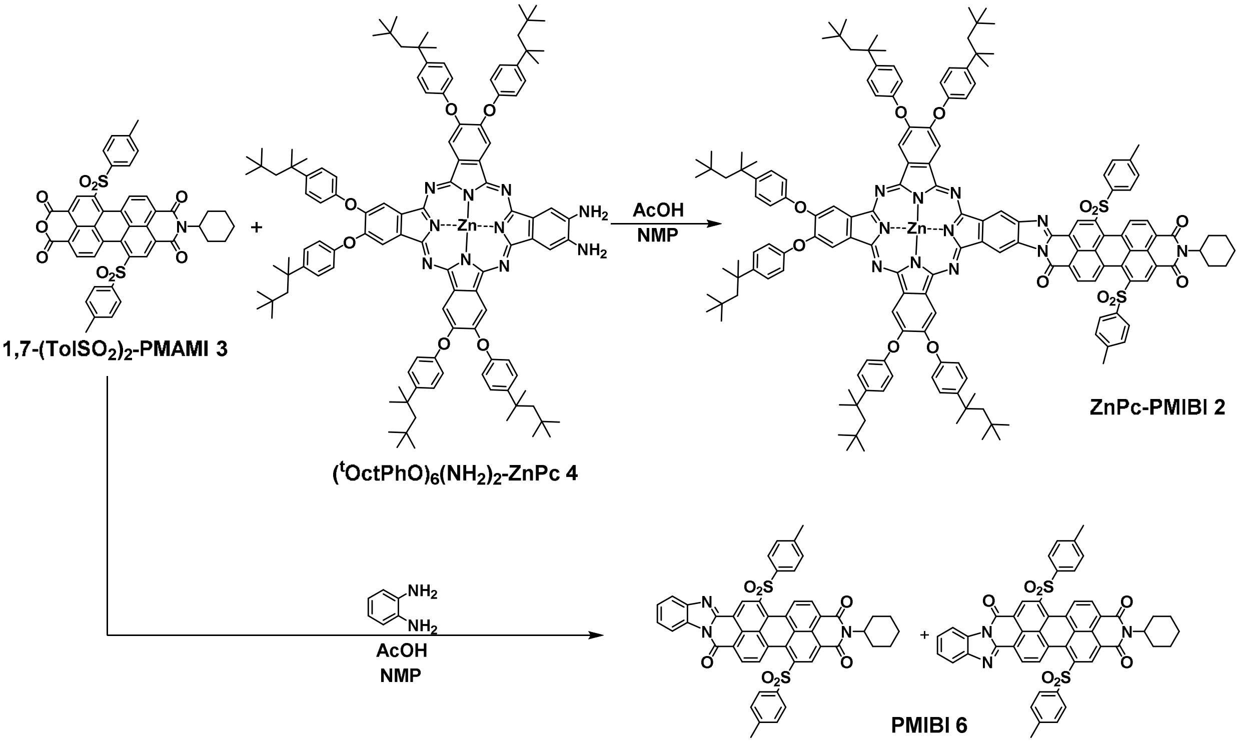
The inspiration for the synthesis of the fused, electronically conjugated dyad came as we realized the accused a bathochromic shift in benzimidazole derivatives of PDIs as a consequence of the conjugation extension.[14] Dyad ZnPc-PMIBI **2** was obtained, as mixture of two regioisomers, by condensing 1,7-ditolylsulfonylperylenemonoanhydridemonoimide, 1,7-$(TolSO_2)_2$-PMAMI **3**,[15,16] with the unsymetrically substituted zinc hexakis(*tert*-octyphenoxy)diaminophthalocyaninate $(^tOctPhO)_6(NH_2)_2$-ZnPc **4** in good yield, 42% (Scheme 1). Although many symmetrically substituted aminoPcs[17] have been synthesized, ZnPc **4** was not described to date. Since the free amino groups are incompatible with phthalonitrile cyclotetramerization, we had to find a suitable protecting group or, even better, a synthon for the *o*-diamine moiety. The 2,1,3-thiadiazole ring,[18] whose electron-withdrawing character would favour the cyclization reaction, demonstrated to be an excellent choice for the latter option. Cyclotetramerization of 5,6-dicyano-2,1,3-benzothiadiazole[19] and 4,5-bis(*p-tert*-octylphenoxy)phthalonitrile[7d] in the presence of zinc acetate afforded zinc hexakis(*p-tert*-octylphenoxy) thiadiazolo[4,5-b] phthalocyaninate $(^tOctPhO)_6$TDZnPc **5** with a very good yield for an statistical condensation (20%). The reductive desulfurization of the thiadiazole group proved to be quite difficult as the usual conditions like $NaBH_4$ in ethanol,[20] $LiAlH_4$ in THF,[21] Zn in AcOH[22] or Mg in MeOH[23] had no effect on the thiadiazolo ZnPc. However, the reaction with $NaBH_4$ in the presence of nickel boride,[24] prepared in situ from nickel (II) acetate, afforded diamino ZnPc **4** in 74% yield. (Scheme 2). On the other hand, 1,7-tolylsulfonyl-perylenemonoimidebenzimidazole 1,7-$(TolSO_2)_2$PMIBI **6** (as a mixture of two regioisomers) was synthesized as reference compound by condensation of 1,7-$(TolSO_2)_2$PMAMI **3** with *o*-phenylenediamine in 77% yield (Scheme 1).

All new compounds were characterized by UV-vis, FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopies, and high resolution mass spectrometry (See ESI). $(^tOctPhO)_6(NH_2)_2$ZnPc **4** and $(^tOctPhO)_6$TDZnPc **5** present a very well resolved ^{1}H-NMR using THF-d_8 as solvent, which is unusual for unsymmetrically substituted Pcs. Both, diamino ZnPc **4** and thiadiazolo ZnPc **5** present four singlets in the aromatic region of the ^{1}H-NMR spectrum as expected due to the C_{2v} symmetry of the compounds. In the case of the diamino ZnPc **4** a shielded proton at 8.51 ppm can be assigned to the Ha in ortho position to the amino group. The other three singlets at, 8.95, 8.96 and 9.00 ppm can be assigned to the Hb, Hc and Hd protons in ortho to the *tert*-octylphenoxy groups by comparison with the already published symmetrically substituted octakis *tert*-octylphenoxy ZnPc that shows only one singlet for the nonperipheral protons of the phthalocyanine core at δ= 8.96 ppm.[12e] In the case of the thiadiazolo ZnPc **5** a more de-shielded proton at 9.31 ppm can be assigned to the Ha due to the influence of the acceptor character of the thiadiazole ring. No explanation was fount for the shifted of the Hb, Hc and Hd protons at 8.51, 8.71 and 8.76 ppm in comparison with δ= 8.96 ppm of the octakis *tert*-octylphenoxy ZnPc (Figure 1).

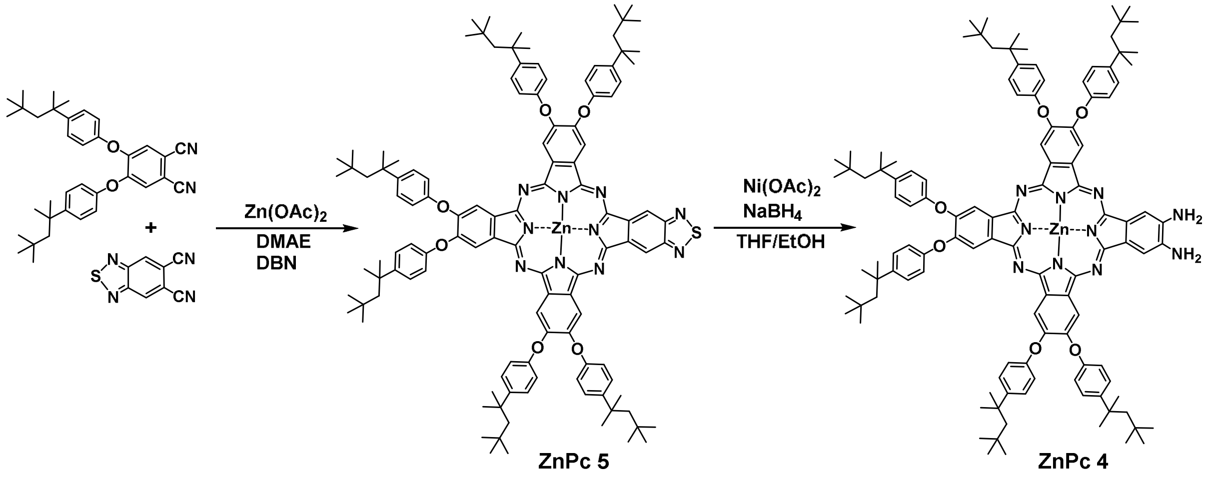
By the contrary, the ^{1}H-NMR of the conjugated ZnPc-PMIBI dyad, even in THF-d_8 as solvent, presents no signals corresponding to the ZnPc and PMIBI in the aromatic region (See ESI, Figure S11). This phenomenon could be explained taking into consideration a charge-transfer interaction in the ground state between ZnPc to PDI units.

The strong acceptor character of the thiadiazole ring was also evidenced by the 29 nm bathochomic shift in the Q-band of the UV-vis spectrum when comparing the diamino ZnPc **4** with the thiadiazolo ZnPc **5**. It is also worth of mention the bigger splitting of the Q band in **5** when compared with that of **4** where only a small splitting of 4 nm is observed due to the presence of electron donor groups in all the peripheral position of the ZnPc. (Figure 2).

Although the maximum of the Q band absorption in both the non-fused and the fused dyad is located at the same wavelength in THF solution, 683 nm, the spectrum of the fully conjugated system shows a broad tail absorption from 700 to 1000 nm, probably due to the conjugation between the Pc and the PDI units (Figure 3). The 0-0 and the 0-1 bands of the reference compound



Scheme 1 Synthesis of the dyad **ZnPc-PMIBI 2** from **ZnPc 4** and **1,7-(TolSO$_2$)$_2$-PMAMI 3** and synthesis of **PMIBI 6**.



Scheme 2 Synthesis of the **ZnPc 4** from **ZnPc 5**

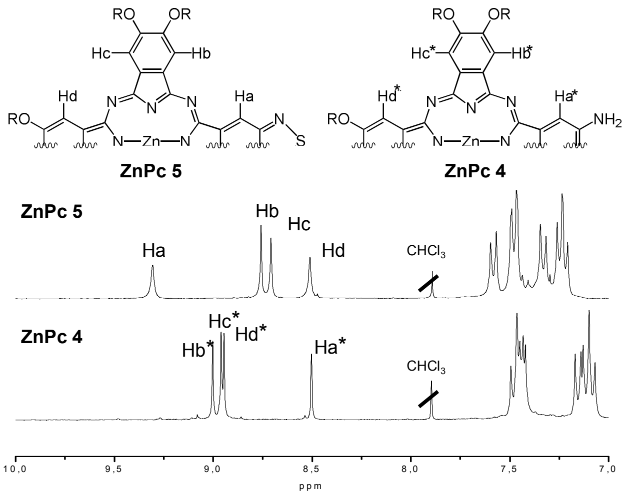


Fig. 1 ^{1}H-NMR spectra of **ZnPc 5** and **ZnPc 4** in THF-d_8 as solvent.

PMIBI **6** appears at 571 and 541 nm. These bands are lower in intensity and with different intensity ratio in the ZnPc-PMIBI 2 which also probe the conjugation of both subunits.

Cyclic voltammetry studies were carried out in a dry PhCN solution with 0.1 M TBAPF$_6$ as supporting electrolyte (Fig. 4 and Table 1). ZnPc-PMIBI dyad **2** presents two reduction potentials at -0.32 and -0.57 V (*vs.* SCE) corresponding to the perylene moiety and two oxidation potentials at 0.52 and 0.92 V that can be assigned to the phthalocyanine ring.[25] Compound **2** and reference compound PMIBI **6** have the same first reduction potential, -0.32 V, indicating that the fusion of the Pc does not affect the perylenebenzimidazole core. On the other hand, the first oxidation potential increases in comparison with the diamino substituted ZnPc **4** (0.34 and 0.79 V) and is higher than the ones of the thiadiazolo ZnPc **5** (0,50 and 0,68 V). It is highly remarkable that conjugated dyad **2** is oxidized and reduced more easily than non-conjugated dyad **1**, whose first oxidation and first reduction potential are respectively 0.61 and -0.34 V, which may attributed to the presence of the doubly fused imidazole ring. These changes also corroborate the coupling between ZnPc and PDI units in the fused ZnPc-PMIBI dyad **2**.

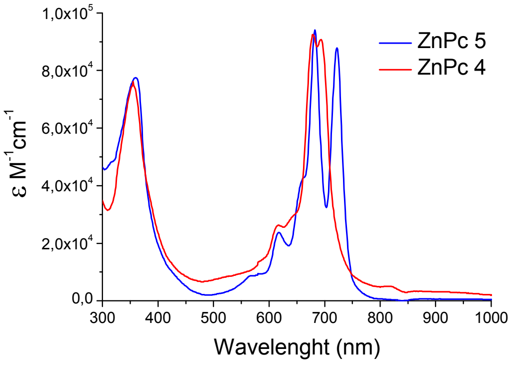


Fig. 2 UV-vis absorption spectra of **ZnPc 4** and **ZnPc 5**.

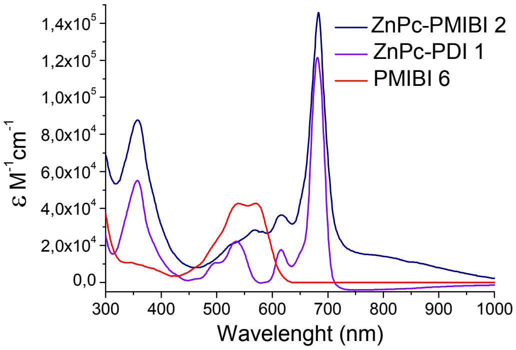


Fig. 3 UV-vis absorption spectra of dyad **1**, dyad **2** and **PMIBI 6.**

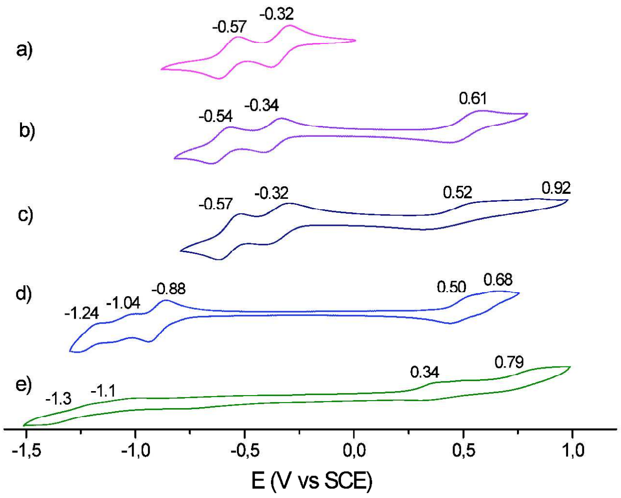


Fig. 4. Cyclic voltammograms of 1.0 mM deaerated PhCN solutions of (a) PMIBIM **6** , (b) ZnPc-PDI **1**, (c) ZnPc-PMIBI **2** (d) ZnPc **5** and (e) ZnPc **4** containing TBAPF$_6$ (0.1 M) at 298 K. Sweep rate: 50 mV s^{-1}.

Table 1. Redox potentials (*vs.* SCE) in deaerated PhCN

Compound	E_{ox1}	E_{ox2}	E_{red1}	E_{red2}	E_{red3}
ZnPc 5	0.50	0.68	-0.88	-1.04	-1.24
ZnPc 4	0.34	0.79	-1.10	-1.3	---
PMIBI 6	---	---	-0.32	-0.57	---
ZnPc-PDI 1	0.61	---	-0.34	-0.54	---
ZnPc-PMIBI 2	0.52	0.92	-0.32	-0.57	---

It is also worthy to note that the energy of the charge-separated state is 0.1 eV lower in dyad **2** (0.85 eV) than in dyad **1** (0.95 eV). This energy value of the CS state in dyad **2**, quite below the energies of the excited triplet states of ZnPc (1.18 eV) and PDI (1.07 eV),[26] suggests the real possibility of obtaining the long time desired long-lived charge-separated state without back electron transfer to the triplet excited states.

Computational Studies. To gain insight into the ground- and excited-state electronic properties of ZnPc-PDI **1** and ZnPc-PMIBI **2**, density functional theory (DFT) calculations were performed. The ground-state geometries of ZnPc-PDI **1** and ZnPc- PMIBI **2** were optimized with DFT at the B3LYP/6-31G(d) level of theory . The centre-to-centre distances (R_{cc}), that is, the distance between the PDI core and the ZnPc unit, was computed to be 14.5 Å for ZnPc-PDI **1**. A shorter centre-to-centre distance was found in the case of ZnPc-PMIBI **2** to be 13.6 Å.

The important frontier molecular orbitals of the ZnPc-PDI dyad **1** and ZnPc-PDI **2** are given in Figs. 5 and 6. In the ZnPc-PMIBI dyad **2**, the localization of the highest occupied frontier molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) on the ZnPc and PDI moieties, respectively, has clearly been demonstrated, together with the extensions of the HOMO^{-1} and LUMO^{+1} into the bridging area. However in the case of ZnPc-PDI dyad **1** the frontier orbitals are localized either on the Pc or in the PDI and no delocalization was found at all.

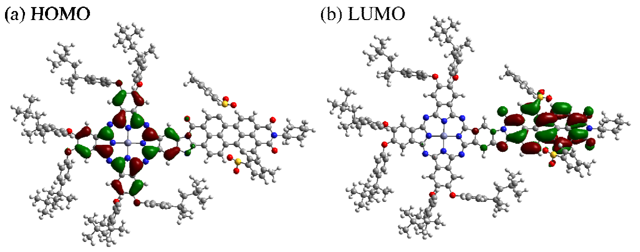


Fig. 5 Optimized structure with (a) HOMO and (b) LUMO of ZnPc-PMIBI **2** calculated by DFT at the B3LYP/6-31G(d) level of theory. The other MOs and coordinates are shown in ESI Fig. S14 and Table S2.

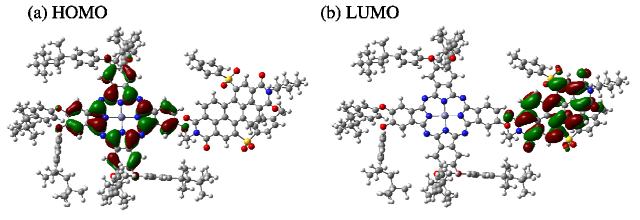


Fig. 6 Optimized structure with (a) HOMO and (b) LUMO of ZnPc-PDI **1** calculated by DFT at the B3LYP/6-31G(d) level of theory. The other MOs and coordinates are shown in ESI Fig. S15 and Table S1.

TD-DFT calculation of a dyad **2** was carried out by TD-B3LYP/6-31G(d)//B3LYP/6-31G(d) basis set. The calculated absorption band was obtained at 626 nm with an oscillator strength of $f = 0.00423$ ascribable to charge transfer from ZnPc to PDI. The calculated results are shown in Table S3 (ESI).

Spectroelectrochemistry. The one-electron oxidation and reduction species of ZnPc-PMIBI **2** are electrochemically stable, because the reversible redox CV waves were observed as shown in Fig. 4c. The electrochemical oxidation and reduction of **2** in a deoxygenated PhCN solution containing n-Bu_4NClO_4 (0.2 M) were examined using a thin-layer electrochemical cell to observe ZnPc radical cation ($ZnPc^{\bullet+}$–PDI) and PDI radical anion (ZnPc–$PDI^{\bullet-}$). Upon the one-electron oxidation of ZnPc–PDI at an applied potential at 0.7 V *vs*. SCE, the absorption band at 690 nm due to the Q-band of ZnPc decreased, accompanied by increase in new absorption bands at 530 and 860 nm with isosbestic points at 397, 607 and 840 nm as shown in Fig. 7a. The observed absorption bands were assigned to $ZnPc^{\bullet+}$–PDI. On the other hand, electrolysis at –0.45 V *vs*. SCE for the one-electron reduction of ZnPc–PDI resulted in disappearance of the absorption bands due to the PDI moiety at 490 and 530 nm, accompanied by increase in a new absorption at 400 nm and also a broad absorption band in the region of 700-1100 nm with isosbestic points (Fig. 7b). The observed absorption bands are assigned to ZnPc–$PDI^{\bullet-}$. The absorption bands of $PDI^{\bullet-}$ without the ZnPc moiety and those of $ZnPc^{\bullet+}$ without the PDI moiety are known to show sharp absorption band(s) at near-IR region. In the case of fully conjugated **2**, the absorption bands of one-electron-oxidized and reduced **2** ($ZnPc^{\bullet+}$–PDI and ZnPc–$PDI^{\bullet-}$) are relatively weak[27,28] and significantly broadened because of the intramolecular orbital conjugation effect between ZnPc and PDI.[29]

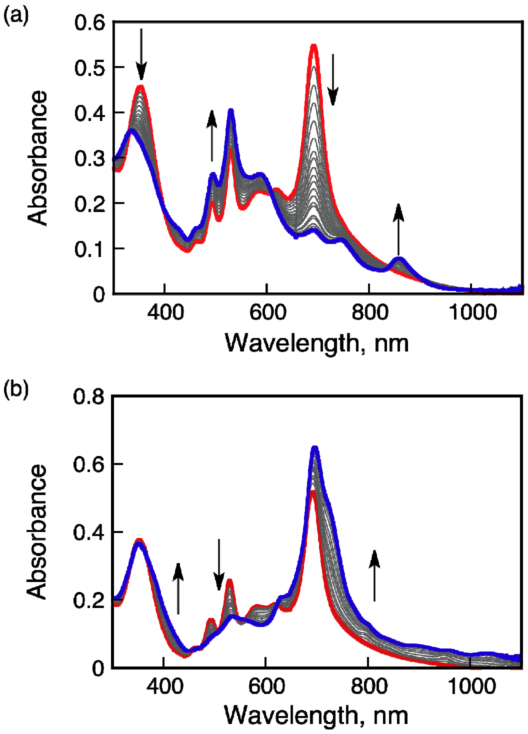


Fig. 7 (a) Absorption spectral changes in the electrolysis at an applied potential of (a) +0.70 V *vs*. SCE for the oxidation and (b) –0.45 V *vs*. SCE for the reduction of **2** in deaerated PhCN containing Bu_4ClO_4 (0.20 M).

Photophysical Studies. Femtosecond laser flash photolysis was conducted on a deaerated PhCN solution of **2** with a 393 nm laser pulse. The detection at 20 ps of the characteristic band at 580 nm and 760 nm indicates the formation of the singlet excited state of ZnPc (^{1}ZnPc*),[27] which decayed to the triplet excited state (^{3}ZnPc*) via intersystem crossing (τ = 2 ns) without photoinduced electron transfer producing the CS state (Fig. 8).

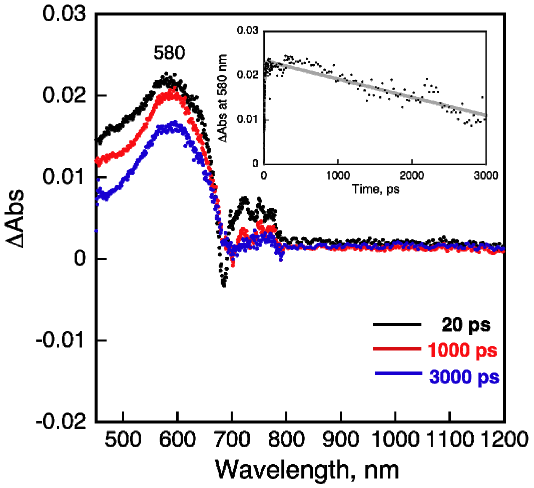


Fig. 8 Transient absorption spectra of **ZnPc-PDI 2** in deaerated PhCN taken by femtosecond laser excitation at 393 nm. Inset: Time profile of the absorbance at 580 nm.

The dynamics of ^{3}ZnPc* thus formed was monitored by nanosecond laser flash photolysis measurements using a 355 nm laser pulse excitation. The transient absorption spectrum observed upon nanosecond laser excitation is shown in Fig. 9a. The observed absorption bands at 410 and 530 nm are assigned to the PDI$^{\bullet-}$ and ZnPc$^{\bullet+}$,[26,27] respectively, because they agree with the those of electrochemically generated PDI$^{\bullet-}$ and ZnPc$^{\bullet+}$ in Fig. 7. The difference absorption spectra have been added in Fig. S16 in ESI, indicating that the absorption bands of PDI$^{\bullet-}$ and ZnPc$^{\bullet+}$ were appeared at 410 nm and 530 nm, respectively. The band at 860 due to ZnPc$^{\bullet+}$ is too weak to be detected as a transient absorption band. The positive absorption band at 730 nm due to PDI$^{\bullet-}$ was cancelled by the bleaching due to the ground state of ZnPc. This result demonstrates doubtlessly formation of the CS state.[9b,c] The decay of the absorbance at 530 nm can be fitted to first-order kinetics affording the CS lifetime of 260 μs (Fig. 9b), which is about four times longer than the lifetime of the CS of dyad **1** (72 μs).[10] The CS lifetime of ZnPc-PMIBI **2** is the longest value ever reported for a covalent phthalocyanine-peryleneimide system in solution, probably resulting form the CS energy lower than the triplet energy of each chromophore, together with the coupling between both units, which allows the fast charge separation.

Such a long-lived CS state was also detected by EPR measurements after photolysis to estimate the spin state of the CS state. The EPR spectrum was observed after photoirradiation by a high-pressure Hg lamp at low temperature at g = 2.0042 (Fig. 10), which is the average value of g = 2.003 for ZnPc$^{\bullet+}$ and g = 2.005 for PDI$^{\bullet-}$.[26,29] The triplet marker signal at g = 4 indicates that the spin state of the CS state is triplet.[30]

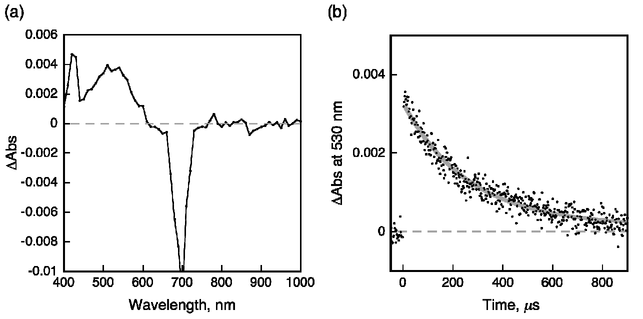


Fig. 9 (a) Transient absorption spectra of **ZnPc-PDI 2** in deaerated PhCN taken at 1 μs after nanosecond laser excitation at 355 nm. (b) Time profile of the absorbance at 530 nm.

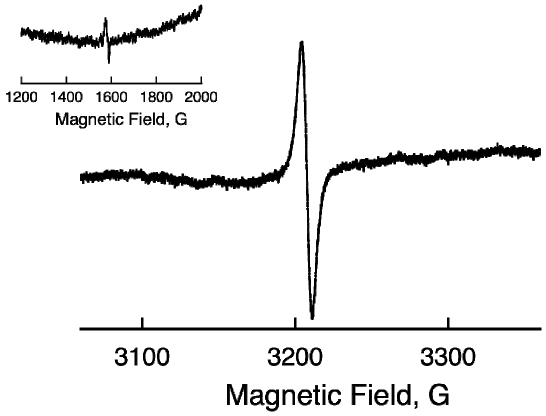
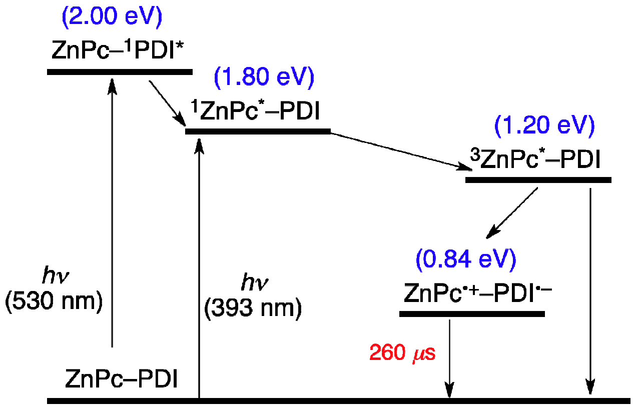


Fig. 10 EPR spectrum measured at 77 K after photoirradiation of a deaerated PhCN solution containing **2** with a high-pressure Hg lamp at 263 K. Inset: EPR spectrum around g = 4.



Scheme 3

The energy diagram with photoinduced reaction course is shown in Scheme 3. Photoexcitation of ZnPc-PDI (**2**) gives the singlet excited state of ZnPc by direct excitation of the ZnPc moiety and also by energy transfer from ^{1}PDI*. Intersystem crossing of ^{1}ZnPc* to generate ^{3}ZnPc* occurs without occurrence of electron transfer from ^{1}ZnPc* to PDI. Photoinduced electron-transfer process at the singlet excited state may be slow probably because the CS process with a large driving force ($-\Delta G_{ET}$ = 0.96 eV) may be in the Marcus inverted region, where the rate of electron transfer decrease with increasing the driving force.[30,31] Instead, photoinduced electron transfer from ^{3}ZnPc* to PDI preferentially occurs to form the CS state. Then, slow back electron transfer occurs to give the ground state.

Conclusions

A fully conjugated phthalocyanine-perylenemonoimide-benzimidazole system, where the conjugation goes through the imide position of the perylene, ZnPc-PMIBI **2**, has been synthesized for the first time. From the electrochemical analysis, the energy of the expected CS state is estimated to be lower than the triplet excited energies of the phthalocyanine and peryleneimide subunits. The rational design implies the substitution of the ZnPc with phenoxy groups and the bay substitution at the perylene with sulfonyl substituents. The preparation was made possible by the synthesis of a diamino substituted phthalocyanine ZnPc(NH$_2$)$_2$. Its condensation with a perylene monoanhidride monoimide generates a fused, electronically conjugated ZnPc-PMIBI dyad **2**. ZnPc-PMIBI undergoes photoinduced electron transfer from the triplet excited state of the phthalocyanine to the perylenemonoimidebenzimidazole to afford the CS state with a rate constant of 3.8×10^3 s^{-1}. A non-conjugated phthalocyanine-perylenediimide system ZnPc-PDI **1** also undergoes electron transfer from the phthalocyanine to the perylediimide with a rate constant of 1.4×10^4 s^{-1}. The lifetimes of the resulting CS states are 0.26 ms for ZnPc-PMIBI **2** and 72 μs for ZnPc-PDI **1**. The CS lifetime in the case of ZnPc-PMIBI **2** is the longest value ever reported for a covalent phthalocyanine-peryleneimide system in solution and is attributed to the synergy of an extremely low CS energy, lower than the triplet energy of each chromophore, together with the coupling between both units, which allows a fast charge separation. Our approach thus holds promise for the design of improved systems for solar energy conversion. Also future tests of the performance of this π-conjugated material for charge transport in molecular electronic applications will be of particular interest.

Experimental

Synthesis of 2,3,9,10,16,17-hexaquis-[*p*-(*tert*-octyl)phenoxy]-22,23-thiadiazolo[4,5-b]-phthalocyaninate zinc (II), ZnPc 5

A mixture of 100 mg (0.537 mmol) of 5,6-dicyano-2,1,3-benzothiadiazole[19], 864 mg (1.61 mmol) of 4,5-bis(*p-tert*-octylphenoxy)phthalonitrile[7d], 234 mg (1.074 mmol) of zinc acetate and two drops of DBN were dissolved in 2 ml of DMAE in argon atmosphere and refluxed for 10 h. Then the mixture was cooled to room temperature and precipitated with MeOH. The crude was purified by column chromatography (CHCl$_3$:EtOAc/93:7), yielding 210 mg of **ZnPc 5** (20%).^{1}H RMN (300 MHz, THF-d_8, 25°C): δ = 9.31(s, 2H; Pc), 8.76 (s, 2H; Pc), 8.71 (s, 2H; Pc), 8.51 (s, 2H; Pc), 7.60-7.47(m, 12H; phenol), 7.34-7.23 (m, 12H; phenol), 1.92-1.83 (m, 12H; -CH$_2$-), 1.49-1.42 (m, 36H; -CH$_3$), 0.85-0.83ppm (m, 54H; *tert*-butyl). UV-vis (THF): λ_{max}/nm (log ε): 360 (4.88), 618 (4.37), 682 (4.97), 722 nm (4.94). HRMS-MALDI-TOF (dithranol): *m/z*: for $C_{116}H_{134}N_{10}O_6SZn$ calcd, 1858.9494; found 1858.9739 (M$^+$). ν_{max} (KBr)/cm^{-1} 3441, 2952, 2901, 1603, 1505, 1486, 1401, 1271, 1216, 1177, 1090, 1024, 892, 828 cm^{-1}.

Synthesis of 2,3,9,10,16,17-hexaquis-[*p*-(*tert*-octyl)phenoxyl]-22,23-diaminophthalocyaninate zinc (II), ZnPc 4

75 mg (0.039 mmol) of ZnPc **5**, 39 mg (0.156 mmol) of nickel acetate tetrahydrate and 9 mg (0.234 mmol) of sodium borohydride were dissolved in a mixture of dried THF:EtOH/1:2 (3 ml) at 0 °C under argon atmosphere. Two hours later the reaction mixture was filtered over celite and the organic layer was washed with NH$_4$Cl (2M) and H$_2$O two times. The organic layer was dried with MgSO$_4$ and concentrate in vacuum. The crude was purified by column chromatography (CHCl$_3$:THF/9:1), yielding 62 mg of **ZnPc 4** (75%). ^{1}H RMN (300 MHz, THF-d_8, 25°C): δ = 9.00 (s, 2H; Pc) 8.96 (s, 2H; Pc), 8.95 (s, 2H; Pc), 8.51 (s, 2H; Pc), 7.49-7.42 (m, 12H; phenol), 7.17-7.07(m, 12H; phenol), 4.94 (s, 4H; (NH$_2$)$_2$), 1.94-1.82 (m, 12H; -CH$_2$-), 1.46-1.41 (m, 36H; -CH$_3$), 0.85-0.83 ppm (m, 54H; *tert*-butyl). UV-vis (THF): λ_{max}/nm (log ε): 355 (4.88), 679 (4.98), 693 nm (4.97). HRMS-MALDI-TOF (dithranol): *m/z*: for $C_{116}H_{138}N_{10}O_6Zn$ calcd, 1831.0086; found 1831.0432 (M$^+$). ν_{max} (KBr)/cm^{-1} 3438, 3352, 2952, 2901, 1603, 1505, 1452, 1399, 1269, 1218, 1176, 1088, 1028, 890, 829 cm^{-1}.

Synthesis of PMIBI 6

5 mg (0.046 mmol) of benzene 1,2-diamine, 27.6 μL (0.3mmol) of AcOH and 25 mg (0.031 mmol) of *N*-1,7-bis(p-tolylsulfonyl)perylene-3,4-dicarboxyanhydride-9,10-dicarboximide[10] were dissolved in 1.5 ml of NMP and heated at 85°C during 72 h. The reaction mixture was diluted with chloroform and the organic layer was washed with H$_2$O two times. The organic layer was dried with MgSO$_4$, concentrated in vacuum and purified by column chromatography (CHCl$_3$:Acetone/100:1), affording 20.8 mg of the **PMIBI** (77 %). ^{1}H RMN (300 MHz, CDCl$_3$, 25°C): δ = 9.18 (dd, *J* = 8, 3.8 Hz, 1H), 9.02-8.91 (m, 2H), 8.81-8.61 (s, 4H), 7.90 (m, 5H), 7.45 (m, 6H), 4.97 (m, 1H), 2.50-2.37 (m, 8H), 1.87-1.36 ppm (m, 8H). ^{13}C NMR (75 MHz, CDCl$_3$, 25°C): δ = 146.4, 146.2, 141.9, 141.3, 136.3, 136, 135.4, 135.3, 135.1, 135, 134.7, 133.6, 133.5, 133.1, 132.9, 131.6, 131.2, 130.9, 130.6 (2C), 130.5 (2C), 129.9, 128.9 (2C), 128.8 (2C), 127.9, 127.8, 127.7, 124.9, 123.4, 120.9, 120.5, 119.4, 117.9, 116.7, 116.3, 54.4, 28.9, 26.3, 25.2, 21.8, 21.7 ppm. UV-vis (THF): λ_{max}/nm (log ε): 541 (4.63), 571 nm (4.63). HRMS-MALDI-TOF (dithranol): *m/z*: for $C_{50}H_{35}N_3O_7S_2$ calcd, 853.191; found 853.189 (M$^+$). ν_{max} (KBr)/cm^{-1} 2924, 2852, 1701, 1661, 1590, 1397, 1340, 1294, 1241, 1141, 1081, 808 cm^{-1}.

Synthesis of dyad ZnPc-PMIBI 2

57.8 mg (0.032 mmol) of ZnPc 4, 20 μL (0.21 mmol) of AcOH and 16.32 mg (0.021 mmol) of *N*-1,7-bis(*p*-tolylsulfonyl)perylene-3,4-dicarboxyanhydride-9,10-dicarboximide[10] were dissolved in 1.5 ml of NMP and heated to 85°C under argon atmosphere during 72 hours. The crude was diluted in CHCl$_3$, washed with NH$_4$Cl (aq) and H$_2$O. The organic layer was dried with MgSO$_4$ and concentrate in vacuum. The crude was purified by column chromatography (CHCl$_3$:Acetone/95:5), affording 22.4 mg of **ZnPc-PMIBI 2**

(42%). UV-vis (THF): λ_{max}/nm (log ε): 358 (4.94), 568 (4.44), 616 (4.55), 683 (5.16). HRMS-MALDI-TOF (dithranol): *m/z*: for $C_{160}H_{165}N_{11}O_{13}S_2Zn$ calcd, 2576.131; found 2576.0272 (M$^+$). ν_{max} (KBr)/cm^{-1} 2951, 2901, 1702, 1664, 1589, 1505, 1452, 1402, 1332, 1270, 1219, 1172, 1092, 1027, 892 cm^{-1}.

Acknowledgements

We thank financial support from Spanish Ministry of Science and Innovation, Generalitat Valenciana and the European FEDER funds (CTQ2011-26455, Prometeo 2012/010, ACOMP/2012/, Prometeo/2009/058 and ISIC/2012/008), an ALCA project from JST (to S.F.) and Grants-in-Aid (Nos. 26620154 and 26288037 to K.O.) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

Notes and references

[a] *División de Química Orgánica Instituto de Bioingeniería, Universidad Miguel Hernández, Elche, Spain. Fax: 34966658408; Tel: 34966658351; E-mail: asastre@umh.es*

[b] *Department of Material and Life Science, Graduate School of Engineering, Osaka University, ALCA, Japan Science and Technology Agency (JST), Suita, Osaka 565-0871, Japan.*

† Electronic Supplementary Information (ESI) available: Characterization spectra of the new compounds, See DOI: 10.1039/b000000x/

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