

Formation of a long-lived charge-separated state of a zinc phthalocyanine-perylenediimide dyad by complexation with magnesium ion†

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Photoexcitation of a zinc phthalocyanine-perylenediimide (ZnPc-PDI) dyad affords the triplet excited state without the fluorescence emission, whereas addition of Mg^{2+} to the photoexcited ZnPc-PDI results in formation of a long-lived charge-separated state ($ZnPc^{++}-PDI^{-}/Mg^{2+}$) in which PDI^{-} forms a complex with Mg^{2+} .

A number of photoactive molecular architectures, such as dyads, triads, and higher order arrays, have been designed and extensively studied as model systems of natural photosynthesis to harvest efficiently solar energy.^{1–3} Upon selective light illumination of a given chromophore, such multi-component model systems are able to undergo directional multi-step electron and/or energy transfer processes. Among many chromophores, porphyrins have most frequently been used as important units in electron donor-acceptor dyads.^{4–7} On the other hand, phthalocyanines, which are porphyrin analogues, exhibit a number of unique electronic properties derived from their two-dimensional highly delocalized 18π -electron system, holding great promise because of more enhanced absorptive cross sections at those wavelengths corresponding to maxima of emission in the solar spectrum as compared with porphyrins.^{8–11} In contrast to donor-acceptor dyads using porphyrins, which undergo efficient photoinduced electron transfer, however, no long-lived charge-separated state of donor-acceptor dyads with phthalocyanine chromophore has so far been reported because of the low lying triplet excited state which is generally lower in energy than the charge-separated (CS) state.¹²

We report herein the formation of a long-lived CS state with a lifetime of 240 μ s in the presence of Mg^{2+} , which forms a complex with PDI^{-} .

ZnPc-PDI was synthesized by reacting the zinc tri-*tert*-butylaminoethoxyphthalocyanine¹³ with *N*-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylic-3,4-anhydride-9,10-imide¹⁴ in melted

imidazole at 170 °C. The reference compounds (ZnPc and PDI) employed in the present study (Chart 1) were prepared according to previously reported procedures.¹⁵

Cyclic voltammograms of ZnPc-PDI, ZnPc, and PDI are shown in Fig. 1a–c, respectively. The one-electron redox waves of ZnPc-PDI largely consist of superposition of those of ZnPc and PDI. The absorption spectrum of ZnPc-PDI is also the superposition of the spectrum of each component (ZnPc and PDI) (see Supplementary Information S1†). This indicates that there is no ground state interaction between ZnPc and PDI moieties.

Laser excitation of ZnPc-PDI at 530 nm in which PDI has the absorption band results in formation of the triplet excited state of ZnPc ($^3ZnPc^*-PDI$) in deaerated benzonitrile (PhCN) as shown in Fig. 2 (open circles). The triplet-triplet (T–T) absorption at 510 nm is changed to the T–T absorption at 700 nm due to the triplet excited state of PDI ($ZnPc-^3PDI^*$), which agrees with the T–T absorption of the reference compound ($^3PDI^*$).

The decay of the T–T absorption at 510 nm due to $^3ZnPc^*-PDI$ coincides with the rise in the T–T absorption at 710 nm due to $ZnPc-^3PDI^*$ (Fig. 3a). The rate constant of energy transfer from $^3ZnPc^*$ to the PDI moiety is determined as $2.0 \times 10^4 \text{ s}^{-1}$ at 298 K. The T–T absorption due to $ZnPc-^3PDI^*$ decays at a longer time scale (Fig. 3b) and the decay rate constant ($6.4 \times 10^2 \text{ s}^{-1}$) agrees with that of the T–T absorbance of the reference compound (PDI). Thus, the photoexcitation of the ZnPc and PDI moieties results in

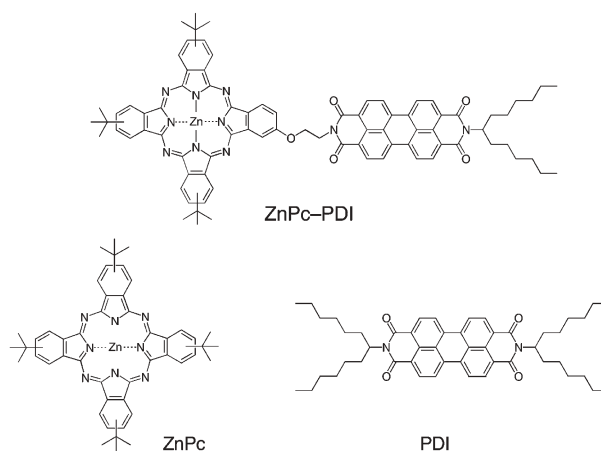


Chart 1 Drawing of ZnPc-PDI and the reference compounds (ZnPc and PDI).

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† Electronic supplementary information (ESI) available: spectral data of ZnPc-PDI, and those of $ZnPc^{++}$ and the $PDI^{-}-Mg^{2+}$ complex, and experimental information of electrochemical and photodynamics measurements. See <http://dx.doi.org/10.1039/b506412k>

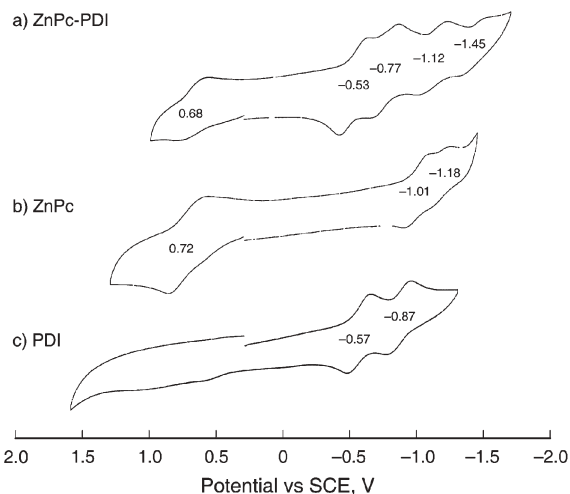


Fig. 1 Cyclic voltammograms of a) ZnPc-PDI ($1.0 \times 10^{-3} \text{ mol dm}^{-3}$); b) ZnPc ($1.0 \times 10^{-3} \text{ mol dm}^{-3}$); c) PDI ($1.0 \times 10^{-3} \text{ mol dm}^{-3}$) in deaerated PhCN containing TBAPF₆ (0.1 mol dm^{-3}) at 298 K; sweep rate: 50 mV s^{-1} .

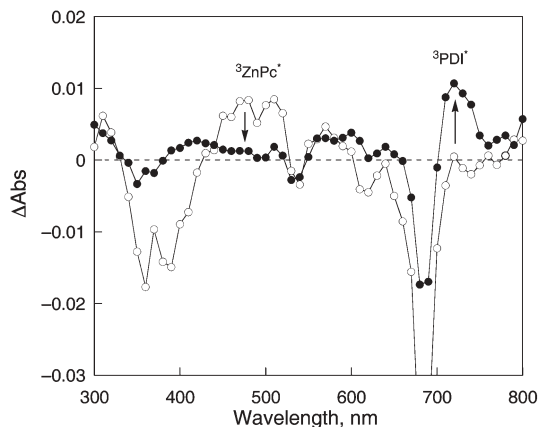


Fig. 2 Transient absorption spectra of ZnPc-PDI ($3.0 \times 10^{-5} \text{ mol dm}^{-3}$) obtained by laser flash photolysis in deaerated PhCN at 298 K at 2.0 (○) and 180 μs (●) after laser excitation ($\lambda = 530 \text{ nm}$).

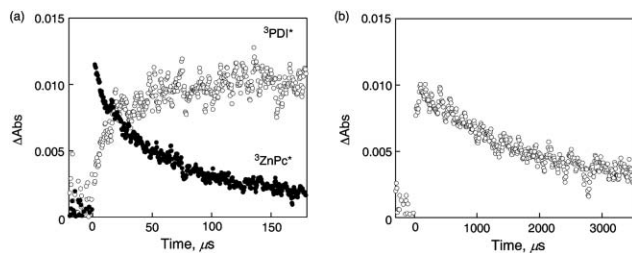


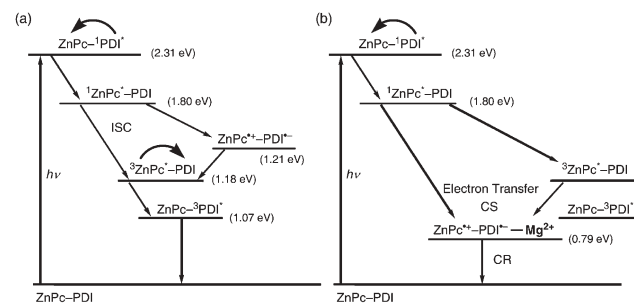
Fig. 3 (a) Decay and rise time profiles of transient absorption of ZnPc-PDI at 510 (●) and 710 nm (○) (short time scale); (b) Decay time profile at 710 nm (long time scale).

delayed and selective formation of the triplet excited state, ZnPc-³PDI*, without the fluorescence emission.

The photoexcitation of ZnPc and PDI affords the fluorescence emission of ¹ZnPc* at 694 nm,¹⁶ and that of ¹PDI* at 544 nm (see Supplementary Information S2†).¹⁷ In the case of ZnPc-PDI,

however, the photoexcitation of the absorption band of the ZnPc and PDI moieties results in no fluorescence emission. The absence of fluorescence emission together with the delayed formation of the triplet excited state (ZnPc-³PDI*) upon photoexcitation of ZnPc-PDI indicates the singlet excited state (ZnPc-¹PDI*: 2.31 eV), which is higher in energy than ¹ZnPc*-PDI (1.80 eV), is efficiently quenched by energy transfer to ZnPc, followed by intersystem crossing (ISC) to give ³ZnPc*-PDI (1.18 eV)^{18,19} as detected by the transient absorption spectrum in Fig. 2 (open circles). Then, energy transfer from ³ZnPc* to PDI occurs to afford the final triplet excited state (ZnPc-³PDI*: 1.07 eV)^{18,20} as shown in Fig. 2 (filled circles). Such a back and forth energy transfer is summarized in Scheme 1a. Since the CS state (ZnPc⁺-PDI⁻: 1.21 eV) is higher in energy than the triplet excited state (³ZnPc*-PDI), no CS state was observed in the transient absorption spectrum. ³ZnPc*-PDI may also be generated from charge-separated state (ZnPc⁺-PDI⁻), which is formed by electron transfer from ¹ZnPc* to PDI in competition with intersystem crossing of ¹ZnPc*-PDI. In any case, the triplet excited state (ZnPc-³PDI*) is the final long-lived species. This demonstrates sharp contrast with the case of zinc porphyrin-PDI dyad which affords the CS state upon the photoexcitation.^{21,22}

In contrast to the above case, the addition of magnesium perchlorate [Mg(ClO₄)₂] (0.1 mol dm^{-3}) to a PhCN solution of ZnPc-PDI and the photoexcitation at 530 nm results in formation of the CS state as indicated by the appearance of the transient absorption band due to ZnPc⁺ at 550 nm together with the one corresponding to PDI⁻/Mg²⁺ complex at 500 nm (Fig. 4a). The formation of the CS state was confirmed by comparing the transient spectra in Fig. 4a with the spectrum of ZnPc⁺ obtained by the electrochemical oxidation of ZnPc and that of the PDI⁻/Mg²⁺ complex produced by photoinduced electron-transfer reduction of PDI with dimeric 1,4-dihydropyridine [(BNA)₂]²³ in the presence of Mg²⁺ in deaerated PhCN (see Supplementary Information S4†). The absorption maxima at 500 nm and 550 nm in Fig. 3a agree with the absorption maximum of the PDI⁻/Mg²⁺ complex (Fig. S4a) and that of ZnPc⁺ (Fig. S4b†), respectively. The absorption band due to the PDI⁻/Mg²⁺ complex ($\lambda_{\text{max}} = 500 \text{ nm}$) is significantly shifted from that of PDI⁻ ($\lambda_{\text{max}} = 720 \text{ nm}$)²¹ due to the complex formation with Mg²⁺, whereas no change in the absorption spectrum of PDI is observed in the presence of Mg²⁺ (0.10 mol dm^{-3}) in PhCN.²⁴ The ESR spectrum of PDI⁻ in the presence of Mg²⁺ (0.10 mol dm^{-3}) was also changed due to the complex formation with Mg²⁺ as compared with that of PDI⁻ in the absence of Mg²⁺ (see Supplementary Information S5†).²⁵ The one-electron reduction



Scheme 1

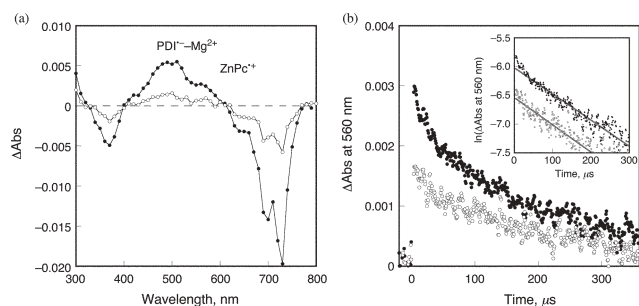


Fig. 4 (a) Transient absorption spectra of ZnPc-PDI ($3.0 \times 10^{-5} \text{ mol dm}^{-3}$) with $\text{Mg}(\text{ClO}_4)_2$ (0.1 mol dm^{-3}) obtained by laser flash photolysis in deaerated PhCN at 298 K at 2.0 (○) and 180 μs (●) after laser excitation ($\lambda = 530 \text{ nm}$). (b) Decay time profiles at 560 nm with different laser power (3.0 mJ per pulse, ●; 1.5 mJ per pulse, ○). Inset: first-order plots.

potential of ZnPc-PDI (-0.53 V vs SCE) was shifted to -0.11 V vs SCE in the presence of $\text{Mg}(\text{ClO}_4)_2$ (0.10 mol dm^{-3}) due to the complex formation with Mg^{2+} in PhCN. The energy of the CS state ($\text{ZnPc}^+-\text{PDI}^-/\text{Mg}^{2+}$) is then determined as 0.79 eV, which is now lower than the energy of the triplet excited state ($\text{ZnPc}^3-\text{PDI}^*$: 1.07 eV).^{18,20} The quantum yield of the CS state was determined as 72% using the comparative method.²⁶

The decay of the CS state in the presence of $\text{Mg}(\text{ClO}_4)_2$ (0.1 mol dm^{-3}) was monitored using different laser power, obeying first-order kinetics with the same slope as shown in the inset of Fig. 4b. The first-order decay with the same slope indicates that no intermolecular reaction is involved in the charge-recombination (CR) process. The lifetime of the CS state was determined as 240 μs in PhCN at 298 K.

In conclusion, the addition of Mg^{2+} to ZnPc-PDI results in drastic change in the photodynamics from the formation of $^3\text{PDI}^*$ (Scheme 1a) to electron transfer to produce long-lived charge-separated state ($\text{ZnPc}^+-\text{PDI}^-/\text{Mg}^{2+}$) in which PDI^- forms a complex with Mg^{2+} (Scheme 1b).

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