Supplementary Information

Formation of a Long-Lived Charge-Separated State of a Zinc Phthalocyanine-Perylenediimide Dyad by Complexation with Magnesium Ion

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Fig. S1 UV-vis spectra of (a) ZnPc, (b) PDI and (c) ZnPc-PDI in PhCN at 298 K.
Fig. S2 Fluorescence spectra of (a) ZnPc ($\lambda_{ex} = 610$ nm) and (b) PDI ($\lambda_{ex} = 530$ nm) in deaerated PhCN at 298 K. No fluorescence emission from the ZnPc or PDI moiety of ZnPc-PDI was observed.
**Fig. S3** Phosphorescence spectra of (a) ZnPc ($\lambda_{ex} = 610$ nm) and (b) PDI ($\lambda_{ex} = 530$ nm) in argon-saturated glassy butyronitrile at 77 K.
Fig. S4 (a) Spectral change in the electrochemical reduction of ZnPc in deaerated PhCN containing TBAPF$_6$ (0.1 mol dm$^{-3}$) applied potential at 0.90 V vs SCE at 298 K; (b) Transient absorption spectra observed in deaerated PhCN solution containing of PDI and (BNA)$_2$ in the presence of Mg(ClO$_4$)$_2$ (0.1 mol dm$^{-3}$) at 3 µs (blue) and 300 µs (red) after laser excitation ($\lambda = 530$ nm) and the difference spectrum (black).
Fig. S5 ESR spectra of PDI\textsuperscript{•–} formed in the photoinduced electron-transfer reduction of PDI (1.0 x 10\textsuperscript{–4} M) by (BNA)\textsubscript{2} (5.0 x 10\textsuperscript{–4} mol dm\textsuperscript{–3}) in the (a) absence and (b) presence of Mg(ClO\textsubscript{4})\textsubscript{2} (0.1 mol dm\textsuperscript{–3}) in deaerated PhCN at 298 K (top column) with the computer simulation spectra (middle column) and the hyperfine splitting constants (in mT) and maximum slope linewidth ($\Delta H_{msl}$) (bottom column).
Electrochemistry: Electrochemical measurements were performed on an ALS630B electrochemical analyzer in deaerated MeCN containing 0.1 M Bu₄NPF₆ (TBAPF₆) as supporting electrolyte at 298 K. A conventional three-electrode cell was used with a platinum working electrode (surface area of 0.3 mm²) and a platinum wire as the counter electrode. The Pt working electrode (BAS) was routinely polished with BAS polishing alumina suspension and rinsed with acetone before use. The measured potentials were recorded with respect to the Ag/AgNO₃ (0.01 mol dm⁻³) reference electrode. All potentials (vs Ag/Ag⁺) were converted to values vs SCE by adding 0.29 V. All electrochemical measurements were carried out under an atmospheric pressure of Ar.

Laser Flash Photolysis: An MeCN solution containing ZnPc–PDI was excited by a Panther OPO pumped by Nd:YAG laser (Continuum, SLII-10, 4-6 ns fwhm) at λ = 531 nm with the powers of 1.5 and 3.0 mJ per pulse. The transient absorption measurements were performed using a continuous xenon lamp (150 W) and an InGaAs-PIN photodiode (Hamamatsu 2949) as a probe light and a detector, respectively. The output from the photodiodes and a photomultiplier tube was recorded with a digitizing oscilloscope (Tektronix, TDS3032, 300 MHz). The transient spectra were recorded using fresh solutions in each laser excitation at 298 K.