Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Multiple photosynthetic reaction centres composed of supramolecular assemblies of zinc porphyrin dendrimers with a fullerene acceptor

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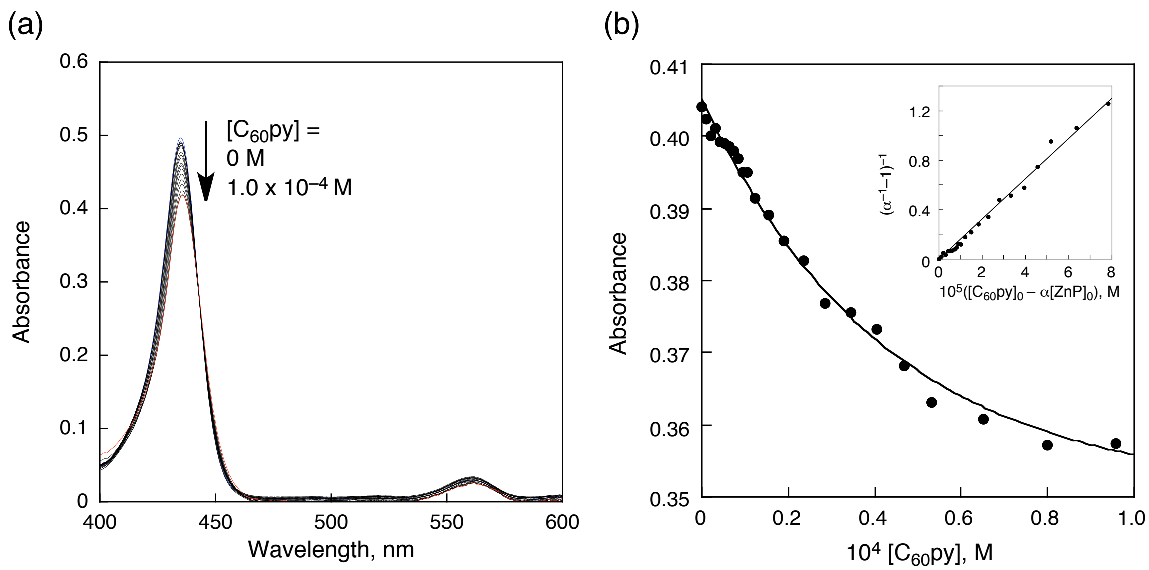

Fig. S1 (a) Change in the absorption of D(ZnP)$_{16}$ (2.9×10^{-6} M based on the number of porphyrin unit) in the presence of various concentrations of C_{60}py (0 to 9.6×10^{-5} M) in deaerated PhCN at 298 K. Inset: Plot of $(\alpha^{-1} - 1)^{-1}$ *vs*. $[C_{60}py]_0 - \alpha[ZnP]_0$. $\alpha = (A - A_0)/(A_\infty - A_0)$; A is the absorption of D(ZnP)$_{16}$ at 435 nm in the presence of C_{60}py, A_0 and A_∞ are the initial and final intensities at the same wavelength in the absence and presence of C_{60}py, respectively. (b) Change in the absorbance at 430 nm of D(ZnP)$_{16}$ (2.9×10^{-6} M) in the presence of various concentrations of C_{60}py (0 to 9.6×10^{-5} M) in deaerated PhCN at 298 K. Inset: Plot of $(\alpha^{-1} - 1)^{-1}$ vs $[C_{60}py]_0 - \alpha[ZnP]_0$. $\alpha = (I - I_0)/(I_\infty - I_0)$; I is the absorbance at 430 nm in the presence of C_{60}py, I_0 and I_∞ are the initial and final absorbances in the absence and presence of C_{60}py, respectively.

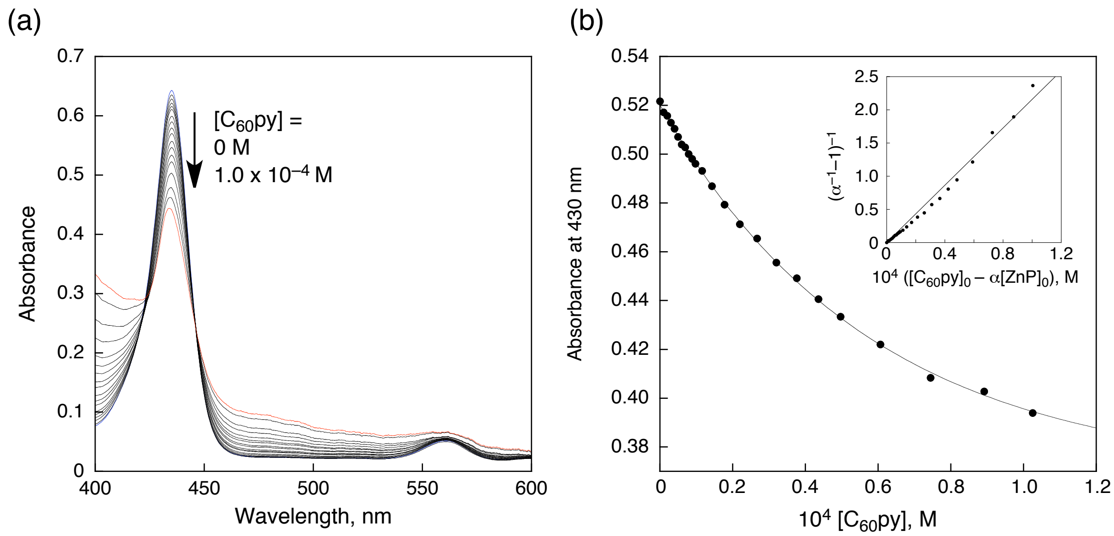

Fig. S2 (a) Change in the absorption of D(ZnP)$_8$ (2.9×10^{-6} M based on the number of porphyrin unit) in the presence of various concentrations of C_{60}py (0 to 9.6×10^{-5} M) in deaerated PhCN at 298 K. Inset: Plot of $(\alpha^{-1} - 1)^{-1}$ vs $[C_{60}py]_0 - \alpha[ZnP]_0$. $\alpha = (A - A_0)/(A_\infty - A_0)$; A is the absorption of D(ZnP)$_{16}$ at 430 nm in the presence of C_{60}py, A_0 and A_∞ are the initial and final intensities at the same wavelength in the absence and presence of C_{60}py, respectively. (b) Change in the absorbance at 430 nm of D(ZnP)$_8$ (2.9×10^{-6} M) in the presence of various concentrations of C_{60}py (0 to 9.6×10^{-5} M) in deaerated PhCN at 298 K. Inset: Plot of $(\alpha^{-1} - 1)^{-1}$ vs $[C_{60}py]_0 - \alpha[ZnP]_0$. $\alpha = (I - I_0)/(I_\infty - I_0)$; I is the absorbance at 430 nm in the presence of C_{60}py, I_0 and I_∞ are the initial and final absorbances in the absence and presence of C_{60}py, respectively.

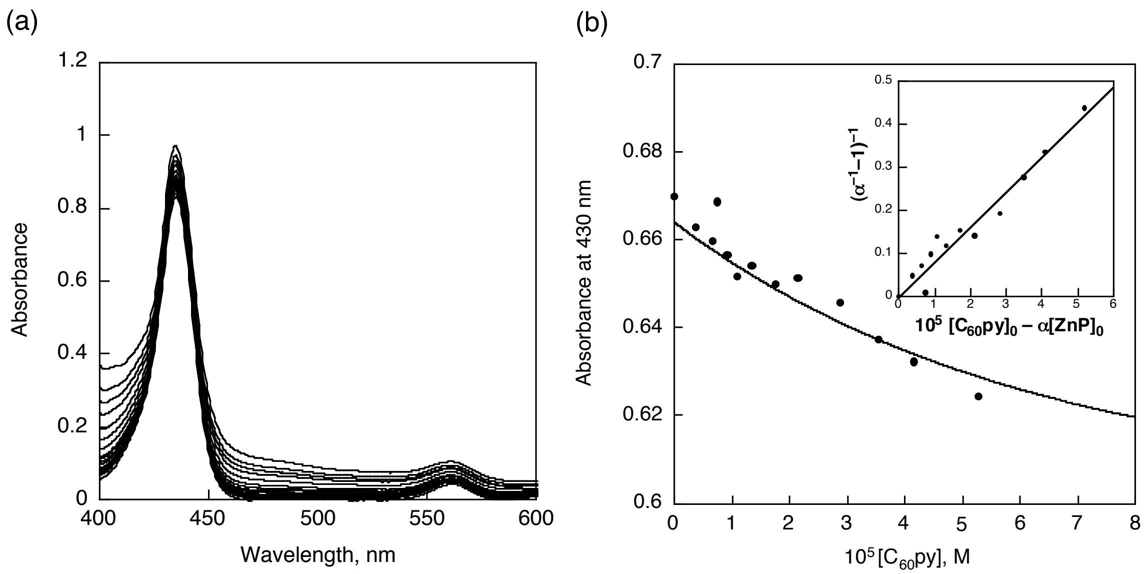

Fig. S3 (a) Change in the absorption of D(ZnP)$_4$ (2.9×10^{-6} M based on the number of porphyrin unit) in the presence of various concentrations of C_{60}py (0 to 9.6×10^{-5} M) in deaerated PhCN at 298 K. Inset: Plot of $(\alpha^{-1} - 1)^{-1}$ vs $[C_{60}\text{py}]_0 - \alpha[\text{ZnP}]_0$. $\alpha = (A - A_0)/(A_\infty - A_0)$; A is the absorption of D(ZnP)$_{16}$ at 430 nm in the presence of C_{60}py, A_0 and A_∞ are the initial and final intensities at the same wavelength in the absence and presence of C_{60}py, respectively. (b) Change in the absorbance at 430 nm of D(ZnP)$_4$ (2.9×10^{-6} M) in the presence of various concentrations of C_{60}py (0 to 9.6×10^{-5} M) in deaerated PhCN at 298 K. Inset: Plot of $(\alpha^{-1} - 1)^{-1}$ vs $[C_{60}\text{py}]_0 - \alpha[\text{ZnP}]_0$. $\alpha = (I - I_0)/(I_\infty - I_0)$; I is the absorbance at 430 nm in the presence of C_{60}py, I_0 and I_∞ are the initial and final absorbances in the absence and presence of C_{60}py, respectively.

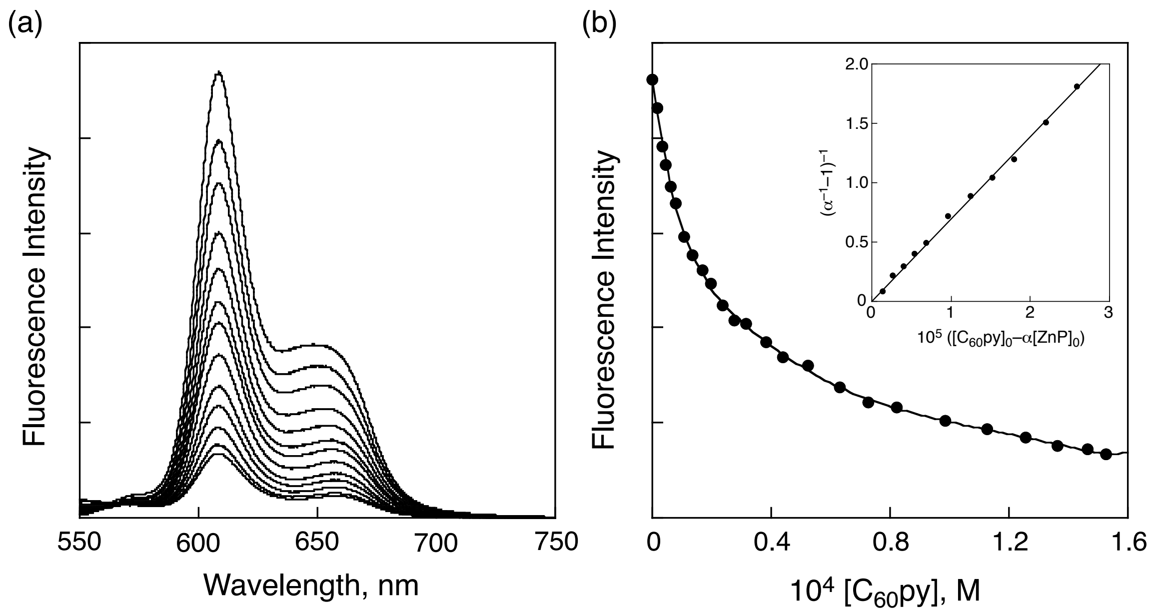

Fig. S4 (a) Fluorescence spectra of $D(ZnP)_8$ (2.9×10^{-6} M based on the number of porphyrin unit) in the presence of various concentrations of C_{60}py (0 to 1.5×10^{-4} M) in deaerated PhCN at 298 K. (b) Change in the fluorescence intensity of $D(ZnP)_8$ (2.9×10^{-6} M based on the number of porphyrin unit) in the presence of various concentrations of C_{60}py (0 to 1.5×10^{-4} M) in deaerated PhCN at 298 K. Inset: Plot of $(\alpha^{-1} - 1)^{-1}$ *versus* $[C_{60}py]_0 - \alpha[ZnP]_0$. $\alpha = (I - I_0)/(I_\infty - I_0)$; I is the fluorescence intensity of $D(ZnP)_8$ at 609 nm in the presence of C_{60}py, I_0 and I_∞ are the initial and final intensities at the same wavelength in the absence and presence of C_{60}py, respectively.

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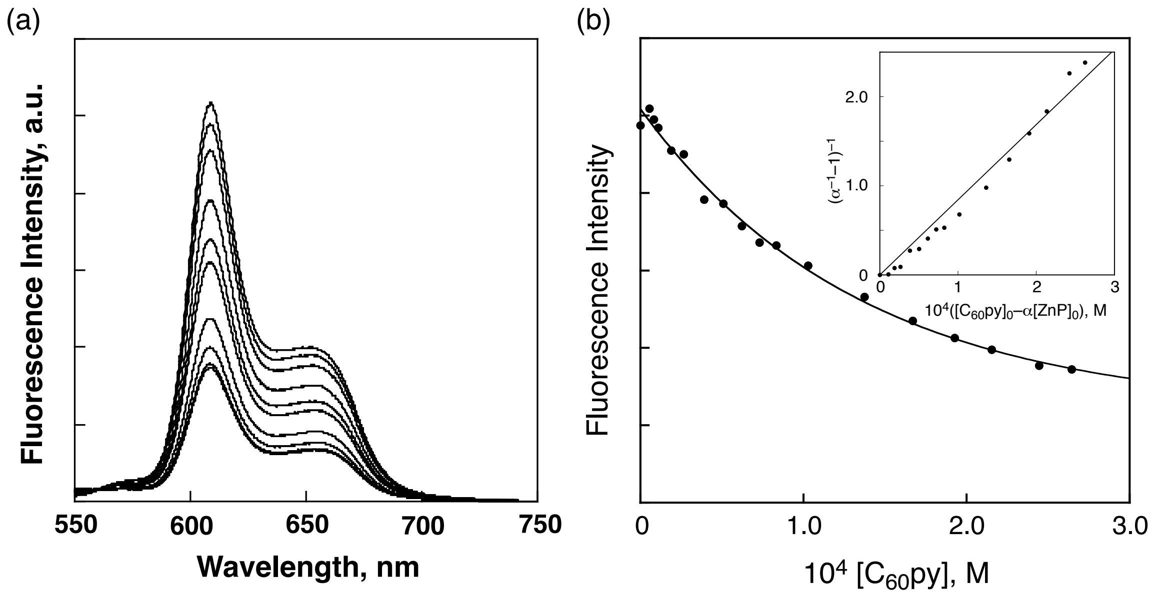

Fig. S5 (a) Fluorescence spectra of $D(ZnP)_4$ (2.9×10^{-6} M based on the number of porphyrin unit) in the presence of various concentrations of C_{60}py (0 to 1.5×10^{-4} M) in deaerated PhCN at 298 K. (b) Change in the fluorescence intensity of $D(ZnP)_4$ (2.9×10^{-6} M based on the number of porphyrin unit) in the presence of various concentrations of C_{60}py (0 to 1.5×10^{-4} M) in deaerated PhCN at 298 K. Inset: Plot of $(\alpha^{-1} - 1)^{-1}$ *versus* $[C_{60}py]_0 - \alpha[ZnP]_0$. $\alpha = (I - I_0)/(I_\infty - I_0)$; I is the fluorescence intensity of $D(ZnP)_4$ at 609 nm in the presence of C_{60}py, I_0 and I_∞ are the initial and final intensities at the same wavelength in the absence and presence of C_{60}py, respectively.

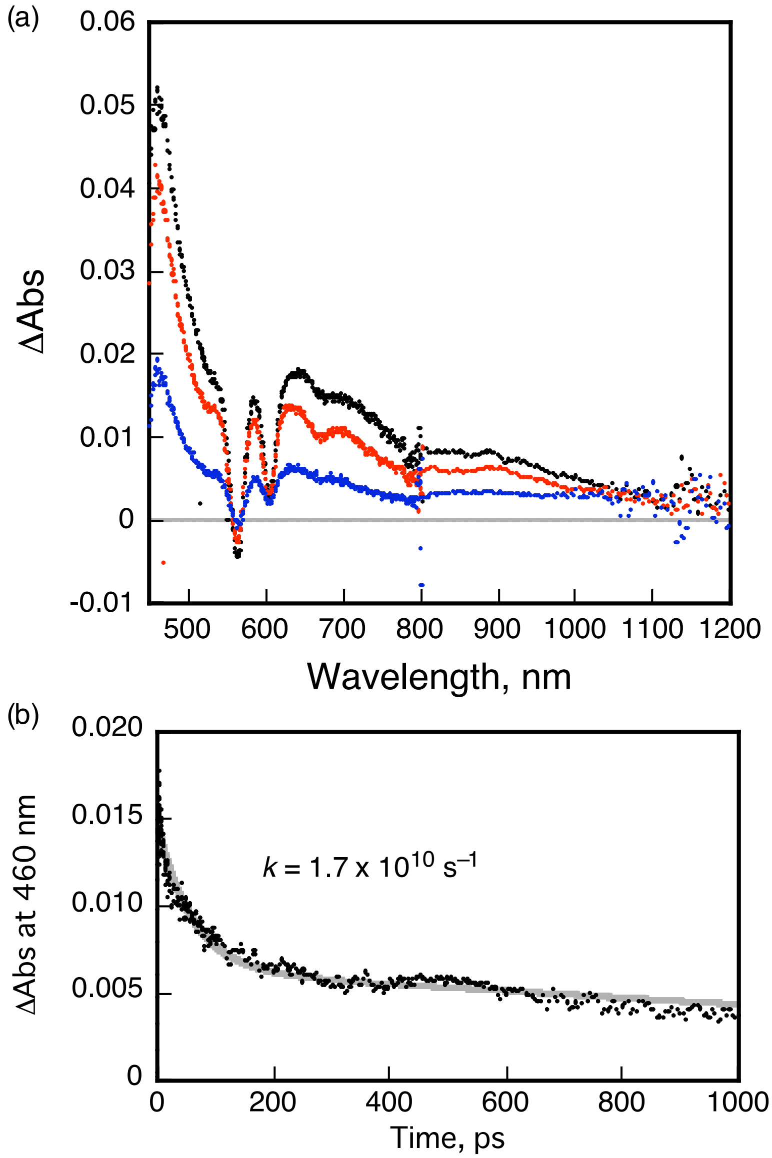

Fig. S6 (a) Transient absorption spectra of D(ZnP)$_8$–C$_{60}$py in deaerated PhCN taken at 1.0 (black), 10 (red) and 350 ps (blue) after femtosecond laser excitation at 438 nm. (b) Decay time profile at 460 nm due to ^{1}ZnP*. Gray line is drawn on the basis of the two-exponential curve fitting with $k = 1.7 \times 10^{10}$ and 1.0×10^8 s^{-1}.

Note: Slow decay component is due to the intersystem crossing of free ZnP.

Materials and methods

Zinc(II) porphyrin dendrimers and fulleropyrrolidine bearing a pyridine were prepared according to the literature.[S1,S2] Absorption spectra were measured on a Shimadzu UV-3100PC spectrometer at 298 K. Corrected fluorescence spectra were taken using a SHIMADZU spectrofluorophotometer (RF-5300PC). Nanosecond transient absorption measurements were also carried out using SHG (532 nm) of a Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-130, fwhm 6 ns) as an excitation source. For transient absorption spectra in the near-IR region (600-1600 nm), monitoring light from a pulsed Xe lamp was detected with a Ge-avalanche photodiode (Hamamatsu Photonics, B2834). All the samples (10^{-4}~10^{-5} M) in a quartz cell (1 x 1 cm) were deaerated by bubbling argon through the solution for 15 min. The quantum yields were measured using the comparative method.[7] ESR spectra were recorded on a JEOL X-band spectrometer (JES-RE1XE) with a quartz ESR tube (4.5 mm i.d.). ESR spectra in frozen PhCN were measured under photoirradiation with a high-pressure mercury lamp (USH–1005D) through a water filter focusing at the sample cell in the ESR cavity at 173 K. The *g* values were calibrated using an Mn^{2+} marker.

S1. T. Hasobe, Y. Kashiwagi, M. A. Absalom, J. Sly, K. Hosomizu, M. J. Crossley, H. Imahori, P. V. Kamat and S. Fukuzumi, *Adv. Mater.*, 2004, **16**, 975.

S2. F. D'Souza, G. R. Deviprasad, M. E. Zandler, V. T. Hoang, A. Klykov, M. VanStipdonk, A. Perera, M. E. El-Khouly, M. Fujitsuka and O. Ito, J. *Phys. Chem. A*, 2002, **106**, 3243.