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 $A_\infty$ 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 $I_\infty$ 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$_\infty$ 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$_\infty$ 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 $[\text{C}_{60}\text{py}]_0 - \alpha[\text{ZnP}]_0$. $\alpha = (A - A_0)/(A_\infty - A_0)$; $A$ is the absorption of D(ZnP)$_{16}$ at 430 nm in the presence of C$_{60}$py, $A_0$ and $A_\infty$ 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 $[\text{C}_{60}\text{py}]_0 - \alpha[\text{ZnP}]_0$. $\alpha = (I - I_0)/(I_\infty - I_0)$; $I$ is the absorbance at 430 nm in the presence of C$_{60}$py, $I_0$ and $I_\infty$ 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 $I_\infty$ are the initial and final intensities at the same wavelength in the absence and presence of C$_{60}$py, respectively.
**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 $[\text{C}_{60}\text{py}]_0 - \alpha[\text{ZnP}]_0$. $\alpha = (I - I_0)/(I_{\infty} - I_0)$; $I$ is the fluorescence intensity of D(ZnP)$_4$ at 609 nm in the presence of C$_{60}$py, $I_0$ and $I_{\infty}$ 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 $1.0 \times 10^8$ 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.\textsuperscript{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.\textsuperscript{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.