Chem. Commun.

Supporting Information

Fullerenes-encapsulated porphyrin hexagonal nanorods. An anisotropic donor-acceptor composite for efficient photoinduced electron transfer and light energy conversion

Taku Hasobe,*[ab] Atula S. D. Sandanayaka,*[a] Takehiko Wada[c] and Yasuyuki Araki[c]

[a]School of Material Science, Japan Advanced Institute of Science and Technology

(JAIST), 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

E-mail: t-hasobe@jaist.ac.jp

[b]PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi,

Saitama, 332-0012, Japan

[c] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,

Katahira, Sendai, 980-8577, Japan

Experimental section

General information. ZnP(Py)$_4$ and cetyltrimethylammonium bromide (CTAB) was purchased from Aldrich. All solvents and reagents of the best grade available were purchased from commercial suppliers and were used without further purification. All experiments were performed at room temperature.

Preparation of ZnP(Py)$_4$ nanotube: ZnP(Py)$_4$ nanotube was prepared as following procedure. 0.4 ml of 0.25 mM ZnP(Py)$_4$ in DMF solution was injected into 3 mL of continuously stirred acetronitrile/0.20 mM CTAB (cetyltrimethylammonium bromide) solution at room temperature (Final concentration; [ZnP(Py)$_4$] = 0.03 mM). The resulting green color solution was employed for analysis of the structures.

C$_{60}$-ZnP(Py)$_4$ nanorod: C$_{60}$-ZnP(Py)$_4$ nanorod was prepared by the same method as ZnP(Py)$_4$ nanotube. 0.4 ml of 0.25 mM ZnP(Py)$_4$ with C$_{60}$ in DMF solution was injected into 3 mL of continuously stirred acetronitrile/0.20 mM CTAB solution at room temperature (Final concentrations; [ZnP(Py)$_4$] = 0.03 mM and [C$_{60}$] = 0.02 mM).

(ZnP(Py)$_4$)$_n$: (ZnP(Py)$_4$)$_n$ was prepared as following procedure 0.4 ml of 0.25 mM ZnP(Py)$_4$ in DMF solution was injected into 3 mL of continuously stirred acetronitrile solution at room temperature (Final concentration; [ZnP(Py)$_4$] = 0.03 mM). The resulting red color solution was employed for analysis of the structures.
(C$_{60}$+ZnP(Py)$_4$)$_n$: (C$_{60}$+ZnP(Py)$_4$)$_n$ was prepared by the same method as (ZnP(Py)$_4$)$_n$, 0.4 ml of 0.25 mM ZnP(Py)$_4$ with C$_{60}$ in DMF solution was injected into 3 mL of continuously stirred acetronitrile solution at room temperature (Final concentrations; [ZnP(Py)$_4$] = 0.03 mM and [C$_{60}$] = 0.02 mM).

Electron micrograph measurements. Transmission electron micrograph (TEM) measurements were recorded by applying a drop of the sample to a copper grid. Images were recorded on a Hitachi H 7100 transmission electron microscope an accelerating voltage of 100 kV for imaging. SEM images of porphyrin assemblies were recorded using a Hitachi S-4100 scanning electron microscope.

Steady-state spectroscopic measurements. Steady-state absorption spectra in the visible and near-IR regions were measured on a Perkin Elmer (Lamda 750) UV-VIS-NIR spectrophotometer. Steady-state fluorescence spectra were measured on a Perkin Elmer (LS-55) spectrofluorophotometer equipped with a photomultiplier tube having high sensitivity in the 400-800 nm region.

Time-resolved fluorescence measurements. The time-resolved fluorescence spectra were measured by single photon counting method using a streakscope (Hamamatsu Photonics, C5680) as a detector and the laser light (Hamamatsu Photonics M10306, laser diode head, 408 nm) as an excitation source. Lifetimes were evaluated with software attached to the equipments.

Nanosecond transient absorption measurements. Nanosecond transient absorption measurements were carried out using THG (532 nm) of a Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-130, 5 ns fwhm) as an excitation source. For transient absorption spectra in the near-IR region (600-1200 nm) and the time-profiles, monitoring light from a pulsed Xe lamp was detected with a Ge-APD (Hamamatsu Photonics, B2834). For the measurements in the visible region (400-1000 nm), a Si-PIN photodiode (Hamamatsu Photonics, S1722-02) was used as a detector.

X-ray diffraction measurement. X-ray diffraction (XRD) measurement was carried out with a BRUKER-axs M18XHF-SRA using filtered Cu Ka radiation. The sample for XRD analysis was prepared by drying suspension liquid over a glass substrate in air.

Preparation of porphyrin-deposited films. ZnP(Py)$_4$ and C_{60} composite films were simply prepared by electrophoretic deposition method. A known amount of ZnP(Py)$_4$, C_{60} or the mixture solution in DMF/acetonitrile (2/15, v/v, 2 mL) was transferred to a 1 cm cuvette in which two optically transparent electrodes were kept at a distance of 6 mm using a Teflon spacer. A DC electric field (~200 V/cm) for 1 minute was applied between these two electrodes using a PowerPac HV (Bio-Rad). The deposition of the film can be visibly seen as the solution becomes colorless with simultaneous brown coloration of the OTE electrode. The OTE electrode coated with C_{60}-ZnP(Py)$_4$ nanorod is referred to OTE/C_{60}-ZnP(Py)$_4$-nanorod.

Measurement of photoelectrochemical solar cells. An optically transparent electrode (OTE) was prepared by casting SnO_2 colloidal solution (Alfa Chemicals) onto an ITO film (Sanyo Vacuum Industires Co., Ltd.). The detail procedure was reported.[4] Photoelectrochemical measurements were carried out in a standard two-compartment cell consisting of a working electrode and a Pt wire gauze counter electrode in the electrolyte. The electrolyte is 0.5 M LiI and 0.01 M I_2 in acetonitrile. KEITHLEY 2400 was used for recording photocurrent generation response and IPCE action spectrum. A collimated light beam from a 300 W Xenon lamp with a AM 1.5 filter was used for excitation of porphyrin assembly film deposited on an OTE. In the case of measurement of IPCE spectra, a monochromator (SM-25, Bunkoh-Keiki Co.,LTD) was introduced into the path of the excitation beam for the selected wavelength. The schematic illustration is shown in Fig. 1 for clarify.

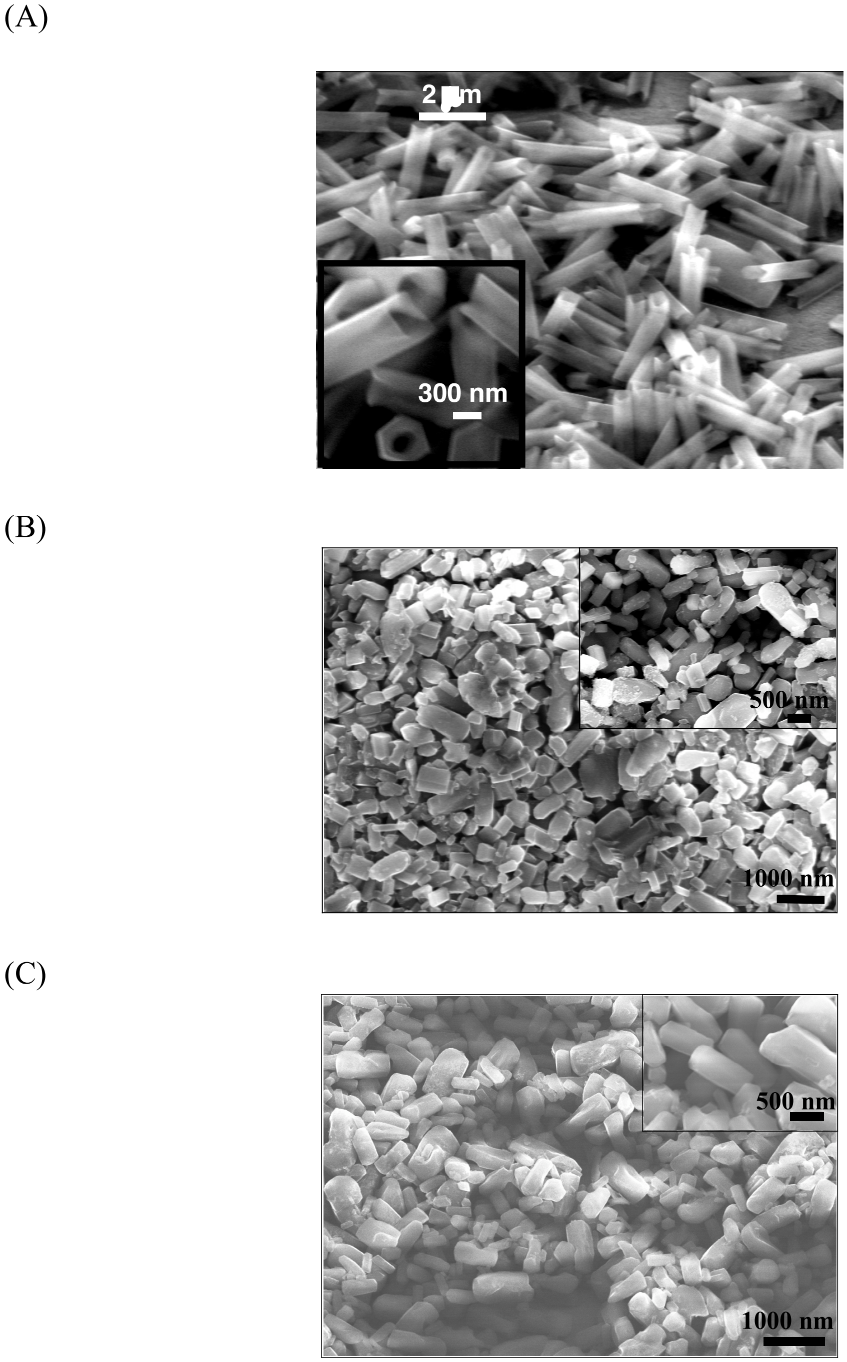


Fig. S1 SEM images of (A) $ZnP(Py)_4$ nanotubes, (B) $(ZnP(Py)_4{+}C_{60})_n$ and (C) $(ZnP(Py)_4)_n$.

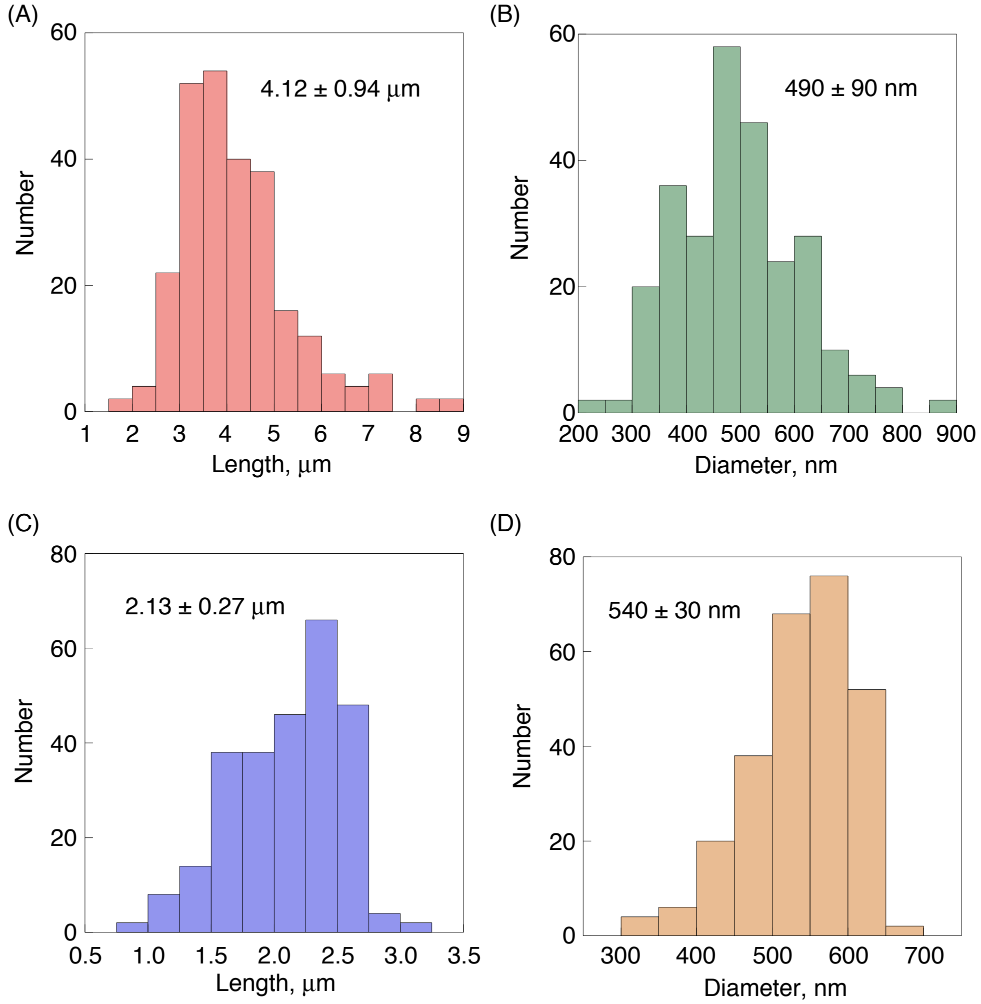


Fig. S2 Length and diameter-distributions. (A) length of C_{60}-ZnP(Py)$_4$ nanorods, (B) diameter of C_{60}-ZnP(Py)$_4$ nanorods, (C) length of ZnP(Py)$_4$ nanotubes and (D) diameter of ZnP(Py)$_4$ nanotubes.

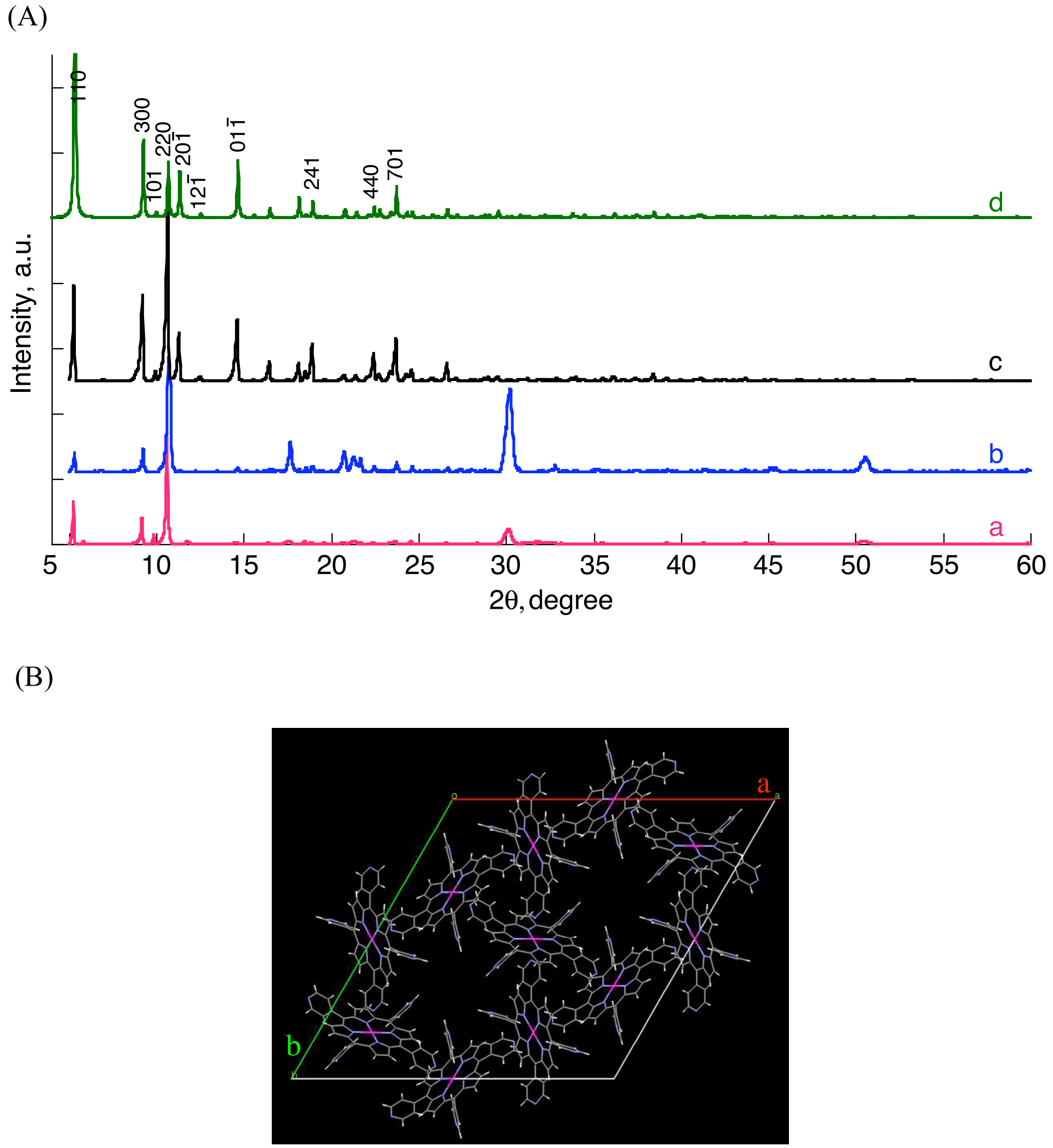


Fig. S3 (A) XRD patterns of (a) C_{60}-ZnP(Py)$_4$ nanorods, (b) ZnP(Py)$_4$ nanotubes, (c) ZnP(Py)$_4$ starting material, and (d) simulated pattern from the crystal structure of ZnP(Py)$_4$. (B) Crystal structures of ZnP(Py)$_4$. The structure was analyzed by supporting materials of the following papers. H. Krupitsky, Z. Stein, I. Goldberg and C. E. Strouse, *J. Inclusion Phenom. Macrocyclic Chem.*, 1994, **18**, 177.

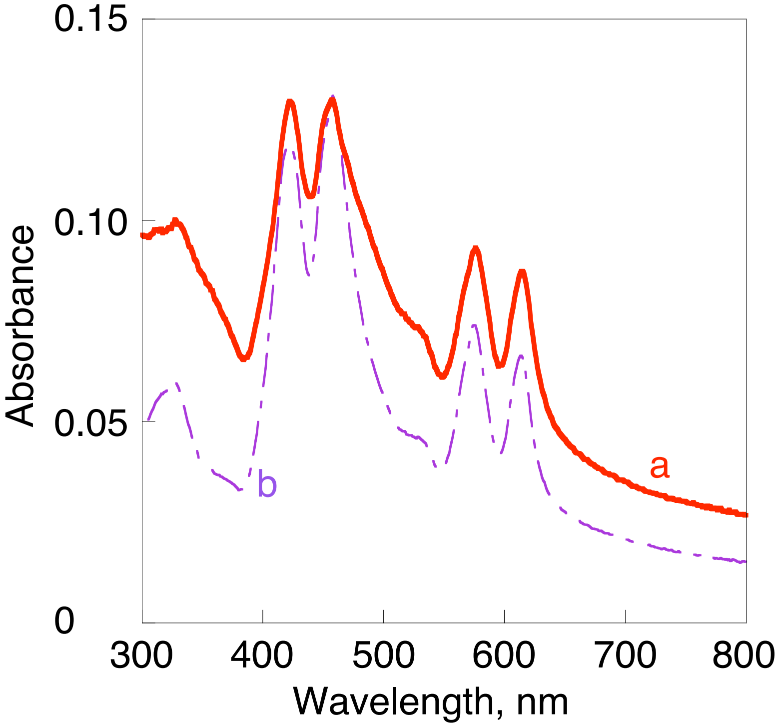
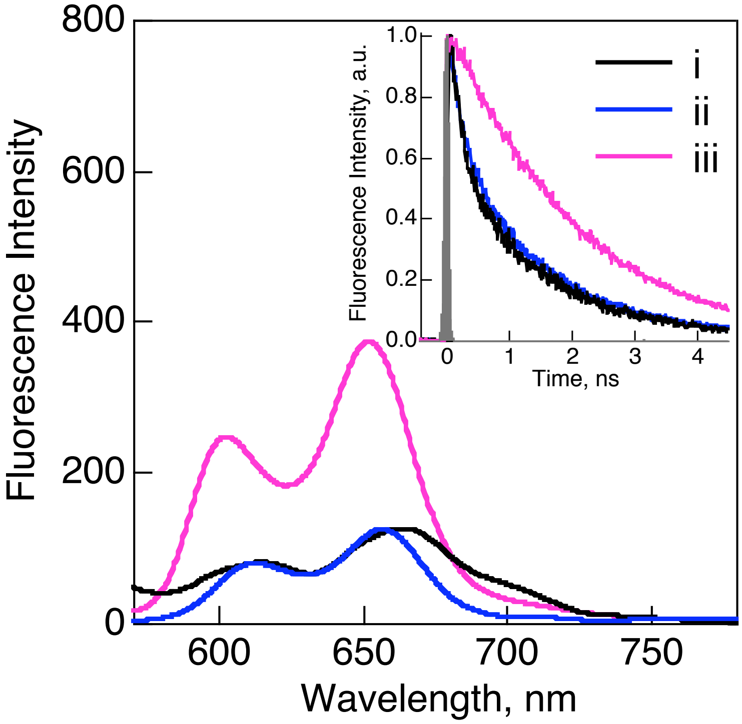


Fig. S4 Steady-state absorption spectra of (a) C_{60}-ZnP(Py)$_4$ nanorods and (b) ZnP(Py)$_4$ nanotubes in DMF/acetonitrile (15/2, v/v). The spectrum *b* is normalized for comparison.



Sample	τ_{f}, ps	Φ^{S}_{q}
C_{60}-ZnP(Py)$_4$ nanorods [trace a in Fig. 3]	180 (85%) 1100 (15%)	0.92
ZnP(Py)$_4$ nanotubes [trace b in Fig. 3]	390 (65%) 1870 (35%)	0.82
(C_{60}+ZnP(Py)$_4$)$_n$ without CTAB [trace (i) in Fig. S6]	420 (55%) 1730 (45%)	0.80
(ZnP(Py)$_4$)$_n$ without CTAB [trace (ii) in Fig. S6]	430 (55%) 1700 (45%)	0.80
ZnP(Py)$_4$ monomer [trace (iii) in Fig. S6]	2200 (100%)	–

Fig. S5 Steady-sate fluorescence spectra of (i) (C_{60}+ZnP(Py)$_4$)$_n$ prepared without CTAB, (ii) (ZnP(Py)$_4$)$_n$ prepared without CTAB and (iii) ZnP(Py)$_4$ monomer in DMF. λ_{ex} = 408 nm. Inset: the corresponding time-resolved fluorescence decays. Table: summarized data of lifetimes (τ_f) and average quenching quantum yield (Φ^{s}_{q}) in all systems.

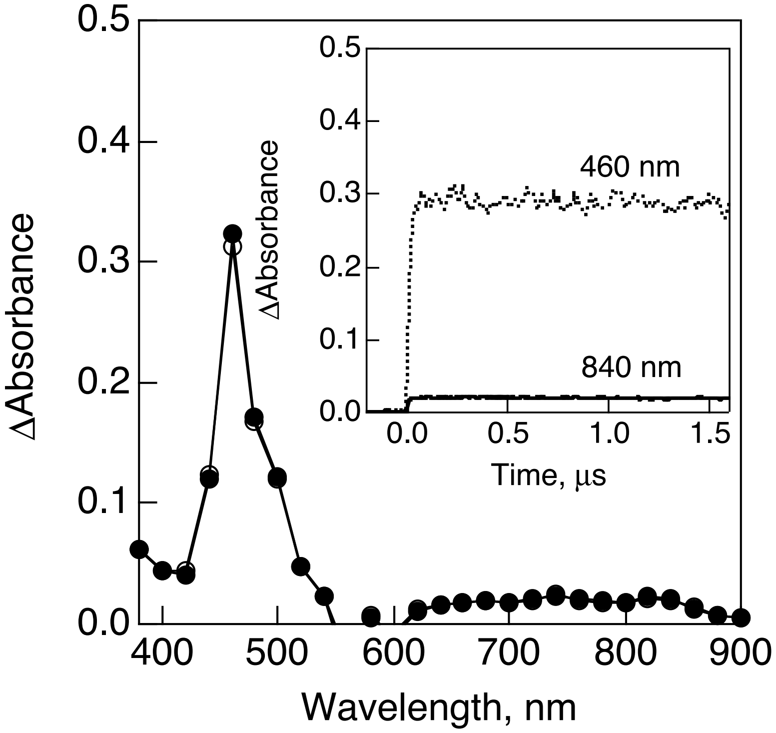


Fig. S6 Nanosecond transient absorption spectrum of 0.03 mM ZnP(Py)$_4$ monomer observed by 532 nm laser light (ca. 3 mJ/pulse) irradiation at 0.1 μs (●) and 1.0 μs (○) in DMF. Inset: Time profiles.

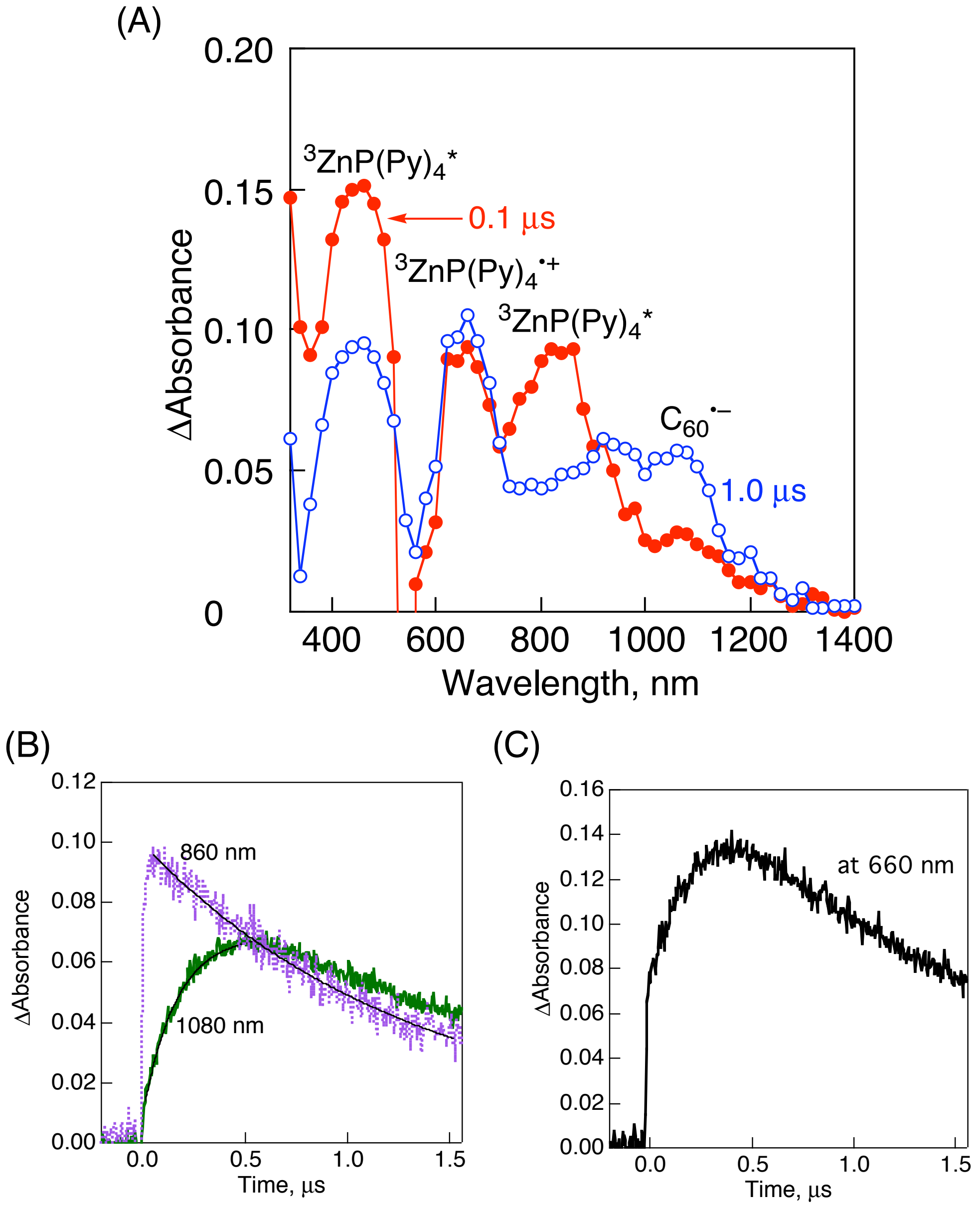


Fig. S7 (A) Nanosecond transient absorption spectra of $(C_{60}+ZnP(Py)_4)_n$ observed by 532 nm laser light (ca. 3 mJ/pulse) irradiation at 0.1 μs (●) and 1.0 μs (○) in DMF/acetonitrile (2/15, v/v). (B) and (C): time profiles at 660, 860 and 1080 nm.

$k^{T}_{CS} = 6.84 \times 10^{6}\ s^{-1}$
$k_{CR} = 5.54 \times 10^{5}\ s^{-1}$
$\tau_{CR} = 1800$ ns