

Supplementary Information for

Effects of Fullerene Encapsulation on Structure and Photophysical Properties of Porphyrin-Linked Single-Walled Carbon Nanotubes

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Experimental

Instruments. X-ray photoelectron spectroscopy (XPS) was carried out with ULVAC-PHI MT-5500 system with Mg K α X-ray source (1253.6 eV) and a hemispherical energy analyzer. Resonance Raman spectra were measured on a Horiba JobinYvon LabRAM HR-800 equipped with 2.54 (488 nm). Atomic force microscopy (AFM) analyses were carried out with an Asylum Technology MFP-3D-SA in the AC mode. DMF solutions of SWNTs were spin-coated on freshly cleaved mica at 1500 rpm. Transmission electron microscope (TEM) images were obtained from a JEOL JEM-2200FS. UV-vis-near infrared (NIR) absorption spectra of solutions and films were measured with a Perkin-Elmer Lambda 900 UV/vis/NIR spectrometer. Steady-state fluorescence spectra were recorded on a HORIBA SPEX Fluoromax-3 spectrofluorometer. A time-correlated single photon counting (TCSPC) method was used for the fluorescence lifetime measurements in the nanosecond and subnanosecond time-scale and the time resolution was 70 ps (FWHM) for the excitation wavelength at 405 nm.^{S1} Pump-probe measurements were carried out using the instrument described previously.^{S2} Briefly, the second harmonic (420 nm) of Ti:sapphire laser was used for excitation and the transient spectra were recorded by a CCD detector coupled with a monochromator in the visible and near infrared ranges. A typical time resolution of the instrument was 150 fs (FWHM).

Materials. SWNT soot produced by the direct-injection-pyrolyticsynthesis (DIPS)^{S3} method was supplied by Nikkiso Co., Ltd. As-received soot was refluxed in 15% H₂O₂ aq., stirred in conc. HCl aq., and oxidized in air at 600 °C, affording purified, open-ended SWNTs (p-SWNT). C₆₀ (99.98%) was obtained from MTR Ltd. and used as-received. All other

solvents and chemicals were of reagent grade quality, purchased, and used without further purification. 4-Iodobenzenediazonium tetrafluoroborate,^{S4} 5-(pinacolboronyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)-porphyrinatozinc(II),^{S5} and 5-phenyl-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrinatozinc(II)^{S6} (ZnP-ref) were prepared according to the reported procedures.

Preparation of C₆₀@SWNT.^{S7} p-SWNT (10 mg) and C₆₀ (50 mg) were sealed in a Pyrex tube under vacuum at 1.5×10^{-5} Torr and heated at 550 °C for 72 h. The obtained material was washed with toluene and CS₂ to remove excess fullerenes, giving 15 mg of C₆₀@SWNT .

Preparation of C₆₀@SWNT-PhI.^{S8} C₆₀@SWNT (2 mg) was dispersed in aqueous medium (160 mL) with sodium dodecylbenzenesulfonate (SDBS) surfactant (1 wt%) by tip-type sonication (BRANSON, Digital Sonifier; Model 250) for 2 h. Immediately after the sonication, the dispersion was centrifuged (BECKMAN COULTER, Optima MAX-XP) at 70,000 *g* for 7 min. Supernatant was then carefully collected, leaving micelle-suspended C₆₀@SWNT solutions. This procedure was repeated five times and the obtained dispersions were combined. 4-Iodobenzenediazonium tetrafluoroborate was added to the dispersion and stirred at room temperature for 1 h. The reaction mixture was diluted with acetone, and filtered through a PTFE (average pore size: 0.1 μm) membrane. The black material on the filter paper was washed with acetone, methanol and DMF to efficiently remove the SDBS surfactant and excess unreacted diazonium salt, and dried under vacuum over night. Then, half of the black precipitate was dispersed in 1,2-dichlorobenzene (10 mL) with 4-iodoaniline (1.4 g, 6.4 mmol). After the cautious, slow addition of isoamyl nitrite (0.99 mL, 7.5 mmol) via syringe, the reaction mixture was stirred at 65 °C for 4 h. The mixture was diluted with

DMF and filtered through a PTFE membrane. The resulting black cake was suspended in DMF, and then filtered and washed with DMF. The resulting solid was dried under vacuum overnight to yield 14 mg of C₆₀@SWNT-PhI.

Preparation of C₆₀@SWNT-ZnP.^{S9} A flask was charged with C₆₀@SWNT-PhI (5.8mg) and DMF (5mL). After bath-type sonication for 10 min at room temperature, Cs₂CO₃ (0.2 g, 0.6 mmol) and 5-(pinacolboronyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrinatozinc(II) (86 mg, 0.08 mmol) were added. This mixture was then degassed via three cycles of freeze-pump-thaw and refilled with argon. Pd(PPh₃)₄ (10 mg) was added and the reaction mixture was stirred for 24 h at 105 °C under argon atmosphere. After cooling to room temperature, the mixture was diluted with THF, sonicated for 5 min, and filtered through a PTFE membrane. The product was washed thoroughly with THF, methanol, water, methanol, and THF to remove excess porphyrin. The resulting black cake was suspended in DMF, and then filtered and washed with DMF. The resulting solid was dried under vacuum overnight to yield 7.5 mg of C₆₀@SWNT-ZnP.

Preparations of p-SWNT-PhI and p-SWNT-ZnP. The same procedures described above were conducted using p-SWNT instead of C₆₀@SWNT to yield 12 mg of p-SWNT-PhI and 6.6 mg of p-SWNT-ZnP.

Estimation of Functionalization Ratios. Upon treatment of C₆₀@SWNT with the iodophenyl diazonium salt, a significant amount of iodine (2%) was detected by XPS (Fig. S4). This corresponds to the existence of one *p*-iodophenyl group in ca. 40 carbon atoms of

the nanotube sidewall, supposing that the ratio of carbon atoms of SWNT and C₆₀ in C₆₀@SWNT is 2 : 1. This ratio was estimated based on the following conditions; (i) SWNT with diameter of 1.5 nm contains C₆₀ molecules at 1.1 nm intervals and (ii) C₆₀@SWNT-PhI sample includes 15% of empty SWNT. These conditions are supported by TEM measurements (Fig. S1) and weight increase with a factor of 1.5 by C₆₀ encapsulation (*vide supra*).

In addition, the degree of the porphyrin functionalization by Suzuki coupling was estimated to be one porphyrin unit in ca. 300 carbons of sidewall by the zinc atom ratio of 0.2%. Thus, the reaction yield of Suzuki coupling on the CCG surface was ca. 13%. The marked drop of iodine content from 2% in C₆₀@SWNT-PhI to 0.05% in C₆₀@SWNT-ZnP (98% decrease) suggests that most of iodine atoms in the iodophenyl group were consumed by incomplete Suzuki coupling reaction.

Table S1. Fluorescence lifetimes (τ) excited at 405 nm and monitored at 600 nm in DMF.

Sample	τ (ns) ^a
C ₆₀ @SWNT-ZnP	<0.07 (70%), 1.9 (30%)
SWNT-ZnP	<0.07 (75%), 2.0 (25%)
ZnP-ref	2.0 (100%)

^a The component ratio of each fluorescence lifetime is given in parenthesis.

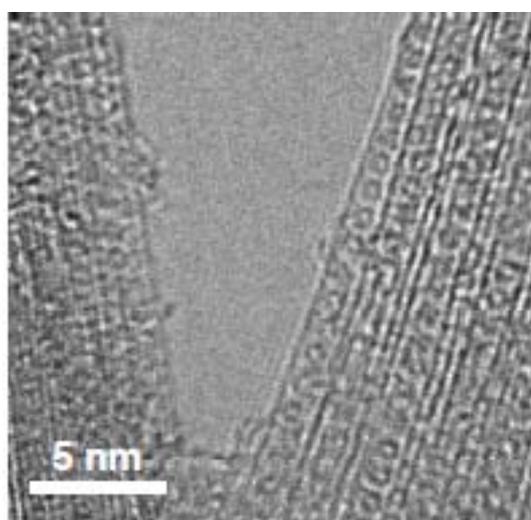


Fig. S1. TEM image of C₆₀@SWNT, drop-cast onto a microgrid from ethanol dispersion.

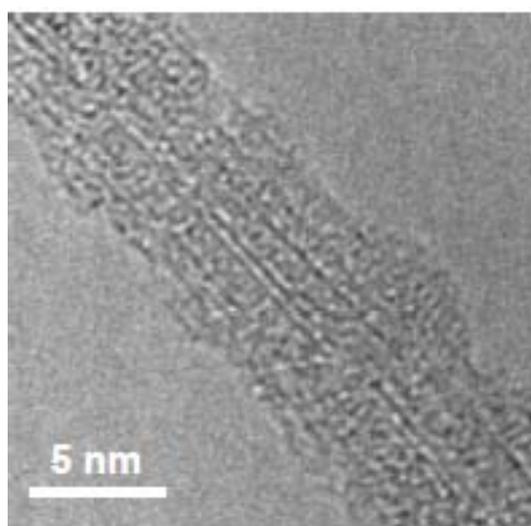


Fig. S2. TEM image of $C_{60}@SWNT-ZnP$, drop-cast onto a microgrid from ethanol dispersion.

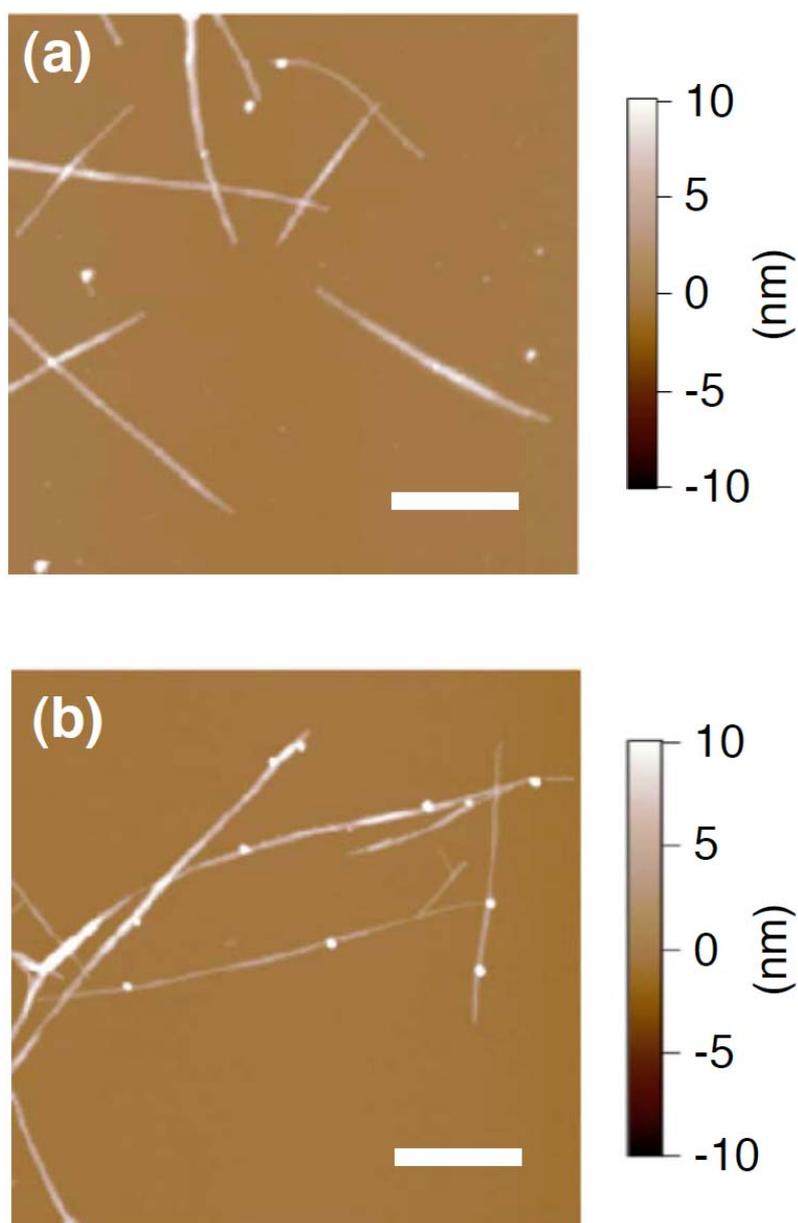


Fig. S3. AFM images of (a) $C_{60}@SWNT-ZnP$ and (b) $C_{60}@SWNT-PhI$ spin-coated on mica from DMF dispersion (scale bar: 500 nm). The average diameters estimated by height profile are 4.5 ± 1 and 6.0 ± 1 nm, respectively.

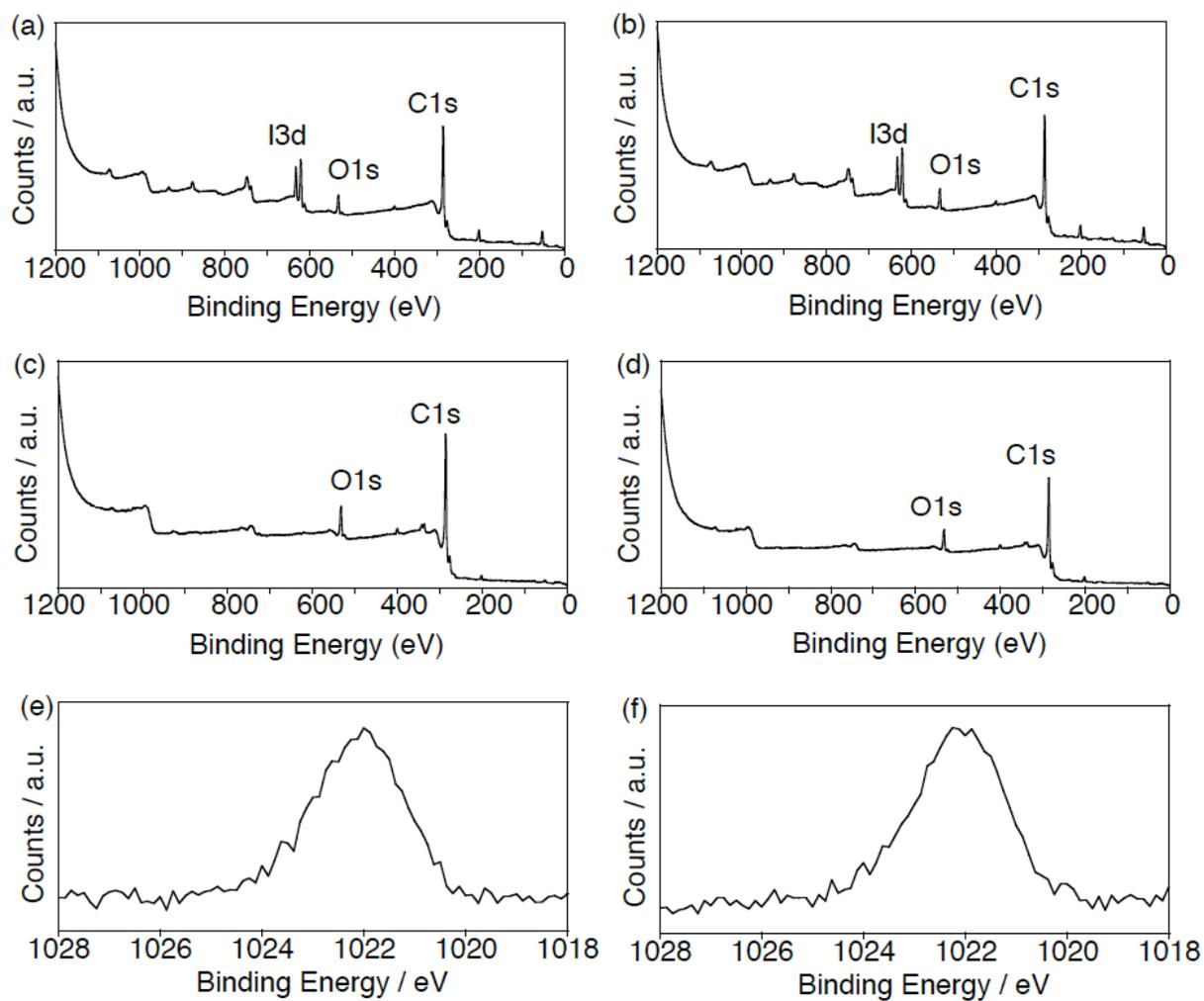


Fig. S4. XPS survey scan of (a) $C_{60}@SWNT-PhI$, (b) $p-SWNT-PhI$, (c) $C_{60}@SWNT-ZnP$ and (d) $p-SWNT-ZnP$. High-resolution XPS $Zn2p$ spectra of (e) $C_{60}@SWNT-ZnP$ and (f) $p-SWNT-ZnP$.

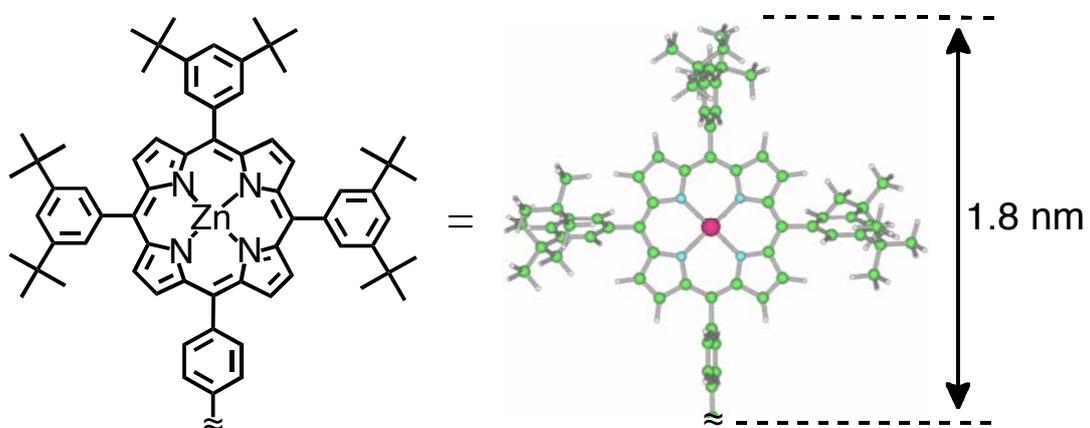


Fig. S5. Structure of the substituted ZnP optimized using B3LYP functional and 6-31G(d) basis set implemented in Gaussian03 program package.^{S10}

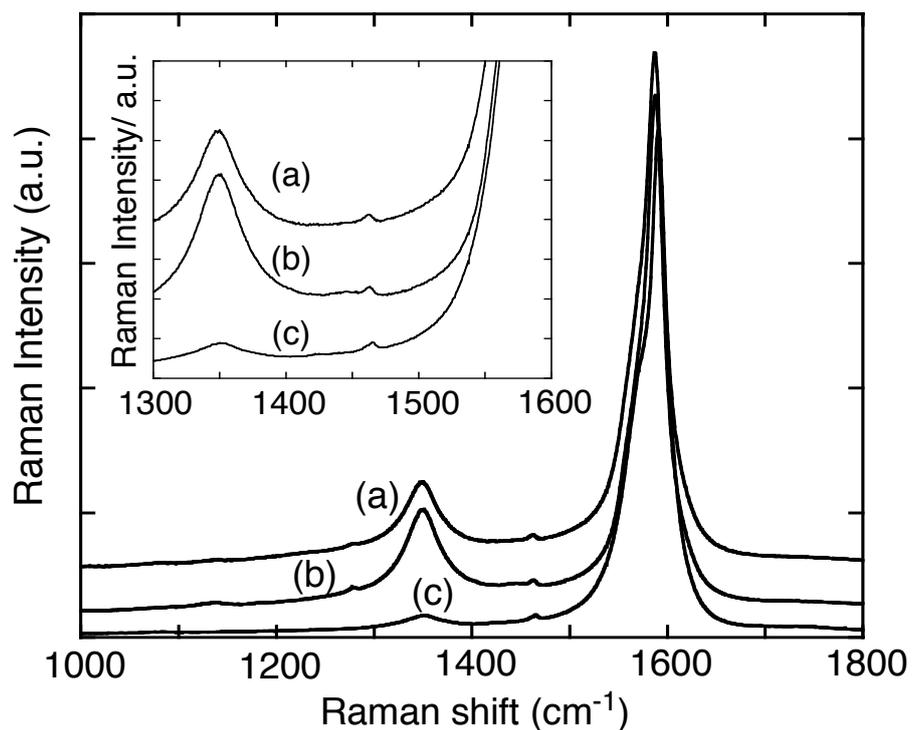


Fig. S6. Resonant Raman spectra of (a) C₆₀@SWNT-ZnP, (b) C₆₀@SWNT-PhI, and (c) C₆₀@SWNT with the excitation wavelength of 488 nm.

The relative peak intensities of tangential mode (G-band) around 1600 cm⁻¹ and of disorder mode (D-band) around 1350 cm⁻¹ (G/D ratio) reflect the relative amounts of sp³ carbon, and are used to determine the degree of sidewall functionalization.^{S11} The G/D ratio of C₆₀@SWNT-PhI (5) is much smaller than that of C₆₀@SWNT (34), which is reasonable considering that the iodophenyl functionalization increases the defect sites on the sidewall of C₆₀@SWNT. On the other hand, The G/D ratio of C₆₀@SWNT-ZnP (6) is almost equal to that of C₆₀@SWNT-PhI (5). It means that the porphyrin compound reacted with iodophenyl group under the Suzuki coupling reaction. The relative peak intensities of Ag (2) mode of C₆₀ molecule around 1460 cm⁻¹ do not change after the functionalization,^{S12} implying that the C₆₀ molecules remain inside the SWNT.

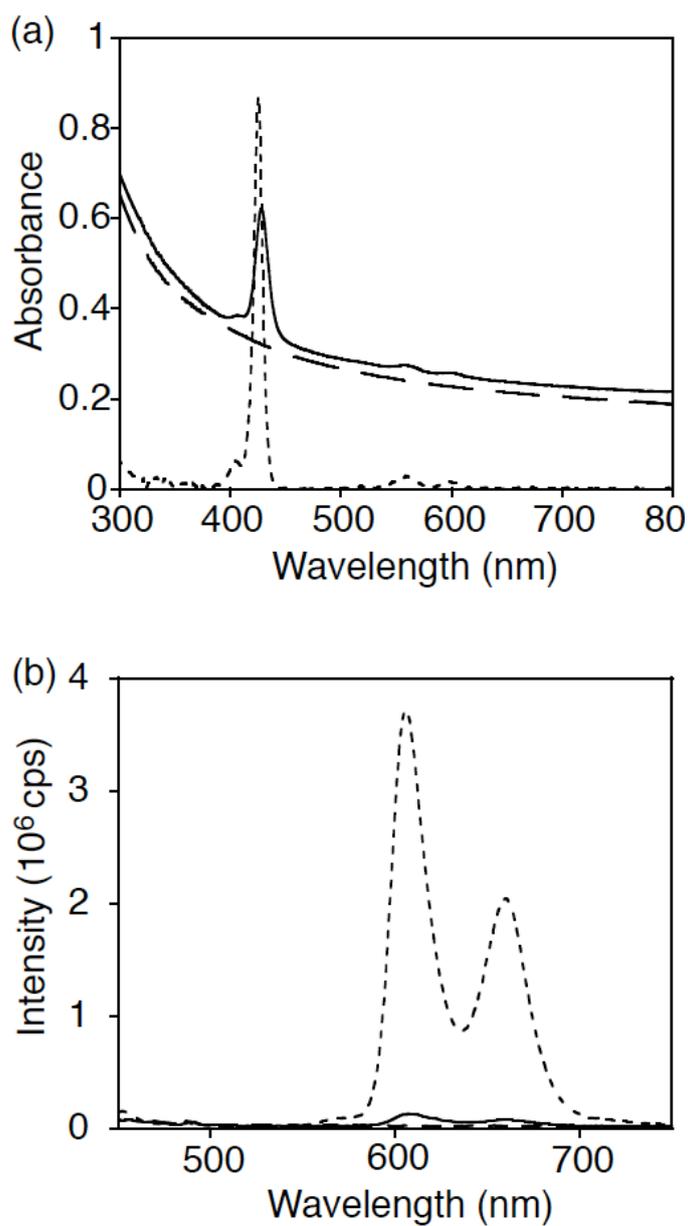


Fig. S7. (a) UV-vis absorption and (b) fluorescence spectra of p-SWNT-ZnP (solid line), p-SWNT-PhI (dashed line), and ZnP-ref (1.6 μM for (a) and 0.3 μM for (b), dotted line) in DMF. For the excitation, the absorbance of the porphyrin moiety was adjusted to be identical at the peak position of the Soret band.

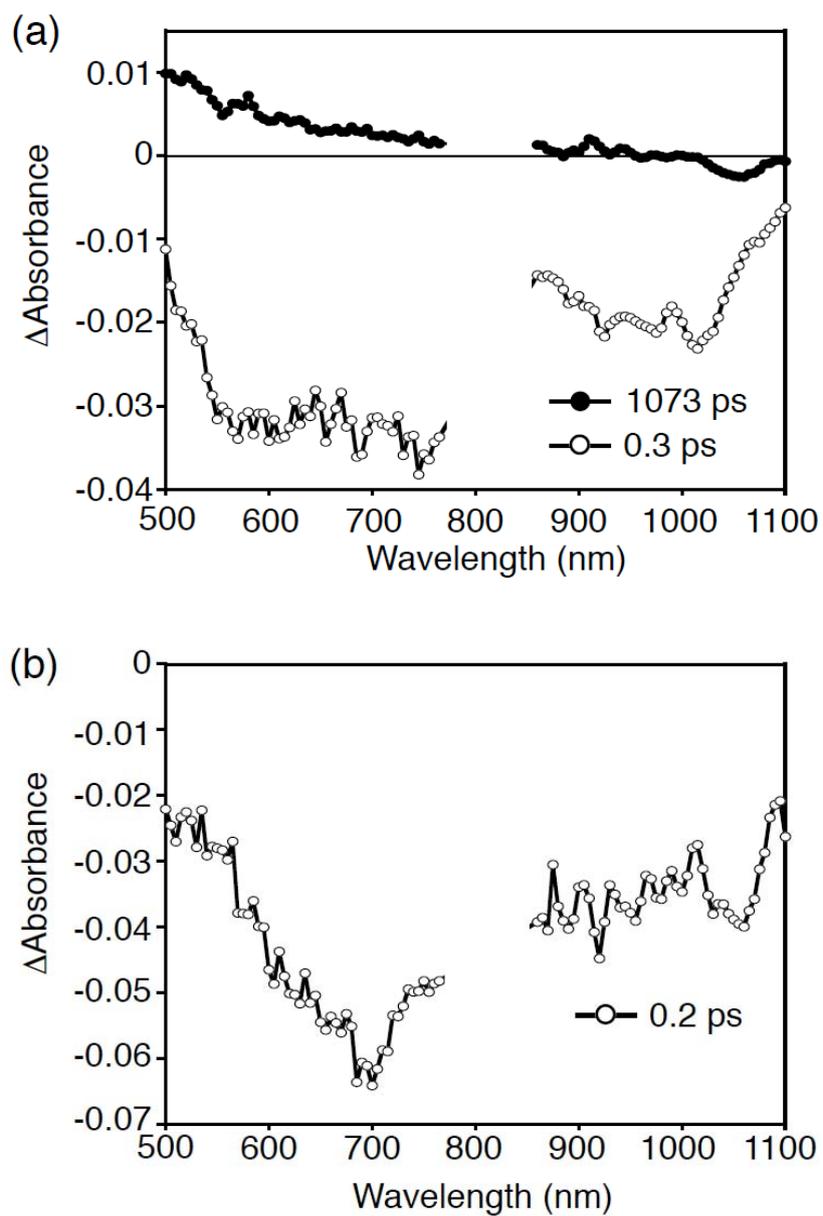


Fig. S8. Transient absorption decay component spectra of (a) p-SWNT-ZnP and (b) p-SWNT-PhI in DMF obtained with global two- or one-component fit of the data. The samples were excited at 420 nm. The fitted time constants are displayed in the figure.

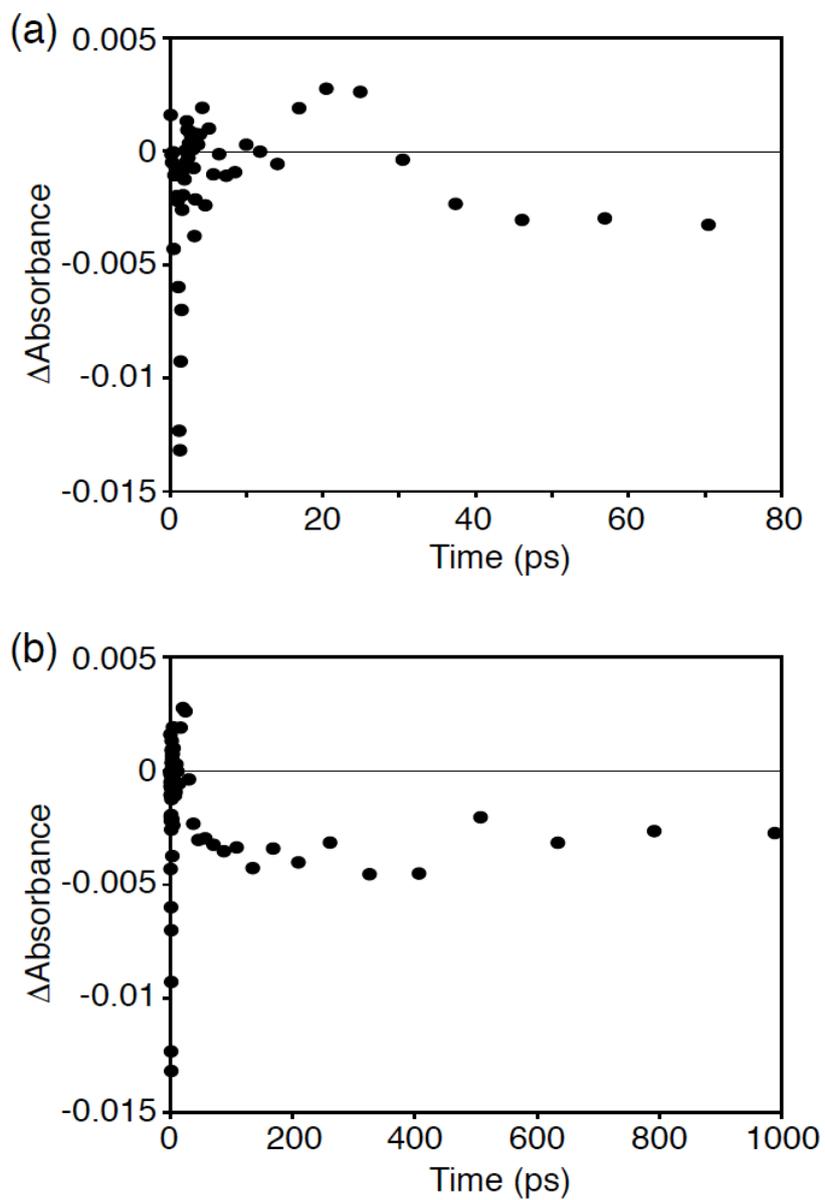


Fig. S9. Time traces of transient absorption signals of $C_{60}@SWNT-ZnP$ at 560 nm in (a) 0 – 80 ps and (b) 0 – 1000 ps regions.

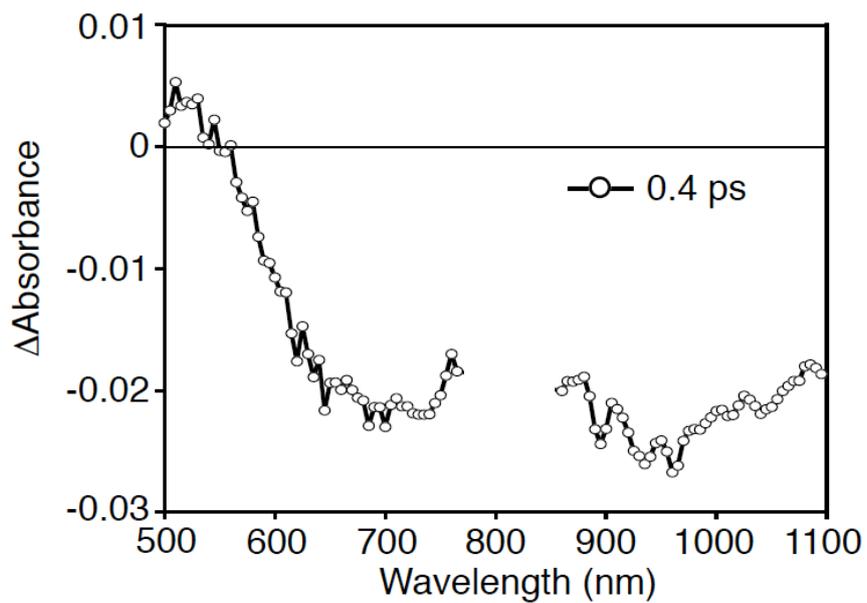


Fig. S10. Transient absorption decay component spectra of C₆₀@SWNT-PhI in DMF obtained with global one-component fit of the data. The sample was excited at 420 nm. The fitted time constants are displayed in the figure.

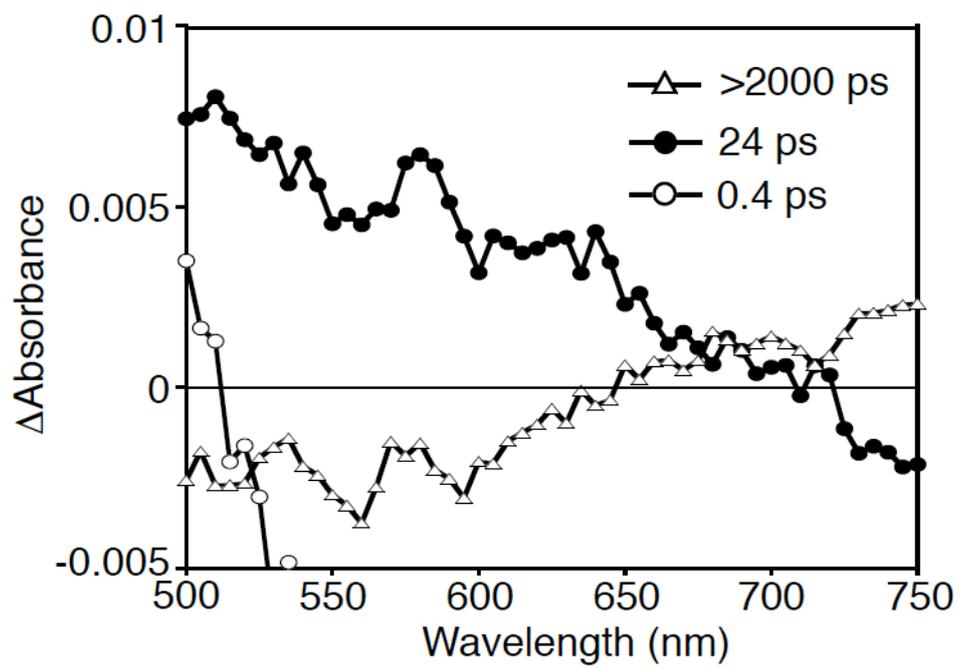


Fig. S11. Enlarged image of Fig. 2 (main text) in the visible region.

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