Supplementary Information for

Photophysics and Photoelectrochemical Properties of Nanohybrids Consisting of Fullerene-Encapsulated Single-Walled Carbon Nanotubes and Poly(3-hexylthiophene)

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Experimental details

Time-resolved spectroscopies. Sub-picosecond to nanosecond time-resolved absorption spectra were collected using a pump-probe technique as described elsewhere.^{S1} The femtosecond pulses of the Ti:sapphire generator (CDP Corp., TiF-50) were amplified by using a multipass amplifier (CDP Corp.) pumped by a second harmonic of the Nd: YAG Q-switched laser (SOLAR TII, LF-114). The amplified pulses were used to generate an excitation pulse (600 nm) through an optical parametric amplifier (CDP Corp., CDP2017) for sample excitation (pump beam) and a white continuum for time-resolved spectrum detection (probe beam). An average of 100 pulses at 10 Hz repetition rate was used to improve the signal-to-noise ratio. The transient spectra were recorded by a charge-coupled device (CCD) detector (Andor Technology, Newton) coupled with a monochromator in the visible and near-infrared ranges. The wavelength range for a single measurement was 296 nm and typically two regions were studied, i.e., 506 - 802 and 810 - 1106 nm. The typical response time of the instrument was 150 fs (full width at half-maximum (FWHM)). A global multi-exponential fitting procedure was applied to process the data. The procedure takes into account the instrument time response function and the group velocity dispersion of the white continuum, and allows one to calculate the decay time constants and dispersion-compensated transient absorption spectra. The excitation energy was adjusted to the highest value at which the photodegradation of the samples during measurements is negligible. All measurements were carried out using a rotating cuvette with 1 mm path at room temperature in air.

Thin film fabrication of SWNT–P3HT hybrids. SWNTs (0.3 mg) and sodium dodecylbenzenesulfonate (SDBS, 10 mg) in D₂O (10 mL) were sonicated using a tip-type sonicator (Astrason, XL2020; 140 W) for 10 min with continuous cooling by water flowing. A thin film of the SWNTs on an indium tin oxide (ITO) electrode (GEOMATEC, $R_s = 7 \sim 10 \ \Omega/\Box$) was prepared by the filtration method.^{S2} In short, 1 mL of the SWNT dispersion in D₂O was filtered with 0.05 µm mixed cellulose ester (MCE) filter ($\phi = 25$ mm). The remaining SWNT film was washed with a copious amount of deionized water to remove SDBS. Then, the film on the filter was first cut to suitable size (typically 7 × 14 mm) together with the attached filter paper and then put and

clamped for a while on the ITO electrode, which was washed by sonication in 2-propanol and cleaned in an O_3 atmosphere in advance. Finally, the filter was dissolved by immersing the whole assembly in acetone bath for 1 day, affording the blackish, semi-transparent film of SWNTs on ITO. Atomic force microscopy (AFM) observation revealed a film thickness of ca. 200 nm.

Reference

S1. N. V. Tkachenko, L. Rantala, A. Y. Tauber, J. Helaja, P. H. Hynninen and H. Lemmetyinen, *J. Am. Chem. Soc.*, 1999, **121**, 9378.

S2. Z. Wu, Z. Chen, X. Du, J. M. Logan, J. Sippel, M. Nikolou, K. Kamaras, J. R. Reynolds, D. B. Tanner, A. F. Hebard and A. G. Rinzler, *Science*, 2004, **305**, 1273.



Fig. S1 XRD patterns of (a) p-SWNT, (b) C_{60} @SWNT, and (c) C_{70} @SWNT.



Fig. S2 Resonance Raman spectra of (a) p-SWNT, (b) C_{60} @SWNT, and (c) C_{70} @SWNT measured with an excitation of 2.33 eV (531.95 nm). Inset in panel (a) shows contracted view of whole spectrum for p-SWNT, whereas that in (b) shows enlarged view of 1400 – 1550 cm⁻¹ region for C_{60} @SWNT. Peaks marked with asterisk are assigned as signals from the encapsulated C_{60} (in (b)) or C_{70} (in (c)).



Fig. S3 TEM images of (a) C_{70} @SWNT and (b) p-SWNT.



Fig. S4 Diameter distributions for the isolated bundles of (a) C_{60} @SWNT-P3HT, (b) C_{70} @SWNT-P3HT, and (c) p-SWNT-P3HT hybrids obtained by AFM observations.



Fig. S5 Representative absorption spectra of (a) C_{60} @SWNT–P3HT in chlorobenzene and (b) C_{60} @SWNT in D₂O dispersed with SDBS. The absorption spectra are normalized to A = 1 at 1500 nm for comparison.



Fig. S6 TGA curves of (a) p-SWNT–P3HT hybrid, (b) p-SWNT, and (c) P3HT obtained under a flowing air at a scan rate of $10 \,^{\circ}\text{C min}^{-1}$.



Fig. S7 Fluorescence emission spectra of (a) C_{70} @SWNT-P3HT and (b) P3HT in chlorobenzene. Excitation wavelength (λ_{ex}) was set at the peak position of P3HT-derived absorption, i.e., 586 nm for C_{70} @SWNT-P3HT and 457 nm for P3HT. Absorbance of the P3HT moiety of C_{70} @SWNT-P3HT was adjusted to be identical (~ 0.1) to that of P3HT at the respective peak positions.



Fig. S8 Fluorescence decay of p-SWNT–P3HT hybrid in chlorobenzene. The sample solution was excited at 400 nm and emission at 690 nm was monitored. Solid line shows the result of bi-exponential fit of the data, from which two time constants (0.75 ps (54%) and > 100 ps (46%)) are reasonably derived. The slow decay component (> 100 ps) probably originates from the emission of trace amount of unbound P3HT, which could not be detected by UV–vis absorption spectroscopy.



Fig. S9 Transient absorption decay component spectra of C_{70} @SWNT–P3HT in chlorobenzene obtained with global two-component fit of the data. The sample was excited at 600 nm. The fitted time constants are displayed in the figure. Dotted line shows recalculated time-resolved spectrum at 0 delay. Inset displays time traces of transient signals at 580 (circle) and 700 nm (square). Solid lines represent the results of bi-exponential fitting.

Fig. S10 Photocurrent action spectra of (a) $ITO/C_{60}@SWNT$ (solid line), (b) $ITO/C_{70}@SWNT$ (dotted line), and (c) ITO/p-SWNT (dashed line) electrodes. Applied potential: -0.05 V vs. SCE. Electrolyte: 0.5 M LiI and 0.01 M I₂ in acetonitrile. Inset shows absorption spectrum of $ITO/C_{60}@SWNT$ electrode.