

Electronic Supplementary Information

Diameter Dependent Electron Transfer in Supramolecular Nanohybrids of (6,5)- or (7,6)- Enriched Semiconducting SWNT as Donors and Fullerene as Acceptor

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Experimental Section

Chemicals. The (6,5) and (7,6) enriched SWNTs were produced by CoMoCAT[®], SouthWest Nano Technologies, Inc., (Norman, OK) marketed by Aldrich Chemicals (Milwaukee, WI). The bulk solvents utilized in the syntheses were from Fischer Chemicals, while all of the chemicals used in the synthesis of pyrene appended fullerene were from Aldrich Chemicals.

Synthesis of Pyrene Functionalized Fullerene

(4-Formyl)-phenyl-4-pyrenylbutanoate, (1): 1-Pyrene butyric acid (590 mg, 2.05 mmol) and 4-hydroxy benzaldehyde (750 mg, 6.00 mmol) were dissolved in 150 mL of dry CH₂Cl₂. Then 1,3-dicyclohexycarbodiimide (600 mg, 2.25 mmol) and 4-(dimethylamino)pyridine (32 mg, 0.524 mmol) were added, and the reaction mixture was stirred for 18 hrs. Then, the solvent was evaporated under the reduced pressure, and the crude compound was purified on silica gel column using hexane:CH₂Cl₂ (94:6 v/v) as eluent. Yield: 170 mg (20 %). ¹H NMR (400 MHz, CDCl₃) (in ppm) : δ 9.99 (s, 1 H, -CHO), 8.33-7.83 (m, 13H, pyrene *H* and phenyl *H*), 3.50 (t, 2 H, -CH₂-), 2.75 (t, 2H, -CH₂-), 2.33 (m, 2H, -CH₂-), Mass (APCI mode in CH₂Cl₂): calcd, 392.45; found 393.80.

2-(Phenoxy pyrenebutyl)-5-methylphenyl-3,4-fulleropyrrolidine (2): The title compound was synthesized according to Prato et al.¹ A solution of C₆₀ (100 mg, 0.138 mmol), phenylalanine (46 mg, 0.277 mmol), and pyrene appended aldehyde (1) (164 mg, 0.416 mmol) in toluene (100 mL) was refluxed for 6 h. The crude product was purified by column chromatography (silica gel, hexane/toluene 40:60) to give the product (23.0 mg, 13.6%). ¹H NMR (300 MHz, CDCl₃): 8.31-7.08 (m, 18H, pyrene *H* and phenyl *H*), 5.68 (s, 1H, -CH- fulleropyrrolidine ring), 5.00 (dd, 1H, -CH-), 4.08 (dd, 1H, -CH-), 3.50 (s, 1H, -CH- fulleropyrrolidine ring) 3.45 (t, 2 H, -CH₂-), 2.91 (broad s, 1H, -NH-) 2.65 (t, 2H, -CH₂-), 2.33 (m, 2H, -CH₂-), Mass (APCI mode in CH₂Cl₂): calcd, 1221.27; found 1222.85

Preparation of SWNT(6,5)/pyrC₆₀, and SWNT(7,6)/pyrC₆₀ nanohybrids

A 1.0 mg sample of SWNT [(6,5) or (7,6) chirality] was added to 2.00 mg of pyrC₆₀ dissolved in 15 mL of dry DMF and the reaction mixture was stirred for 48 hrs at room temperature. The resulting mixture was sonicated (Fisher Scientific, 60 Hz, 40 W) for 6 hrs at

20°C followed by centrifugation (Fisher Scientific, 50/60 CY) for 2 hrs. The excess of C₆₀ pyrene was removed by separating the centrifugate (speed of 3300 rpm giving a RCF force of 1380g) from the black precipitate. Further purification is carried out by dissolving the black mixture in 5 mL of fresh DMF, sonicating for 30 min at 20 °C, followed by centrifugation for 1 hr, and removal of unadsorbed C₆₀ pyrene by separating from the black centrifugate. This process was repeated (at least twice) until the solution in the centrifuge tube turned colorless. At the end, 10 mL of fresh solvent was added to the resulting deposit and was sonicated for 15 min at 20 °C. This homogenous black dispersion was used for mentioned studies.

Instrumentation. The UV-visible-NIR spectral measurements were carried out with a Perkin-Elmer (Lambda 750) or Jasco V-670 spectrophotometers. The steady-state fluorescence emission was monitored by using a Perkin-Elmer (LS-55) or a Horiba Jobin Yvon Nanolog UV-vis-NIR spectrofluorometer equipped with PMT (for UV-vis) and InGaAs (for NIR) detectors. The ¹H NMR studies were carried out either on a Varian 400 MHz spectrometer. Tetramethylsilane (TMS) was used as an internal standard. All the solutions were purged prior to spectral measurements using nitrogen gas.

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-7650 transmission electron microscope an accelerating voltage of 120 kV for imaging. A TEM equipped with EDX (H-2300; Hitachi) was operated at 120 kV, and the elemental map was obtained by using a scanning spot size of 0.5 nm and a scanning rate of 0.5 nm/ms.

Raman spectroscopy measurements were performed using a Tokyo Instruments Nanofinder 30) with three different laser excitations, namely, λ =441.6 nm (HeCd), 532.0 nm (Nd:YAG), and 632.8 nm (HeNe) and the laser spot size was about 2 mm in diameter.

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

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.

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 I₂ in acetonitrile. In the case of IPCE measurement, a monochromator (SM-25, Bunkoh-Keiki Co.,LTD) was introduced into the path of the excitation beam (300 W Xenon lamp, Bunkoh-Keiki Co.,LTD) for the selected wavelength. The lamp intensity at each wavelength was determined by Si photodiode (Hamamatsu Photonics S1337-1010BQ) and corrected.

References

1. M. Maggini, G. Scorrano, M. Prato, *J. Am. Chem. Soc.* **1993**, 115, 9798

Estimation of ratio of C₆₀pyr to SWCNT

- 1) MW of C₆₀pyr $\approx$ 1000, mole of 2 mg of C₆₀pyr $\approx$ 0.002/1000 $\approx$ 2 x 10⁻⁶ M.
- 2) MW of SWCNT(ϕ 1nm x 800 nm) $\approx$ 150000, mole of 1.5 mg of SWCNT $\approx$ 0.0015/150000 $\approx$ 1 x 10⁻⁸ M.
- 3) C₆₀pyr/ SWCNT $\approx$ 200 molecules per one SWCNT.
- 4) Size of C₆₀pyr $\approx$ 1 nm/ 800 nm SWCNT, 200 nm/800nm = 1/4 (each C₆₀pyr every 4 nm).
- 5) Feed; Wt% of SWCNT in solution = 1.5 mg/1.5 mL x d_{DMF} = 0.098 Wt% $\approx$ 0.1 Wt%.
- 6) Feed; Wt% of C₆₀pyr vs. total weight (=SWCNT+ C₆₀pyr) = 2/3.5=57%.

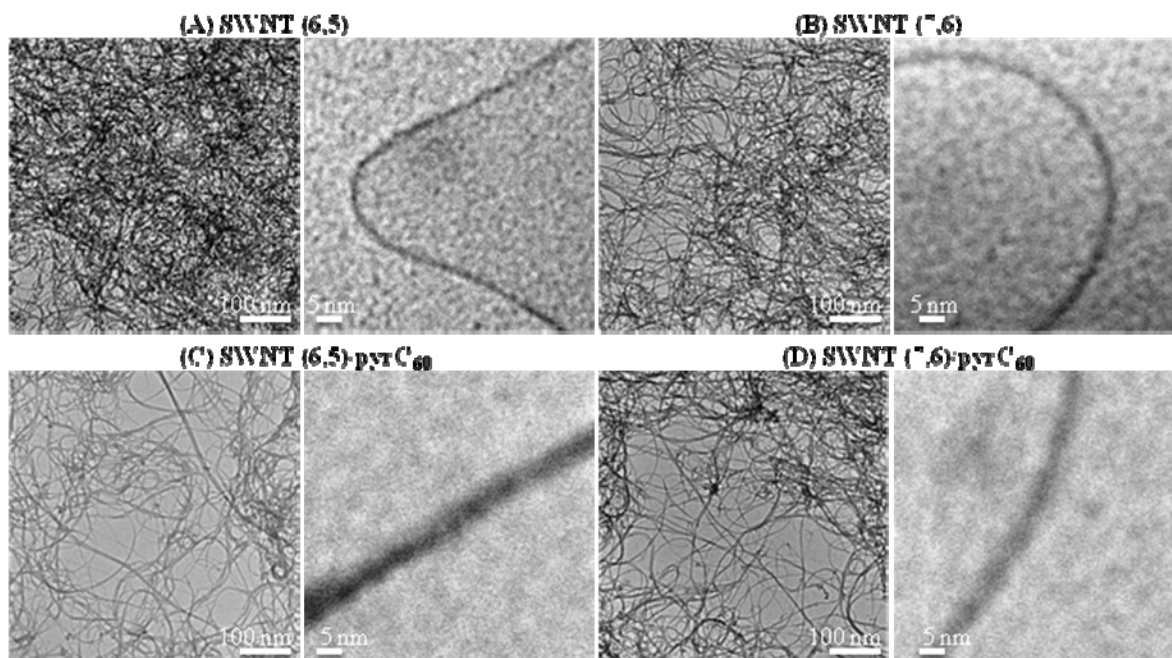


Fig. S1. TEM images of (A) SWNT (6,5), (B) SWNT (7,6), (C) SWNT(6,5)/pyrC₆₀, and (D) SWNT(7,6)/pyrC₆₀ nanohybrids. Every 5 nm, one bulge is recognized.

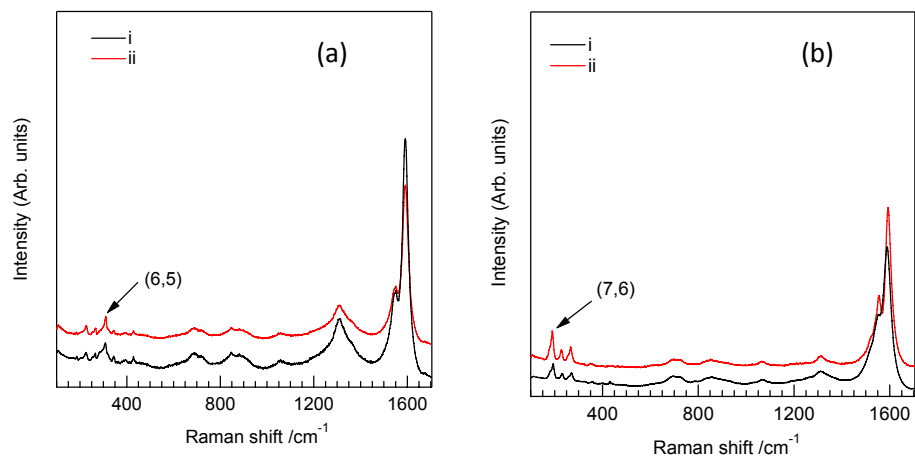


Fig. S2. Raman spectra of (a) (i) SWNT(6,5)/pyC₆₀, and (ii) SWNT(6, 5), and (b) (i) SWNT(7,6)/pyC₆₀, and (ii) SWNT(7, 6) at the laser excitation wavelength of 632.8 nm.

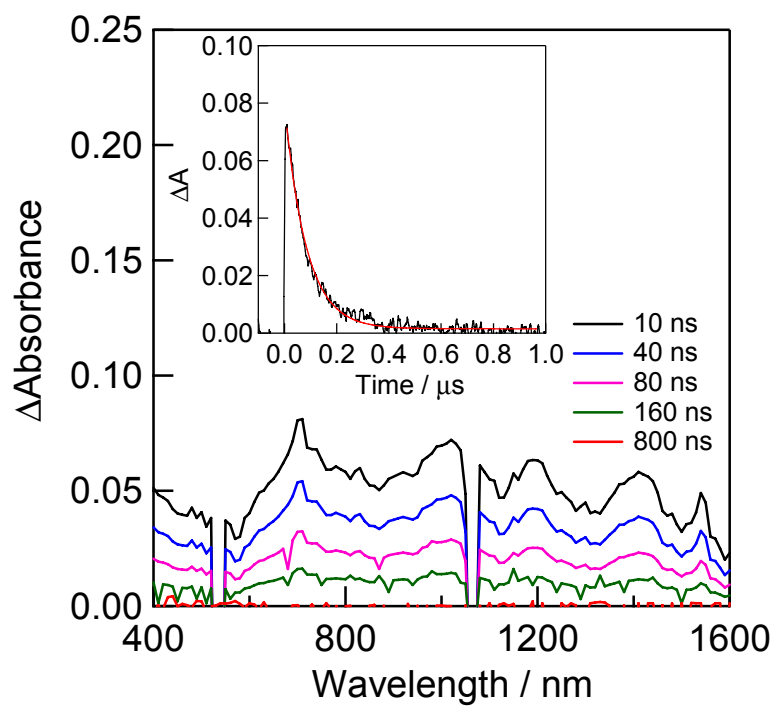


Fig. S3. Nanosecond transient absorption spectra of SWNT(6,5)/pyrC₆₀ hybrids in DMF. λ_{ex} = 532 nm (ca. 3 mJ/pulse).

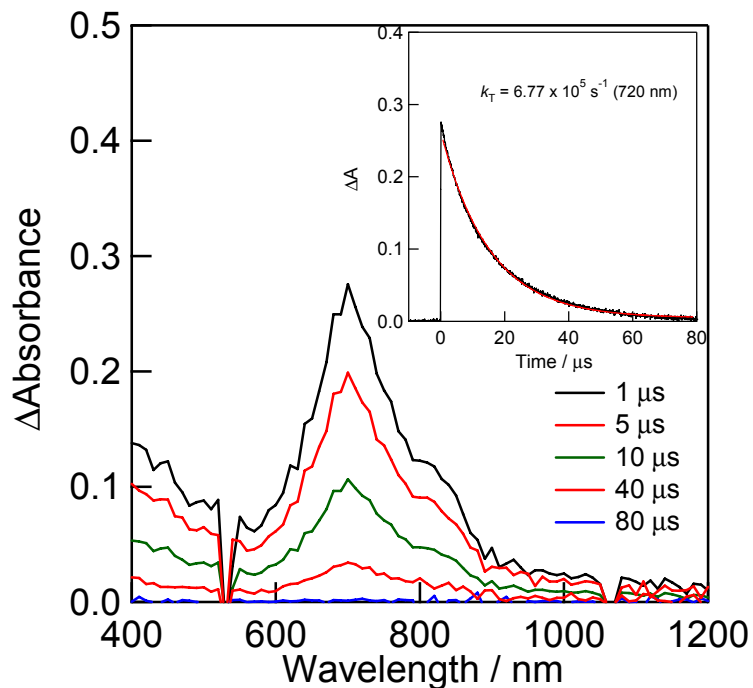


Fig. S4. Nanosecond transient absorption spectra of C₆₀pyr observed by 532 nm (ca. 3 mJ/pulse) laser irradiation in Ar-saturated DMF. Inset: Absorption-time profile.

Note: No transient absorption bands in nanosecond time-region from pristine SWNT(*n,m*) in DMF (by 532 nm (ca. 3 mJ/pulse) laser irradiation) are observed.

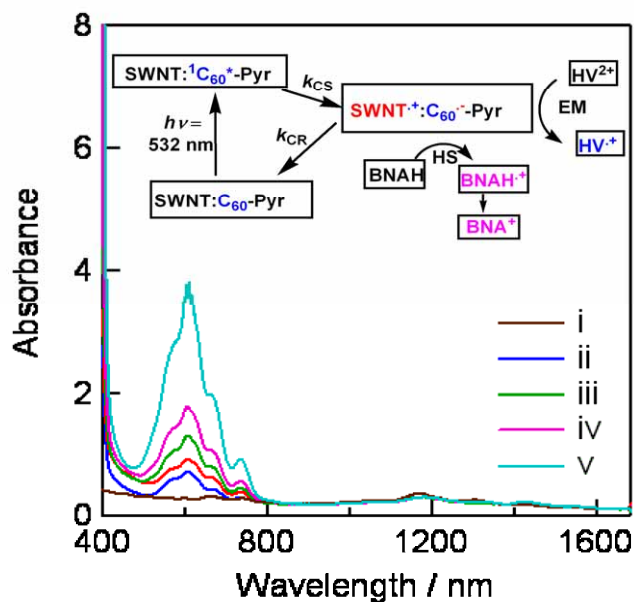


Fig. S5. Steady-state absorption spectra of SWNT(6,5)/pyC₆₀ in Ar-saturated DMF solution measured after 5 laser-shots with laser light (6-ns pulse width) at 532-nm in the presence of HV²⁺ (0.5 mM) and BNAH (i) 0, (ii) 0.5, (iii) 1.0, (iv) 1.5, (v) 2.0 (vi) 2.5 (vii) 3.0 (viii) 3.5 and (ix) 4.0 mM.

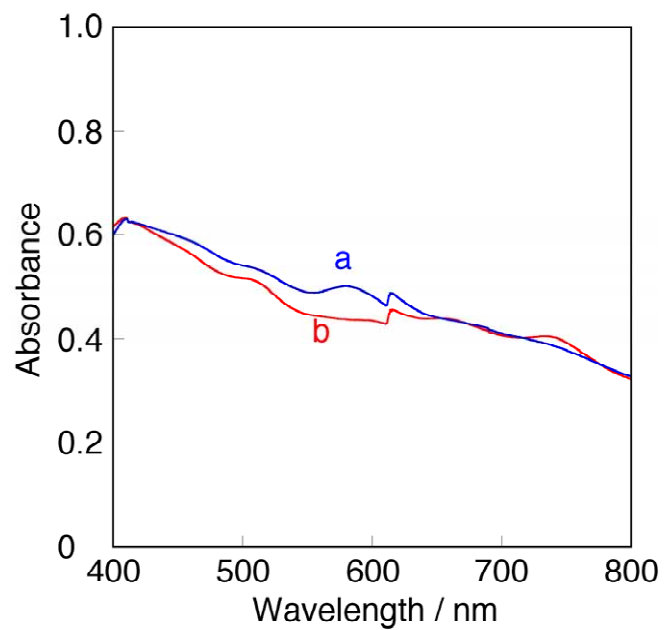


Fig. S6. Steady-state absorption spectra of (a) OTE/SnO₂/C₆₀pyr/SWNT(6,5) and (b) OTE/SnO₂/C₆₀pyr/ SWNT(7,6).