Supplementary Material (ESI) for Chemical Communications

Supplementary Information for

Dispersion of Carbon Nanotubes by Photo- and Thermal-Responsive Polymers Containing Azobenzene Unit in the Backbone

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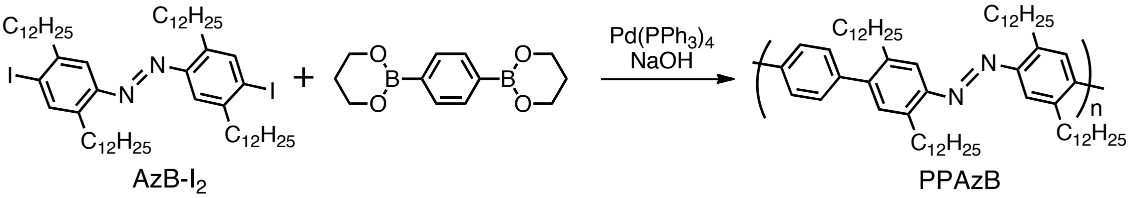
Experimental Details

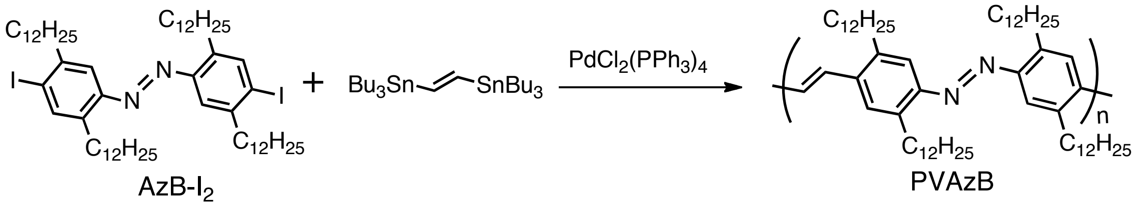
Instruments. UV-vis-NIR absorption spectra were measured on a Perkin-Elmer Lambda 900 UV/VIS/NIR spectrometer. ^{1}H NMR spectra were obtained with a JEOL JNM-EX400 NMR spectrometer. IR spectra were recorded on a JASCO FT/IR-470 Plus spectrometer, using KBr pellets. Gel permeation chromatography (GPC) measurements were carried out on a SHIMADZU Prominence equipped with JAIGEL-2.5HAF column, using chloroform as an eluent after calibration with standard polystyrene. Atomic force microscopy (AFM) images were obtained from MFP-3D-SA (Asylum Technology) in the AC mode. TEM analysis was carried out on a JEOL JEM-2200FS. For sample preparation, a THF solution of the polymer-SWNT composite was dropped on microgrids and evaporated. Contour plots of NIR photoluminescence spectra were recorded by SHIMADZU NIR-PL System.

Materials. SWNTs (Purified HiPco SWNTs) were purchased from Carbon Nanotechnologies, Inc., and used as-received. Other solvents and chemicals were of reagent grade quality, purchased commercially and used without further purification unless otherwise noted. 4,4’-Diiodo-2,2’,5,5’-tetradodecylazobenzene (AzB-I_2) and 1,4-bis(1,3,2-dioxaborinan-2-yl)benzene were prepared according to the literature.[S1]

Synthesis of Azobenzene Polymers



PPAzB. A solution of dehydrated *N,N*-dimethylacetamide (0.87 mL) containing AzB-I_2 (88.5 mg, 0.08 mmol), 1,4-bis(1,3,2-dioxaborinan-2-yl)benzene (19.7 mg, 0.08 mmol), $Pd(PPh_3)_4$ (2.5 mg, 2.2 μmol), NaOH (11.2 mg, 0.28 mmol), water (0.14 mL), and a stirring bar in a Schlenk flask charged with argon was stirred at 110 °C for 48 h. Then, the reaction mixture was poured into 300 mL of methanol. The precipitated solids were filtrated and washed with water/methanol (1:1), methanol and *n*-hexane. The resulting precipitate was dissolved in 80 mL chloroform and filtered. Addition of methanol (20 mL) to the filtrate with vigorous stirring and filtration yielded PPAzB as orange powder, which was dried under vacuum (11.2 mg, 0.01 mmol, 15%). The number-average molecular weight (M_n) of the polymer obtained was estimated to be 15000 with a polydispersity index (PDI) of 1.7 by GPC analysis. IR (KBr): ν_{max}/cm^{-1} 2957, 2921, 2851, 1605, 1561, 1515, 1467, 1376, 1261, 1170, 1097, 1021, 906, 854, 803, 721, 505. ^{1}H NMR: δ_H(400 MHz; $CDCl_3$; Me_4Si) 7.64 (2H, =N-Ar'*H*), 7.45 (2H, =N-Ar'*H*), 7.30 (4H, -Ar*H*), 3.20 (4H, =N-Ar'*CH_2*), 2.70 (4H, =N-Ar'*CH_2*), 1.90−1.11(64H, -CH_2-), 0.88 (12H, -CH_3).



PVAzB. A solution of dehydrated *N,N*-dimethylformamide (1 mL) containing AzB-I_2 (90.0 mg, 0.08 mmol), *trans*-bis(tributylstannyl)ethylene (70.0 mg, 0.12 mmol), $PdCl_2(PPh_3)_2$ (27.0 mg, 0.04 mmol), and a stirring bar in a 10 mL round-bottom flask charged with argon was stirred at 110 °C for 48 h. The reaction mixture was poured into 300 mL of methanol. The precipitate was filtered and washed with methanol and *n*-hexane to give PVAzB as red powder, which was dried under vacuum (58.2 mg, 0.07 mmol, 83%). M_n of the polymer obtained was estimated to be 18000 with PDI of 2.6 by GPC analysis. IR (KBr): ν_{max}/cm^{-1} 3018, 2954, 2921, 2851, 1601, 1557, 1467, 1374, 1342, 1247, 1170, 1101, 962, 903, 721. ^{1}H NMR: δ_H(400 MHz; $CDCl_3$; Me_4Si) 7.60 (2H, =N-Ar'*H*), 7.54 (2H, =N-Ar'*H*), 7.38 (2H, -CH=CH-) 3.20 (4H, =N-Ar'*CH_2*), 2.83 (4H, =N-Ar'*CH_2*), 1.90−1.11(64H, -CH_2-), 0.88 (12H, -CH_3).

Isomerization of Azobenzene Polymers in THF (1 g L^{-1}). A THF solution of PPAzB (1 g L^{-1}) in a vial was placed at a distance of 5 cm from a 250 W ultra-high-pressure mercury lamp equipped with a power source (USH-250D, USHIO) and irradiated to cause *trans*-to-*cis* isomerization. The appropriate UV light irradiation wavelengths were selected with UV-35 (Toshiba) and UTVAF-50S-33U (Sigma Koki) filters for irradiation at 350 nm < λ < 400 nm. UV-vis absorption spectra were measured after a dilution by 50-fold with THF. The ratios of *trans* : *cis* were estimated from the peak absorbance for π–π^* transition bands of *trans*-azobenzene units around 380 nm, assuming that the absorption of *cis*-azobenzene is negligible at the wavelength.[S1] Since all azobenzene units exist as the stable *trans* form at the initial stage, the decrease of absorbance at 380 nm corresponds to that of the *trans* form and the concomitant increase of the *cis* form.[S1] Similarly, PVAzB in THF were irradiated by UV light, and the absorption spectra were recorded. Moreover, *cis*-PPAzB-39% in THF was heated at 70 °C or irradiated by visible light at room temperature, to cause *cis*-to-*trans* isomerization. The visible light irradiation wavelengths were selected with Y-47 (Toshiba) for irradiation at > 470 nm. All the absorption spectra are depicted in Fig. S1.

Photo-isomerization of PPAzB in THF (0.02 g L^{-1}). A THF solution of PPAzB (0.02 g L^{-1}) in a vial was irradiated by UV light to cause *trans*-to-*cis* isomerization. Subsequently, photoirradiation by visible light was conducted to cause *cis*-to-*trans* isomerization. Changes in the absorption spectra are depicted in Fig. S2. The photo-isomerization reached a plateau within 25 sec, which was much faster than that in the concentrated solution (1 g L^{-1}) in Fig. S1.

Thermal-isomerization of PPAzB in the Film State. *cis*-PPAzB-39% prepared by UV-light irradiation in THF (1 g L^{-1}) was cast on a glass plate and the film was heated at 200 °C to cause *cis*-to-*trans* isomerization. The absorption spectra before and after the heating are depicted in Fig. S3.

Preparation and Photoirradiation of SWNT–*cis*-PPAzB-9% Dispersion in THF without Excess, Unbound Polymer. The dispersion of SWNT prepared with *cis*-PPAzB-9% (1 g L^{-1}) in THF was filtered through a membrane filter (pore size = 100 nm), and washed by THF to remove the unbound *cis*-PPAzB-9% from the SWNT-based film. The resulting SWNT–*cis*-PPAzB-9% without excess, unbound polymer on the filter was redispersed in THF with the aid of bath sonication. The visible light was irradiated to the dispersion and the UV-vis-NIR absorption spectra were recorded (Fig. S13).

Preparation of Composite Film of SWNTs with *cis*-PPAzB-9% and Thermal- and Photo-Isomerization and Removal of the Polymer. The dispersion of

SWNT–*cis*-PPAzB-9% in THF was filtered through a membrane filter (pore size = 100 nm), and washed thoroughly by THF to remove the unbound *cis*-PPAzB-9% from the SWNT-based film. The resulting material on the filter was redispersed in THF with the aid of bath sonication, and the suspension was cast on a glass plate for the absorption measurement as well as on an electrode for the resistivity measurement. Then, the composite film was heated at 200 °C for 15 min or irradiated by visible light for 20 min to cause *cis*-to-*trans* isomerization, and rinsed with THF repeatedly after cooling to room temperature.

Measurements of Resistivities by Four-Point Probe Techniques. The composite film of SWNT–*cis*-PPAzB-9% was formed on an inter-digit electrode prepared by photolithography method. To ensure conductivity of these electrodes, a thin chrome layer of about 20 nm was firstly sputtered onto silicon (Si) wafer. An ultra-thin gold film of ca. 15 nm was then sputtered. The current source is Keithley 6487 picoammeter. The voltage was monitored with a Keithley 6517A electrometer.

Structure Optimizations. Structure optimizations for *cis*-PPAzB-10% and *cis*-PPAzB-20% were performed with Universal force field implemented within the FORCITE module of the Materials Studio Modeling Software 4.4. As the models of *cis*-PPAzB-10% and *cis*-PPAzB-20%, docosamer with two (at the 7th and 14th units) and four (at the 5th, 10th, 15th, and 20th units) *cis* isomers were employed.

Reference

S1. A. Izumi, M. Teraguchi, R. Nomura and T. Masuda, *Macromolecules*, 2000, **33**, 5347.

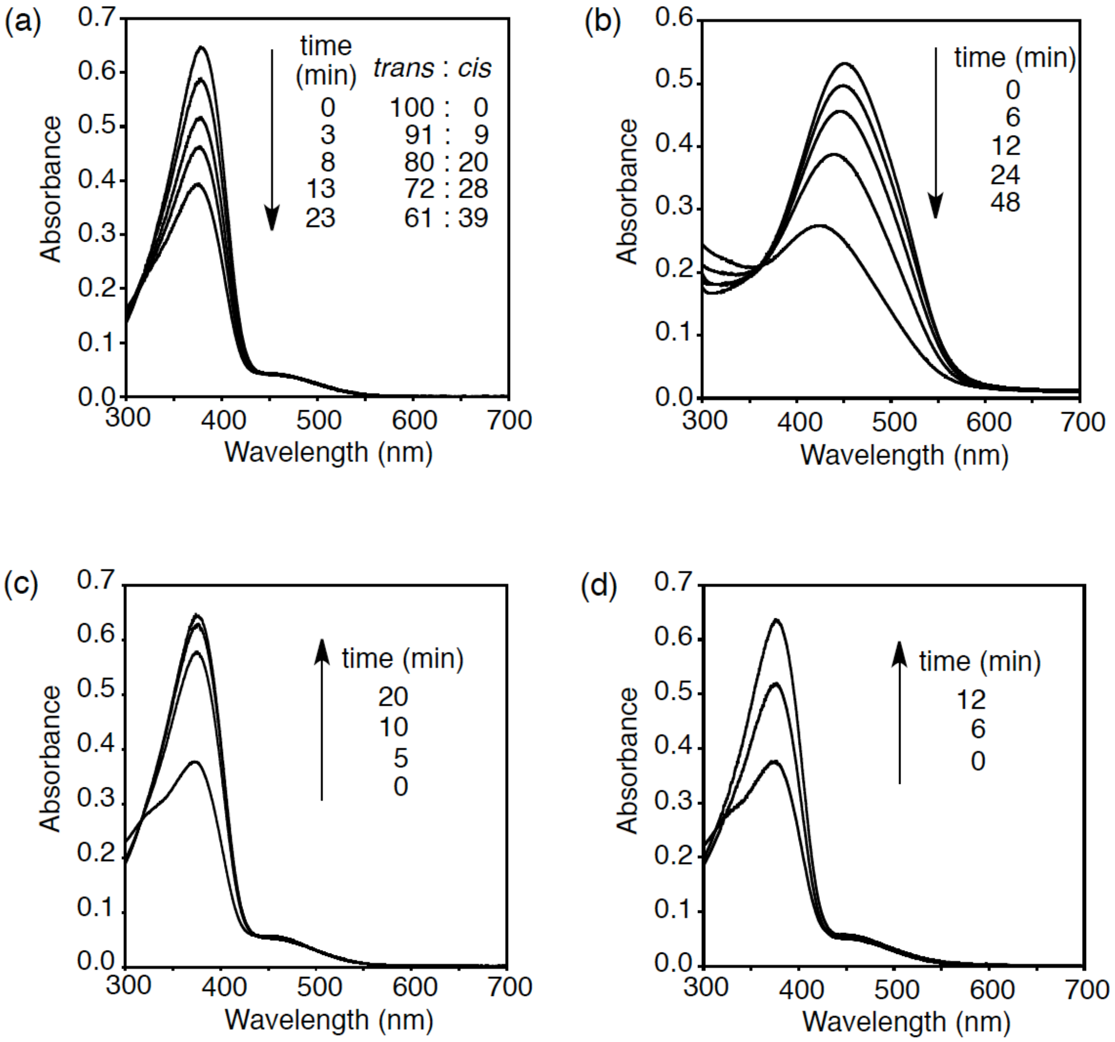


Fig. S1 Change in the UV-vis absorption spectra of (a) PPAzB and (b) PVAzB in THF (1 g L^{-1}) as a function of irradiation time ($350 < \lambda < 400$ nm). Subsequent change in the UV-vis absorption spectra of PPAzB as a function of (c) irradiation time of visible light ($\lambda > 470$ nm) and (d) heating time at 70 °C in THF. The ratios of *trans* : *cis* are listed in (a).

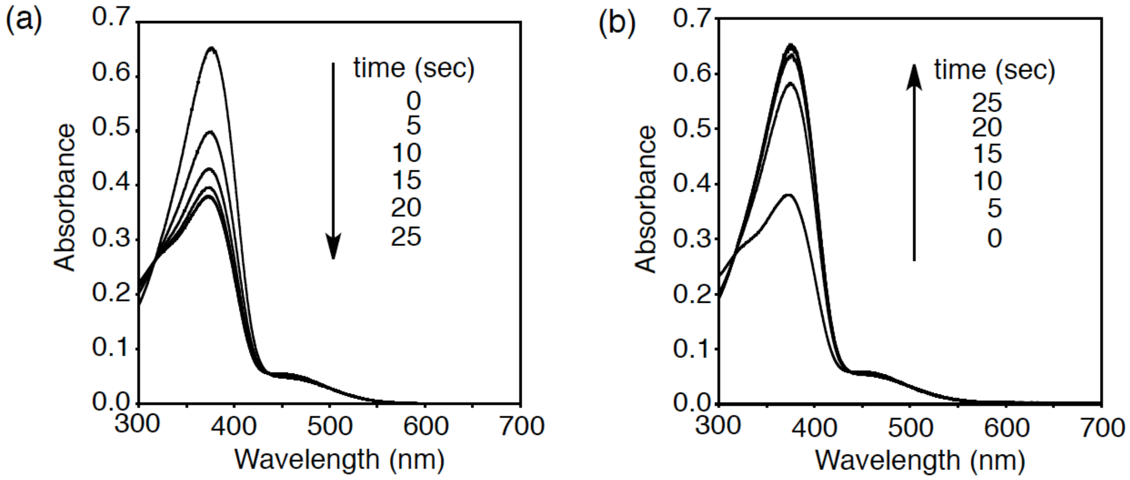


Fig. S2 (a) Change in the UV-vis absorption spectra of PPAzB in THF (0.02 g L^{-1}) as a function of irradiation time of UV light ($350 < \lambda < 400$ nm). (b) Subsequent change in the UV-vis absorption spectra of PPAzB as a function of irradiation time of visible light ($\lambda > 470$ nm).

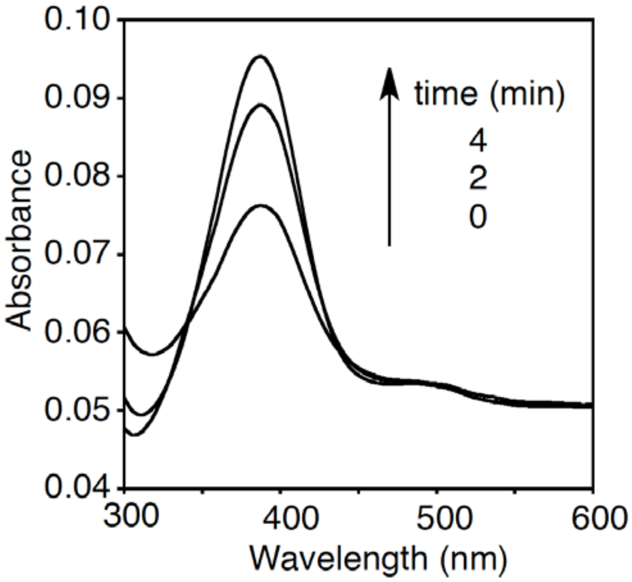


Fig. S3 Change in the UV-vis absorption spectra of PPAzB film (*cis*-PPAzB-39%), prepared by casting the THF solution of PPAzB (1 g L^{-1}) after UV light irradiation for 23 min, as a function of heating time at 200 °C on a glass plate.

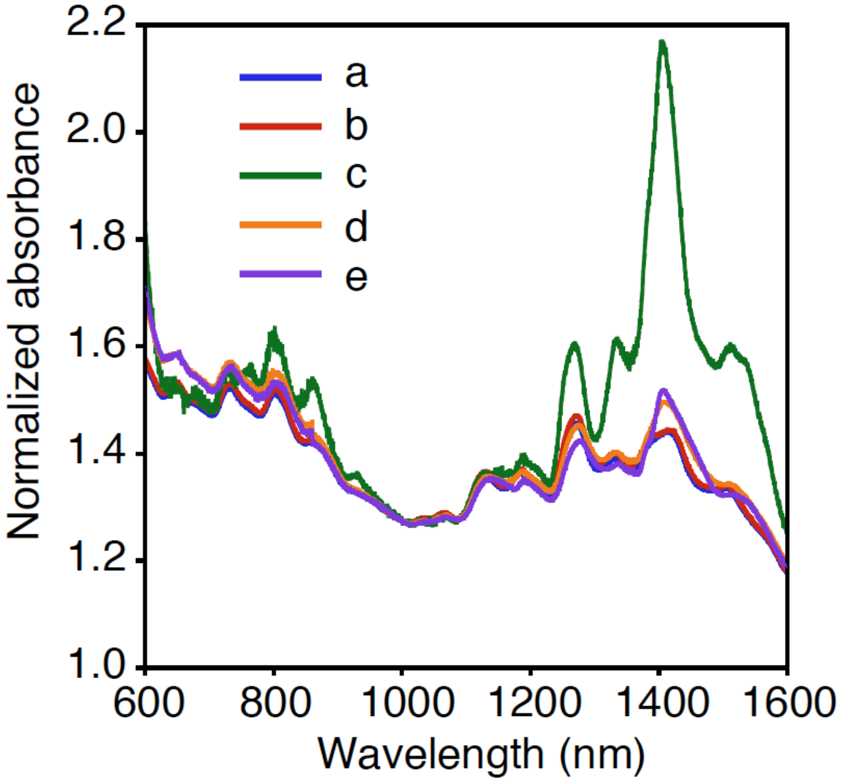


Fig. S4 Vis-NIR absorption spectra of SWNTs dispersed by PPAzB with *cis* contents of (a) 0, (b) 9, (c) 20, (d) 28, and (e) 39 % in THF. The spectra were normalized to the absorbance of (b) at 1000 nm for comparison.

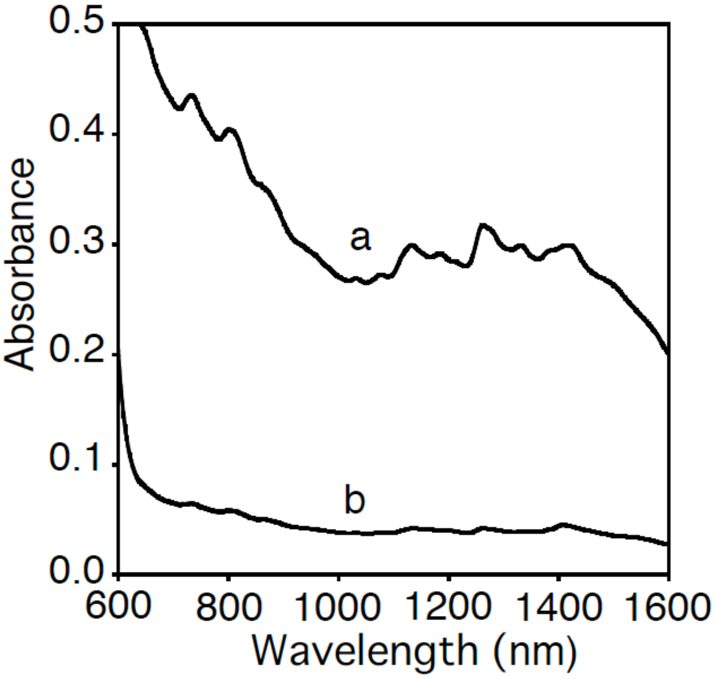


Fig. S5 Vis-NIR absorption spectra of SWNTs dispersed in THF by PVAzB (a) before and (b) after the photoirradiation for 48 min.

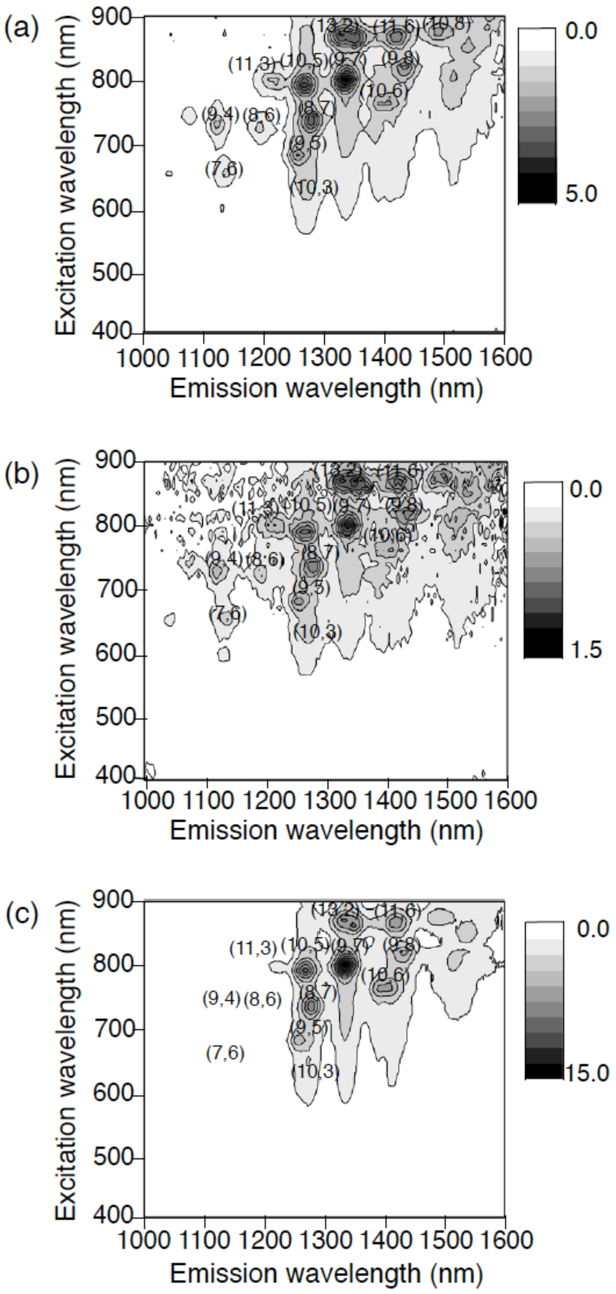


Fig. S6 Contour plots of photoluminescence spectra with the assignment of chiral indices for SWNTs dispersed by PPAzB with *cis* contents of (a) 0, (b) 9 and (c) 20% in THF. The gray scale represents the relative intensity of emission.

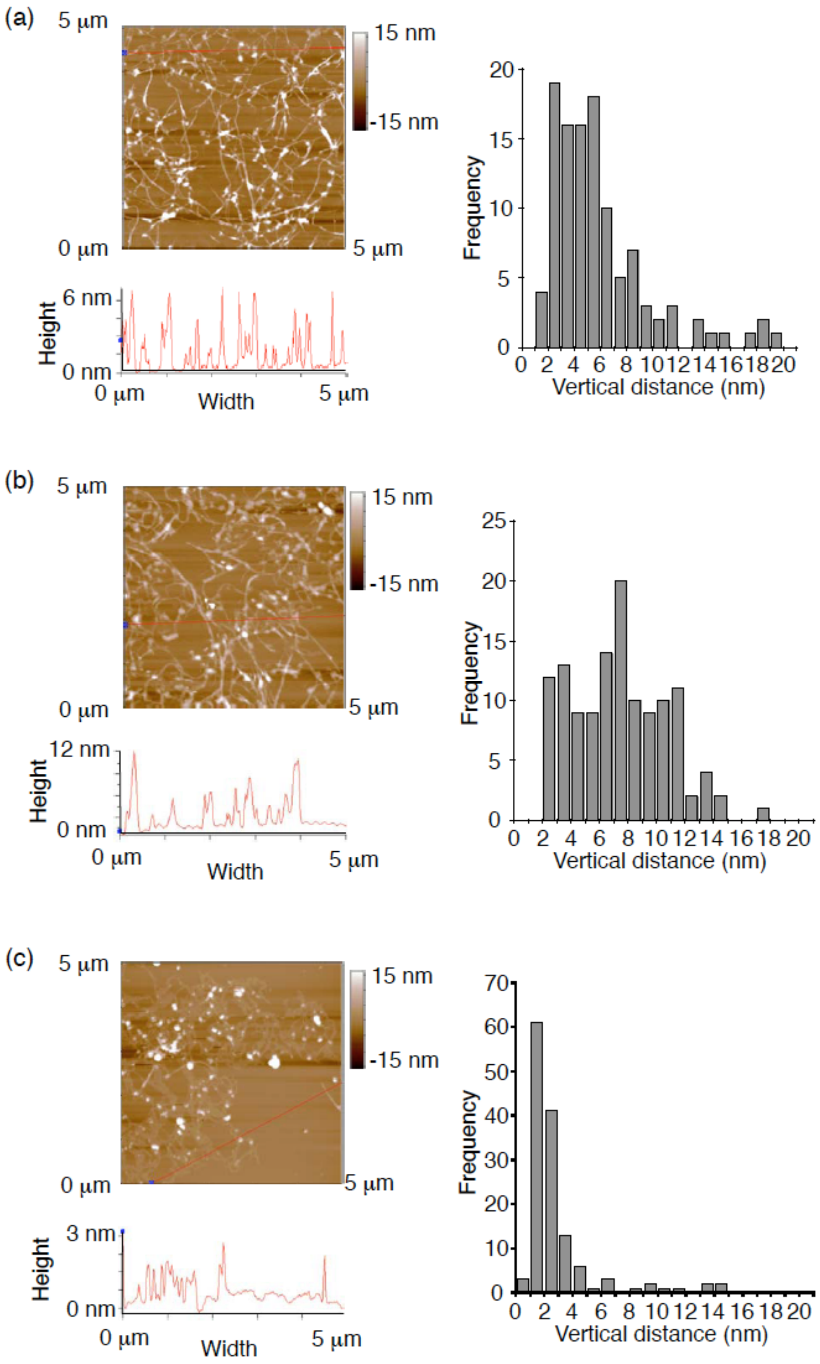


Fig. S7 AFM images of (a) SWNT–PPAzB, (b) SWNT–*cis*-PPAzB-9%, and (c) SWNT–*cis*-PPAzB-20% on mica. The cross section profiles and diameter distribution are also shown. The color scale represents the height topography, with bright and dark representing the highest and lowest features, respectively.

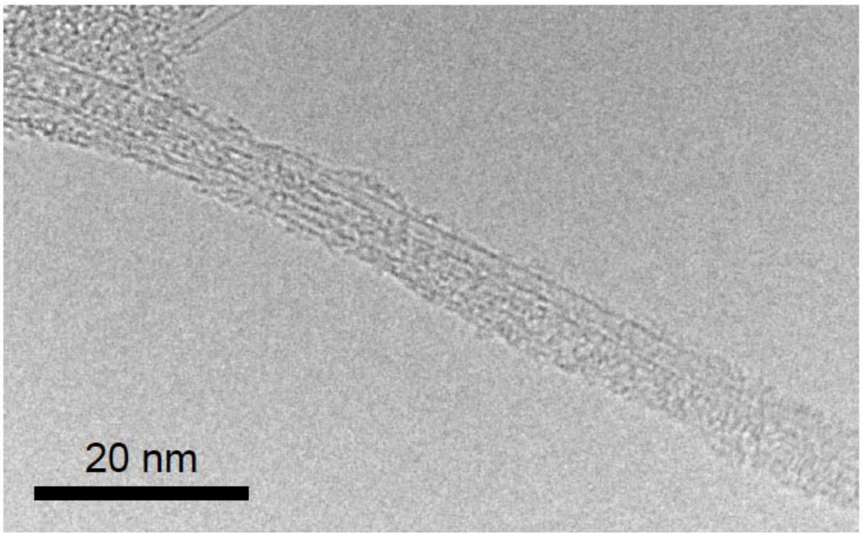


Fig. S8 TEM image of SWNT–*cis*-PPAzB-9%.

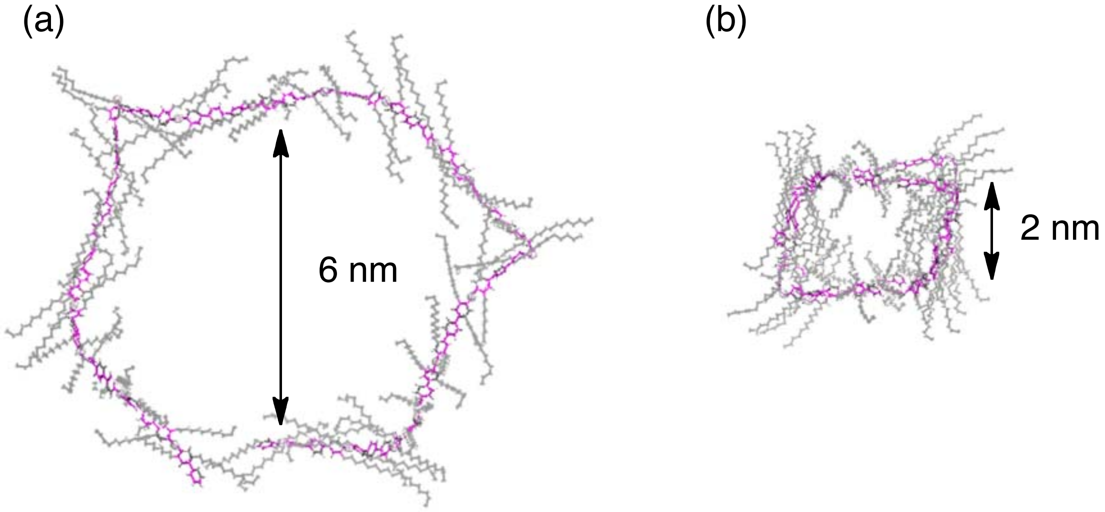


Fig. S9 Optimized structures of (a) *cis*-PPAzB-10% and (b) *cis*-PPAzB-20% models.

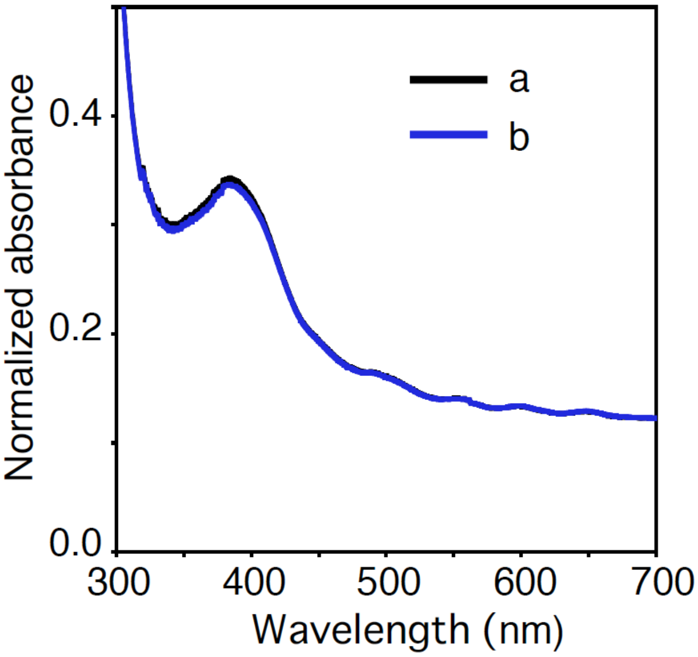


Fig. S10 UV-vis absorption spectra of the SWNT–*cis*-PPAzB-9% film on a glass plate (a) before and (b) after the visible light irradiation and washing with THF. The absorbance of (b) was normalized at 600 nm for comparison.

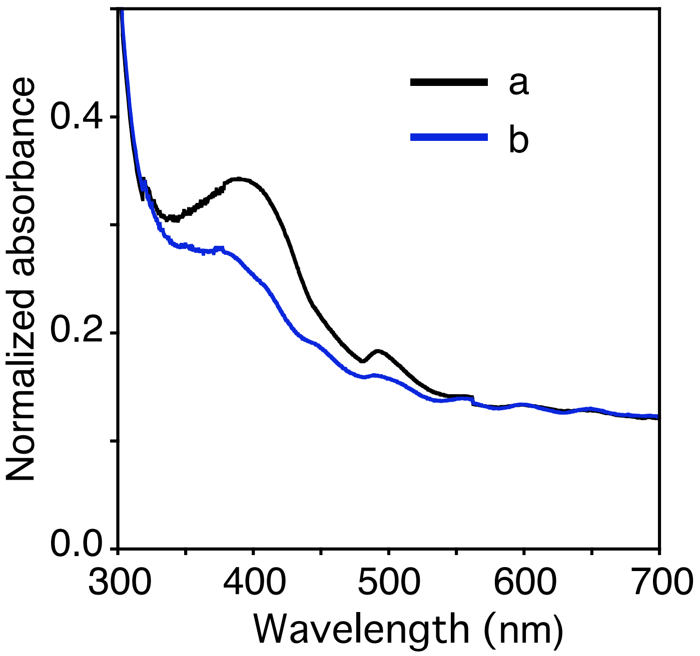


Fig. S11 UV-vis absorption spectra of the SWNT–*cis*-PPAzB-9% film on a glass plate (a) before and (b) after the thermal-isomerization and removal of the wrapping polymer. The absorbance of (b) was normalized at 600 nm for comparison.

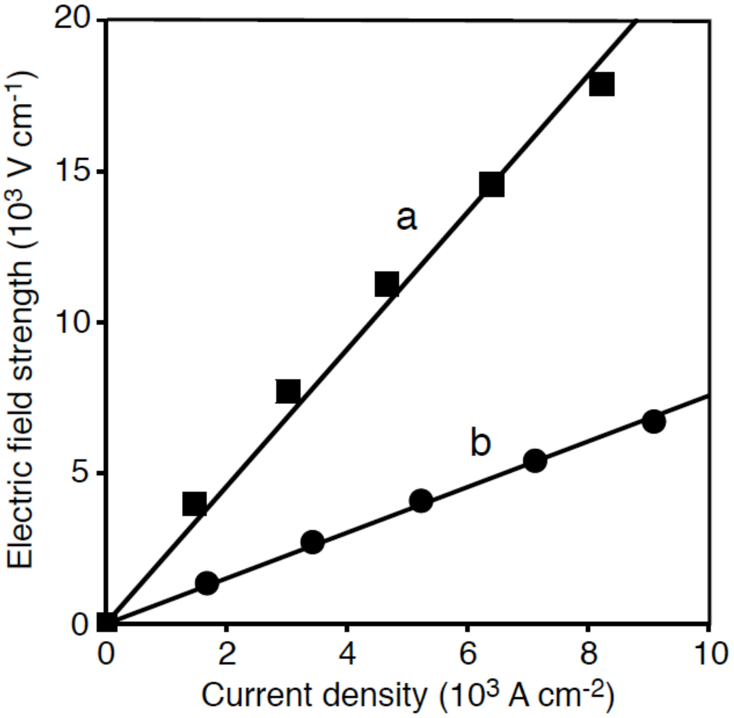


Fig. S12 Current density vs. electric field characteristic of SWNT-*cis*-PPAzB-9% film (a) before and (b) after the thermal-isomerization and removal of the wrapping polymer.

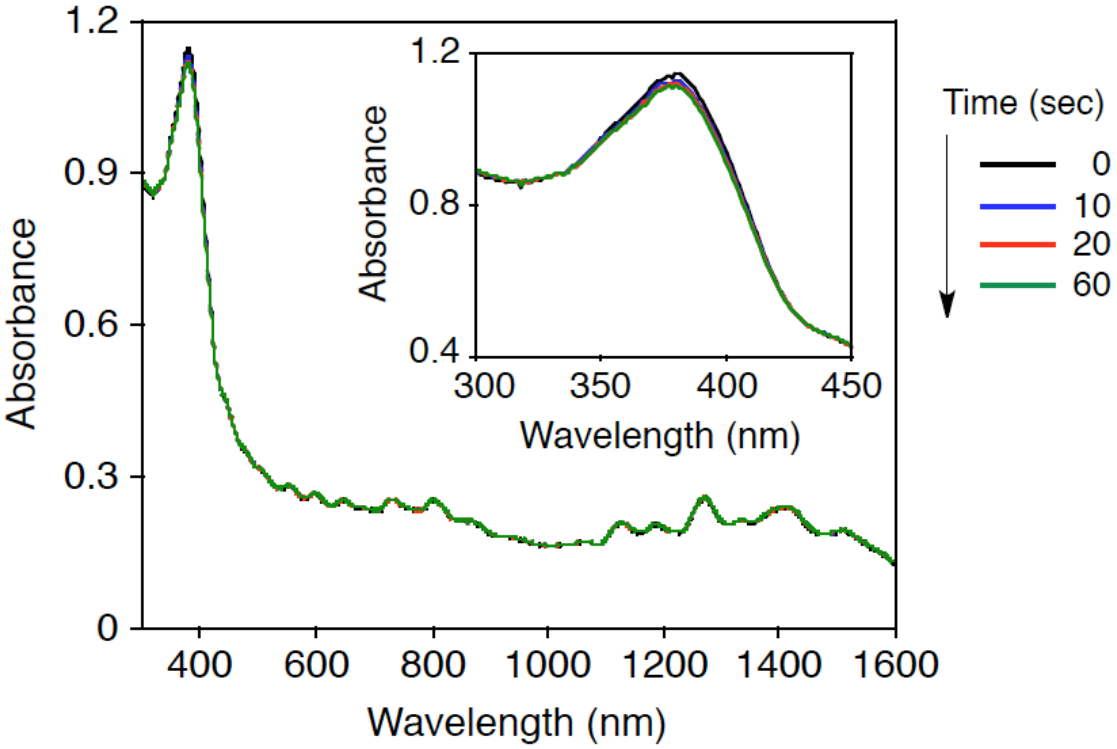


Fig. S13 Change in the UV-vis-NIR absorption spectra of SWNT–*cis*-PPAzB-9% in THF without excess, unbound polymer as a function of irradiation time of visible light ($\lambda > 470$ nm).