SUPPORTING INFORMATION

Decoration of Polyfluorene-Wrapped Carbon Nanotubes via Strain-Promoted Azide-Alkyne Cycloaddition

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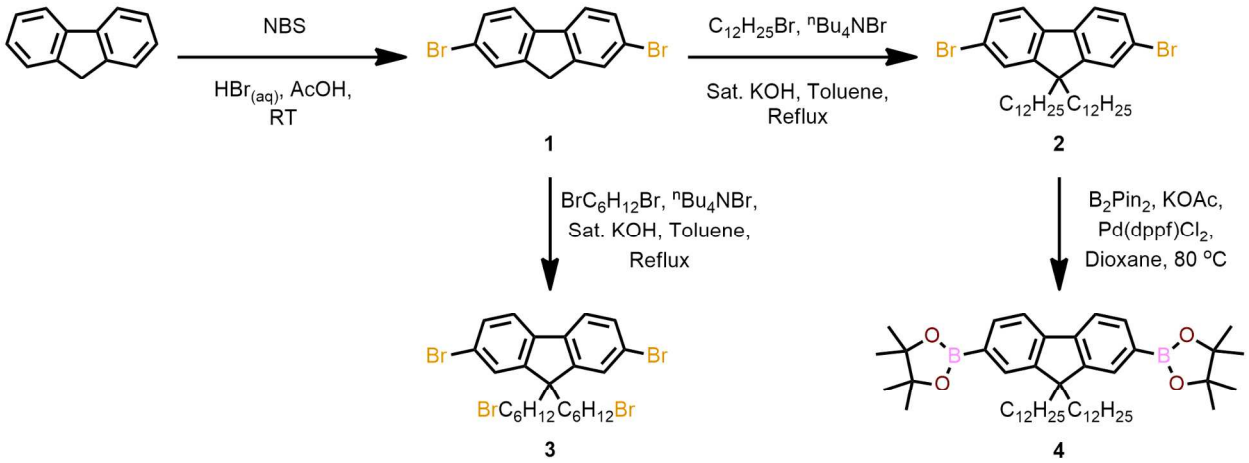
Experimental

General

Semi-purified plasma torch SWNTs (RN120, batch #RNB735-120-X464) were purchased from Raymor Industries Inc. and used without further purification. Raw HiPCO SWNTs were purchased from NanoIntegris (batch #HR27-104, 10 wt % in anhydrous EtOH) and also used without further purification. Reagents were purchased from commercial suppliers and used as received. Monomethyl ether $mPEG_{5000}$ was purchased from Fluka. Flash chromatography was performed using an IntelliFlash 280 system from Analogix. Unless otherwise noted, compounds were monitored using a variable wavelength detector at 254 nm. Solvent amounts used for gradient or isocratic elution were reported in column volumes (CV). Columns were prepared in Biotage® SNAP KP-Sil cartridges using 40 – 63 μm silica or 25 – 40 μm silica purchased from Silicycle. NMR was performed on a Bruker Avance 600 MHz or 700 MHz instrument and shift-referenced to the residual solvent resonance. Polymer molecular weights and dispersities were analyzed (relative to polystyrene standards) via GPC using a Waters 2695 Separations Module equipped with a Waters 2414 refractive index detector and a Jordi Fluorinated DVB mixed bed column in series with a Jordi Fluorinated DVB 10^5 Å pore size column. THF with 2% acetonitrile was used as the eluent at a flow rate of 2.0 mL/min. Sonication was performed in a Branson Ultrasonic B2800 bath sonicator. Centrifugation of the polymer-SWNT samples was performed using a Sorvall Legend X1R centrifuge (semi-purified plasma torch SWNT dispersions) or a Beckman Coulter Allegra X-22 centrifuge (raw HiPCO SWNT dispersions). Infrared spectra were recorded using a Thermo Scientific Nicolet 6700 FT-IR spectrometer equipped with a Smart iTX attenuated total reflectance (ATR) sample analyzer. UV-Vis-NIR spectra were recorded on a Cary 5000 spectrometer in dual beam mode, using matching 10 mm quartz cuvettes. Fluorescence spectra were measured on a Jobin-Yvon SPEX Fluorolog 3.22 equipped with a 450 W Xe arc lamp, digital photon counting photomultiplier, and an InGaAs detector, also using a 10 mm quartz cuvette. Slit widths for both

excitation and emission were set to 10 nm band-pass, and correction factor files were applied to account for instrument variations. Photoluminescence maps were obtained at 25 °C, with 5 nm intervals for both the excitation and emission. Raman spectra were collected using a Renishaw InVia Laser Raman spectrometer, with three different lasers: a 25 mW argon ion laser (514 nm, 1800 L/mm grating); a 500 mW HeNe Renishaw laser (633 nm, 1800 L/mm grating); and a 300 mW Renishaw laser (785 nm, 1200 L/mm grating). Laser intensity was set to 0.5% for the 785 nm excitation wavelength and 5% for the 514 nm and 633 nm excitations for the polymer-SWNT samples. For the SWNT sample dispersed in $CHCl_3$, laser intensity was set to 1% for 514 nm and 633 nm, and 10% for 785 nm.



Scheme S1. Synthesis of monomers **3** and **4**.

Synthetic Procedures

2,7-dibromofluorene (1) (adapted from reference 1)

A round bottom flask equipped with a stir bar was charged with fluorene (33.2 g, 200 mmol), NBS (89.0 g, 500 mmol) and acetic acid (400 mL). While the mixture was stirring, conc. HBr (10 mL) was slowly added and then the reaction mixture was stirred at RT for 1.5 h. Water (200 mL) was added and the resulting suspension was filtered and washed with water to obtain an orange-white solid. The solid was recrystallized from a 1.5:1 v/v mixture of EtOH:acetone (~1.8 L total volume), and the mother

liquor was recrystallized again from the same solvent mixture (~1.5 L total volume). The crops were combined to afford **1** (41.2 g, 64%) as a white solid. ^{1}H-NMR (600 MHz; $CDCl_3$): δ 7.67 (d, *J* = 1.1 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.51 (dd, *J* = 8.1, 1.8 Hz, 2H), 3.88 (s, 2H).

2,7-dibromo-9,9-didodecylfluorene (2) (adapted from reference 1)

A round bottom flask equipped with a stir bar was charged with **1** (5 g, 15.4 mmol), 1-bromododecane (7.88 g, 31.6 mmol), toluene (31 mL), and sat. KOH (31 mL). $^nBu_4NBr$ (1.0 g, 3.1 mmol) was then added and the reaction mixture was heated to 60 °C and stirred vigorously for 1 h under a nitrogen atmosphere. The biphasic mixture was allowed to separate, and the organic layer was isolated. The aqueous phase was extracted twice with diethyl ether (2 x 120 mL) and the organic extracts were combined and concentrated *in vacuo* to obtain a viscous green oil. The crude mixture was purified by flash chromatography (100 g column, 100% hexanes) to afford **2** as a white solid (9.34 g, 92%). ^{1}H-NMR (600 MHz; $CDCl_3$): δ 7.51 (d, *J* = 8.0 Hz, 1H), 7.45-7.43 (m, 2H), 1.92-1.89 (m, 2H), 1.29-1.04 (m, 18H), 0.87 (t, 3H), 0.59-0.56 (m, 2H).

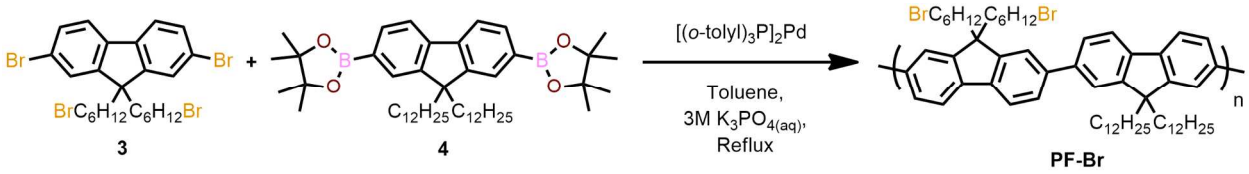
2,7-dibromo-9,9-bis(6-bromohexyl)fluorene (3) (adapted from reference 1)

A round bottom flask equipped with a stir bar was charged with **1** (5 g, 15.4 mmol), 1,6-dibromohexane (37.7 g, 154 mmol), toluene (31 mL), and sat. KOH (31 mL). $^nBu_4NBr$ (1.0 g, 3.1 mmol) was then added and the reaction mixture was heated to 60 °C and stirred vigorously for 1 h under a nitrogen atmosphere. The biphasic mixture was allowed to separate, and the organic layer was isolated. The aqueous phase was extracted twice with diethyl ether (2 x 120 mL) and the organic extracts were combined and concentrated *in vacuo* to obtain a viscous green oil. Excess 1,6-dibromohexane was removed using vacuum distillation (1 mbar, 115 °C) to obtain a viscous yellow oil. The crude mixture was purified by flash chromatography (100 g column, 0 to 20% CH_2Cl_2 in hexanes over 10 CV) to obtain a white solid containing two spots by TLC. The crude product was recrystallized from MeOH (~250 mL) to afford **3** as a white solid (4.4 g, 44%). ^{1}H-NMR (600 MHz; $CDCl_3$): δ 7.53-

7.52 (m, 1H), 7.47-7.43 (m, 2H), 3.31-3.28 (t, 2H), 1.94-1.91 (m, 2H), 1.68-1.66 (m, 2H), 1.22-1.19 (m, 2H), 1.10-1.07 (m, 2H), 0.60-0.57 (m, 2H).

2,2'-(9,9-didodecylfluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**4**) (adapted from reference 1)

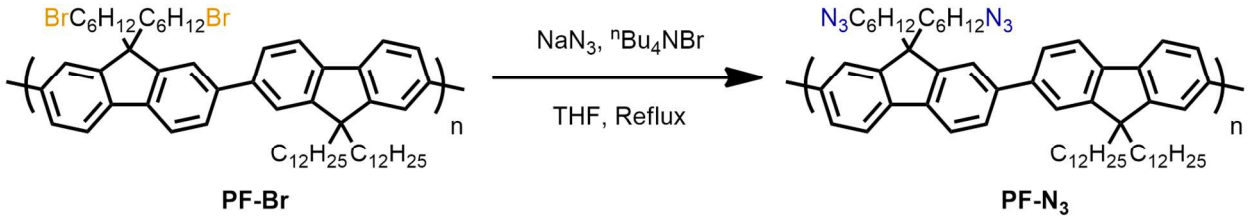
A round bottom flask equipped with a stir bar was charged with **2** (7.0 g, 10.6 mmol), B_2Pin_2 (5.92 g, 23.3 mmol), KOAc (3.12 g, 31.8 mmol), and dioxane (100 mL). $Pd(dppf)_2Cl_2$ (260 mg, 318 µmol) was added and the reaction mixture was stirred at 80 °C for 12 h. The reaction mixture was partitioned with water and extracted thrice with Et_2O. The organic extracts were combined and dry loaded onto silica (10 g). The crude mixture was purified by flash chromatography (100 g column, 0 to 80% CH_2Cl_2 in hexanes over 10 CV) to obtain a yellow solid. The solid was recrystallized from a 1.25:1 v/v mixture of MeOH:acetone (~450 mL total volume) to afford **4** as a white solid (4.88 g, 63%). ^{1}H-NMR (600 MHz; $CDCl_3$): δ 7.80 (d, J = 7.6 Hz, 1H), 7.74-7.71 (m, 2H), 2.00-1.97 (m, 2H), 1.39 (s, 12H), 1.26-0.99 (m, 18H), 0.86 (t, J = 7.1 Hz, 3H), 0.54 (m, 2H).



Poly(didodecylfluorene-*alt*-bis(bromohexyl)fluorene) (PF-Br)

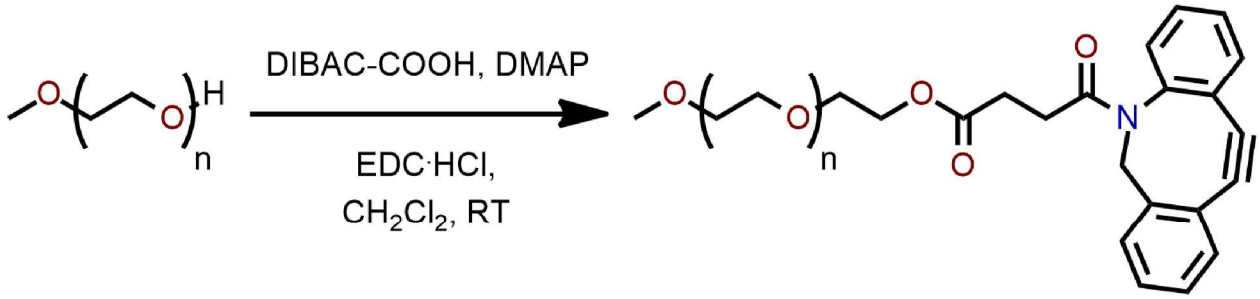
A Schlenk tube equipped with a stir bar was charged with **3** (646 mg, 0.99 mmol), **4** (750 mg, 0.99 mmol), toluene (7.1 mL), and 3M $K_3PO_{4(aq)}$ (7.1 mL). The biphasic mixture was degassed by three freeze-pump-thaw cycles, then, while frozen under liquid nitrogen, $[(o\text{-tol})_3P]_2Pd$ (36 mg, 50 µmol) was added under a positive pressure of nitrogen. The Schlenk tube was evacuated and backfilled with nitrogen four times, and the reaction mixture was vigorously stirred at 80 °C for 12 h. The phases were allowed to separate, and the organic layer was isolated and filtered through a single plug of celite and neutral alumina. The plug was thoroughly washed with THF and the flow-through was concentrated *in vacuo*. The crude polymer was precipitated into MeOH (~400 mL) and then filtered to afford **P1** as a

yellow solid (760 mg, 77%). ^{1}H-NMR (600 MHz; $CDCl_3$): δ 7.86-7.83 (m, 4H), 7.73-7.66 (m, 8H), 3.31-3.28 (m, 4H), 2.20-2.10 (m, 4H), 1.72-1.69 (m, 4H), 1.29-1.11 (m, 50H), 0.86 (t, J = 7.1 Hz, 12H).



Poly(didodecylfluorene-*alt*-bis(azidohexyl)fluorene) (PF-N_3)

A round bottom flask equipped with a stir bar and reflux condenser was charged with **PF-Br** (600 mg, 0.61 mmol), NaN_3 (394 mg, 6.1 mmol), $^nBu_4NBr$ (390 mg, 1.2 mmol), and THF (90 mL) and the reaction mixture was heated to reflux for 12 h. The reaction mixture was filtered through an alumina plug and washed thoroughly with THF, then the solution was concentrated *in vacuo* and precipitated into MeOH (~400 mL) to afford **PF-N_3** as a yellow solid (407 mg, 73%). ^{1}H-NMR (600 MHz; $CDCl_3$): δ 7.86-7.83 (m, 4H), 7.73-7.64 (m, 8H), 3.15-3.12 (m, 4H), 2.16-2.11 (m, 4H), 1.45-1.42 (m, 4H), 1.27-1.10 (m, 50H), 0.86 (t, J = 7.0 Hz, 12H).



mPEG$_{5000}$-DIBAC. A round bottom flask equipped with a stir bar was charged with mPEG$_{5000}$-OH (250 mg, 50 μmol), DIBAC-COOH (46 mg, 150 μmol) and 4-dimethylaminopyridine (3 mg, 25 μmol) and CH_2Cl_2 (1 mL). To the solution, *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (EDC·HCl) (33 mg, 175 μmol) was added, and the reaction mixture was stirred overnight at RT. The reaction mixture diluted with 5 mL of CH_2Cl_2 and then precipitated into 1:1 Et_2O:hexanes (~100 mL).

The precipitate was collected on a Hirsch funnel, then washed with ice cold ethanol (3 x 20 mL), Et_2O (3 x 20 mL), and dried *in vacuo* to afford **mPEG$_{5000}$-DIBAC** as a fine white powder (246 mg, 93%). ^{1}H NMR (600 MHz; DMSO-d6): δ 7.66 (dd, J = 7.6, 1.2, 1H), 7.62 (d, J = 7.3, 1H), 7.52-7.45 (m, 3H), 7.38 (td, J = 7.4, 1.5, 1H), 7.34 (td, J = 7.4, 1.3, 1H), 7.30 (dd, J = 7.5, 1.2, 1H), 5.03 (d, J = 14.2, 1H), 4.03-3.99 (m, 1H), 3.95-3.91 (m, 1H), 3.51 (s, 1H), 3.24 (s, 3H), 2.67-2.62 (m, 2H), 2.37-2.35 (m, 1H), 2.29 (dt, J = 17.1, 6.4, 1H), 1.81 (dt, J = 16.7, 6.3, 1H).

General SPAAC procedure. A glass vial was charged with 4 mL of polymer-SWNT dispersion and 2.05 equivalents of DIBAC derivative was added directly. Equivalents were calculated by determining the polymer concentration in solution (based on the SWNT dispersion protocol), calculating the mass of polymer present, and then using the molecular weight of the repeat unit to determine the number of moles of azide moiety (two per repeat unit). The glass vial was agitated until the DIBAC derivative was dissolved, and then the reaction progress was monitored by IR spectroscopy.

SPAAC with DIBAC-COOH. 4 mL of **PF-N$_3$**-SWNT dispersion, 1.4 mg of DIBAC-COOH.

SPAAC with mPEG$_{5000}$-DIBAC (plasma torch SWNTs). 4 mL of **PF-N$_3$**-SWNT plasma torch dispersion, 23.7 mg of mPEG$_{5000}$-DIBAC.

SPAAC with mPEG$_{5000}$-DIBAC (HiPCO SWNTs). 4 mL of **PF-N$_3$**-SWNT HiPCO dispersion, 35.5 mg of mPEG$_{5000}$-DIBAC.

HiPCO Dispersion with PF-N$_3$-mPEG$_{5000}$

PF-N$_3$ (3 mg) and mPEG$_{5000}$-DIBAC (35.5 mg) were dissolved in toluene (4 mL) and allowed to stand at RT overnight. HiPCO SWNTs (3 mg dry weight) were then added and the mixture was sonicated for 2 h in a bath sonicator chilled with ice. The suspension was centrifuged at 8,346 *g* for 30 min, and the supernatant was carefully removed and filtered through a cotton plug. The as-produced sample was

analyzed using UV-Vis-NIR spectroscopy, and was diluted 16-fold (200 µL of the as-produced dispersion was added to 3.0 mL of toluene) to obtain the spectrum shown in Figure S10.

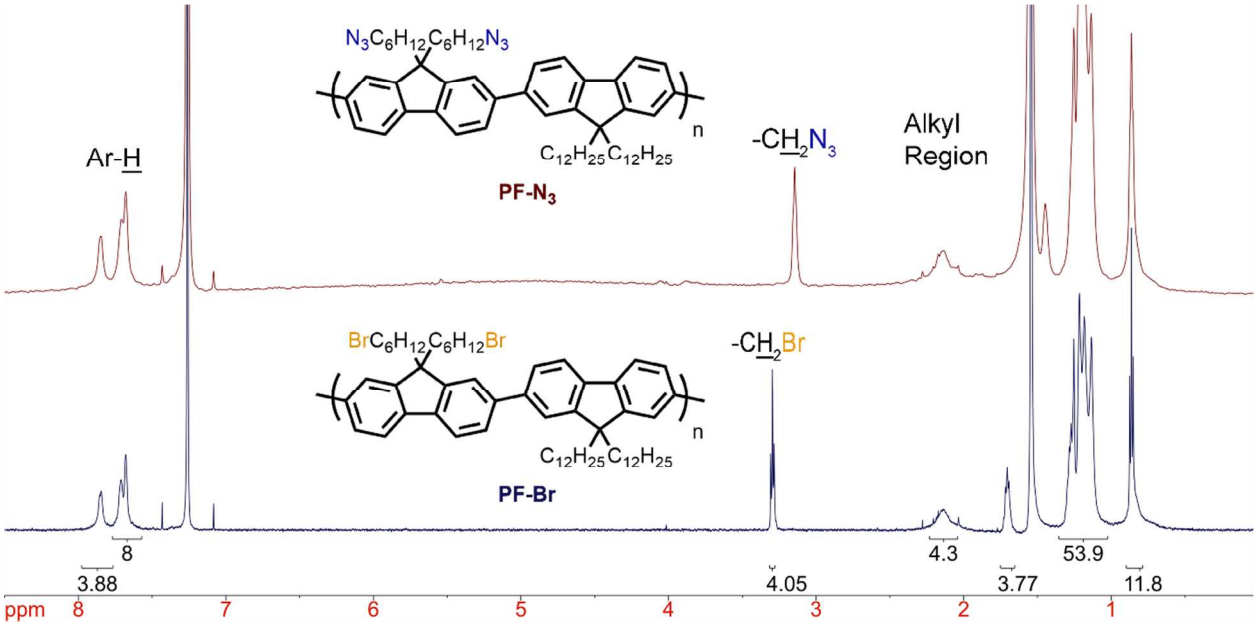


Figure S1. ^{1}H NMR overlay of (a) **PF-Br** (blue) and (b) **PF-N$_3$** (red).

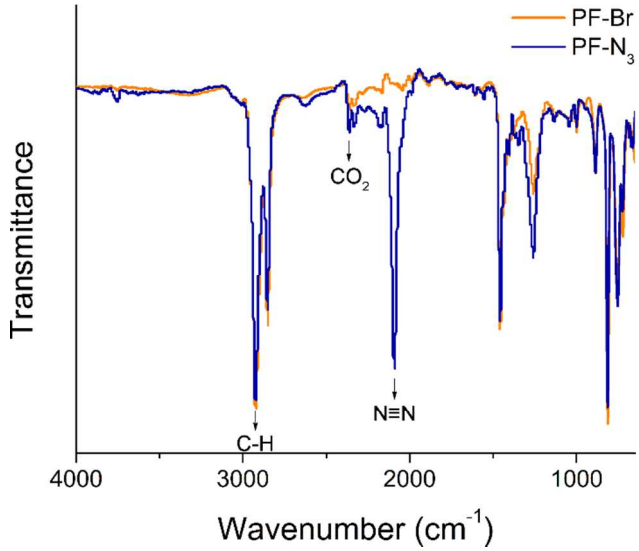


Figure S2. FT-IR overlay of (a) **PF-Br** (orange) and (b) **PF-N$_3$** (blue).

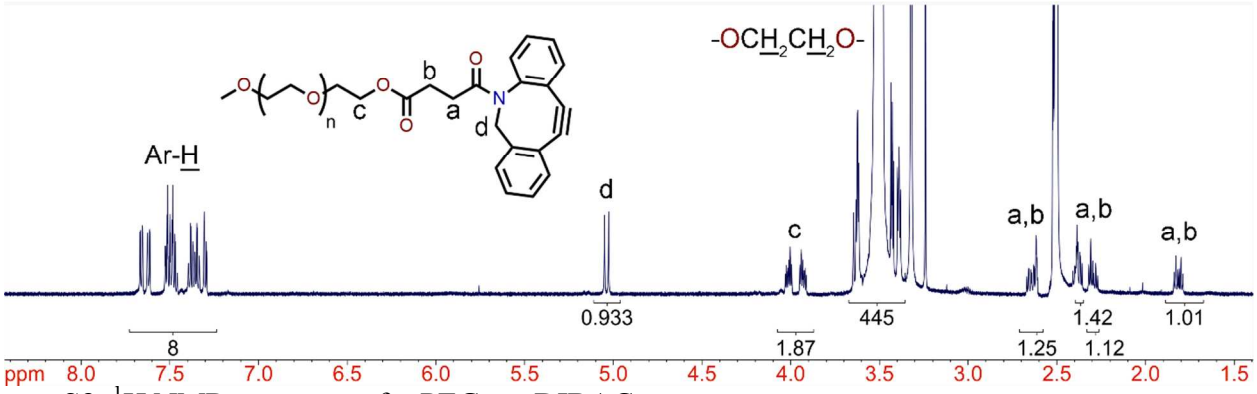


Figure S3. ^{1}H NMR spectrum of mPEG$_{5000}$-DIBAC.

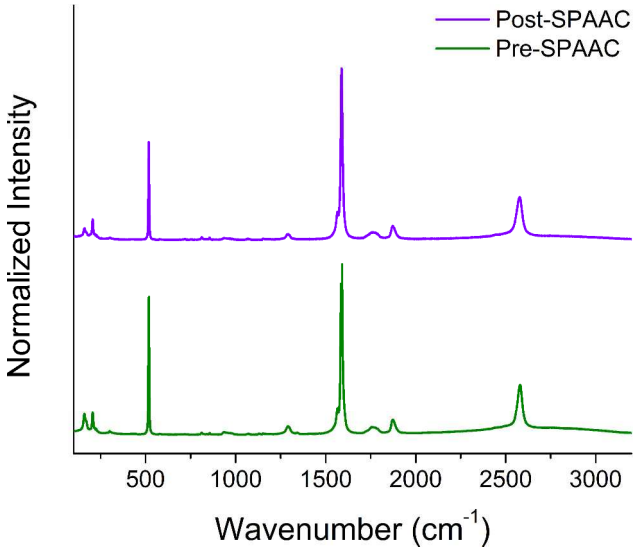


Figure S4. Raman spectra collected at 785 nm of **PF-N$_3$**-SWNT dispersions (a) pre- (green) and (b) post-SPAAC (purple) with DIBAC-COOH. Spectra were normalized to the G-band at ~1590 cm^{-1} and offset for clarity.

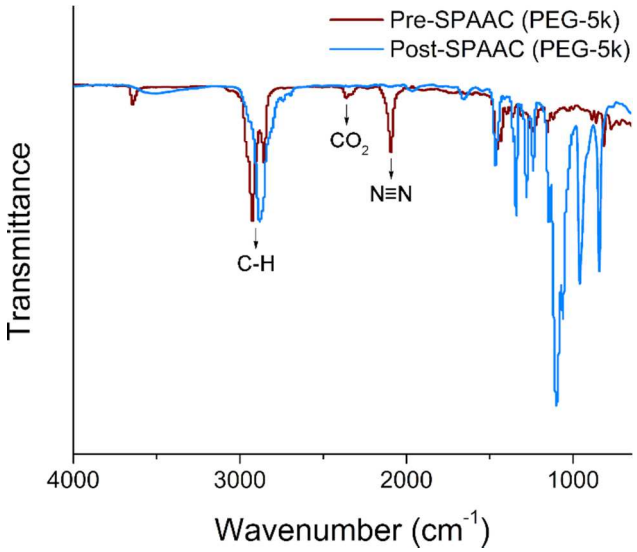


Figure S5. FT-IR overlay of the SPAAC reaction between **PF-N$_3$**-SWNT and mPEG$_{5000}$-DIBAC (a) pre- (dark red) and (b) post-SPAAC (light blue). The post-SPAAC spectrum was obtained after 30 min.

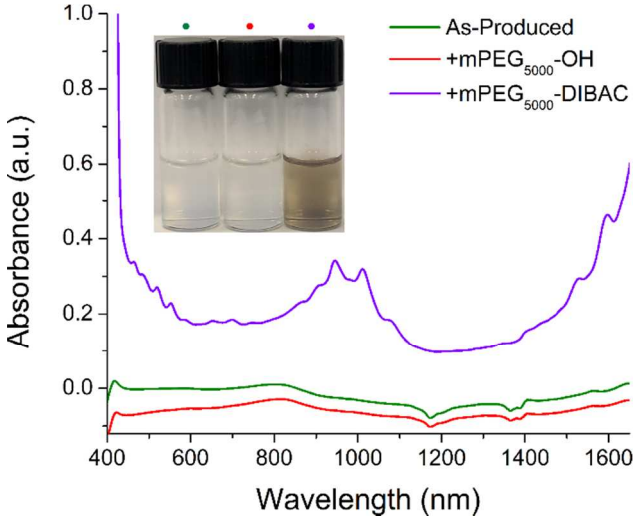


Figure S6. UV-Vis-NIR spectra of **PF-N$_3$**-SWNT dispersions in 50/50 THF:D_2O with (i) nothing, (ii) two equivalents of mPEG$_{5000}$-OH (containing no DIBAC), or (iii) two equivalents of mPEG$_{5000}$-DIBAC. Photographs of the filtered dispersions are colour-coded accordingly with coloured dots above.

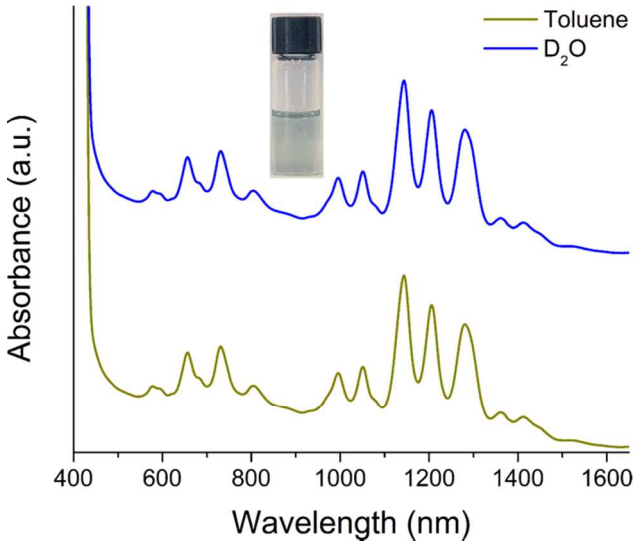


Figure S7. UV-Vis-NIR spectra of **PF-N$_3$-**HiPCO dispersions pre-SPAAC (toluene, dark yellow trace) and post-SPAAC with mPEG$_{5000}$-DIBAC (D_2O, blue trace). Spectra are offset for clarity. The photograph shows the pre-SPAAC polymer-SWNT dispersion in toluene.

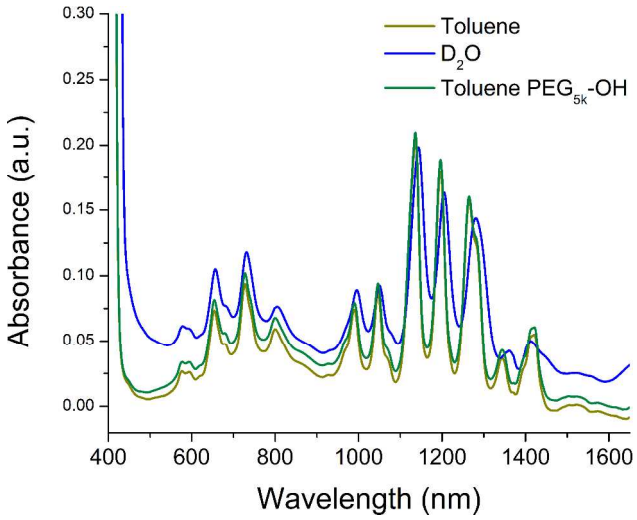


Figure S8. UV-Vis-NIR spectra of **PF-N$_3$**-HiPCO dispersions diluted for PL mapping.

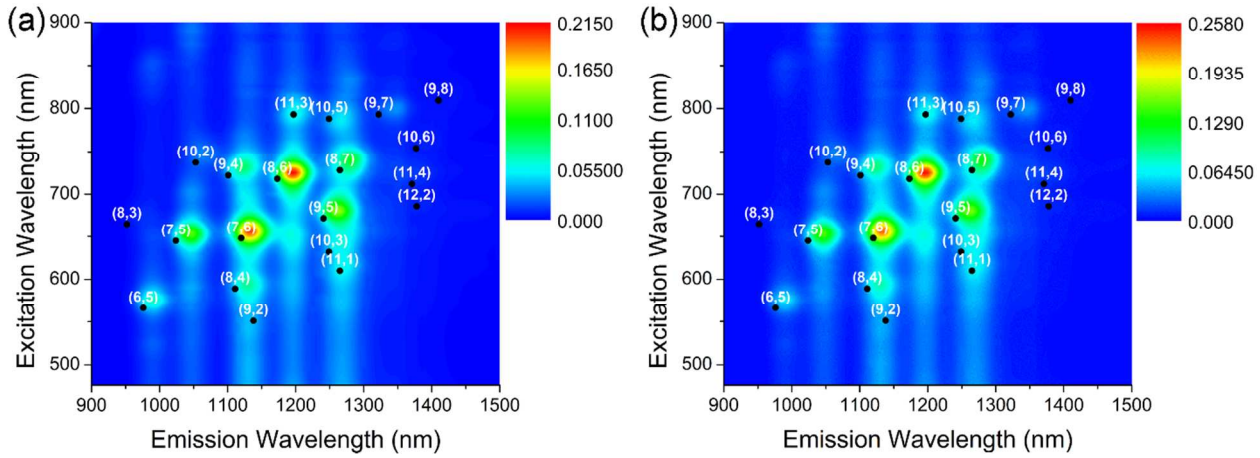


Figure S9. PL maps of **PF-N$_3$**-HiPCO in (a) toluene and (b) toluene mixed with 2.05 eq of mPEG$_{5000}$-OH.

Table S1. Emission Wavelengths of sc-SWNT Chiralities Dispersed by **PF-N$_3$** in Toluene and Toluene with mPEG$_{5000}$-OH

Chirality	λ_{em} (nm) (-PEG$_{5k}$)	λ_{em} (nm) (+PEG$_{5k}$)	$\Delta[\lambda_{em}]$ (nm)
(6,5)	990	990	0
(7,5)	1047	1046	-1
(7,6)	1133	1133	0
(8,4)	1131	1130	-1
(8,6)	1196	1196	0
(8,7)	1280	1279	-1
(9,4)	11245	1126	+1
(9,5)	1265	1264	-1

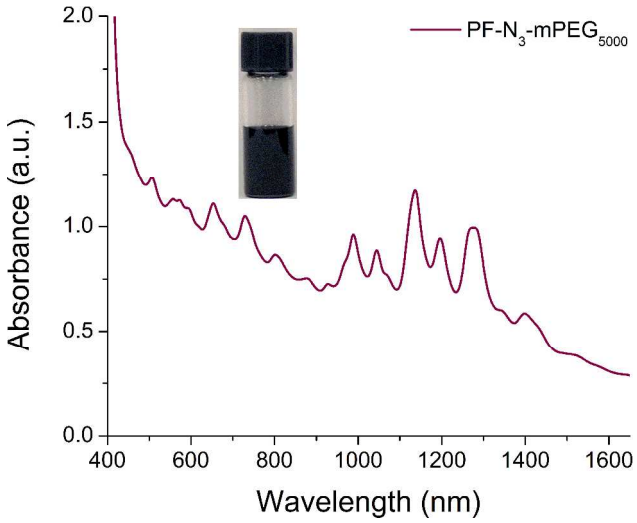


Figure S10. UV-Vis-NIR spectrum of **PF-N$_3$-mPEG$_{5000}$** used to disperse HiPCO SWNTs in toluene. Note that the spectrum was obtained by diluting the as-produced dispersion by a factor of 16 in toluene. The photograph shows the as-produced polymer-SWNT dispersion (undiluted).

References

(1) Xia, C.; Advincula, R. C. Decreased Aggregation Phenomena in Polyfluorenes by Introducing Carbazole Copolymer Units. *Macromolecules* **2001**, *34*, 5854–5859.