

SUPPORTING INFORMATION

Decoration of Polyfluorene-Wrapped Carbon Nanotube Thin Films via Strain-Promoted Azide-Alkyne Cycloaddition

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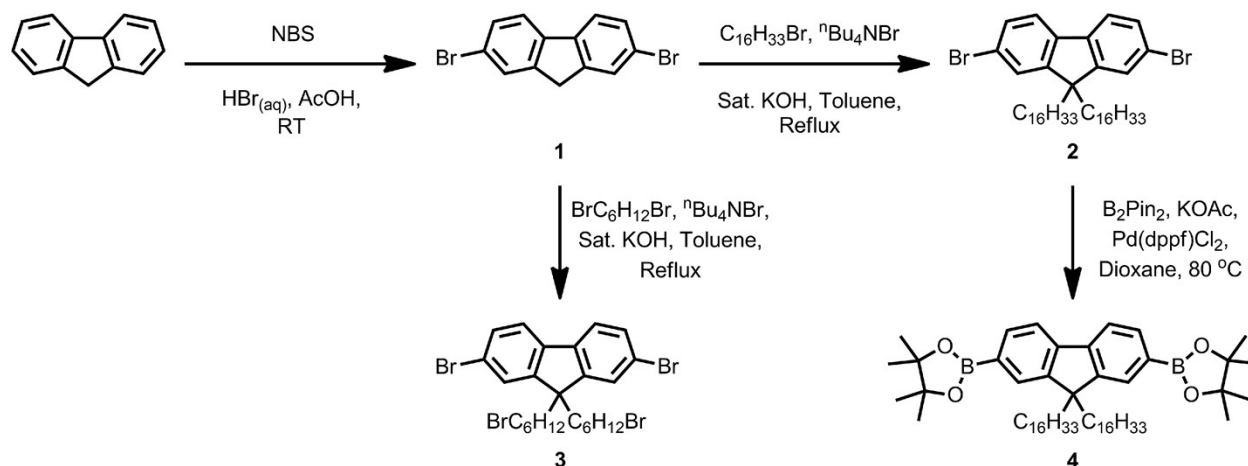
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Experimental

General

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. 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 $2.0\text{ mL}\cdot\text{min}^{-1}$. Sonication was performed in a Branson Ultrasonic B2800 bath sonicator. Centrifugation of the polymer-SWNT samples was performed using a Beckman Coulter Allegra X-22 centrifuge. Thin film thickness was measured using an optical profilometer (Veeco WYKO NT1100, DYMEK Company Ltd.) in VSI mode. Polymer-SWNT thin films were prepared by filtering the polymer-SWNT dispersion through a Teflon membrane (0.2 μm pore diameter). A straight boundary was prepared between the polymer-SWNT thin film and Teflon membrane by placing a glass slide over half of the polymer-SWNT thin film and using a Kim wipe to remove exposed thin film. The average maximum profile of the ten greatest peak-to-valley separations in the evaluation area, R_z , was used to quantify the thin film thickness. Infrared spectra were recorded using a Thermo Scientific Nicolet 6700 FT-IR spectrometer equipped with a Smart iTX attenuated total reflectance (ATR) sample analyzer. Raman spectra were collected using a Renishaw InVia Laser Raman spectrometer, with a 500 mW HeNe

Renishaw laser (633 nm, 1800 L/mm grating). Laser intensity was set to 1% for the 633 nm excitation wavelength for the polymer-SWNT samples. 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 to instrument variations. Photoluminescence maps were obtained at 25 °C, with 5 nm intervals for both the excitation and emission. Thermogravimetric analysis was performed on a Mettler Toledo TGA/DSC 3+, and all measurements were conducted under an argon atmosphere, with sample masses ranging from 0.5 to 1.0 mg. Contact angle measurements were obtained using an Optical Contact Angle (OCA 25) instrument from DataPhysics Instruments (Filderstadt, Germany). Conductivity measurements were recorded using the Model 2450 Interactive Source Meter Instrument (Keithley) with Pt-wire probes. X-ray photoelectron spectroscopy (XPS) survey spectra were collected using a K-Alpha X-ray photoelectron spectrometer system from Thermo Scientific.



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 magnetic 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. ¹H-NMR (600 MHz; CDCl₃): 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-dihexadecylfluorene (**2**) (adapted from reference 2)

A round bottom flask equipped with a magnetic stir bar was charged with **1** (2.7 g, 8.3 mmol), 1-bromohexadecane (6.36 g, 20.8 mmol), ⁿBu₄NBr (537 mg, 1.7 mmol), toluene (16.6 mL), and sat. KOH_(aq) (16.6 mL). 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 20 mL) and the organic extracts were

combined and concentrated *in vacuo* to obtain a viscous green oil. The crude product was purified by flash chromatography (100 g column, 100% hexanes over 10 CV) to afford **2** as a white solid (5.19 g, 81%). ¹H-NMR (600 MHz; CDCl₃): δ 7.51 (d, *J* = 8.0 Hz, 1H), 7.46-7.43 (m, 2H), 1.92-1.88 (m, 2H), 1.24-1.03 (m, 26H), 0.88 (t, *J* = 7.0 Hz, 3H), 0.59-0.57 (m, 2H).

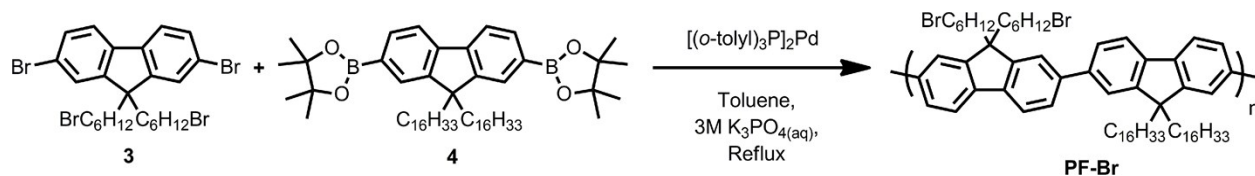
2,7-dibromo-9,9-bis(6-bromohexyl)fluorene (3) (adapted from reference 1)

A round bottom flask equipped with a magnetic 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). ⁿBu₄NBr (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% CH₂Cl₂ in hexanes over 10 CV) to obtain a white solid. TLC analysis of this product indicated that it was composed of two components. Subsequent recrystallization from MeOH (~250 mL) afforded **3** as a pure white solid (4.4 g, 44%). ¹H-NMR (600 MHz; CDCl₃): 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-dihexadecylfluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4) (adapted from reference 2)

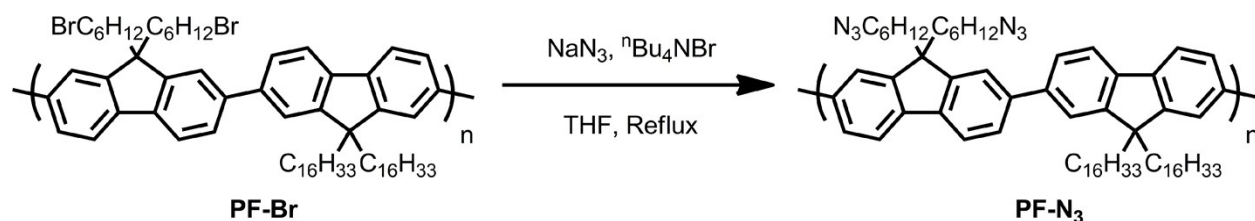
A round bottom flask equipped with a magnetic stir bar was charged with **2** (5.2 g, 6.7 mmol), B₂Pin₂ (3.76 g, 14.8 mmol), KOAc (1.98 g, 20.2 mmol), and dioxane (28 mL). Pd(dppf)₂Cl₂ (165 mg, 202 μmol) was added and then the reaction mixture was stirred at 80 °C for 12 h. The reaction mixture was partitioned with water and extracted thrice with Et₂O. The organic extracts were combined and dry loaded onto silica (9.9 g). The crude product was purified by flash chromatography (100 g column, 0 to 70%

CH₂Cl₂ in hexanes over 10 CV) to afford **3** as a white solid (4.88 g, 63%). ¹H-NMR (600 MHz; CDCl₃): δ 7.80 (d, *J* = 7.5 Hz, 1H), 7.74-7.71 (m, 2H), 2.00-1.97 (m, 2H), 1.39 (s, 12H), 1.24-0.99 (m, 26H), 0.87 (t, *J* = 7.0 Hz, 3H), 0.55-0.53 (m, 2H).



Poly(dihexadecylfluorene-*alt*-bis(bromohexyl)fluorene) (PF-Br) (adapted from Ref 3)

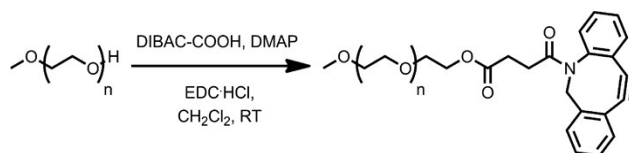
A Schlenk tube equipped with a magnetic stir bar was charged with **3** (447.7 mg, 0.69 mmol), **4** (597 mg, 0.69 mmol), toluene (4.9 mL), and 3M K₃PO_{4(aq)} (4.9 mL). The biphasic mixture was degassed by three freeze-pump-thaw cycles, then, while frozen under liquid nitrogen, [(*o*-tol)₃P]₂Pd (18 mg, 2.5 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 heated to 80 °C and vigorously stirred 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 (~300 mL) and then filtered to afford **PF-Br** as a yellow solid (478 mg, 63%). ¹H-NMR (700 MHz; CDCl₃): δ 7.85-7.83 (m, 4H), 7.73-7.68 (m, 8H), 3.30 (t, 4H), 2.17-2.11 (m, 4H), 1.72-1.69 (m, 4H), 1.30-1.13 (m, 60H), 0.87 (t, 6H).



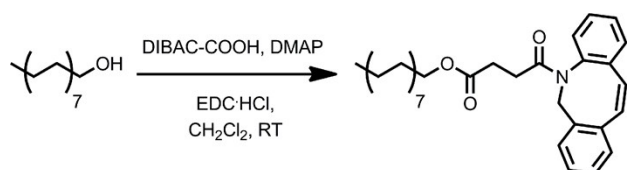
Poly(dihexadecylfluorene-*alt*-bis(azidoheptyl)fluorene) (PF-N₃) (adapted from Ref 3)

A round bottom flask equipped with a magnetic stir bar and reflux condenser was charged with **PF-Br** (400 mg, 0.36 mmol), NaN₃ (236 mg, 3.6 mmol), ⁿBu₄NBr (234 mg, 0.73 mmol), and THF (60 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 (~200 mL) to afford **PF-N₃** as a yellow solid (328 mg, 86%). ¹H-NMR (700 MHz; CDCl₃): δ 7.86-7.84 (m, 4H), 7.71-7.68 (m, 8H), 3.15 (t, 4H), 2.21-2.08 (m, 4H), 1.45-1.42 (m, 4H), 1.29-1.14 (m, 60H), 0.87 (t, 6H).



mPEG₅₀₀₀-DIBAC (adapted from reference 3). A round bottom flask equipped with a magnetic stir bar was charged with mPEG₅₀₀₀-OH (250 mg, 50 μmol), DIBAC-COOH (46 mg, 150 μmol) and 4-dimethylaminopyridine (DMAP; 3 mg, 25 μmol) and CH₂Cl₂ (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 for 12 h at RT. The reaction mixture was diluted with 5 mL of CH₂Cl₂ and then precipitated into 1:1 Et₂O:hexanes (~100 mL). The precipitate was collected on a Hirsch funnel, then washed with ice cold ethanol (3 x 20 mL), Et₂O (3 x 20 mL), and dried *in vacuo* to afford **mPEG₅₀₀₀-DIBAC** as a fine white powder (246 mg, 93%). ¹H 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).



DIBAC-C₁₆ (adapted from reference 3). A round bottom flask equipped with a magnetic stir bar was charged with 1-hexadecanol (0.099 g, 0.404 mmol), DIBAC-COOH (0.130 g, 0.426 mmol), DMAP (0.013 g, 0.106 mmol), and CH₂Cl₂ (1 mL). To the solution, EDC·HCl (0.122 g, 0.639 mmol) was added and then the reaction mixture was stirred for 2 h. The reaction mixture was purified by flash chromatography (25 g column, gradient of 0 to 35% EtOAc in hexanes over 20 CV) to afford **DIBAC-C₁₆** as a slightly waxy, colourless solid after cooling to -20 °C in a freezer for 2 h (227 mg, 98%). ¹H NMR (700 MHz; CDCl₃): δ 7.69 (d, J = 7.6, 1H), 7.51-7.50 (m, 1H), 7.42-7.40 (m, 1H), 7.39-7.37 (m, 2H), 7.35 (td, J = 7.5, 1.4, 1H), 7.29 (td, J = 7.5, 0.7, 1H), 7.25 (dd, J = 7.5, 1.1, 1H), 5.17 (d, J = 13.9, 1H), 4.00-3.93 (m, 2H), 3.67 (d, J = 13.9, 1H), 2.73 (ddd, J = 16.7, 8.2, 6.6, 1H), 2.62 (ddd, J = 17.2, 8.2, 6.5, 1H), 2.32 (dt, J = 17.2, 6.3, 1H), 1.95 (dt, J = 16.8, 6.2, 1H), 1.52 (t, J = 6.7, 2H), 1.27 (dd, J = 26.9, 6.1, 26H), 0.88 (t, J = 7.1, 3H). ¹³C NMR (176 MHz; CDCl₃): δ 173.1, 171.8, 151.6, 148.2, 132.4, 129.4, 128.6, 128.39, 128.20, 127.8, 127.2, 125.6, 123.3, 122.8, 115.1, 107.9, 64.8, 55.6, 32.1, 29.84, 29.80, 29.72, 29.67, 29.61, 29.50, 29.39, 28.6, 26.0, 22.8, 14.3. HRMS (ESI) (m/z) for C₁₆[M + H]⁺ calculated: 530.3629, found: 530.3641.

General SPAAC procedure. PF-N₃-SWNT thin film was prepared by filtering the dispersion through a Teflon membrane with a pore diameter of 0.2 μm. Thin films were washed with THF until the flow-through did not fluoresce at 365 nm, as monitored using a handheld UV lamp. Thin film samples were functionalized by either soaking the thin film in a solution of DIBAC derivative (for organic solvents) or by filtering the DIBAC solution through the thin film using vacuum filtration (for aqueous solvents). Reaction progress was monitored using IR spectroscopy for the disappearance of the polymer azide stretch at ~2090 cm⁻¹.

TGA Calculations

f is the mass percentage of a given subset of atoms.

Pre-SPAAC:

PF-N₃ repeat unit mass: 1027.60 g·mol⁻¹

N x 5 = 14.01 g·mol⁻¹ x 5 = 70.05 g·mol⁻¹

$$f_{5N} = \frac{70.05}{1027.60} \times 100\% = 6.8\% \quad (\text{measured: } 6.8\%)$$

Total side chain mass: [C₁₆H₃₃ + C₆H₁₂N₃] x 2 = C₄₄H₉₀N₆ = 703.40 g·mol⁻¹

Post-SPAAC:

DIBAC-COOH MW: 305.33 g·mol⁻¹

Side chain mass: C₄₄H₉₀N₆ + DIBAC-COOH x 2 = [703.40 + 305.33] g·mol⁻¹ x 2 = 1314.06 g·mol⁻¹

$$\% \text{ side chain mass increase} = \frac{\text{side chain mass (post - SPAAC)}}{\text{side chain mass (pre - SPAAC)}} = \frac{1314.06}{703.40} \times 100\% = 186.8\%$$

Expected mass loss post-SPAAC:

$$\text{Initial observed mass loss (TGA)} \times \text{side chain mass increase} = 15.4\% \times 1.868 = 28.8\% \quad (\text{measured: } 27.2\%)$$



Figure S1. Photograph of the **PF-N₃**-SWNT functionalization process. A 1 cm² **PF-N₃**-SWNT thin film is soaked in a solution of strained cyclooctyne.

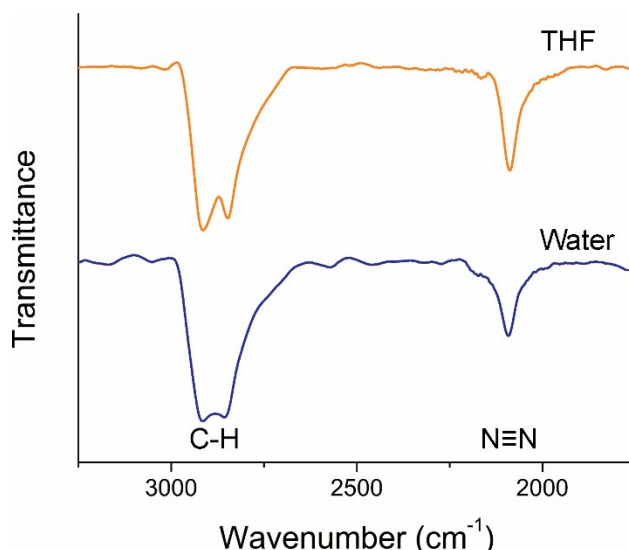


Figure S2. FT-IR overlay of the **PF-N₃-SWNT** thin film soaked in a 0.5 mg·mL⁻¹ solution of mPEG₅₀₀₀-DIBAC in THF (orange) or H₂O (blue).

Table S1. Atomic %s of C, N, and O for **PF-N₃-SWNT** Thin Film Pre- and Post-SPAAC With mPEG₅₀₀₀-DIBAC or DIBAC-C₁₆

Sample	C (%)	N (%)	O (%)
Pristine	91.04	3.38	5.58
mPEG ₅₀₀₀ -Functionalized	81.83	2.07	16.09
C ₁₆ -Functionalized	90.10	3.65	6.25

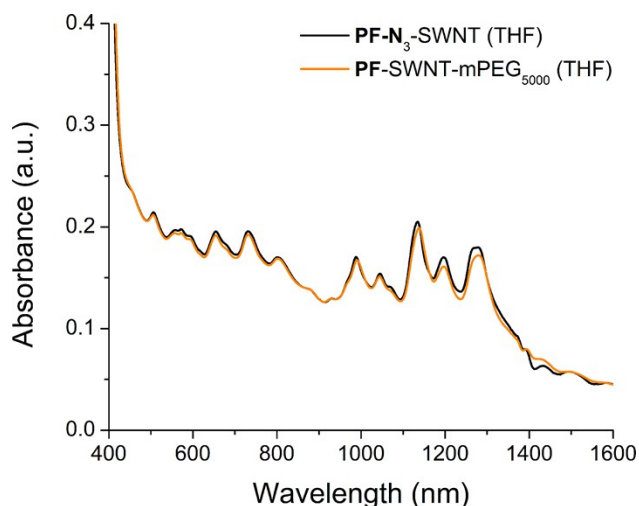


Figure S3. UV-Vis-NIR spectra of **PF-N₃-SWNT** samples in THF used for PL mapping (i) prior to any functionalization (black), (ii) functionalized with mPEG₅₀₀₀-DIBAC (orange). The samples were prepared by sonicating the corresponding thin film in THF for 1 h and then filtering the resulting dispersion through a cotton plug.

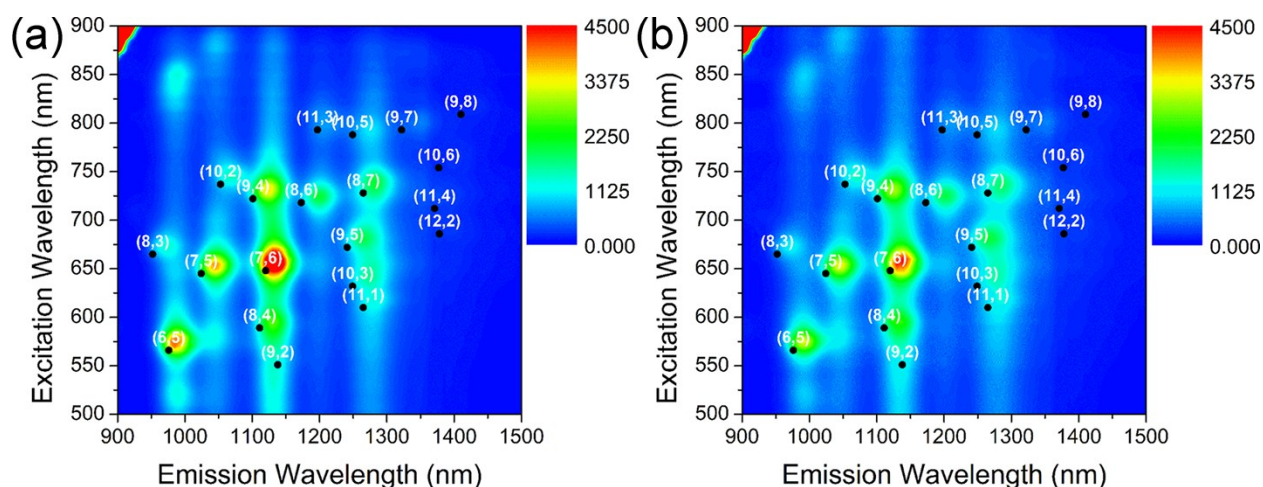


Figure S4. PL maps of **PF-N₃-SWNT** samples in THF (a) prior to any functionalization, (b) functionalized with mPEG₅₀₀₀-DIBAC. The samples were prepared by sonicating the corresponding thin film in THF for 1 h and then filtering the resulting dispersion through a cotton plug.

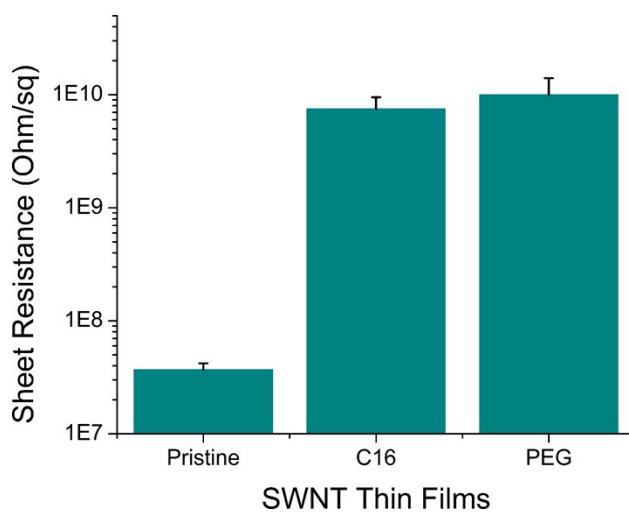


Figure S5. Bar chart of sheet resistance measurements for (i) pristine, (ii) C₁₆-functionalized, and (iii) mPEG₅₀₀₀-functionalized polymer-SWNT thin films.

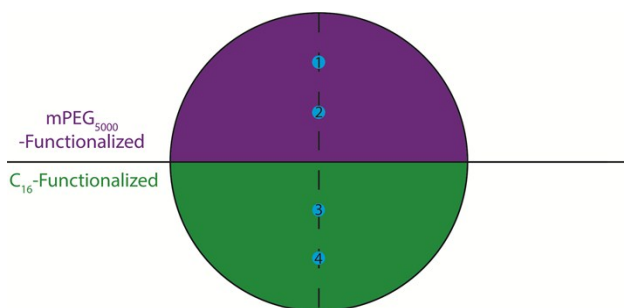


Figure S6. Idealized cartoon showing the location of XPS measurements made on the Janus polymer-SWNT thin film.

Table S2. Atomic %s of C, N, and O for Janus Polymer-SWNT Thin Film Functionalized With mPEG₅₀₀₀-DIBAC or DIBAC-C₁₆

Location	C (%)	N (%)	O (%)
1	88.24	3.26	8.50
2	88.33	2.93	8.74
3	90.25	3.59	6.16
4	90.49	3.42	6.08

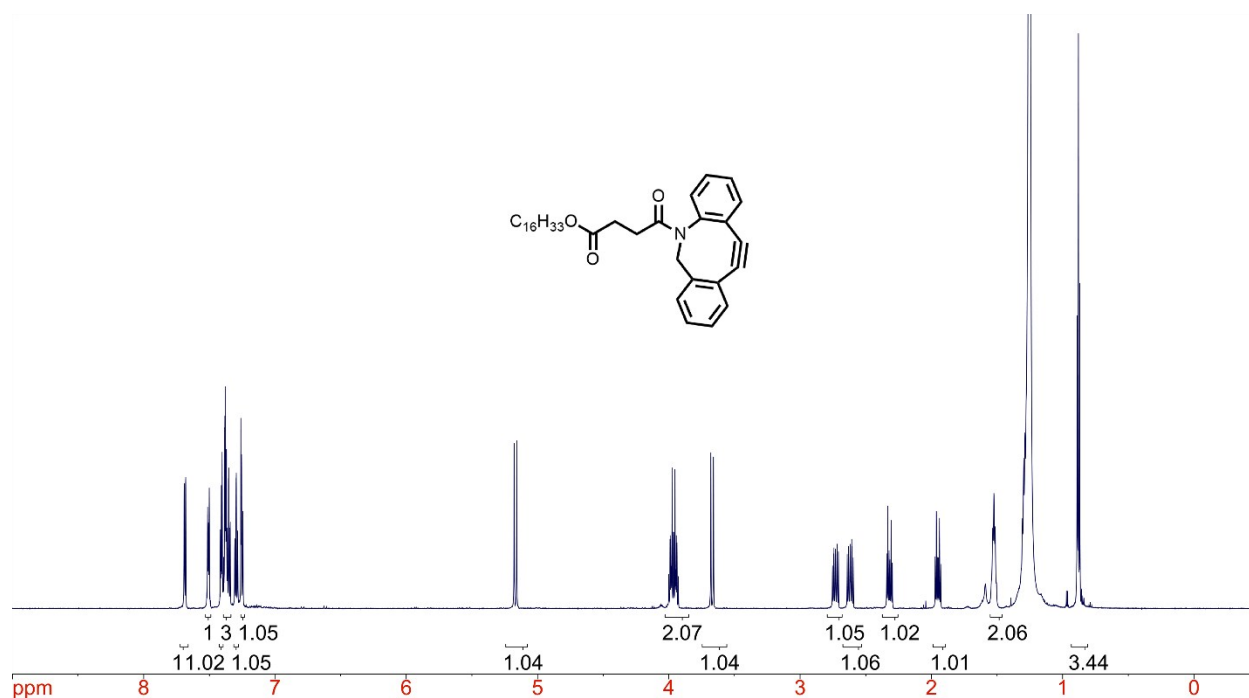


Figure S7. ¹H NMR spectrum of **DIBAC-C₁₆** in CDCl₃.

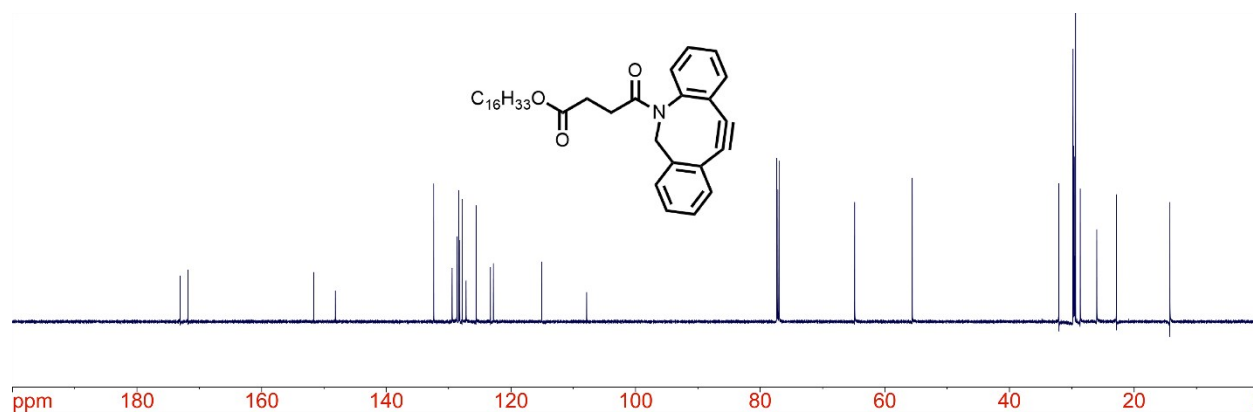


Figure S8. uDEFT spectrum of **DIBAC-C₁₆** in CDCl₃.

References

- 1 C. Xia and R. C. Advincula, *Macromolecules*, 2001, **34**, 5854–5859.
- 2 D. Fong and A. Adronov, *Macromolecules*, 2017, **50**, 8002–8009.
- 3 D. Fong, J. Yeung, S. A. McNelles and A. Adronov, *Macromolecules*, 2018, **51**, 755–762.