

SUPPORTING INFORMATION

Supramolecular Interactions of Fluorene-Based Copolymers Containing 3,4-Propylenedioxythiophene and Phenazine Units with SWNTs

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Experimental

General

Single-walled carbon nanotubes (HiPco SWNTs) were purchased from NanoIntegris (batch number: R1-901) and used without any further treatment. Reagent grade chemicals and solvents were purchased from commercial suppliers. ^1H NMR spectra were obtained on Bruker Avance 600 MHz or 200 MHz instruments, and the non-deuterated solvent signal was used as the internal standard for ^1H -NMR spectra. Polymer molecular weight and polydispersity index (PDI) were estimated by gel permeation chromatography (GPC) analysis using a Waters 2695 Separations Module equipped with a Waters 2996 photodiode array detector, a Waters 2414 refractive-index detector, and two Jordi Labs Jordi Gel DVB columns. Polystyrene standards were used for calibration, and THF was used as the eluent at a flow rate of 1.0 mL/min. Raman spectra were collected with a Renishaw InVia Laser Raman spectrometer equipped with a 500 mW HeNe Renishaw laser (633 nm, 1800 L/mm grating), and a 300 mW Renishaw laser (785 nm, 1200 L/mm grating). The Raman system was also equipped with a Leica microscope having 5 \times , 20 \times , and 50 \times objectives as well as a USB camera for sample viewing. The 785 nm laser was operated at 1% intensity, and the 633 nm laser was operated at 5% intensity to avoid damage to the sample. Samples were prepared by drop-casting the polymer (or SDBS) and SWNT dispersions onto a clean silicon substrate. Ultrasonication was carried out in a Branson Ultrasonics B2510 bath sonicator. Filtration carried out through a 200 nm-pore Teflon membrane (Millipore). UV/vis-NIR absorption spectra were measured using a Varian Cary 5000 spectrophotometer. Fluorescence spectra were measured using a Jobin-Yvon SPEX Fluorolog 3.22 equipped with 450 W Xe lamp and an InGaAs detector, also using a 10 mm quartz cuvette. Slit widths for both excitation and emission were set to 8 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 (TGA) was carried out on a TA Instruments Q50 thermogravimetric analyzer under Argon with a temperature range from 20 to 800 °C and the temperature gradient of 5 deg/min. All measurements were done under Ar, with sample masses ranging from 1~ 2.0 mg.

Synthesis of monomers and polymers

All of the precursors, monomers, and corresponding polymers were prepared according to literature procedures or by modification of reported procedures.

2,3,4,5-Tetrabromothiophene (1):¹ A 250 mL round bottom flask equipped with a magnetic stir bar was charged with thiophene (8.4 g, 0.10 mmol) and CHCl₃ (10 mL). After cooling down the reaction mixture to 0 °C in ice bath, a mixture of bromine (80 g, 0.50 mmol, 5 equiv) and CHCl₃ (30 mL) was added dropwise into the solution over a 2 h period. Upon complete addition of the bromine, the reaction was allowed to warm up to room temperature under constant stirring. The reaction mixture was kept stirring at room temperature for 15 h and then heated to reflux and continued for 2 h. After cooling down to room temperature, aqueous NaOH (~20% w/w) was added slowly until an alkaline pH was obtained, and then the mixture was stirred for additional 1 h. After addition of 50 mL of methanol, light brown slurry was obtained. The resulting mixture was filtered, and the collected solid was washed with 5% aqueous Na₂CO₃ (100 mL) and water (200 mL) separately. Then the solid sample was dissolved in a minimum amount of hot CHCl₃ and was precipitated into 500 mL methanol. The resulting precipitate was collected by filtration, and dried under vacuum to yield a white powder (35 g, 90%). ¹³C NMR (150 MHz, CDCl₃), δ_H [ppm]: 117.15, 110.49.

3,4-Dibromothiophene (2):^{1,2} A 500 mL round-bottom flask equipped with a magnetic stir bar was charged with an acetic acid/water mixture (1:2 v/v, 180 mL) followed by the addition of powdered zinc (60 g, 0.92 mol) and 2,3,4,5-tetrabromothiophene (113 g, 0.28 mol) in small portions. The resulting mixture was subsequently stirred at room temperature for 1 h, and then under reflux for 3 h under argon atmosphere. The mixture was passed through a plug of celite (~4 cm thick), and then the filtrate was extracted with diethyl ether. After drying with anhydrous Na₂SO₄, the solvent was removed via rotary evaporation, and the crude product was distilled under vacuum to yield a colorless liquid (68 g, 86%). ¹H NMR (600 MHz, CDCl₃), δ_H [ppm]: 7.73 (s, 2H).

3,4-dimethoxythiophene (3):¹⁻³ A flame dried 250 mL round-bottom flask equipped with a magnetic stir bar was charged with with 120 mL anhydrous methanol, and sodium metal (~10 g, 0.44 mol) was added slowly over 30 min. 3,4-dibromothiophene (24.2 g, 0.10 mol) was added to the alkaline solution at room temperature. The cupric oxide (5.6 g, 70 mmol) and KI (1.7 g, 10 mmol) were quickly added to the above mixture, and then the reaction mixture was stirred and heated to reflux for 3 days under argon atmosphere. After cooling to room temperature and the most of the solvent was removed and 150 mL of water was added and stirred 10 min. Then it was extracted three times with diethyl ether (3×100 mL), and the combined organic layer was washed with water (100 mL) and brine (100 mL), respectively. The organic layer was dried over MgSO₄, and concentrated via rotary evaporation. The resulting product was purified via distillation under reduced pressure and compound **3** was obtained as a clear oil (10.9 g, 76 %). ¹H NMR (600 MHz, CDCl₃), δ_H [ppm]: 6.20 (s, 2H), 3.88 (s, 6H).

2,2-didodecyl malonic acid diethyl ester (4):^{3,4} A 1 L three-neck flask equipped with a magnetic stir bar and a reflux condenser was charged with 500 mL of ethanol, and sodium metal (~15 g, 0.65 mol) was added slowly and stirred to dissolve all of the sodium. After slow addition of diethyl malonate (32 g, 0.20 mol), the reaction mixture was heated to reflux. When the mixture started to reflux, 1-bromododecane (130 g, 0.70 mol, 3.5 equiv) was added slowly, and then the reaction mixture was stirred at reflux for 2 days. After removal of ethanol, 120 mL of cold water was added, and then the mixture was extracted with diethyl ether (3×100 mL). Organic layer was dried over anhydrous MgSO₄, and solvent was removed via rotary evaporation. The remained organic residue was distilled at reduced pressure to yield 2,2'-didodecyl malonic acid diethyl ester (55.7 g, 80%). ¹H-NMR (600 MHz, CDCl₃), δ_H [ppm]: 4.15 (q, *J* = 7.02 Hz, 4H), 1.82(q, *J* = 4.60 Hz, 4H), 1.00~1.40 (m, 46H), 0.87 (t, *J* = 5.60 Hz, 6H).

2,2'-Didodecyl-1,3-Propanediol (5):^{1,4} A flame dried 1L three-neck flask equipped with a magnetic stir bar and a reflux condenser was charged with LiAlH₄ (9.5 g, 0.25 mol) under N₂ atmosphere, and 500 mL of dry ether was added slowly to the reaction flask. 2,2'-didodecyl malonic acid diethyl ester **4** (51.4 g, 0.14 mol) was added slowly, and the reaction mixture was stirred at reflux for 24 h. After cooling the reaction mixture with ice-bath, distilled water was slowly added until evolving hydrogen gas was ceased. 5% aqueous sulfuric acid was added until all of the white solid precipitates were dissolved, and the resulting solution was extracted with diethyl ether (3×100 mL). The organic layer was dried with anhydrous MgSO₄ to get crude 2,2'-didodecyl-1,3-propanediol (37.3 g, 95%), which was used for the next reaction without further purification. ¹H NMR (600 MHz, CDCl₃), δ_H [ppm]: 3.64 (d, *J* = 14.40 Hz, 2H), 1.42 (s, 4H), 1.36 ~ 1.20 (m, 44H), 0.90 (t, *J* = 7.02 Hz, 6H).

3,3'-didodecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (6)(ProDOT):^{1,4} A 250 mL round-bottom flask equipped with a magnetic stir bar was charged with 120 mL of toluene. 3,4-dimethoxythiophene (1.97 g, 13.6 mmol), 2,2'-didodecyl-1,3-propanediol (7.45 g, 27.2 mmol) and *p*-toluenesulfonic acid monohydrate (0.26 g, 1.36 mmol) were added. The resulting mixture was stirred at reflux for 2 days under N₂ atmosphere. After cooling down to room temperature, the reaction mixture was washed with water (100 mL). The toluene was removed under reduced pressure, and the crude product was purified by column chromatography on silica gel with methylene chloride/hexane (1:9, v/v) as an eluent to yield colourless oil (3.7 g, 78%). ¹H NMR (600 MHz, CDCl₃), δ_H [ppm]: 6.39 (s, 2H), 3.81 (s, 4H), 1.00 ~ 1.40 (m, 44H), 0.90 (t, *J* = 6.60 Hz, 6H).

2,5-dibromo-3,3'-didodecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (7):⁵ A 250 mL flame-dried round-bottom flask equipped with a magnetic stir bar was charged with compound **6** (2.46 g, 5 mmol) and 10 mL of CHCl₃. *N*-bromosuccinimide (2.67 g, 15 mmol, 3 equiv) was dissolved in a 2:1 solvent mixture of CHCl₃ (100 mL) and acetic acid (50 mL), and added slowly to the reaction flask at 0-5 °C under argon atmosphere. Then the reaction was quenched by adding 100 mL cold water, and the layers were separated. The aqueous layer was extracted with chloroform (2×100 mL). The organic layer was neutralized with 5% Na₂CO₃ aqueous solution, and washed with distilled water (100 mL). The organic layer was dried over anhydrous MgSO₄ and concentrated via rotary evaporation. The residue was purified using silica gel column chromatography eluted with hexane/EtOAc (9:1, v/v) to give a product as colourless oil (3.1 g, 95%). ¹H NMR (600 MHz, CDCl₃), δ_H [ppm]: 3.93 (s, 4H), 1.38~1.42 (m, 4H), 1.32~1.14 (br, 40H), 0.90 (t, *J* = 7.20 Hz, 6H).

4,7-Dibromo-2,1,3-benzothiadiazole (8):^{6,7} A 250 mL two-neck round-bottom flask equipped with a magnetic stir bar was charged with 2,1,3-benzothiadiazole (1.36 g, 10 mmol) and 15 mL of HBr (45% water solution), and heated to reflux. A mixture of 4.8 g (1.53 mL, 30 mmol) of bromine and 10 mL of HBr was added slowly, and the mixture was stirred at reflux for additional 3 h. The mixture was then filtered, washed well with water (3×100 mL), recrystallized from chloroform, and dried over night to give white needle crystals (2.78 g, 95%). ¹H NMR (600 MHz, CDCl₃), δ_H [ppm]: 7.73 (s, 2H).

1,2-diamino-3,6-dibromobenzene (9):^{6,8} A 250 mL two-neck round-bottom flask equipped with a magnetic stir bar was charged with 4,7-dibromo-2,1,3-benzothiadiazole (1.46 g, 5 mmol) and 50 mL ethanol, and stirred for 10 min. To this suspension, NaBH₄ (3.8 g, 100 mmol) was added very slowly followed by addition of catalytic amount of CoCl₂·6H₂O (0.01g, 0.04 mmol, ~1 mol %). Black solid was obtained instantly and in a few minutes the evolution of H₂S was noticed. The mixture was heated to reflux and allowed to react for 3 more hours. After cooling down to room temperature, the mixture was filtered to separate the black solid. The solvent was evaporated, 60 mL of water was added, and the product was extracted with diethyl ether (3×30 mL). The combined organic extracts were dried over Na₂CO₃, and the solvent was removed under vacuum, resulting in the diamine 1,2-diamino-3,6-dibromobenzene. Due to instability, the resulting compound was used immediately without further purification to avoid fast decomposition. The product was off-white solid with a yield of 90% (1.2 g). ¹H NMR (600 MHz, CDCl₃), δ_H [ppm]: 6.74 (s, 2H), 3.86 (s, 4H).

6,9-dibromophenazine-2,3-diol (10):⁹ A 250 mL two-neck round-bottom flask equipped with a magnetic stir bar was charged with 1,2-diamino-3,6-dibromobenzene (1.30 g, 5 mmol) and 50 mL of absolute ethanol. After the solid was dissolved, 2,5-dihydroxyl-1,4-benzoquinone (1.12 g, 8 mmol, 1.6 equiv) was added at once, and the reaction mixture was stirred at reflux for 24 hours under an argon atmosphere. The reaction mixture was cooled down slightly, and the solvent was removed. The solid was washed with 100 mL of water, and dried under vacuum for overnight. Most of the impurities were removed by short silica column chromatography using hexane and chloroform (9:1 to 7:3/v:v, progressively increasing polarity) as the elution solvent. The dark brown product (1.48 g, 40%) was used for next step without further purification. ¹H NMR (200 MHz, DMSO-d₆), δ_H [ppm]: 8.02 (s, 2H), 7.37 (s, 2H), 1.48 (br, 2H).

2,3-didodecyl- 6,9-dibromophenazine (11):⁹ To a 500 mL round-bottom flask equipped with a magnetic stir bar, a suspension of K₂CO₃(13.4 g, 100 mmol) and KI (0.17 g, 10 mmol) in 200 mL acetone was added and degassed by bubbling with argon for 10 min. Compound **10** (1.85 g, 5 mmol) and *n*-bromododecane (~5 g, 20 mmol, 4 equiv) and small amounts of 18-crown-6 (~0.1 g, 0.4 mmol) catalyst were added. The mixture was stirred at room temperature for 2 days. Then inorganic salts were removed by hot filtration, and the solvent was removed via rotary evaporation. The light yellow solid was washed with water (100 mL) and ethanol (100 mL) repeatedly in order to remove leftover inorganic salts and other organic impurities. The final pure product was obtained after silica column chromatography using hexane and dichloromethane (7:3/v:v) as the elution solvent. The product was isolated as pale yellow flakes in 70% yield (2.47 g). ¹H NMR (200 MHz, CDCl₃), δ_H [ppm]: 7.94 (s, 2H), 7.50 (s, 2H), 4.28 (t, *J* = 6.18 Hz, 4H), 1.98 (t, *J* = 6.90 Hz, 4H), 1.20~1.40 (m, 40H), 0.90 (t, *J* = 6.20 Hz, 6H).

General Procedure for Suzuki-Miyaura Cross-Coupling Polymerization:^{10,11} To a 50 mL Schlenk tube charged with a mixture 10 mL toluene, 5 mL aqueous 2 M K₂CO₃(aq.) and 1-2 drops of Aliquat 336, monomer 9,9'-dioctylfluorene-2,7-bis(trimethyleneboronate) (0.167 g, 0.3 mmol) and 2,5-dibromo-3,3'-didodecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (0.195 g, 0.3 mmol) or equal molar amount of monomer **11** (0.212 g, 0.3 mmol) were added, then the mixture was degassed via sonication under continuous bubbling with Ar for 30 min. Pd(PPh₃)₄ (35 mg, ~ 1.0 mol %) was added, and the resulting mixture was stirred at 90 °C under Ar for 48 h. After the mixture was cooled to room temperature, it was poured into methanol (~250 mL). The precipitated material was recovered by filtration. The resulting solid material was washed for 24 h using methanol (2×250 mL) and acetone (150 mL), separately, to remove oligomers and catalyst residues. The solid was dissolved in minimum amount of CHCl₃ (5~10 mL), and re-precipitated into 300 mL of methanol, filtered and the solid was dried under vacuum for 24 h at 50 °C.

Poly[(9,9'-dioctylfluorene)-*alt*-(3,3'-didodecyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine)] (PFO-ProDOT): The general procedure was followed, and resulted in a beige fibrous material (0.215 g, 80%). ¹H NMR (600 MHz, CDCl₃), δ_H [ppm]: 7.79 (b, 2H), 7.68 (b, 4H), 4.06 (b, 4H), 6.21 (d, 2 H), 2.02 (b, 4H), 1.10~1.38 (b, 68H), 0.80~0.90 (b, 12H). UV-vis (THF): λ_{max} = 432 nm, Mn=11.5 KDa, PDI=1.7

Poly[(9,9'-dioctylfluorene)-*alt*-(2,3-didodecyloxyphenazine)] (PFO-DPZ): The general procedure was followed, and resulted in a pale yellow fibrous material (0.210 g, 75%). ¹H NMR (CDCl₃, 600 MHz), δ_H [ppm]: 8.01 (b, ~8H), 7.34 (b, overlapped with CHCl₃, ~4H), 4.20 (m, 4H), 1.95 (m, 4H), 1.42 (m, 4H), 1.10-1.34 (b, 64 H), 0.80-0.90 (b, 12 H). UV-vis (THF): λ_{max} = 450, 395, 338 nm; Mn=18.0 kDa, PDI=2.4.

Preparation of polymer-SWNT complexes: ^{11,12}

A mixture of SWNTs (2.5 mg) and the copolymer (7.5 mg) in 10 mL of THF was sonicated for 30 min. The homogeneous solution was then filtered through a 200 nm-pore-diameter Teflon membrane, and the black residue was repeatedly washed with THF in order to remove excess free polymer (this is determined by disappearance of fluorescence of the filtrate). Then the polymer-SWNT complex was dissolved in THF again by sonicating for another 30 minutes, and undissolved parts were removed using centrifugation at 8300 g for 30 min. The dark, clear supernatant solution was found to remain stable, without visible precipitation of nanotubes for a long time. In order to examine the effect of solvents on polymer selectivity towards SWNTs, above experimental process was carried out in other organic solvents such as toluene and xylene using same protocols, respectively.

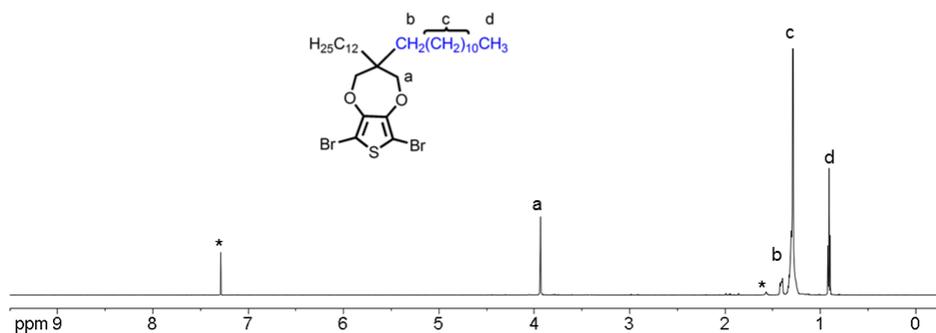


Figure S1. ^1H NMR spectra of the monomer **10** in CDCl_3 . Signals marked with an asterisk arise from CHCl_3 (~ 7.26 ppm) and water (~ 1.54 ppm).

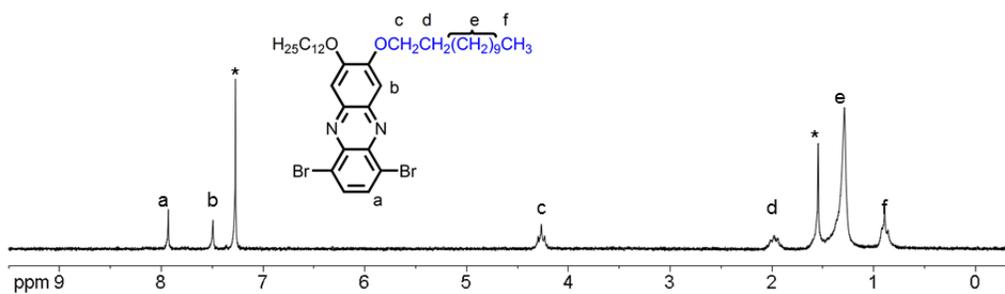


Figure S2. ^1H NMR spectra of the monomer **11** in CDCl_3 . Signals marked with an asterisk arise from CHCl_3 (~ 7.26 ppm) and water (~ 1.54 ppm).

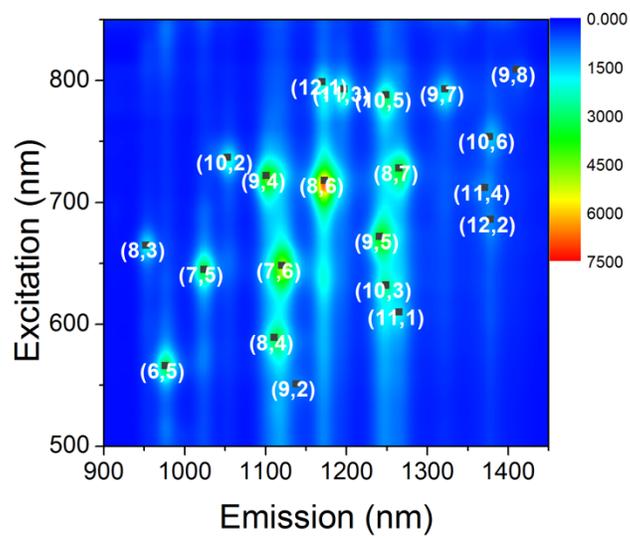


Figure S3. PL contour map of the reference sample of HiPco SWNTs dispersed with SDBS in D_2O .

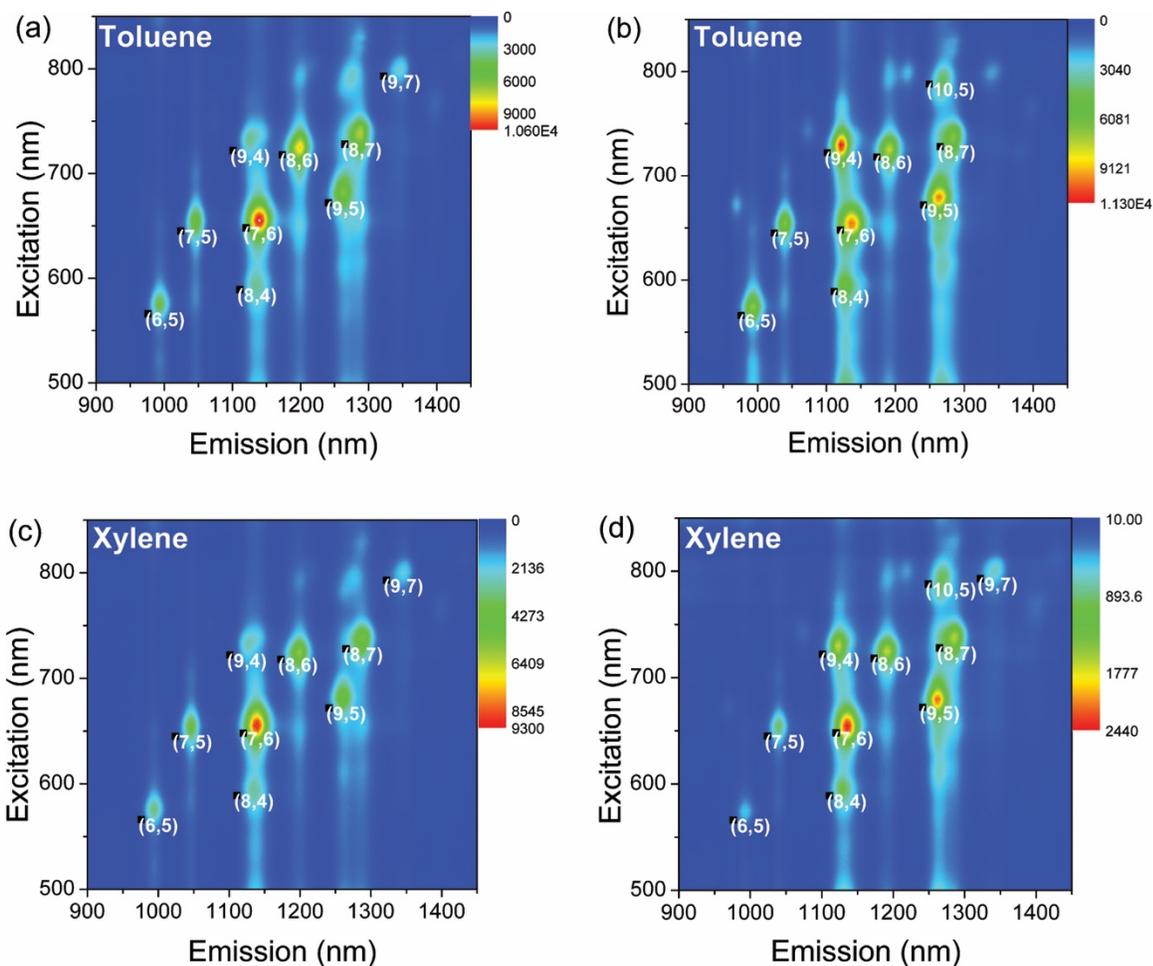


Figure S4. PL contour maps of HiPco SWNTs dispersed with polymers **PFO-ProDOT** (a and c), and **PFO-DPZ** (b and d). Sample dispersions with the two polymers were prepared in toluene (a and b) and xylene (c and d).

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