Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPORTING INFORMATION

Effect of Side-Chain Halogenation on the Interactions of Conjugated Polymers with SWNTs

Mokhtar Imit, Alex Adronov*

Department of Chemistry and Chemical Biology, the Brockhouse Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada

Email: adronov@mcmaster.ca

[*] Department of Chemistry and Chemical Biology

McMaster University

1280 Main St. W.

Hamilton, ON

L8S 4M1

Tel: (905) 525-9140 x 23514

Fax: (905) 521-2773

Experimental

Materials and Characterization: Single-walled carbon nanotubes (HiPco SWNTs) were purchased from Nanointegris (batch number: R1-901) and used without any further treatment. Chemicals and solvents were of reagent grade and purchased from Aldrich, ACROS Chemical Co., and other chemical suppliers and used as received. Solvents were dried according to standard procedures and degassed using Ar bubbling under sonication at room temperature (when necessary). ^{1}H NMR spectra were obtained on Bruker Avance 600 MHz, and the nondeuterated solvent signal was used as the internal standard for ^{1}H-NMR spectra. Polymer molecular weight and polydispersity index (PDI) were estimated from gel permeation chromatography (GPC) analyses by 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 25 mW argon ion laser (514 nm), a 300 mW Renishaw 785 nm laser, and 1800 L/mm and 1200 L/mm gratings for the two lasers, respectively. The Raman system is also equipped with a Leica microscope having 5×, 20×, and 50× objectives as well as a USB camera for sample viewing. The 785 nm laser was operated at 1% intensity to avoid damage to the sample. Ultrasonication was done in a Branson Ultrasonics B2510 bath sonicator. Filtration was done through a 200 nm-pore Teflon membrane (Millipore). UV/vis, 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 a 450 W Xe arc lamp, double-excitation and double-emission monochromators, and a digital photon-counting photomultiplier. Slit widths were set to 8 nm band-pass on both excitation and emission. Spectral measurements were carried out using standard 1 cm quartz cells at room temperature.

Synthesis of monomers and polymers

All of the precursors, monomers, and corresponding polymers were prepared according published literature, and characterized using ^{1}H NMR and other instrumental methods.

2,7-Diiodofluorene (1):[1,2] Fluorene (5.0 g, 30 mmol) was dissolved in 330 mL of a mixed solvent (CH_3COOH:H_2O:H_2SO_4/ 50:4:1) at 80 °C, followed by addition of KIO_3 (2.6 g, 12 mmol) and I_2 (10 g, 78 mmol). Then the mixture was stirred at this temperature for 10 h. Precipitate was formed during the course of the reaction. Upon cooling to room temperature, the precipitate was collected by filtration and washed with Na_2CO_3 (~10%), $NaHSO_3$ (~5%) and water. The crude material was recrystallized from dichloromethane to give the product (9.8 g, 80 %) as off-white solid. ^{1}H NMR (600 MHz, $CDCl_3$), δ_H [ppm]: 7.88 (s, 2H), 7.71 (d, *J* = 8.06 Hz, 2H), 7.51 (d, *J* = 8.06 Hz, 2H), 3.85 (s, 2H).

9,9'-Dihexyl-2,7-Diiodofluorene (2):[2] 10 mL of 1-bromohexane (40 mmol) and 2,7-diiodofluorene (2.1g, 5 mmol) were added to a mixture of tetrabutylammonium bromide (TBAB) (0.1 g, 0.3 mmol) and aqueous KOH (10 mL, 50% v/v) in a 150 mL round-bottom flask with a stir bar, and the reaction was allowed to proceed overnight at room temperature under stirring. Then, to the reaction was added a mixture water and hexane, and then the organic layer was separated. After the aqueous phase was extracted with hexanes (2×50 mL), the organic fractions were combined with previous organic phase and washed with water (50 mL) and aqueous HCl (0.1 M, 50 mL), and dried ($MgSO_4$). After filtering off $MgSO_4$, hexanes was removed in vacuo and the product purified using silica gel column chromatography (hexane:$CHCl_3$ = 9:1) to give a white product with a yield of 90% (2.6 g). ^{1}H NMR (600 MHz, $CDCl_3$), δ_H [ppm]: 7.66 (d, *J* = 9.36 Hz, 2H), 7.65 (s, 2H), 7.42 (d, *J* = 7.89 Hz, 2H), 1.90 (t, *J* = 8.30 Hz, 2H), 1.16~1.10 (m, 2H), 1.06~1.02 (m, 2H), 0.80 (t, *J* = 7.23 Hz, 2H), 0.60~0.56 (m, 2H).

2,7-Diiodo-9,9'-Bis(6-bromohexyl)fluorene (3):[2,3] A mixture of tetrabutylammonium bromide (TBAB, 0.1 g, 0.3 mmol) and aqueous KOH (10 mL, 50% v/v) in a 150 mL round-bottom flask with a stir bar was heated to 75 °C and stirred. Then 10 mL 1,6-dibromohexane (40 mmol) was added to the mixture and, after stirring several minutes, 2,7-diiodofluorene (3.3 g, 8 mmol) was added in one portion. The reaction was allowed to proceed for 50 min under vigorous stirring at 75 °C. After cooling down to room temperature, 20 mL water was added and the mixture was extracted with ethyl acetate (3×60 mL). The organic layer was washed with 50 mL water and aqueous HCl (0.1 M, 50 mL), 50 mL brine, and the organic layer was dried over $MgSO_4$. After filtering off $MgSO_4$, the solvents were evaporated in vacuo and pure product was obtained after silica column chromatography using hexane and dichloromethane (9:1 v:v) as the elution solvent. The product was isolated as a white powder in 80% yield. ^{1}H NMR (600 MHz, $CDCl_3$), δ_H [ppm]: 7.68 (d, *J* = 8.06 Hz, 2H), 7.65 (s, 2H), 7.42 (d, *J* = 7.86 Hz, 2H), 3.28 (t, *J* = 7.08 Hz, 2H), 1.90 (t, *J* = 8.20 Hz, 2H), 1.67~1.62 (m, 2H), 1.20~1.15 (m, 2H), 1.10~1.06 (m, 2H), 0.60~0.56 (m, 2H).

2,7-Diiodo-9,9'-Bis(6-iodohexyl)fluorene (4):[4] 2,7-Diiodo-9,9'-Bis(6-bromohexyl)fluorene) (1.22 g, 1.5 mmol) was dissolved in 25 mL acetone, and NaI (2.3 g, 15 mmol) was added to the reaction flask. The reaction was brought to reflux and stirred for 12 h. After evaporating the acetone, 50 mL of water and 30 mL chloroform were added to the yellowish white solid and extracted twice using the same amount of organic solvent. The organic layer was dried with $MgSO_4$, and evaporated in vacuo, leaving a pale yellow solid. Yield: 1.40 g (98%). ^{1}H NMR

(600 MHz, $CDCl_3$), δ_H [ppm]: 7.68 (d, J = 8.06 Hz, 2H), 7.65 (s, 2H), 7.42 (d, J = 7.89 Hz, 2H), 3.09 (t, J = 6.98 Hz, 2H), 1.90 (t, J = 8.22 Hz, 2H), 1.67~1.62 (m, 2H), 1.20~1.15 (m, 2H), 1.10~1.06 (m, 2H), 0.60~0.56 (m, 2H).

General Procedure for Suzuki-Miyaura Cross-Coupling Polymerization:[4–6] To a 50 mL Schlenk tube charged with a mixture of 10 mL toluene, 6 mL aqueous 2 M K_2CO_3(aq.) and 1-2 drops of Aliquat 336, 9,9'-Dihexyl-2,7-Diiodofluorene or other equimolar amount of corresponding monomer (0.3 mmol) and 9,9'-dioctylfluorene-2,7-bis(trimethyleneboronate) (0.167 g, 0.3 mmol) were added, then the mixture was degassed via sonicating under continuous bubbling with Ar for 30 min. $Pd(PPh_3)_4$ (~ 1.0 mol %) was added, and the resulting mixture was stirred at 90°C under Ar for 4~48 h (Mn was monitored by GPC to obtain the desired molecular weight polymer). After the mixture was cooled to room temperature, it was poured into methanol. The precipitated material was recovered by filtration. The resulting solid material was washed for 24 h using about 250 mL methanol and 250 mL acetone, separately, to remove oligomers and catalyst residues.

***PFO-FH*:** beige powder, 80 % yield, ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ: 7.88~7.80 (b, 4H), 7.66~7.56 (b, 8H), 2.12~1.98 (b, 4H), 1.26~1.04 (b, 40 H), 0.92~0.76 (b, 18H). UV-vis (THF): λ_{max} = 385 nm, GPC: Mn=9.6 KDa, PDI=3.

***PFO-FHBr*:** beige powder, 76 % yield, ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ: 7.90~7.80 (b, 4H), 7.76~7.60 (b, 8H), 3.12~3.04 (b, 4H), 2.26~2.04 (b, 12H), 1.76~1.64 (b, 6H), 1.32~1.06 (b, 54H), 0.94~0.76 (b, 24H). UV-vis (THF): λ_{max} = 386 nm, GPC: Mn=10.2 KDa, PDI=3.4.

PFO-FHI**:** beige powder, 52 % yield, ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ: 7.90~7.80 (b, 4H), 7.76~7.60 (b, 8H), 3.10~3.02 (b, 4H), 2.20~2.08 (b, 4H), 1.70~1.64 (b, 4H), 1.32~1.08 (b, 38H), 0.94~0.78 (b, 18H). UV-vis (THF): λ_{max} = 384 nm, Mn=9.8 KDa, PDI=3.0.

Preparation of the polymer and SWNT supramolecular complexes: [5,6] A mixture of SWNTs (2.5 mg) and polymer (7.5 mg) in 15 mL THF was sonicated for 60 min using a Branson Ultrasonics B2510 bath. The homogeneous solution was then filtered through a 200 nm-pore-diameter Teflon membrane and was repeatedly washed with THF in order to remove excess free polymer (this was determined by disappearance of fluorescence of the filtrate). Then the polymer-SWNT complex was dispersed in THF again by sonicating for another 45 minutes, and undissolved parts were removed using centrifugation at 8300 g for 35 min. The dark, clear supernatant solution was found to remain stable, without visible precipitation of nanotubes, for more than one year.

Dispersion of SWNTs in SDBS/D_2O.[4,5] A SWNT sample (5 mg) was added to a solution of sodium dodecylbenzene sulfonate (SDBS) (350 mg) in 35 mL D_2O. The resulting mixture was sonicated for 60 min using a bath sonicator, and centrifugation was done with an ultracentrifuge at 65,000 g for 4 h. The supernatant was carefully pipetted out of the centrifuge tube and used for subsequent studies.

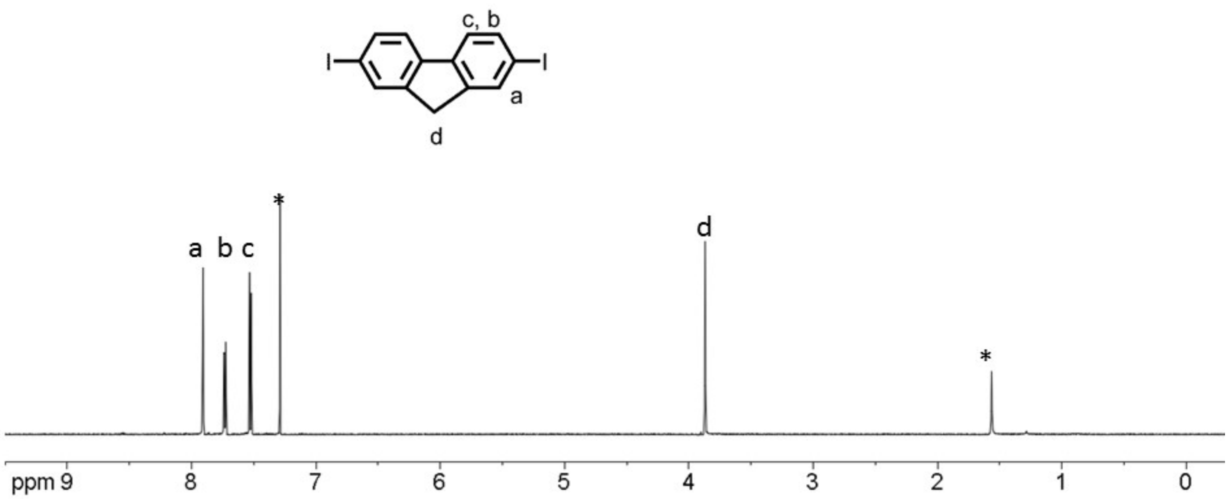

Figure S1. ^{1}H NMR spectra of 2,7-diiodofluorene in $CDCl_3$. Signals marked with * are due to solvent impurities.

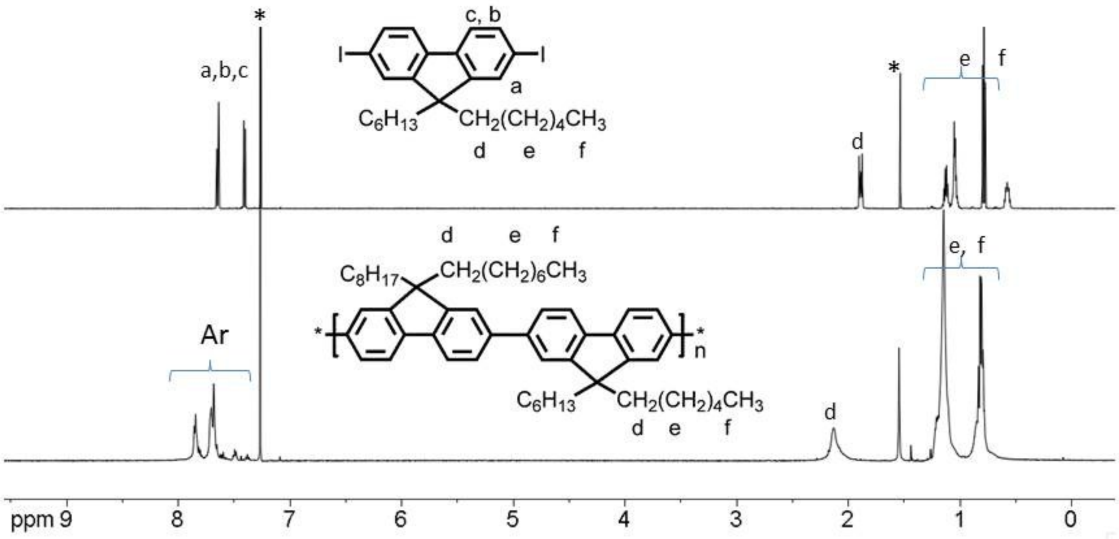

Figure S2. ^{1}H NMR spectra of the monomer **2** and its copolymer PFO-FH in $CDCl_3$. Signals marked with * are due to solvent impurities.

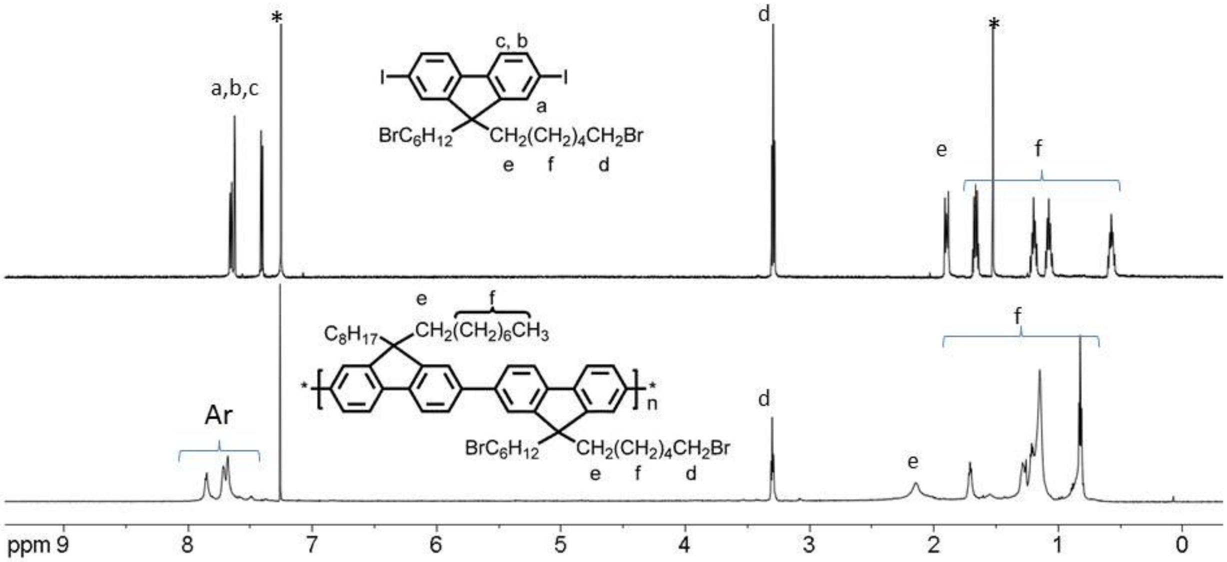

Figure S3. ^{1}H NMR spectra of the monomer **3** and its copolymer PFO-FHBr in $CDCl_3$. Signals marked with * are due to solvent impurities.

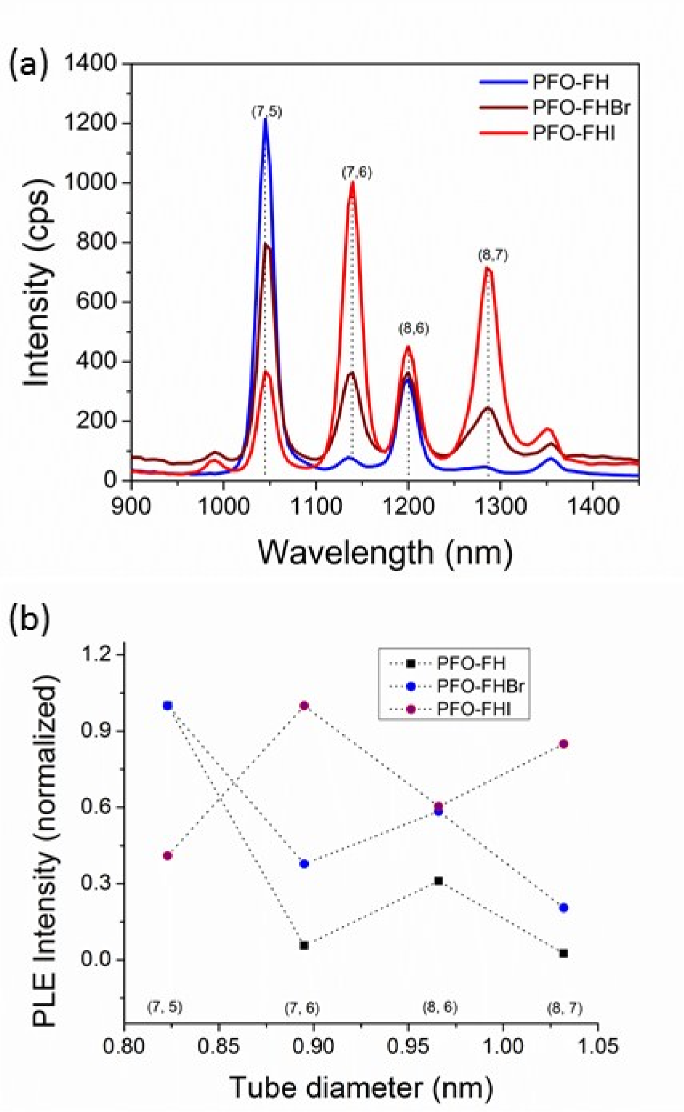

Figure S4. (a) Comparison of fluorescence signal intensity using an excitation wavelength of 550 nm for the **PFO-FHI**-SWNT, **PFO-FHBr**-SWNT, and **PFO-FH**-SWNT dispersions in THF, (b) converting the plot (a) to photoluminescence emission (PLE) intensity to tube diameter d(nm); trends of selectivity.

References

(1) Huang, Y.-Q.; Fan, Q.-L.; Zhang, G.-W.; Chen, Y.; Lu, X.-M.; Huang, W. *Polymer (Guildf).* **2006**, *47* (15), 5233–5238.

(2) Zeng, W.; Liu, S.; Zou, H.; Wang, L.; Beuerman, R.; Cao, D. *J. Polym. Sci. Part a-Polymer Chem.* **2010**, *48* (19), 4168–4177.

(3) Leclerc, M. *J. Polym. Sci. Part A Polym. Chem.* **2001**, *39* (17), 2867–2873.

(4) Stay, D.; Lonergan, M. C. *Macromolecules* **2013**, *46* (11), 4361–4369.

(5) Imin, P.; Imit, M.; Adronov, A. *Macromolecules* **2011**, *44* (23), 9138–9145.

(6) Imin, P.; Imit, M.; Adronov, A. *Macromolecules* **2012**, *45* (12), 5045–5050.