Supporting information

Anthanthrene-Based Conjugated Polymers for the Dispersion of Single-Walled Carbon Nanotubes

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Apparatus:

NMR spectra were recorded using a Varian Inova AS400 spectrometer (Varian, Palo Alto, USA) at 400 MHz or an Agilent DD2 500 MHz. Signals are reported as m (multiplet), s (singlet), d (doublet), t (triplet), dd (doublet of doublets), dt (doublet of triplets) and coupling constants are reported in hertz (Hz). The chemical shifts are reported in ppm (δ) relative to residual solvent peak. High-resolution mass spectra (HRMS) were recorded using an Agilent 6210 time-of-flight (TOF) LCMS apparatus equipped with an APPI ion source (Agilent Technologies, Toronto, Canada) or ESI. Number-average (Mn) and weight-average (Mw) molecular weights were obtained by size exclusion chromatography (SEC) using a high temperature Varian Polymer Laboratories GPC220 equipped with an RI detector. The column set consists of 2 PL gel Mixed C (300 x 7.5 mm) columns and a PL gel Mixed C guard column. The flow rate was mixed at 1 mL min-1 using 1,2,4- trichlorobenzene (TCB) (with 0.0125% BHT w/v) as the eluent. The temperature of the system was set to 110 ° C. All the samples were prepared at a nominal concentration of 1.0 mg mL-1 in TCB. Dissolution was performed using a Varian Polymer Laboratories PL-SP 260VC sample preparation system. The sample vials were held at 110 °C with shaking for 1 h for complete dissolution. The solutions were filtered through a 2 mm porous stainless-steel filter used with a 0.40 mm glass filter into a 2 mL chromatography vial. The calibration method used to generate the reported data was the classical polystyrene method using narrow polystyrene standards Easi-Vials PS-M from Varian Polymer Laboratories which were dissolved in TCB. UVvisible absorption and photoluminescence spectra of monomers were recorded on a

Varian diode-array spectrophotometer (model Cary 500) and Varian Cary Eclipse Fluorescence Spectrofluorimeter respectively, using 10-mm path length quartz cells. UVvisible absorption spectra of SWNTs dispersions were recorded using a Varian diodearray spectrophotometer (Cary 5000 model).

General Methods

Chemical reagents were purchased from Sigma–Aldrich Co. Canada, Alfa Aesar Co. or TCI America Co. and were used as received. 4,10-Dibromoanthanthrone was a courtesy from Heubach GmbH as Monolite Red 316801 product. Solvents used for organic synthesis were purified using a Solvent Purifier System (Vacuum Atmosphere Co., Hawthorne, USA). 2,2'-(9,9-didodecyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) and 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)-9H-carbazole were purchased from Brillant Matters, Canada. 2,2'-(1,5a1-dihydropyrene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) was synthesized according to literature procedure.¹

Carbon nanotubes dispersion procedure

HiPCo CNTs were purchased from NanoIntegris and RN220 CNTs from Raymor Industries Inc. Dispersions of CNTs were prepared with a 20 mL vial charged with 7.5 mg of polymer, 5.0 mg of CNTs and 10 mL of solvent (toluene or THF). The resulting suspensions were pre-sonicated at room temperature for 1 minutes in a standard Branson® 2510 sonicator bath, followed by ultrasonication with a Q700 sonicator from Qsonica, equipped with a 6.4 mm microtip. The suspension is sonicated at 40% of its maximum power for 30 minutes in an ice-water bath. The dispersion was then centrifuged at 13000 rpm for 20 minutes before the supernatant was carefully collected using a pipette. UV-Vis-NIR analysis of the resulting solution was performed on an Agilent Cary 5000 UV-Vis-NIR spectrophotometer. The 2D photoluminescence (PL) spectra were measured with a Horiba Jobin Yvon Nanolog spectrofluorimeter equipped with a 450 W xenon lamp as a source, a double monochromator for excitation, a iHR320 imaging spectrometer and a NIR (950-1700 nm) Hamamatsu photomultiplier tube (PMT) for the detection. Raman analysis are conducted with a confocal Raman Senterra II (Bruker Optics Inc. Milton, ON) with x50 lens.

Synthesis



4,10-Dibromo-6,12-bis (octyldodecyloxy)anthanthrene: A flask was charged with 4,10-Dibromo-anthanthrone (5.00 g, 10.8 mmol), aqueous NaOH (0.1M, 53.9 mmol), Aliquat 336 (5.22 g, 12.9 mmol), Na₂S₂O₄ (4.88 g, 28.0 mmol), and 9-(bromomethyl)nonadecane (31.2 g, 86.2 mmol) under argon. The mixture was degassed with a flow of argon for 10 min and heated at 60°C for 3 h until the mixture turned yellow. The water was decanted

and MeOH (30 mL) was added, resulting in the precipitation of a yellow solid. The crude product was filtered and washed with MeOH. Purification by silica gel column chromatography (CH₂Cl₂/hexanes 50:50 v/v) and two successive recrystallizations in hexanes afforded the final compound as a yellow solid (4.14 g, 37%). ¹H NMR (400 MHz, CDCl₃): δ 8.63 (d, *J* = 8.2 Hz, 2H), 8.59 (s, 2H), 8.52 (d, *J* = 7.5 Hz, 2H), 8.10 (t, *J* = 7.9 Hz, 2H), 4.11 (d, *J* = 5.2 Hz, 4H), 2.14 – 2.03 (m, 2H), 1.91 – 1.77 (m, 4H), 1.75 – 1.62 (m, 4H), 1.60 – 1.20 (m, 56H), 0.98 – 0.83 (m, 12H. ¹³C NMR (100 MHz, CDCl₃): δ 148.70, 130.07, 126.04, 125.79, 125.24, 124.30, 123.24, 121.67, 121.55, 118.70, 79.08, 39.74, 32.03, 31.38, 30.28, 29.88, 29.84, 29.77, 29.51, 29.46, 27.25, 22.78, 22.76. HRMS (ESI+): C₆₂H₉Br₂O₂ (M + H)⁺ 1024.53374, found 1024.53076.



Figure S1. ¹H NMR spectra of 4,10-Dibromo-6,12-bis (octyldodecyloxy)anthanthrene



Figure S2. ¹³C NMR spectra of 4,10-Dibromo-6,12-bis (octyldodecyloxy)anthanthrene

Polymerization procedure: A tube-shaped flask was charged with the bisborylated compound (1.00 eq), 4,10-dibromo-6,12-bis(octyldodecyloxy)anthanthrene (200 mg, 195 μ mol, 1.00 eq), tetrakis(triphenylphosphine)palladium(0) (11.5 mg, 0.05 eq) and Aliquat 336 (1 drop) under inert atmosphere. The solvents were added, and the resulting solution was degassed for 40 minutes. Toluene (2.00 ml, 0.1 M) and 2 M K₂CO₃ aqueous solution (400 μ l, 4.10 eq) were added before sealing the tube. The mixture was heated at 80 °C for three days. Once cooled to room temperature, the polymer was precipitated in cold MeOH and directly filtered in an extraction thimble. The residue was purified by Soxhlet extraction with methanol and acetone and the polymer was recovered using chloroform

and chlorobenzene (if needed). The solvent was evaporated and the solid was precipitated again in MeOH, filtered and dried under vacuum for 24 h to obtain the desired polymer.

Anth-P:



1,4-bis(1,3,2-dioxaborinan-2-yl)benzene (48.8 mg, 195 μ mol, 1.00 eq), 4,10-dibromo-6,12-bis(octyldodecyloxy)anthanthrene (200 mg, 195 μ mol, 1.00 eq), tetrakis(triphenylphosphine)palladium(0) (11.5 mg, 0.05 eq), Aliquat 336 (1 drop), toluene (2.00 ml, 0.1 M) and 2 M K₂CO₃ solution (400 μ l, 4.10 eq). Yield (184 mg, 98%), ($\overline{Mn} = 9.7$ kDa, $\overline{Mw} = 16.3$ kDa, D = 1.6)



Figure S3. GPC chromatogram of Anth-P



Figure S4. ¹H NMR spectra of Anth-P

Anth-Py:

1,3,2-Dioxaborolane, 2,2'-(2,7-pyrenediyl)bis[4,4,5,5-tetramethyl-] (90.6 mg, 195 µmol, 1.00 eq), 4,10-dibromo-6,12-bis(octyldodecyloxy)anthanthrene (200 mg, 195 µmol, 1.00 eq), tetrakis(triphenylphosphine)palladium(0) (11.5 mg, 0.05 eq), Aliquat 336 (1 drop), toluene (2.00 ml, 0.1 M) and 2 M K₂CO₃ solution (400 µl, 4.10 eq). Yield (47 mg in chloroform fraction, 143 mg in chlorobenzene fraction, 91%), (CHCl₃ fraction: $\overline{Mn} = 5.7$ kDa, $\overline{Mw} = 6.6$ kDa, PDI = 1.5; Chlorobenzene fraction: $\overline{Mn} = 14.8$ kDa, $\overline{Mw} = 22.4$ kDa, D = 1.5)



Figure S5. GPC chromatogram of Anth-Py



Figure S6. ¹H NMR spectra of Anth-Py

Anth-F:



2,2'-(9,9-didodecyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (150 mg, 195 µmol, 1.00 eq), 4,10-dibromo-6,12-bis (octyldodecyloxy)anthanthrene (200 mg, 195 µmol, 1.00 eq), tetrakis(triphenylphosphine)palladium(0) (11.5 mg, 0.05 eq), Aliquat 336 (1 drop), toluene (2.00 ml, 0.1 M) and 2 M K₂CO₃ solution (400 µl, 4.10 eq). Yield (222 mg, 84%), ($\bar{M}n = 17.2$ kDa, $\bar{M}w = 29.6$ kDa, D = 1.7)



Figure S7. GPC chromatogram of Anth-F



Figure S8. ¹H NMR spectra of Anth-F

Anth-C:



9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (131 mg, 195 µmol, 1.00 eq), 4,10-dibromo-6,12-bis(octyldodecyloxy)anthanthrene (200 mg, 195 µmol, 1.00 eq), tetrakis(triphenylphosphine)palladium(0) (11.5 mg, 0.05 eq), Aliquat 336 (1 drop), toluene (2.00 ml, 0.1 M) and 2 M K₂CO₃ solution (400 µl, 4.10 eq). Yield (234 mg, 95%), ($\overline{Mn} = 15.1$ kDa, $\overline{Mw} = 26.3$ kDa, D = 1.7)



Figure S9. GPC chromatogram of Anth-C



Figure S10. ¹H NMR spectra of Anth-C

Sample Name	Max. RT	Start RT	End RT	Мр	Mn	Mw	PD
Anth-P	14,4500	13,4333	16,1667	16331	9713	15619	1,6081
Anth-Py	14,7500	12,8833	15,4667	11634	14770	22440	1,5193
Anth-F	14,0167	12,7000	15,6167	26661	17218	29644	1,7217
Anth-C	14,1500	12,8500	15,8167	22927	15077	26325	1,7460





Figure S11. Thermogravimetric analysis (TGA) curves (20°C.min⁻¹) of Anth-P, Anth-Py, Anth-F and Anth-C

Figures



Figure S12. Full Raman spectra showing the extended spectra using the A) 532, B) 633, and C) 785 nm excitation wavelength of Anth-F:SWNT dispersion in toluene and THF.

TGA measurements and Calculation of the polymer:SWNT

mass ratio



Figure S13. Thermogravimetric analysis (TGA) curves under nitrogen (20°C.min⁻¹)of Anth-Py and Anth-Py:Plasma Torch complex

 $\Psi_{\rm P}$ is defined as the measured mass loss of the polymer alone and $\Psi_{\rm C}$ is defined as the measured mass loss for the polymer:SWNT complex after filtration. SWNTs don't decompose under inert atmosphere, polymer fraction $f_{\rm P}$ can be expressed as:

$$f_P = \frac{\Psi_C}{\Psi_P}$$

And SWNTs fraction $f_{\rm C}$ can then be calculated as:

$$f_{\mathcal{C}} = 1 - f_{\mathcal{P}}$$

At 600°C, 54% of mass loss was observed for Anth-Py and 31% for Anth-Py:Plasma Torch complex which give polymer and SWNTs ratios of :

$$f_P = \frac{\Psi_C}{\Psi_P} = \frac{0.31}{0.54} = 0.57$$
 $f_C = 1 - 0.57 = 0.43$



Figure S14. Photoluminescence map of (A) **Anth-P:Plasma Torch , (B) Anth-Py:Plasma Torch , (C) Anth-F:Plasma Torch and (D) Anth-C:Plasma Torch** dispersions.

Anth-F:HiPCO dispersion					
(n,m)	Diameter (nm)				
7,6	0.89				
8,6	0.96				
9,4	0.92				
9,5	0.98				
8,4	0.84				
8,7	1.03				
7,5	0.83				
6,5	0.76				
10,3	0.94				
10,5	1.05				
11,1	0.92				
11,3	1.01				

Table S2- Summary of the SWNT chirality and the corresponding diameter for **Anth-F** dispersion with HiPCO SWNTs obtained with PLE map attribution corresponding to the Kataura plot values from literature.²

Anth-P:PlasmaTorch			Anth-F:PlasmaTorch			Anth-C:PlasmaTorch		
(n,m)	Diameter	Chiral	(n,m)	Diameter	Chiral	(n,m)	Diameter	Chiral
	(nm)	angle (°)		(nm)	angle (°)		(nm)	angle (°)
13,5	1.28	15.61	13,5	1.28	15.61	13,5	1.28	15.61
14,3	1.25	9.52	14,3	1.25	9.52	12,7	1.32	21.36
12,7	1.32	21.36	15,1	1.23	3.2	10,9	1.31	28.26
10,9	1.31	28.26				10,8	1.24	26.33
10,8	1.24	26.33						
11,6	1.19	20.36						
11,7	1.24	22.69						
9,8	1.17	28.05						

Table S3- Summary of the SWNT chirality and the corresponding diameter for **Anth-P**, **Anth-F** and **Anth-C** dispersion with PlasmaTorch SWNTs obtained with PLE map attribution corresponding to the Kataura plot values from literature.²

References

- (1) Liu, Z.; Wang, Y.; Chen, Y.; Liu, J.; Fang, Q.; Kleeberg, C.; Marder, T. B. Ir-Catalyzed Direct Borylation at the 4-Position of Pyrene. *J. Org. Chem.* **2012**, 77 (16), 7124–7128.
- (2) Strano, M. S.; Doorn, S. K.; Haroz, E. H.; Kittrell, C.; Hauge, R. H.; Smalley, R. E. Assignment of (n, m) Raman and Optical Features of Metallic Single-Walled Carbon Nanotubes. *Nano Lett.* **2003**, *3* (8), 1091–1096.