Enrichment of Metallic Carbon Nanotubes Using a Two-Polymer Extraction Method

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Supporting Information

Experimental

General

Raw HiPCO SWNTs were purchased from NanoIntegris (batch #HR27-104) and used without further purification. Plasma-torch SWNTs were purchased from Raymor Industries Inc. (RNB-661-120-X466) and were also used without further purification. All reagents were purchased from commercial chemical suppliers and used as received. Flash chromatography was performed using an Intelliflash280 by 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. $^1$H-NMR and $^{13}$C-NMR spectra were recorded on Bruker Avance 600 MHz and 700 MHz spectrometers 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 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 Beckman Coulter Allegra X-22 centrifuge (raw HiPCO SWNT dispersions) or a Sorvall Legend X1R centrifuge (semi-purified plasma torch SWNT dispersions). UV-Vis-NIR absorption spectra were recorded on a Cary 5000 spectrometer in dual beam mode, using matched 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 (PL) maps were obtained at 25 °C with 5 nm intervals for both the excitation and emission. Raman spectra were collected with a Renishaw InVia Laser Raman spectrometer, using three different lasers: a 25 mW argon ion laser (514 nm, 1800L/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 for both 514 and 633 nm excitations was set to 5% for all SWNT dispersions. For spectra obtained at 785 nm, laser intensity was set to 1% for the SWNT sample and for the polymer-SWNT samples.

**Synthetic Procedures**

**Scheme S1.** Synthesis of N-(2'-decyltetradecane)-2,7-dibromocarbazole.

1-bromo-2-decyl-4-tetradecane (1) (adapted from reference 1)

A 100 mL round bottom flask equipped with a magnetic stir bar was charged with 2-decyl-1-tetradecanol (20 g, 56.4 mmol), triphenylphosphine (17.8 g, 67.7 mmol), and CH₂Cl₂ (30 mL).
The mixture was cooled to 0 °C and then the CBr₄ (22.4 g, 67.7 mmol) powder was added portion-wise. The reaction mixture was warmed to RT and stirred for 2 h. The crude mixture was filtered through a silica plug and hexanes was used to elute the product. The filtrate was concentrated in vacuo to afford 1 as a colourless oil (20.0 g, 85%). ¹H NMR (600 MHz; CDCl₃): δ 3.45 (d, 2H), 1.59 (m, 1H), 1.37-1.26 (m, 40H), 0.88 (t, 6H).

2-nitro-4,4'-dibromobiphenyl (2) (adapted from reference 1)

A 250 mL round bottom flask equipped with a magnetic stir bar was charged with 4,4'-dibromobiphenyl (10 g, 32.0 mmol), glacial acetic acid (120 mL), and conc. HNO₃ (40 mL). The reaction mixture was heated to reflux for 16 h and then precipitated into ice water and filtered. The slurry was filtered to obtain a yellow solid, which was then recrystallized in EtOH to afford 2 as a yellow solid (10.1 g, 88%). ¹H NMR (600 MHz; CDCl₃): δ 8.03 (d, J = 2.0, 1H), 7.76 (dd, J = 8.2, 2.0, 1H), 7.58-7.55 (m, 2H), 7.29 (d, J = 8.2, 1H), 7.17-7.15 (m, 2H).

9H-2,7-dibromocarbazole (3) (adapted from reference 1)

A 200 mL round bottom flask equipped with a magnetic stir bar and condenser was charged with 2-nitro-4,4'-dibromobiphenyl (14.0 g, 39.2 mmol), triphenylphosphine (25.7 g, 98.0 mmol), and tetralin (84 mL). The reaction mixture was heated to reflux under an inert atmosphere for 1 h. Solvent was removed by distillation (1 mbar, 60-70 °C). The crude residue was purified by flash chromatography (100 g column, 20 to 50% CH₂Cl₂ in hexanes over 10 CV) to afford 3 as a tan solid (10.3 g, 81%). ¹H NMR (600 MHz; CDCl₃): δ 8.08-8.06 (s, 1H), 7.88 (d, 2H), 7.58 (d, 2H), 7.37-7.34 (dd, 2H).

N-(2'-decyltetradecane)-2,7-dibromocarbazole (4) (adapted from reference 1)

A 200 mL round-bottom flask equipped with a magnetic stir bar was charged with 1 (5.65 g, 13.5 mmol), toluene (17 mL), and sat. KOH (34 mL). The biphasic mixture was sparged with nitrogen
for 1 h, and then 3 (4.0 g, 12.3 mmol) and nBu₄NBr (783 mg, 2.46 mmol) were added. The reaction mixture was heated to 80 °C under an inert atmosphere for 48 h. The organic phase was isolated and concentrated in vacuo to afford a light brown oil that solidified overnight. The solid was dissolved in hexanes (~50 mL) and filtered through a silica plug, eluting the product using hexanes. The crude residue was dissolved in hot hexanes (~50 mL) and cooled to -20 °C to afford 4 as a colourless crystalline solid (6.34 g, 71%). ¹H NMR (600 MHz; CDCl₃): δ 7.88 (d, J = 8.2, 2H), 7.50 (d, J = 1.5, 2H), 7.33 (dd, J = 8.3, 1.6, 2H), 4.05 (d, J = 7.6, 2H), 2.08-2.07 (m, 1H), 1.37-1.21 (m, 40H), 0.88 (t, J = 7.1, 6H).

2,7-dibromofluorene (5) (adapted from reference 2)

A 250 mL round bottom flask equipped with a magnetic stir bar was charged with fluorene (8.3 g, 50 mmol), NBS (17.4 g, 100 mmol), and acetic acid (100 mL). To the reaction mixture, conc. HBr (2.5 mL) was added dropwise. The reaction mixture was stirred at RT for 3 h, and then dH₂O (50 mL) was added and the resulting suspension was filtered to obtain an orange solid. The crude product was recrystallized from a 2.5:1 mixture of EtOH:acetone (~425 mL total volume), then the mother liquor was concentrated in vacuo and recrystallized using the same solvent mixture (~300 mL total volume). The crops were combined to afford 5 as a white solid (8.8 g, 54%). ¹H
NMR (600 MHz; CDCl₃): δ = 7.67 (d, J = 0.9 Hz, 2H), 7.61 (d, J = 8.1 Hz, 2H), 7.52-7.50 (m, 2H), 3.88 (s, 2H).

2,7-dibromo-9,9-didodecylfluorene (adapted from reference 3) (6)

A 300 mL round bottom flask equipped with a magnetic stir bar was charged with 1-bromododecane (9.62 g, 38.6 mmol), toluene (30 mL), and sat. KOH (60 mL). The biphasic mixture was sparged with nitrogen for 1 h, and then 5 (5.0 g, 15.4 mmol) and nBu₄NBr (993 mg, 3.1 mmol) were added. The mixture was stirred at 60 °C under an inert atmosphere for 6 h. The organic phase was isolated and concentrated in vacuo to afford a light brown oil that solidified overnight. The solid was dissolved in hexanes (~50 mL) and filtered through a silica plug, eluting the product using hexanes. The product was evaporated to dryness and transferred to a 50 mL round bottom flask equipped with a magnetic stir bar and condenser, then excess alkyl bromide was removed by distillation (0.2 mbar, 140 °C). The residue was then recrystallized in hexanes (~50 mL) to afford 6 as a colourless crystalline solid (7.44 g, 73%). ¹H NMR (600 MHz; CDCl₃): δ 7.51 (s, 2H), 7.46- 7.44 (m, 4H), 1.92-1.89 (m, 4H), 1.28-1.04 (m, 36H), 0.87 (t, J = 7.1 Hz, 6H), 0.57 (s, 4H).

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

A 300 mL round bottom flask equipped with a magnetic stir bar was charged with 6 (7 g, 10.6 mmol), B₂Pin₂ (5.92 g, 23.3 mmol), KOAc (3.12 g, 31.8 mmol), DMSO (25 mL), and dioxane (75 mL) and sparged with nitrogen for 1 h. Pd(dppf)₂Cl₂ (260 mg, 318 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 CH₂Cl₂. The organic extracts were combined and concentrated in vacuo, then the extract was passed through a single celite/silica plug. The plug was washed thoroughly
with CH₂Cl₂ and the filtrate was concentrated \textit{in vacuo}. The crude product was purified by flash chromatography (100% CH₂Cl₂) to obtain a yellow solid. The solid was recrystallized from a 1.25:1 mixture of MeOH:acetone (~450 mL total volume) to afford 7 as a white solid (4.88 g, 63%). \(^1\)H NMR (700 MHz; CDCl₃): \(\delta\) 7.80 (dd, \(J = 7.5, 0.8\) Hz, 2H), 7.74 (s, 2H), 7.72 (d, \(J = 7.6\) Hz, 2H), 1.99 (dt, \(J = 7.9, 4.1\) Hz, 4H), 1.39 (s, 24H), 1.26-1.00 (m, 36H), 0.86 (t, \(J = 7.2\) Hz, 6H), 0.55 (s, 4H).

\textbf{Scheme S3.} Syntheses of P1 and P2.

Poly(9,9'-didodecylfluorene-\textit{co-N}(2'-decyltetradecane)-carbazole) (P1) (adapted from reference 4)

A 25 mL Schlenk tube was equipped with a magnetic stir bar and charged with 4 (200 mg, 0.30 mmol), 7 (226 mg, 0.30 mmol), toluene (2.5 mL), and 3M K₃PO₄ (2.5 mL) and the reaction mixture was degassed via three freeze-pump-thaw cycles. The biphasic mixture was frozen under liquid nitrogen, then (\((o\text{-tol})_3\)P)₂Pd (10.8 mg, 7.5 \(\mu\)mol) was added under a positive pressure of nitrogen. The Schlenk tube was evacuated and backfilled with nitrogen three times, and the reaction mixture was vigorously stirred at 85 °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 (1:1 composition). The plug was thoroughly washed with THF and the filtrate was concentrated in vacuo. The crude polymer was precipitated into MeOH (~150 mL) and then filtered to afford P1 as a yellow solid (272 mg, 90%). ¹H NMR (600 MHz; CDCl₃): 8.21 (m, 2H), 7.86 (m, 2H), 7.72 (m, 2H), 7.61 (m, 2H), 4.34 (m, 2H), 2.31 (m, 1H), 2.10 (m, 4H), 1.28 (m, 80H), 0.84 (m, 12H).

Poly(9,9’-didodecylfluorene-co-pyridine) (PF-Py) (adapted from reference 3)
A Schlenk tube equipped with a magnetic stir bar was charged with 7 (700 mg, 0.93 mmol), 2,5-dibromopyridine (219.7 mg, 0.93 mmol), toluene (6.75 mL), and 3M K₃PO₄(aq) (7.4 mL) and the mixture was degassed by three freeze-pump-thaw cycles. The biphasic mixture was frozen under liquid nitrogen and [(o-tol)₂P]₂Pd (33.2 mg, 46 µmol) was added under a positive pressure of nitrogen. The Schlenk tube was evacuated and backfilled with nitrogen four times and then the reaction mixture was vigorously stirred at 85 °C for 3 days. The phases were allowed to separate and the organic layer was isolated then filtered through a single celite and neutral alumina plug (1:1 composition). The plug was thoroughly washed with THF and the filtrate was concentrated in vacuo. The crude polymer was precipitated into MeOH (200 mL) and then filtered to afford PF-Py as a yellow solid (460 mg, 86%). ¹H NMR (700 MHz; CDCl₃): δ 9.07 (m), 8.60-8.59 (m), 8.14-7.66 (m), 2.15 (m), 1.27-0.82 (m).

Methylated PF-Py (P2) (adapted from reference 3)
A Schlenk tube equipped with a magnetic stir bar was charged with PF-Py (50 mg, 87 µmol), MeI (123 mg, 870 µmol, 540 µL), and CHCl₃ (5 mL) and the reaction mixture was heated to reflux for 12 h. The reaction mixture was then transferred to a pre-weighed glass vial and the solvent was removed by passing a stream of nitrogen over the vial, followed by drying the sample under high
vacuum overnight. Polymer **P2** was isolated as a red solid (62 mg, 98%). $^1$H NMR (600 MHz; CDCl$_3$): $\delta$ 9.06-7.43 (m), 4.84 (m), 4.72 (m), 2.27-2.09 (m), 1.25-0.85 (m).
**Plasma-torch SWNT dispersions.** 5 mg of plasma-torch SWNTs were added to a solution of 5 mg of P1 dissolved in 10 mL of toluene. The sample was sonicated for 1.5 h in an ice-chilled bath sonicator, followed by centrifugation at 15,000g for 20 min. The supernatant was removed from the centrifuge tube, filtered through a Teflon membrane with 0.2 µm pore-diameter, and thoroughly rinsed with solvent until the filtrate did not fluoresce at 365 nm. The polymer-SWNT thin film was then re-dispersed in 10 mL of toluene using an ice-chilled bath sonicator for 30 min. Meanwhile, the residue in the centrifuge tube was sonicated in 10 mL of toluene for 10 min, then filtered through a 0.2 µm pore-diameter Teflon membrane and washed to remove unbound polymer. The residue could then be re-dispersed using either 5 mg of P1 in toluene (to further extract sc-SWNTs) or 5 mg of P2 in THF (to disperse m-SWNTs). It should be noted that P2 is not soluble in toluene, necessitating the use of THF. For this study, we use “ExPy” nomenclature, where x indicates the number of extractions (0 – 4) and y indicates the polymer used to re-disperse the residue (1 or 2). Using this process, we produced nine polymer-SWNT dispersions, which were evaluated for sc- and m-SWNT content based on the number of extractions and the final polymer dispersant.

**Figure S1.** Unnormalized UV-Vis-NIR absorption spectra for the polymer-SWNT extraction study using HiPCO SWNTs with A) P1 or B) P2. Polymer-SWNT dispersions were diluted 3-fold.
Figure S2. UV-Vis-NIR absorption data directly comparing P1- and P2-SWNT dispersions after A) 0 extractions, B) 1 extraction, C) 2 extractions, and D) 3 extractions. Spectra are normalized to the local minimum at ~905 nm to highlight relative m-/sc-SWNT content.

Figure S3. Photograph of polymer-SWNT dispersions produced using HiPCO SWNTs (left to right): E0P1, E3P1, E1P2, and E4P2.
Figure S4. Raman spectra of the RBM region for HiPCO polymer-SWNT samples after sc-SWNT extractions (0 – 4 times) at $\lambda_{ex} = 785$ nm for samples prepared using A) P1 or B) P2 as the final dispersant and at $\lambda_{ex} = 514$ nm for samples prepared using C) P1 or D) P2 as the final dispersant. Pink boxes represent signals arising from m-SWNTs, while the grey boxes represent signals arising from sc-SWNTs.
Figure S5. Full Raman spectra for HiPCO polymer-SWNT samples after sc-SWNT extractions (0 – 4 times) dispersed using P1 as the final dispersant at A) $\lambda_{ex} = 514$ nm, B) $\lambda_{ex} = 633$ nm, or C) $\lambda_{ex} = 785$ nm and P2 as the final dispersant at D) $\lambda_{ex} = 514$ nm, E) $\lambda_{ex} = 633$ nm, or F) $\lambda_{ex} = 785$ nm.

Figure S6. UV-Vis-NIR absorption spectra for the polymer-SWNT dispersions used for photoluminescence mapping. Samples were concentration-matched at the peak centered at 1135 nm.
Figure S7. Photoluminescence maps of A) E0P1, B) E1P1, C) E2P1, and D) E3P1 polymer-SWNT dispersions.
Figure S8. Photoluminescence maps of A) E1P2, B) E2P2, C) E3P2, and D) E4P2 polymer-SWNT dispersions.

Figure S9. UV-Vis-NIR absorption spectra of polymer-SWNT dispersions concentration-matched at 1135 nm and used for conductivity studies.
Figure S10. Photograph of polymer-SWNT dispersions produced using plasma-torch SWNTs (left to right): E0P1, E3P1, E1P2, and E4P2.

Figure S11. Unnormalized UV-Vis-NIR absorption spectra for the polymer-SWNT extraction study using plasma-torch SWNTs with A) P1 or B) P2.
Figure S12. Raman spectra for plasma-torch polymer-SWNT samples after sc-SWNT extractions (0 – 4 times) at $\lambda_{\text{ex}} = 633$ nm for samples prepared using A) P1 or B) P2 as the final dispersant and at $\lambda_{\text{ex}} = 785$ nm for samples prepared using C) P1 or D) P2 as the final dispersant. Pink boxes represent signals arising from m-SWNTs, while the grey boxes represent signals arising from sc-SWNTs.
**Figure S13.** Full Raman spectra for plasma-torch polymer-SWNT samples after sc-SWNT extractions (0 – 4 times) at $\lambda_{ex} = 633$ nm for samples prepared using A) P1 or B) P2 as the final dispersant and at $\lambda_{ex} = 785$ nm for samples prepared using C) P1 or D) P2 as the final dispersant.

**Figure S14.** UV-Vis-NIR absorption data for plasma-torch polymer-SWNT samples using A) P1 or B) P2 as the final dispersant. M$_{11}$ (600-750 nm) and S$_{22}$ (750-1150 nm) regions used for integrations are indicated with the black lines.
Table S1. Relative amounts of m- and sc-SWNTs calculated from integrations of the $M_{11}$ and $S_{22}$ regions from the UV-Vis-NIR spectra.

|     | P1  | %$M_{11}$ | %$S_{22}$ | P2  | %$M_{11}$ | %$S_{22}$ |
|-----|-----|-----------|-----------|-----|-----------|-----------|
| E0  | 5   | 95        |           | E0  | 35        | 65        |
| E1  | 10  | 90        |           | E1  | 50        | 50        |
| E2  | 10  | 90        |           | E2  | 55        | 45        |
| E3  | 10  | 90        |           | E3  | 65        | 35        |
|     | -   | -         |           | E4  | 70        | 30        |

Figure S15. $^1$H NMR spectrum of P1 in CDCl$_3$.

Figure S16. UV-Vis-NIR absorption spectra of polymer-SWNT dispersions compared to a SWNT dispersion in SDBS surfactant normalized to local minimum at 905 nm. A) shows the full-spectral range and B) shows a zoom-in of the $S_{22}$ and $M_{11}$ regions.
Figure S17. Polymer-SWNT dispersions at different polymer:nanotube mass ratios using A) P1 and B) P2 in THF with HiPCO nanotubes and C) P1 in toluene and D) P2 in THF with plasma-torch nanotubes.

Figure S18. Normalized absorption and emission spectra corresponding to A) P1 in THF ($\lambda_{\text{max}} = 394$ nm; $\lambda_{\text{em}} = 531$ nm) and Toluene ($\lambda_{\text{max}} = 391$ nm; $\lambda_{\text{em}} = 526$ nm), and B) P2 in THF ($\lambda_{\text{max}} = 384$ nm; $\lambda_{\text{em}} = 566$ nm).

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