

Electronic Supplementary Information

**Dispersing As-Prepared Single-Walled Carbon Nanotube
Powders with Linear Conjugated Polymers**

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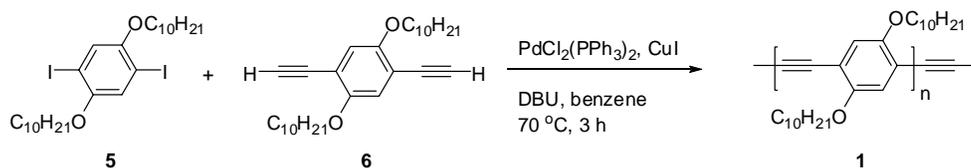
Table of Content

1. Synthesis and Characterization of Polymers **1-4**
2. Preparation of [Polymer + SWNTs] Suspensions
3. Summary of Physical and Optical Properties for Polymers and [Polymer + SWNTs] Complexes
4. Electronic Absorption Spectroscopic Data
5. Fluorescence Spectroscopic Data
6. Atomic Force Microscopic (AFM) Images of Polymer and [Polymer + SWNTs] Samples
7. NMR Spectroscopic Data
8. Deconvoluted Raman Spectra for [Polymer + SWNTs] Composite Films

1. Synthesis and Characterization of Polymers 1-4

1.1 General. Chemicals and reagents were purchased from commercial suppliers and used without further purification. Benzene and toluene were all distilled from LiH before use. Polymers **1** and **2** were prepared using the Sonogashira coupling as described in the literature¹ with slight modifications. Polymer **3** was prepared according to the homocoupling procedure reported by Swager and co-workers,² and polymer **4** was synthesized following the procedure reported by Bunz.³ All reactions were performed in standard, dry glassware under an inert atmosphere of N₂ unless otherwise mentioned. Thin-layer chromatography (TLC) was carried out with silica gel 60 F254 covered on plastic sheets and visualized by UV light or KMnO₄ stain. Infrared spectra (IR) were recorded on a Bruker Tensor 27 spectrometer using a MIRacle attenuated reflectance (ATR) sample stage (Thermo Electron Corporation). Raman spectra were obtained on a Jobin Yvon Horiba LabRAM spectrometer, 532 nm excitation wavelength. ¹H NMR spectra were measured on the Bruker Avance 500 MHz spectrometer. UV-Vis spectral analyses were performed on an Agilent 8453 or a Varian Cary 5E UV-Vis-NIR spectrophotometer. Atomic force microscopic (AFM) analyses were carried out on an Asylum Research MFD-3D-SA microscope with analysis in IGOR (Wavemetric Inc.) using home-built routines as well as codes from Asylum Research.

1.2 Synthesis of Polymer 1



In a 50 mL round bottom flask 1,4-bis(decyloxy)-2,5-diiodobenzene (**5**) (77 mg, 0.12 mmol), 1,4-bis(decyloxy)-2,5-diethynylbenzene (**6**) (50 mg, 0.11 mmol), DBU (240 mg, 1.74 mmol), PdCl₂(PPh₃)₂ (8 mg, 0.01 mmol), and CuI (6.5 mg, 0.034 mmol) were added into 13 mL of benzene. The mixture was immediately degassed by three freeze-pump-thaw cycles and protected with pure N₂. Then the mixture was heated to 70 °C under stirring 3 h. The reaction was quenched with MeOH after cooling to room temperature. The resulting dark yellowish precipitates were filtered and sequentially rinsed with aq. ammonia, water, and a large amount of MeOH to remove the catalysts and low-molecular weight components. The resulting solid was dried under vacuum to afford polymer **1** as a dark yellow solid (80 mg, 66%). IR (neat) 2921, 2850 (ν C-H), 2200 (ν

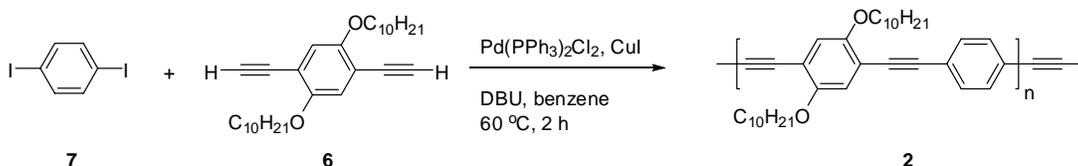
(1) H. Li, D. R. Powell, R. K. Hayashi, and R. West, *Macromolecules*, 1998, **31**, 52.

(2) V. E. Williams and T. M. Swager, *J. Polym. Sci.: Part A*, 2000, **38**, 4669.

(3) U. H. F. Bunz, V. Enkelman, L. Kloppenburg, D. Jones, K. D. Shimizu, J. B. Claridge, H.-C. zur Loye and G. Lieser, *Chem. Mater.*, 1999, **11**, 1416; (c) J. N. Wilson, P. M. Windscheif, U. Evans, M. L. Myrick, and U. H. F. Bunz, *Macromolecules*, 2002, **35**, 8681.

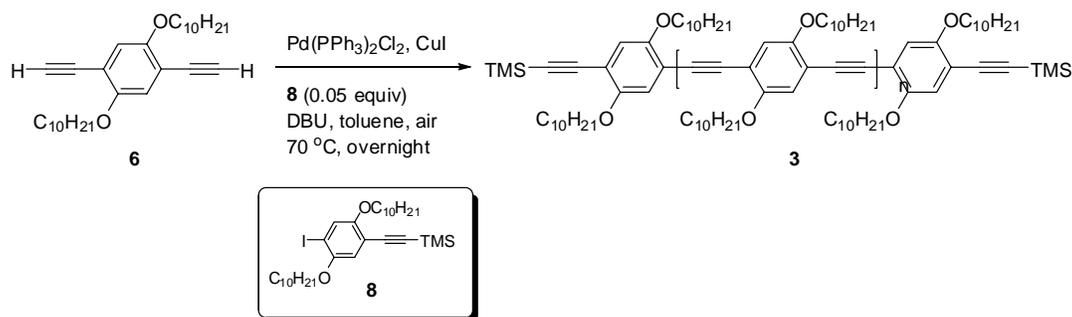
$\text{C}\equiv\text{C}$), 1564, 1497. ^1H NMR (500 MHz, CDCl_3)⁴ δ 7.02 (bm, 2H, ArH), 4.06 (bm, 4H, OCH₂), 1.86 (bm, 4H), 1.53 (bm, 4H), 1.45-1.25 (bm, 24H), 0.94-0.88 (bm, 6H, CH₃).

1.2 Synthesis of Polymer 2



In a 50 mL round bottom flask diiodobenzene (**7**) (25 mg, 0.075 mmol), 1,4-bis(decyloxy)-2,5-diethynylbenzene (**6**) (35 mg, 0.079 mmol), DBU (240 mg, 1.74 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (5.5 mg, 0.0076 mmol), and CuI (4.3 mg, 0.023 mmol) were added into 8 mL of benzene. The mixture was immediately degassed by three freeze-pump-thaw cycles and protected with pure N_2 . Then the mixture was heated to $60\text{ }^\circ\text{C}$ under stirring 3 h. The reaction was quenched with MeOH after cooling to room temperature. The resulting dark yellowish precipitates were filtered and sequentially rinsed with aq. ammonia, water, and a large amount of MeOH to remove the catalysts and low-molecular weight components. The resulting solid was dried under vacuum to afford polymer **2** as a dark yellow solid (25 mg, 66%). IR (neat) 2919, 2851 (ν C-H), 2207 (ν $\text{C}\equiv\text{C}$), 1619, 1572, 1453. ^1H NMR (500 MHz, CDCl_3) δ 7.54 (bm, 4H, phenylene ArH), 7.05 (bm, 2H, bis(decyloxy)phenylene ArH), 4.07 (bm, 4H, OCH₂), 1.89 (bm, 4H), 1.58 (bm, 4H), 1.46-1.25 (bm, 24H), 0.92 (bm, 3H, CH₃).

1.3 Synthesis of Polymer 3

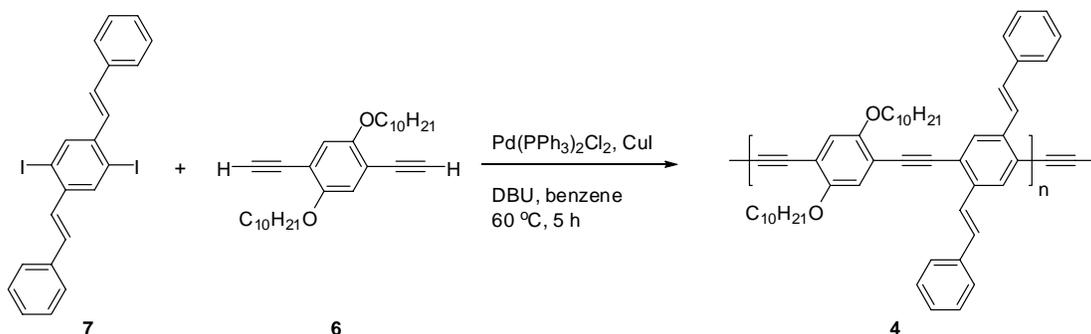


In a 50 mL round bottom flask 1,4-bis(decyloxy)-2,5-diethynylbenzene (**6**) (44 mg, 0.100 mmol) and 5% equiv of endcapping agent, 1,4-bis(decyloxy)-2-ethynyl-5-iodobenzene (**8**) (3.4 mg, 0.0050 mmol), were dissolved in 8 mL of toluene under air. Then DBU (240 mg, 1.74 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (7 mg, 0.01 mmol) and CuI (5 mg, 0.03 mmol) were added sequentially. The flask was capped with a septum and heated to $70\text{ }^\circ\text{C}$ under stirring overnight. The reaction was then quenched with MeOH after cooling to room temperature. The resulting dark yellowish precipitates were filtered and

(4) For NMR data of the polymers, relative integration values were reported based on the structure of each repeating unit.

sequentially rinsed with dilute aq. ammonia, 10% HCl, satd. NaHCO₃, water, MeOH, and hexanes to remove the catalysts, and other low-molecular weight components and then dried under vacuum to afford a golden yellow solid **3** (43 mg, 99%). IR (neat) 2923, 2851 (ν C-H), 2204, 2142 (ν C \equiv C), 1644, 1528 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 6.97 (bs, 2H, ArH), 3.99 (bm, 4H, OCH₂), 1.83 (bm, 4H), 1.55-1.46 (bm, 8H), 1.38-1.26 (bm, 20 H), 0.87 (bm, 6H, CH₃), 0.27 (s, 1.06H, Si(CH₃)₃).

1.4 Synthesis of Polymer 4



In a 50 mL round bottom flask 1,4-bis(styryl)-2,5-diiodobenzene (**7**) (104 mg, 0.195 mmol), 1,4-bis(decyloxy)-2,5-diiodobenzene (**6**) (90 mg, 0.21 mmol), DBU (720 mg, 5.22 mmol), PdCl₂(PPh₃)₂ (14 mg, 0.021 mmol), and CuI (12 mg, 0.062 mmol) were added in 30 mL of benzene. The flask was degassed as described in the synthesis of **1** and then heated to 70 °C under stirring for 3h. The reaction was then quenched with MeOH after cooling to room temperature. The resulting dark yellowish precipitates were filtered and sequentially rinsed with aq. ammonia, water, and a large amount of MeOH to remove the catalysts, and other low-molecular weight components and then dried under vacuum to afford a yellow solid **4** (137 mg, 95%). IR (neat) 3025 (alkene ν C-H), 2922, 2851 (ν C-H), 2208 (ν C \equiv C), 1596, 1497, 1466. ¹H NMR (500 MHz, CDCl₃) δ 7.99 (bm, 1H, bisstyrylphenylene ArH), 7.85-7.77 (bm, 1H, bis(styryl)phenylene ArH), 7.68-7.29 (bm, 14H, ArH and alkene =CH), 7.18-7.01 (bm, 2H, bis(decyloxy)phenylene ArH), 4.15-4.00 (bm, 4H, OCH₂), 1.93-1.74 (bm, 4H), 1.60-1.14 (bm, 28H), 0.92-0.85 (bm, 6H, CH₃).

2. Preparation of [Polymer + SWNTs] Suspensions

To a small glass vial suitable amounts of polymer was added in chloroform. The mixture was heated over a steam bath for a few minutes to ensure that the polymer was completely dissolved. After cooling the polymer solution to room temperature, excess amounts of as-prepared SWNT powders (purchased from Carbon Solution Inc.) were added. The mixture was bath-sonicated for 5 min at room temperature and filtered through a cotton plug to remove all the visible particle contents, affording the [polymer + SWNT] suspension.

Polymer **1** could temporarily form a homogeneous dark-colored solution with as-prepared SWNTs, which precipitated out quickly after a few minutes (see Figure 2a). Polymer **2** did not show any visible signs of SWNT dissolution (Figure 2b). Both

polymers **3** and **4** formed very stable homogeneous solutions with as-prepared SWNTs (Figures 2c and d), which could last for months without precipitation.

2.1 Photographs of polymer and [polymer + SWNTs] suspensions

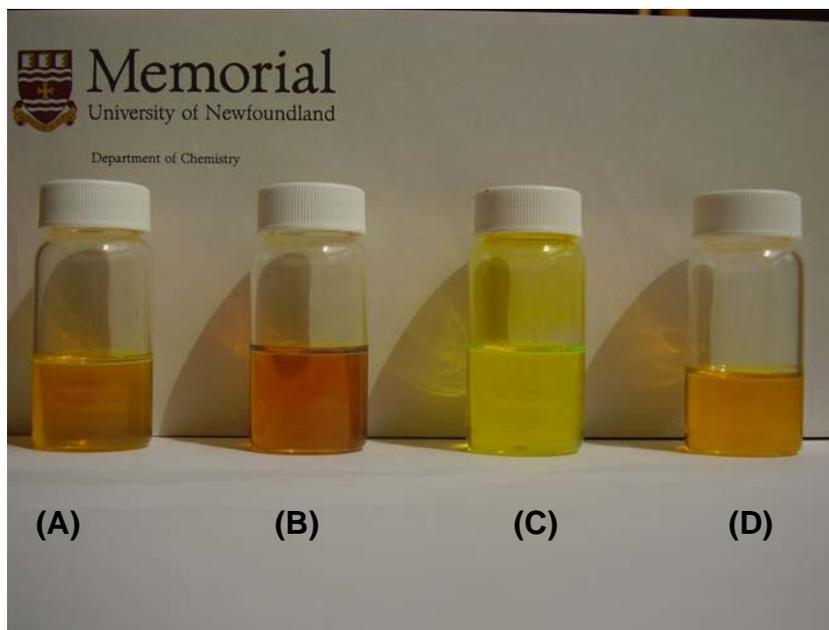


Figure 1. Photographs of chloroform solutions of polymers **1** (A), **2** (B), **3** (C), and **4** (D).

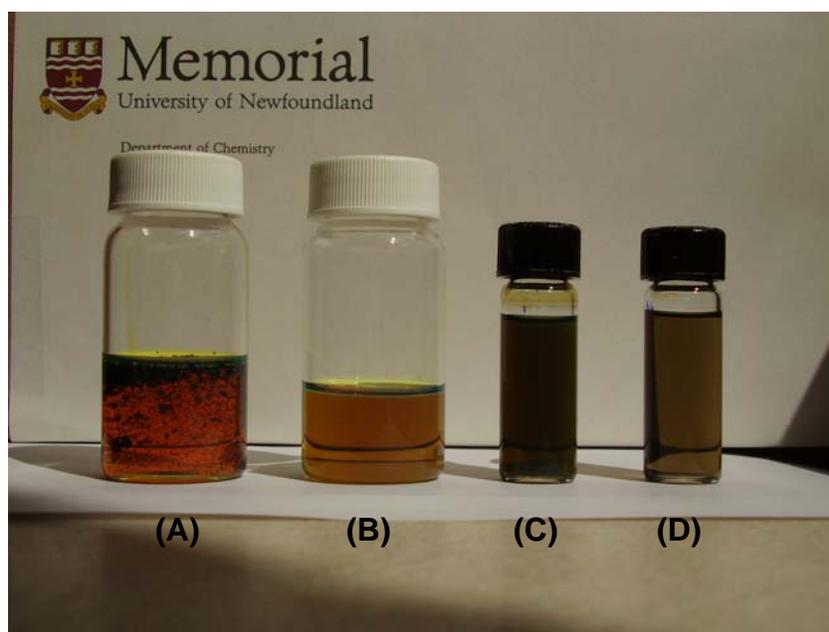


Figure 2. Photographs of [polymer + SWNTs] suspensions in chloroform after 5 min bath-sonication and cotton plug filtration. [SWNTs + **1**] (A), [SWNTs + **2**] (B), [SWNTs + **3**] (C), and [SWNTs + **4**] (D).

3. Summary of Physical and Optical Properties for Polymers and [Polymer + SWNTs] Complexes

Entry	Solubility of polymer in CHCl ₃ ^a (mg/mL at 25 °C)	Solubility of SWNTs in CHCl ₃ ^b (mg/mL at 25 °C)	Dynamic viscosity at 25 °C ^c (Relative to pure CHCl ₃)	Abs. λ _{max} (nm)	Optical bandgap ^d (eV)	Em. λ _{max} (nm)
1	2.31	–	–	438, 337 (sh), 299	2.59	509, 475
[1 + SWNTs]	–	–	–	–	–	–
2	0.62	–	–	421, 331, 315 (sh)	2.69	495 (sh), 458
[2 + SWNTs]	–	–	–	–	–	–
3	0.51	–	1.004	453, 341, 315	2.56	518, 477
[3 + SWNTs]	–	0.94	1.095	494, 453	–	–
4	0.83	–	1.052	443, 369, 338	2.61	499 (sh), 468
[4 + SWNTs]	–	1.30	1.138	504 (sh), 441, 369, 338	–	–

^a Solubility of the polymer was determined by weighing the solid residue after vacuum evaporation of a polymer solution with an accurately measured volume.

^b Solubility of SWNTs in a saturated polymer solution was determined as following: First, the mass of the solid residue resulting from vacuum evaporation of a [polymer + SWNTs] solution with accurately measured volume was determined. This mass value was then subtracted by the mass of the polymer dissolved in CHCl₃, which was calculated based on the solubility of the pure polymer in CHCl₃, giving the solubility of SWNTs in the polymer solution.

^c Saturated polymer solutions in CHCl₃ were used for dynamic viscosity measurements.

^d Optical bandgaps were calculated based on the wavelength value at the cross-point between the x-axis of the absorption spectrum and a tangential line passing through the turning point of the longest-wavelength absorption band.

4. Electronic Absorption Spectroscopic Data

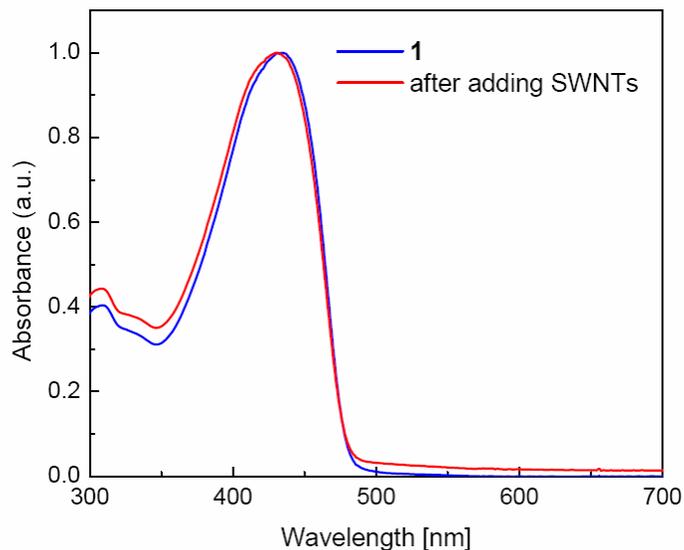


Figure 3. Comparison of UV-Vis absorption spectra for polymer **1** in CHCl_3 before and after adding as-prepared SWNT powders.

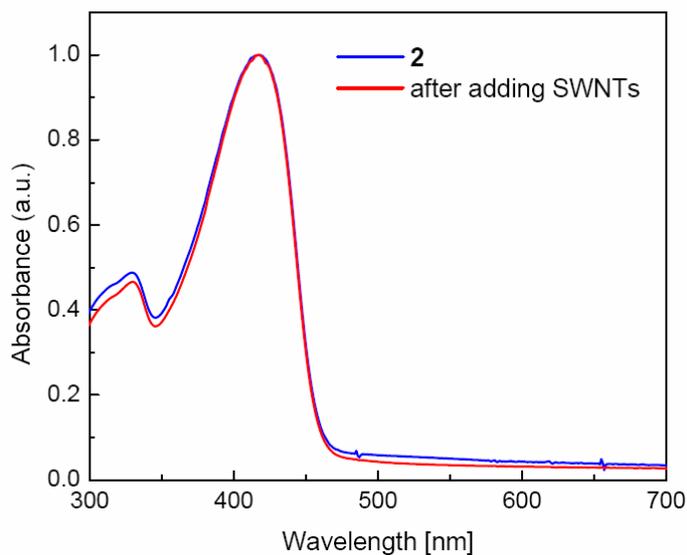


Figure 4. Comparison of UV-Vis absorption spectra for polymer **2** in CHCl_3 before and after adding as-prepared SWNT powders.

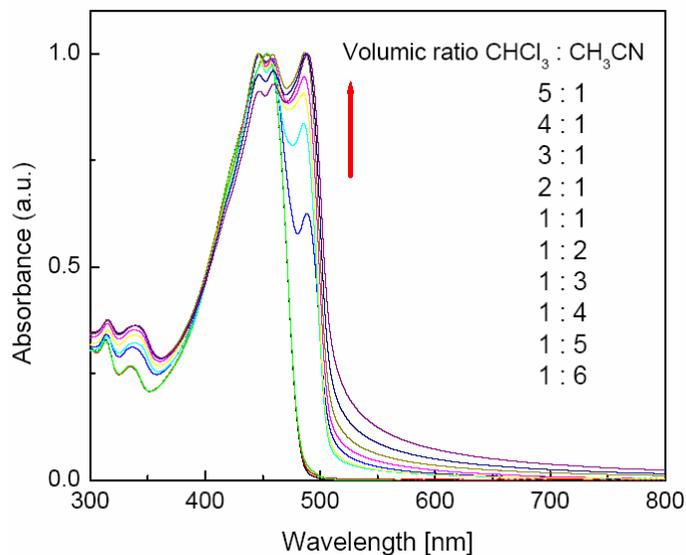


Figure 5. Normalized UV-Vis absorption spectra for polymer **3** in various solvents. The red arrow indicates the steadily growing aggregation band at *ca.* 502 nm with increasing solvent polarity.

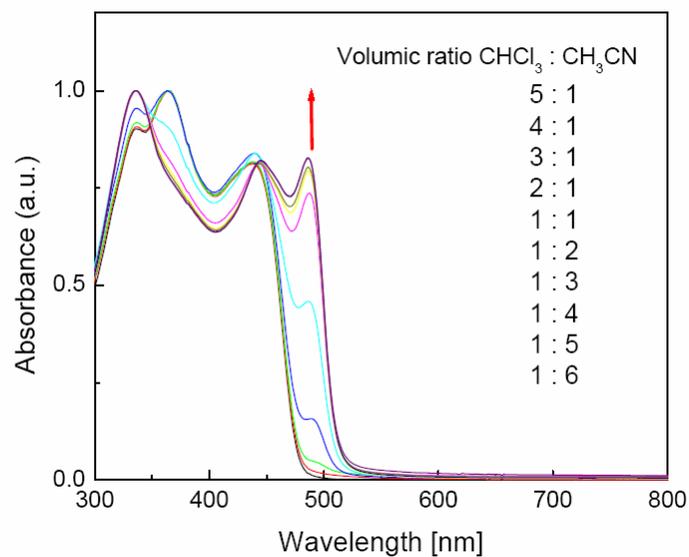


Figure 6. Normalized UV-Vis absorption spectra for polymer **4** in various solvents. The red arrow indicates the steadily growing aggregation band at *ca.* 494 nm with increasing solvent polarity.

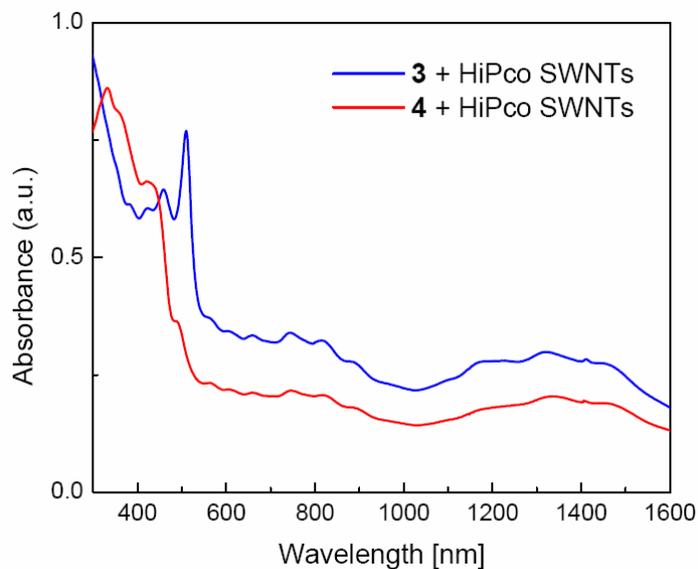


Figure 7. UV-Vis-NIR absorption spectra for HiPco SWNTs dispersed in the chloroform solutions of polymer **3** and **4**.⁵

(5) In order to address the interactions between the linear conjugated polymers and other types of SWNTs, the dispersion of HiPco SWNTs (obtained from Rice University) with polymers **1–4** in chloroform was attempted following the same procedure as that for as-prepared SWNTs (obtained from Carbon Solutions Inc.). The dispersion outcomes of HiPco SWNTs were similar to those of as-prepared SWNTs. Polymers **1** and **2** were not able to lead to stable suspensions of HiPco SWNTs, while polymers **3** and **4** afforded very stable dark solutions with HiPco SWNTs (see above UV-Vis-NIR absorption spectra). Further experimental efforts to understand the interactions between polymers **3** and **4** with various types of SWNTs are currently underway in our laboratory, and detailed results will be reported elsewhere.

5. Fluorescence Spectroscopic Data

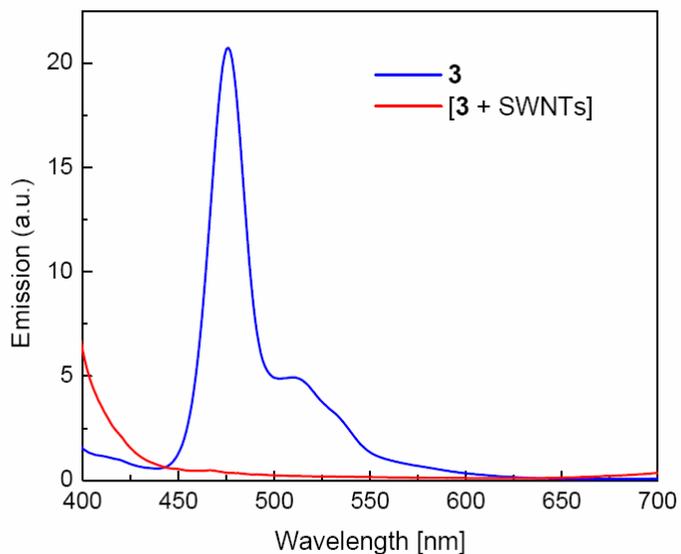


Figure 8. Fluorescence spectra for polymer **3** and [**3** + SWNTs] as measured in degassed CHCl_3 at room temperature ($\lambda_{\text{ex}} = 370 \text{ nm}$).

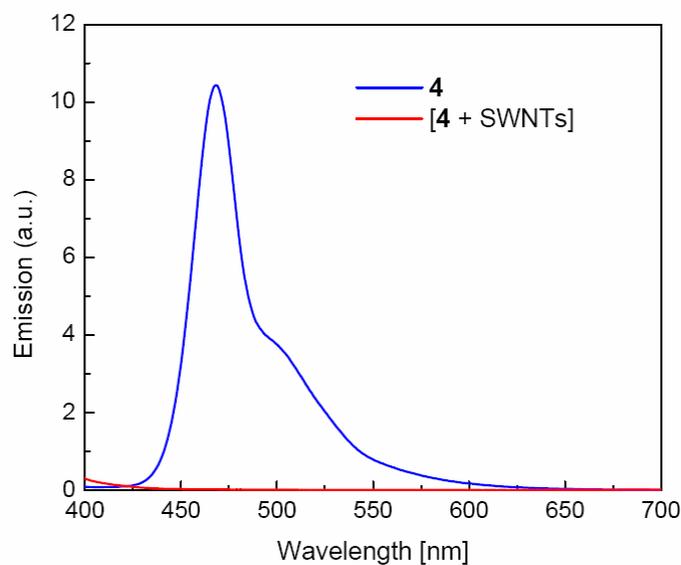


Figure 9. Fluorescence spectra for polymer **4** and [**4** + SWNTs] as measured in degassed CHCl_3 at room temperature ($\lambda_{\text{ex}} = 370 \text{ nm}$).

6. Atomic Force Microscopic (AFM) Images of Polymer and [Polymer +SWNTs] Samples

Thin films for all AFM imaging were prepared by either drop-casting or spin-coating corresponding dilute solutions on a freshly cleaved mica surface. Data were collected in AC mode with simultaneous acquisition of height, amplitude, and phase traces using Si cantilevers of resonant frequency ~100-300 kHz (NSC35, MikroMasch) with a reflective aluminum coating. All images are presented here with minimal post-processing (flattening/planefitting) of raw data.

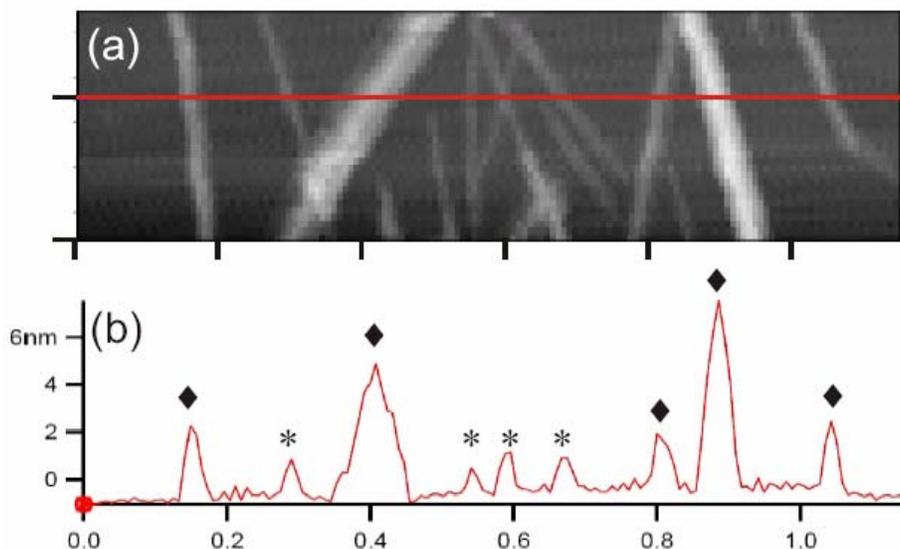


Figure 10. (a) Zoom-in AFM image of [3 + SWNTs], and (b) a line scan analysis showing individual nanotubes, uncoated (*) and coated with polymer 3 (♦). (Heights rather than widths are used to estimate diameters to eliminate broadening effects resulting from tip shape.)

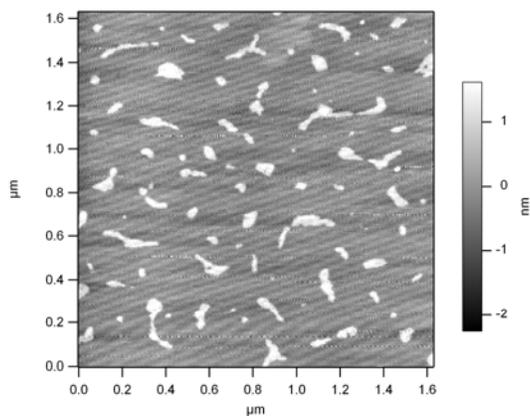


Figure 11. AFM image of a thin film of polymer 4 showing random, amorphous surface features.

7. NMR Spectroscopic Data

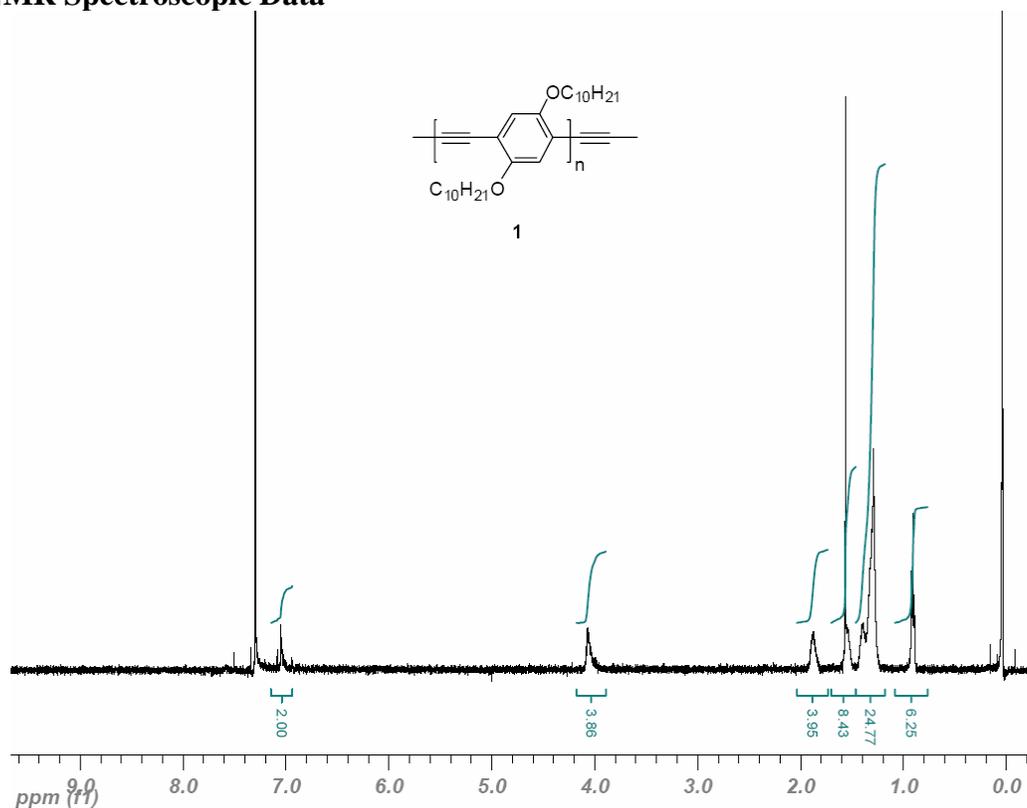


Figure 12. ^1H NMR spectrum of polymer **1** in CDCl_3 .

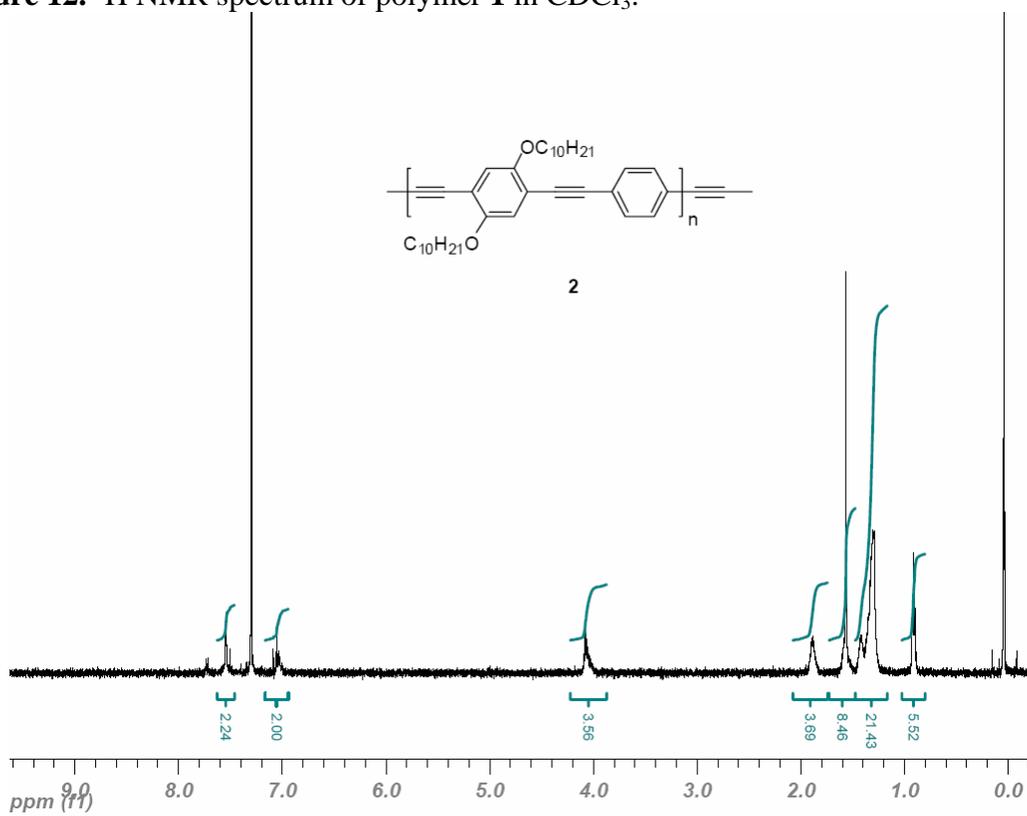
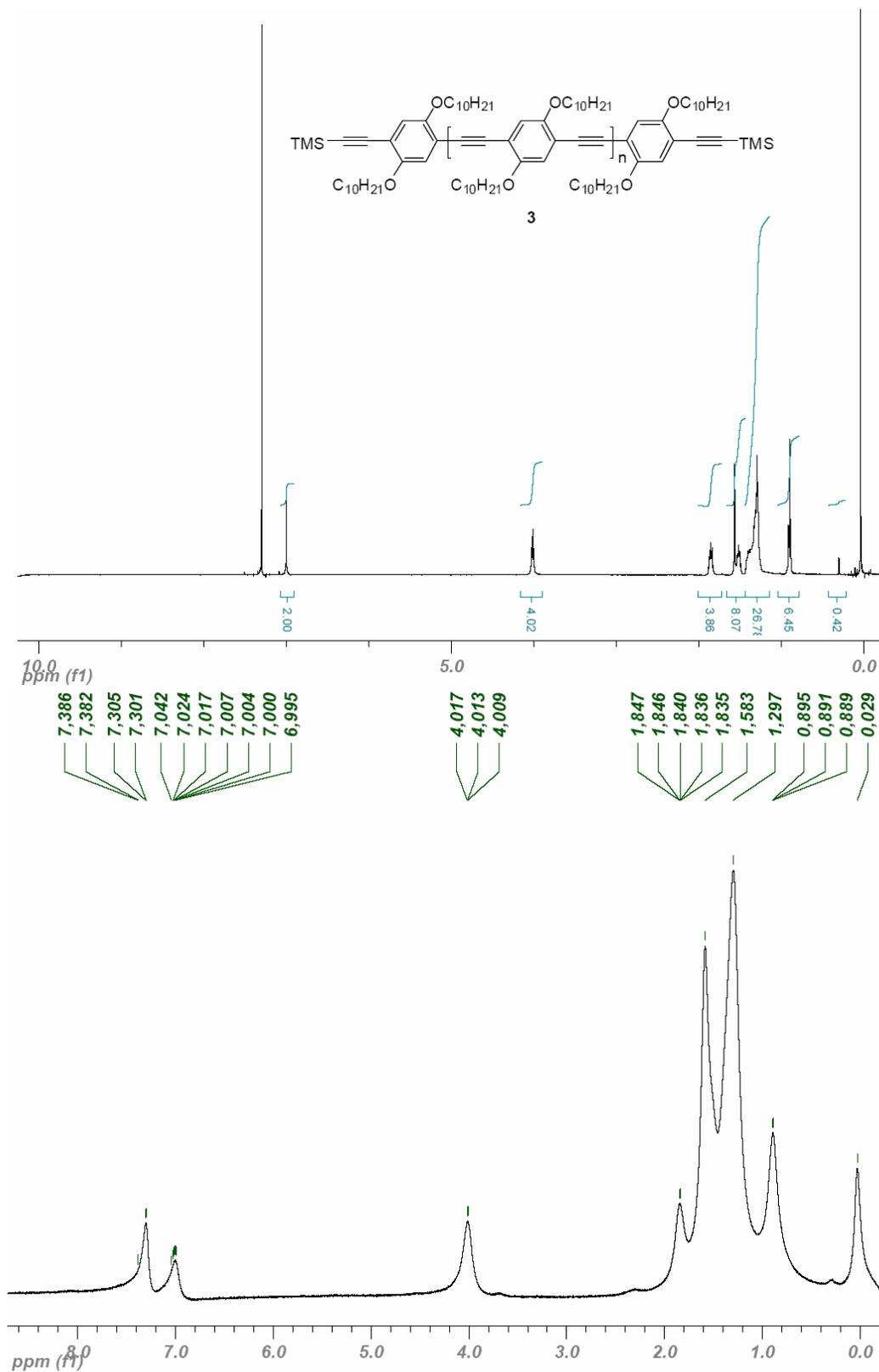


Figure 13. ^1H NMR spectrum of polymer **2** in CDCl_3



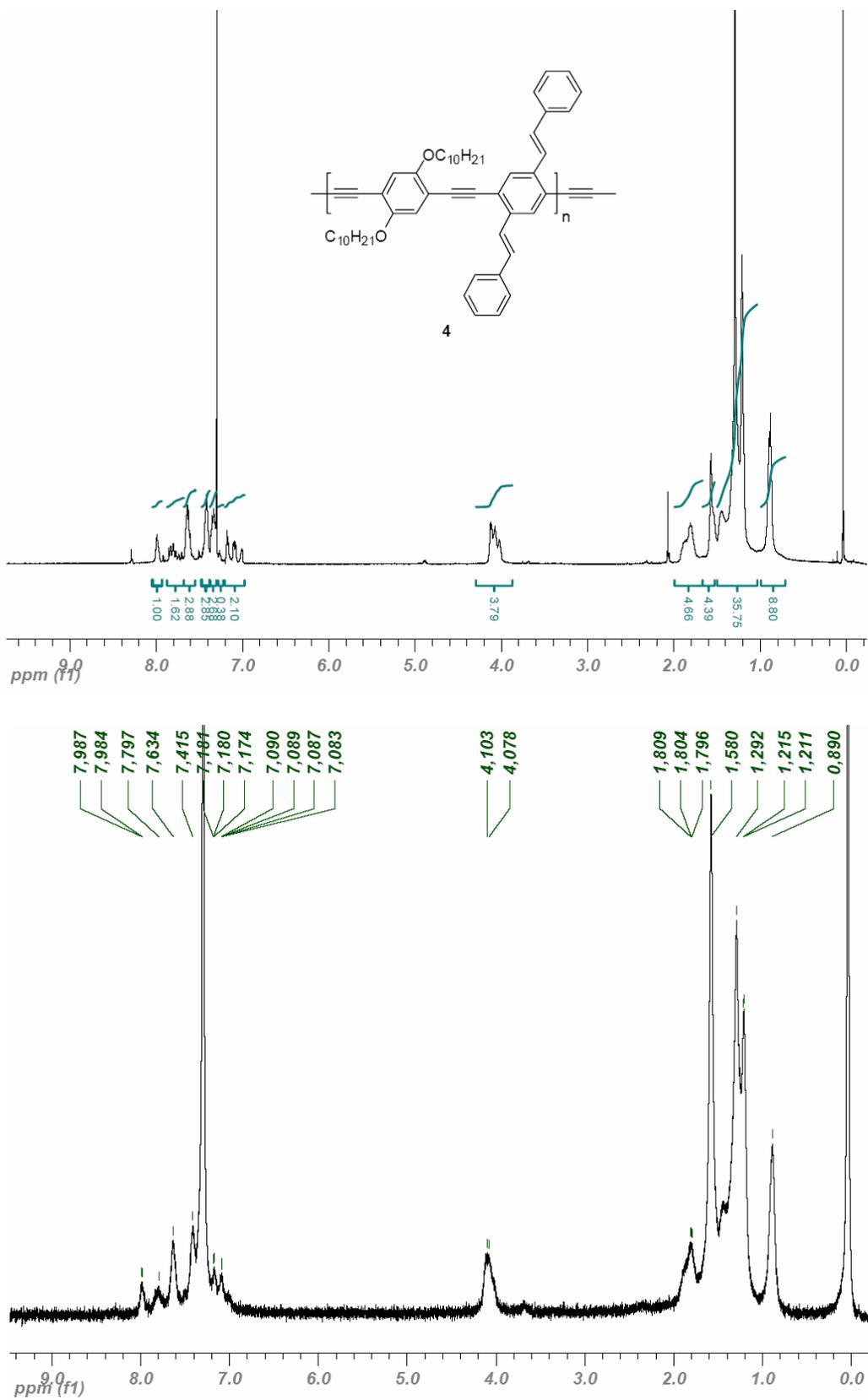


Figure 15. ¹H NMR spectra of polymer 4 (top) and [4 + SWNTs] (bottom) in CDCl₃.

8. Deconvoluted Raman Spectra for [Polymer + SWNTs] Composite Films

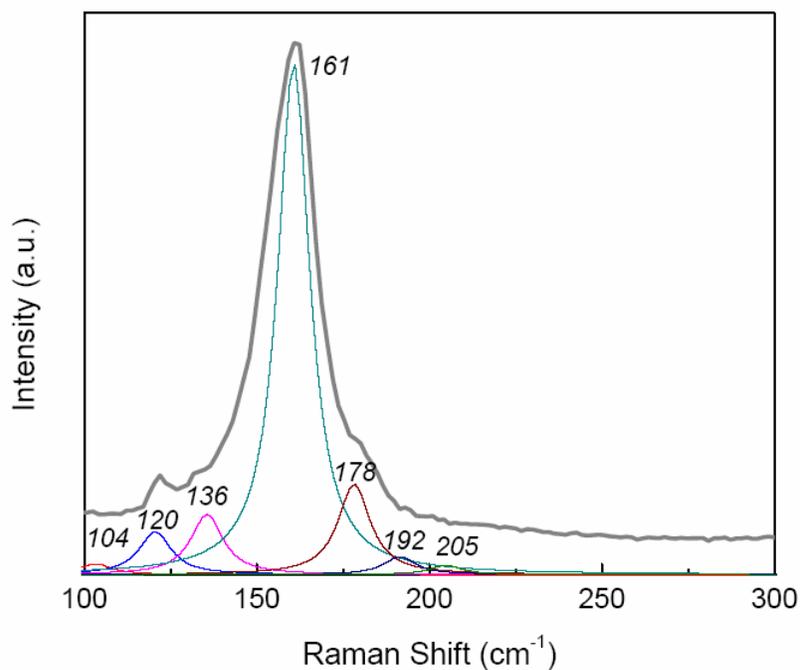


Figure 16. Deconvoluted Raman spectrum of [3 + SWNTs] in the RBM region.

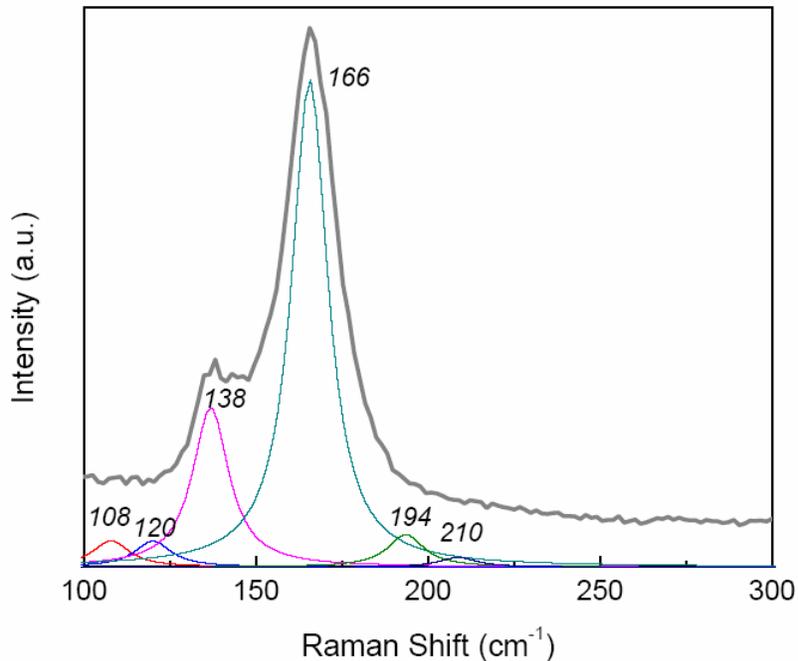


Figure 17. Deconvoluted Raman spectrum of [4 + SWNTs] in the RBM region.