

Dithiafulvenyl-grafted phenylene ethynylene polymers as selective and reversible dispersants for single-walled carbon nanotubes

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1. Experimental

1.1 General

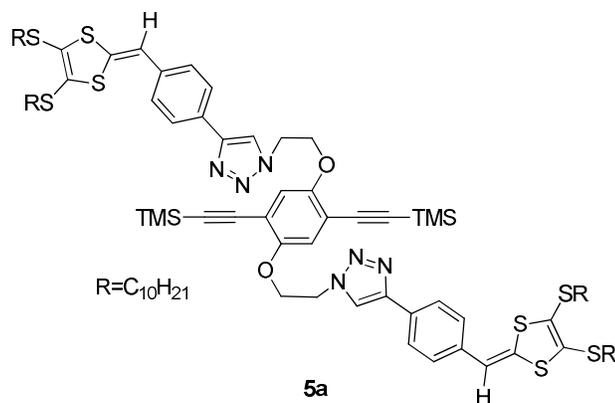
Chemicals and reagents were purchased from commercial suppliers and used without further purification. HiPCO SWNTs were purchased from Carbon Nanotechnologies Inc. The as-produced HiPCO nanotubes were prepared by the so-called high-pressure CO conversion process and contain a mixture of metallic and semiconducting tubes as well as other carbonaceous impurities. CoMoCAT SWNTs were purchased from Southwest Nano Technologies Inc. The CoMoCAT nanotubes, featuring relatively narrow distribution of tube diameters, were grown via the CO disproportionation process catalyzed with Co and Mo based systems. All reactions were performed in standard dry glassware under an inert atmosphere of N₂ unless otherwise noted. Evaporation and concentration was done at H₂O-aspirator pressure. Flash column chromatography was carried out with silica gel 60 (230-400 mesh) from VWR International. Thin-layer chromatography (TLC) was carried out with silica gel 60 F254 covered on plastic sheets and visualized by UV light. ¹H and ¹³C NMR spectra were measured on a Bruker Avance 500 MHz spectrometer or a Tecmag APOLLO 300 MHz spectrometer. Chemical shifts (δ) are reported in ppm downfield from the signal of the internal reference SiMe₄ or relative to the signals of residual solvents (CHCl₃: $\delta_{\text{H}} = 7.24$ ppm, $\delta_{\text{C}} = 77.2$ ppm; CH₂Cl₂: $\delta_{\text{H}} = 5.32$ ppm, $\delta_{\text{C}} = 54.0$ ppm). Coupling constants (J) are given in Hz. UV-Vis-NR absorption spectra were recorded on a Cary 6000i spectrophotometer. Infrared spectra (IR) were recorded on a Bruker Tensor 27 spectrometer equipped with a ZnSe ATR module. MALDI-TOF mass spectra were measured on an Applied Biosystems Voyager instrument using dithranol as the matrix. Polymer molecular weight and polydispersity index (PDI) were estimated from gel permeation chromatography (GPC) 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. Atomic force microscopy (AFM) images were taken with a Q-Scope AFM operated in tapping mode. Scanning electron microscopy (SEM) images were taken with a Hitachi S570 SEM operated at 15 kV. Raman spectra were performed with a Renishaw InVia Laser Raman spectrometer, equipped with a 300 mW Renishaw laser

(785 nm, grating 1200 lines/mm). Photoluminescence excitation (PLE) mapping was carried out using the Jobin-Yvon SPEX Fluorolog 3.22 equipped with a 450 W Xe lamp, and fitted with a liquid-nitrogen cooled InGaAs photodiode detector. Slit widths were set to 10 nm band-pass on both excitation and emission, and samples were illuminated in a quartz cell using 5 nm wavelength steps. Cyclic voltammetric (CV) analyses were carried out in a standard three-electrode setup controlled by a BASi Epsilon workstation. Compounds **3**, **4**, **6** and **7** were prepared according to literature procedures.

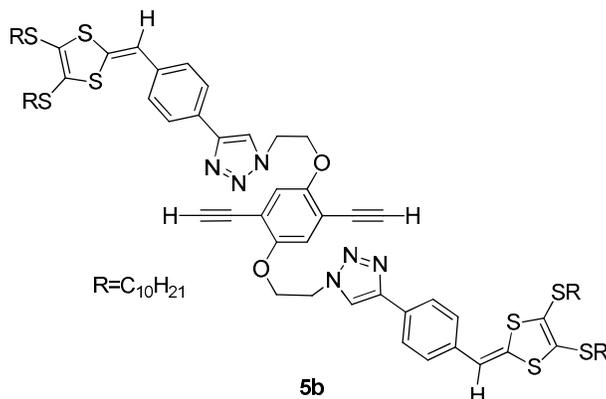
UV-Vis-NIR monitoring of SWNT dispersion in mixed solvents. An excess amount of raw HiPCO SWNTs was added to a polymer solution of polymer **1** (40 mg) in toluene (8 mL). The resulting mixture was subjected to sonication in a bath sonicator that was cooled with ice, followed by centrifugation for 30 min at 8,346 g. The mixture was then filtered through a pipette packed tightly with cotton to give the extremely dark and stable SWNT dispersion. The original dispersion was first analyzed by UV-Vis-NIR spectroscopy. Then 4 mL of hexanes was added to the above dispersion to trigger the precipitation of SWNTs. The released SWNTs were separated by filtration. The filtrate was still a black solution and analyzed by UV-Vis-NIR spectroscopy to monitor the compositional change. Then additional 4 mL of hexanes was added to the filtrate to trigger another round of SWNT precipitation. The released SWNTs were separated by filtration and the filtrate was analyzed by UV-Vis-NIR spectroscopy again. Then another 4 mL of hexanes was added to the filtrate again and the released SWNTs were separated by filtration. At this point, the filtrate was observed as a yellow color solution. UV-Vis-NIR spectroscopic analysis of the filtrate showed no absorption peaks indicative of the presence of SWNTs in the filtrate solution. The obtained UV-Vis-NIR spectral data were compiled and shown in Fig. 5 in the main text.

1.2 Synthetic procedures

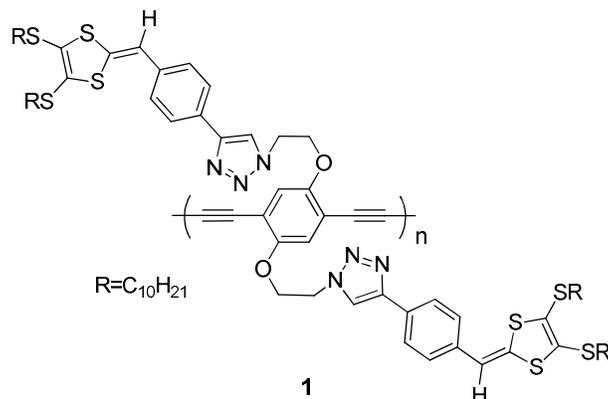
Compound 5a



To a solution of acetylenic phenyl-DTF **3** (1.28 g, 2.28 mmol) and diazido-phenylacetylene **4** (0.502 g, 1.14 mmol) in dry THF (100 mL) were added CuI (80.3 mg, 0.436 mmol) and diisopropylethylamine (DIPEA) (1 mL). The reaction mixture was degassed by bubbling N₂ at rt for 5 min before it was heated to 60 °C overnight. After that, the solvent THF was evaporated off under reduced pressure. The obtained residue was dissolved in CH₂Cl₂ and filtered through a MgSO₄ pad. The filtrate was sequentially washed with brine and water. The organic layer was dried over MgSO₄ and concentrated under vacuum to give crude compound **5a**, which was further purified by silica column chromatography (EtOAc/hexanes, 4:6) to yield pure **5a** (1.04 g, 0.665 mmol, 65%) as a pale yellow solid. m.p. 120-123 °C; IR (neat): 2918, 2148, 1570, 1497, 1393, 1356, 1212, 1047, 977, 930, 852, 757 cm⁻¹; ¹H NMR (500 MHz, CD₂Cl₂): δ 8.22 (s, 2H), 7.80 (d, *J* = 8.4 Hz, 4H), 7.26 (d, *J* = 8.3 Hz, 4H), 6.92 (s, 2H), 6.49 (s, 2H), 4.83 (t, *J* = 4.5 Hz, 4H), 4.36 (t, *J* = 4.8 Hz, 4H), 2.83 (t, *J* = 7.3 Hz, 8H), 1.70-1.59 (m, 8H), 1.41-1.27 (m, 56H), 0.90-0.84 (m, 12H), 0.24 (s, 18H); ¹³C NMR (75 MHz, CDCl₃): δ 153.1, 136.2, 132.9, 127.9, 127.7, 127.2, 126.0, 121.1, 117.6, 114.2, 113.9, 101.7, 100.4, 77.2, 67.9, 49.8, 36.2, 31.9, 29.9, 29.7, 29.6, 29.5, 29.4, 29.21, 29.19, 28.62, 28.60, 22.7, 14.2; MS (MALDI-TOF, positive) *m/z* calcd for C₈₄H₁₂₄N₆O₂S₈Si₂ 1560.7090, found 1560.6237 [M]⁺.

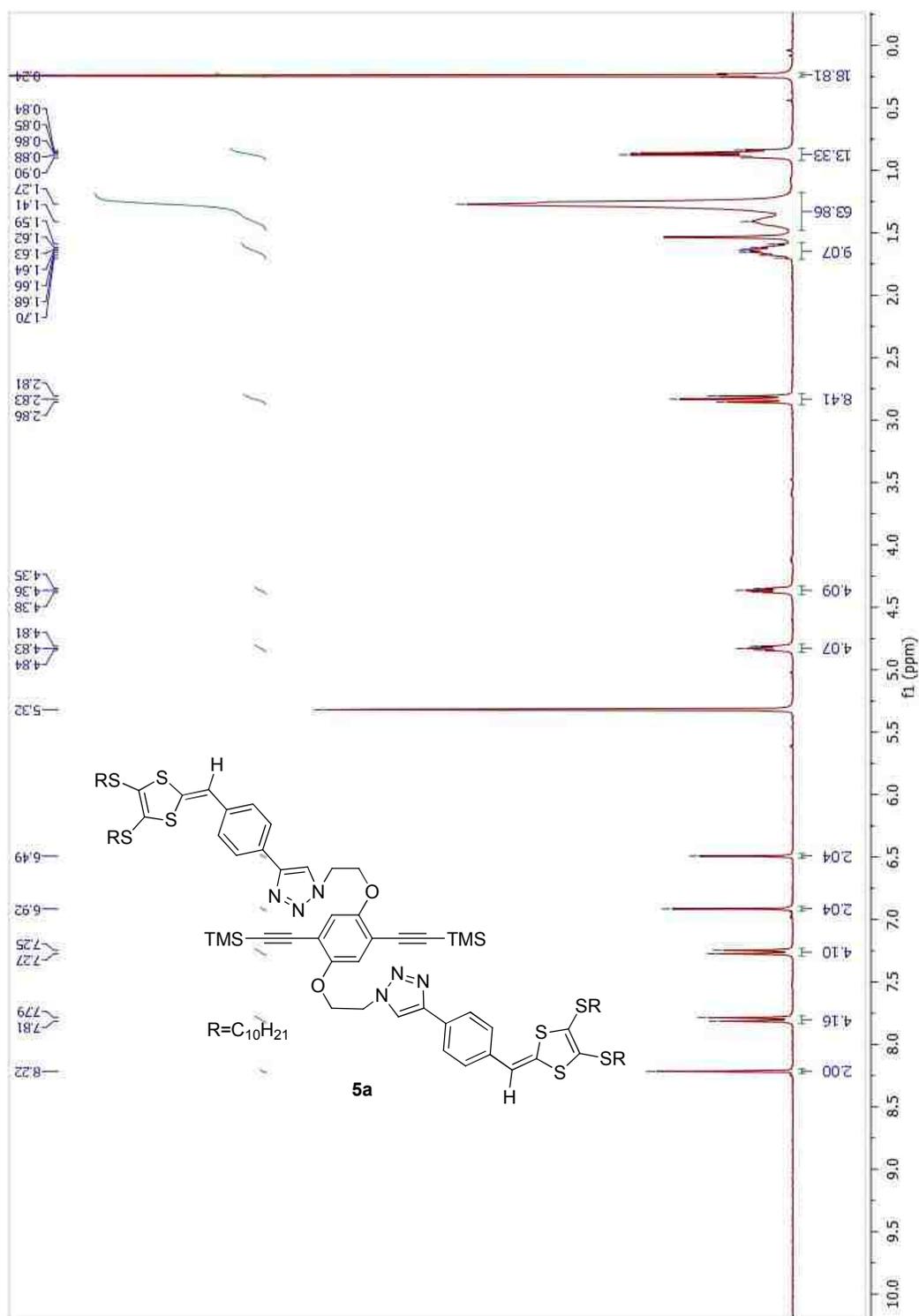
Compound 5b

To the solution of compound **5a** (0.50 g, 0.32 mmol) in THF/MeOH (40 ml, 2:1 v/v) was added K_2CO_3 (0.13 g, 0.96 mmol). The reaction mixture was stirred at rt for 2 h. After that, the solvent was evaporated off under reduced pressure. The residue was dissolved in CH_2Cl_2 , washed with water, dried over MgSO_4 , concentrated and dried under vacuum to obtain pure compound **5b** (0.38 g, 0.27 mmol, 85%) as a pale yellow solid. m.p. 109-112 °C; IR (neat): 3295, 2960, 2919, 2848, 2101, 1497, 1275, 1220, 1040, 1028, 973, 929, 894, 862, 830, 795, 714 cm^{-1} . ^1H NMR (500 MHz, CD_2Cl_2): δ 8.21 (s, 2H), 7.80 (d, $J = 8.1$ Hz, 4H), 7.27 (d, $J = 8.3$ Hz, 4H), 6.96 (s, 2H), 6.49 (s, 2H), 4.82 (t, $J = 4.5$ Hz, 4H), 4.35 (t, $J = 4.6$ Hz, 4H), 3.48 (s, 2H) 2.84 (t, $J = 7.2$ Hz, 8H), 1.69-1.61 (m, 8H), 1.41-1.28 (m, 56H), 0.89-0.85 (m, 12H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 153.8, 147.6, 136.4, 133.3, 128.5, 128.2, 127.5, 125.9, 125.1, 121.9, 118.1, 114.0, 113.9, 83.9, 79.6, 68.3, 50.1, 36.5, 36.4, 32.3, 30.3, 30.1, 29.97, 29.94, 29.7, 29.5, 28.94, 28.91, 23.1, 14.3; HRMS (MALDI-TOF, positive) m/z calcd for $\text{C}_{78}\text{H}_{108}\text{N}_6\text{O}_2\text{S}_8$ 1416.6299, found 1417.6313 $[\text{M} + \text{H}]^+$.

Homo-coupled polymer 1

To a solution of compound **5b** (110 mg, 0.070 mmol) in $\text{CHCl}_3/\text{acetone}$ (50 mL 1:1 v/v) were added CuI (7.30 mg, 0.038 mmol) and $\text{PdCl}_2(\text{PPh}_3)_2$ (10.8 mg, 0.015 mmol) and then TMEDA (0.5 mL). The reaction mixture was degassed by bubbling N_2 at rt for 5 min before it was heated to 60 °C for 2 h. Then the solvent was evaporated off under reduced pressure. The obtained residue was dissolved in CH_2Cl_2 and sequentially washed with brine and water. The organic layer was dried over MgSO_4 and concentrated under vacuum to give a deep brown colored solid. This solid was re-dissolved in CH_2Cl_2 and to the solution MeOH was slowly added to induce precipitation of the product. Filtration followed by vacuum drying finally afforded pure polymer **1** (88 mg, 0.056 mmol, 80%) as a brown solid. IR (neat): 2921, 2850, 1614, 1563, 1496, 1458, 1362, 1171, 1066, 1014, 846, 801, 699 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 8.18 (m, 2H), 7.87 (m, 4H), 7.05 (m, 4H), 6.79 (m, 2H), 6.22 (m, 2H), 4.69 (m, 4H), 4.17 (m, 4H), 2.83-2.67 (m, 8H), 1.56-1.23 (m, 64H), 0.86 (m, 12H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 153.9, 147.7, 136.4, 133.3, 128.5, 128.2, 127.5, 125.9, 121.9, 118.2, 114.0, 113.9, 87.3, 83.8, 79.6, 68.3, 50.1, 36.5, 36.4, 32.3, 30.3, 30.1, 29.97, 29.94, 29.7, 29.5, 28.93, 28.91, 23.1, 14.3. GPC: $M_n = 6233$ g/mol, $M_w = 10504$ g/mol, PDI = 1.7.

2. NMR Spectra for New Compounds

**Fig. S-1** ^1H NMR (500 MHz, CD_2Cl_2) spectrum of compound **5a**.

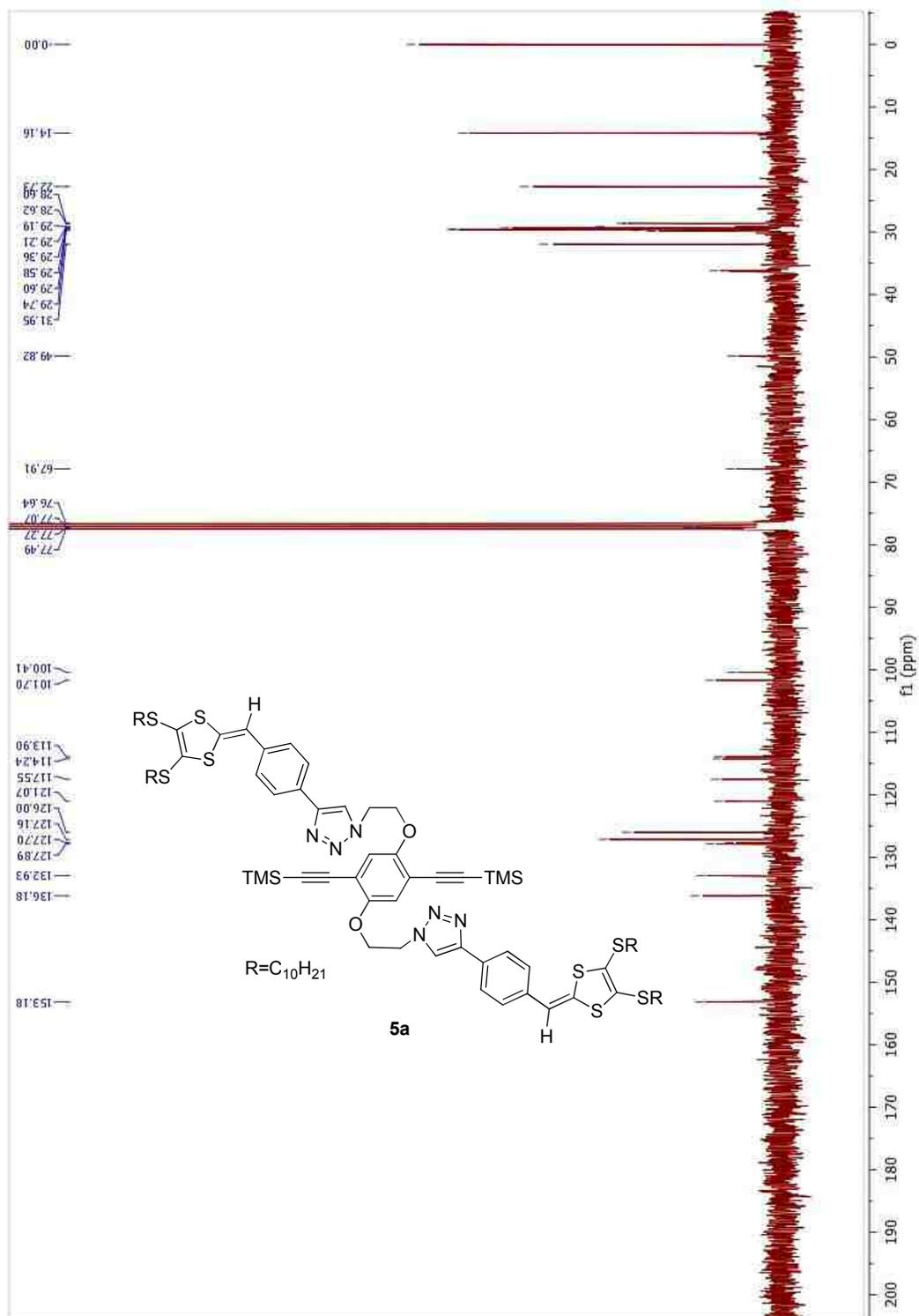


Fig. S-2 ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound **5a**.

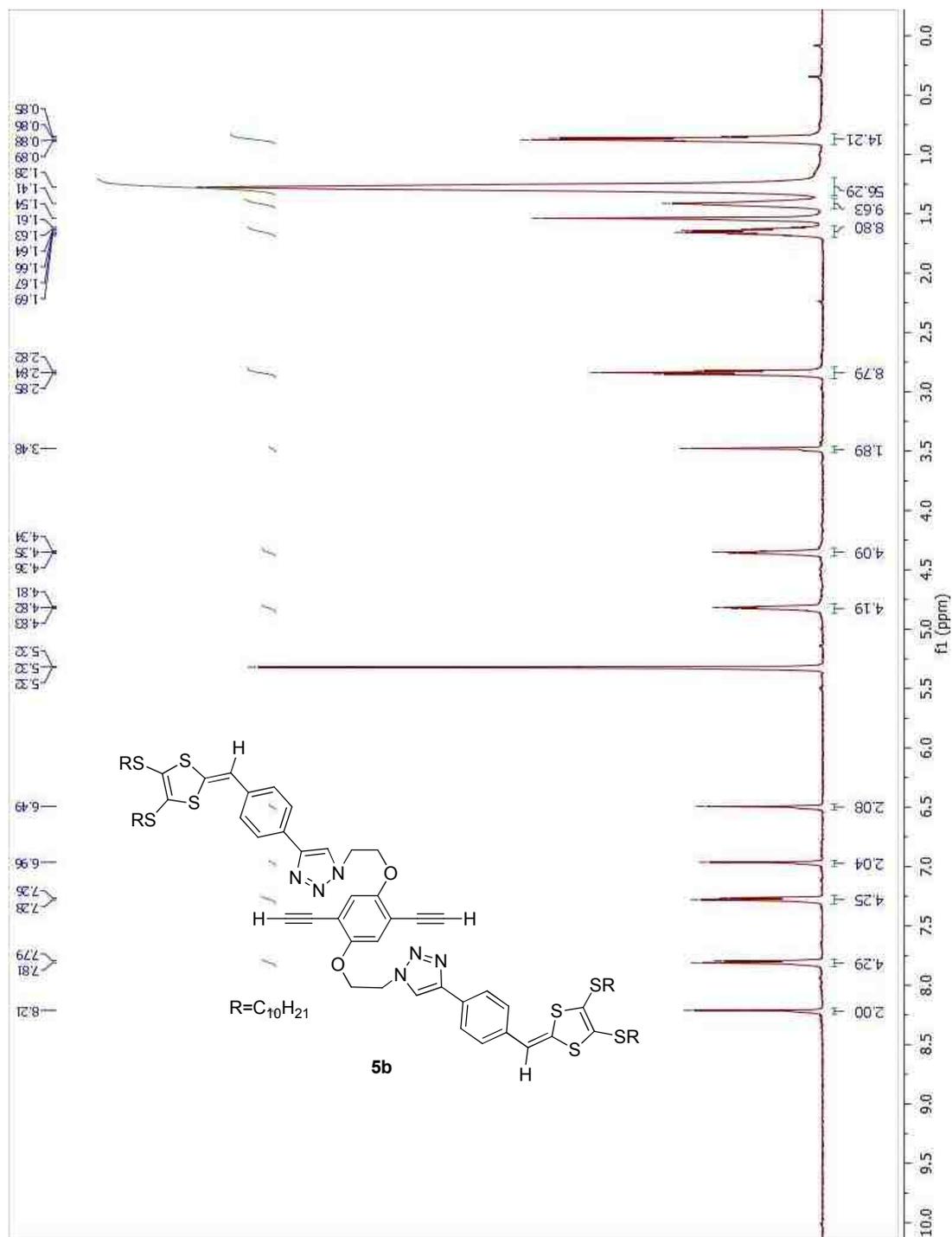


Fig. S-3 ^1H NMR (500 MHz, CD_2Cl_2) spectrum of compound **5b**.

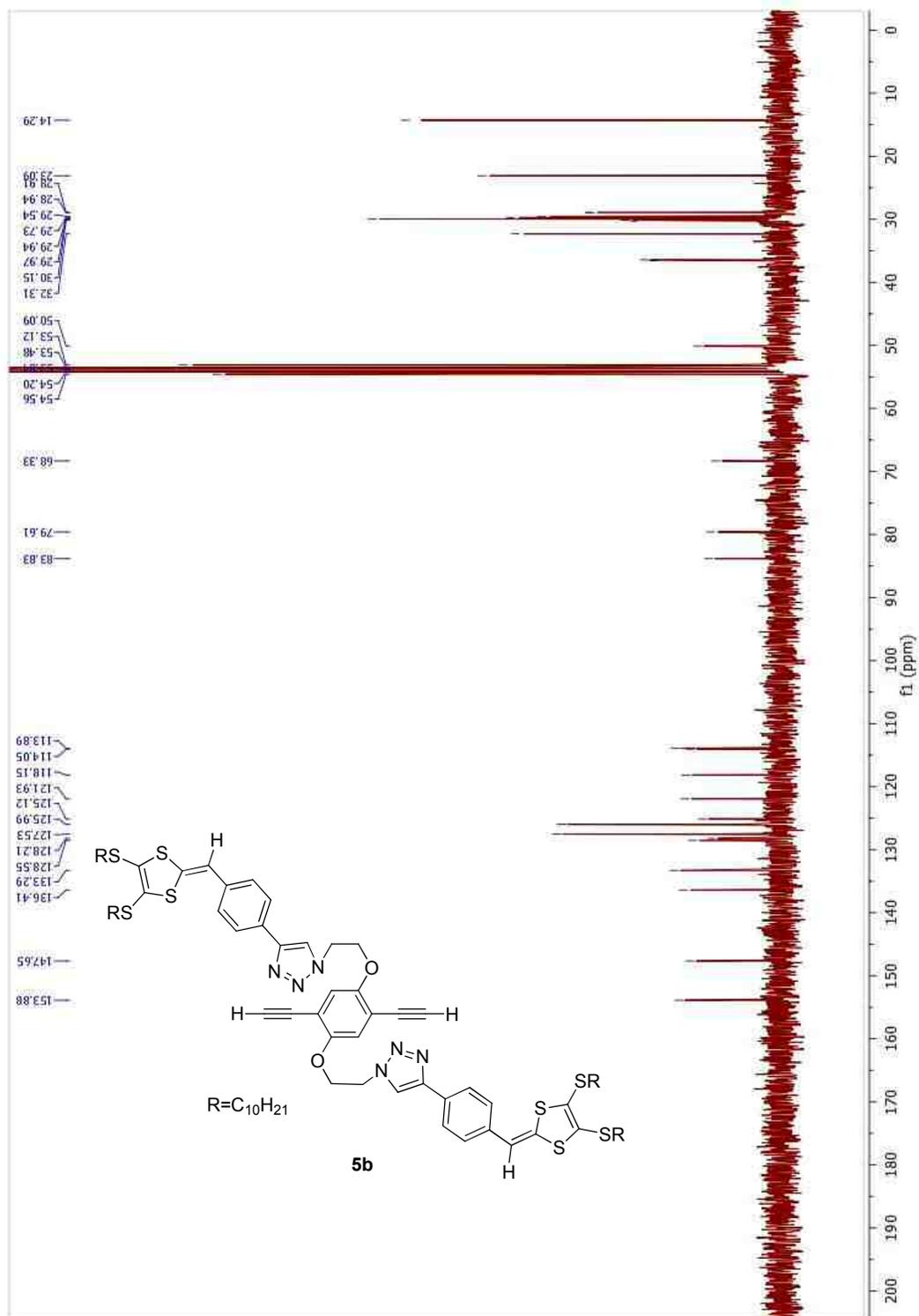


Fig. S-4 ^{13}C NMR (75 MHz, CD_2Cl_2) spectrum of compound **5b**.

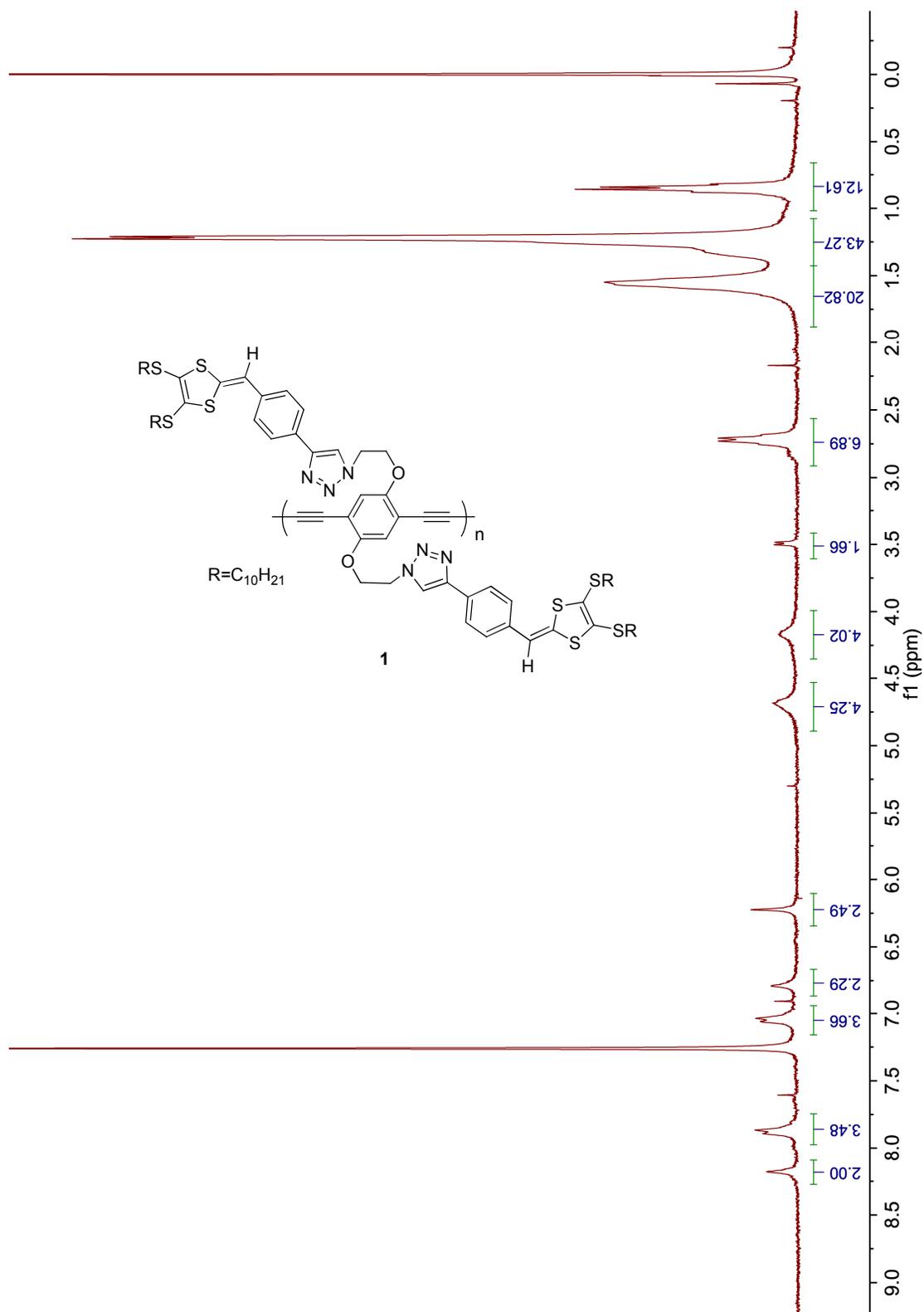
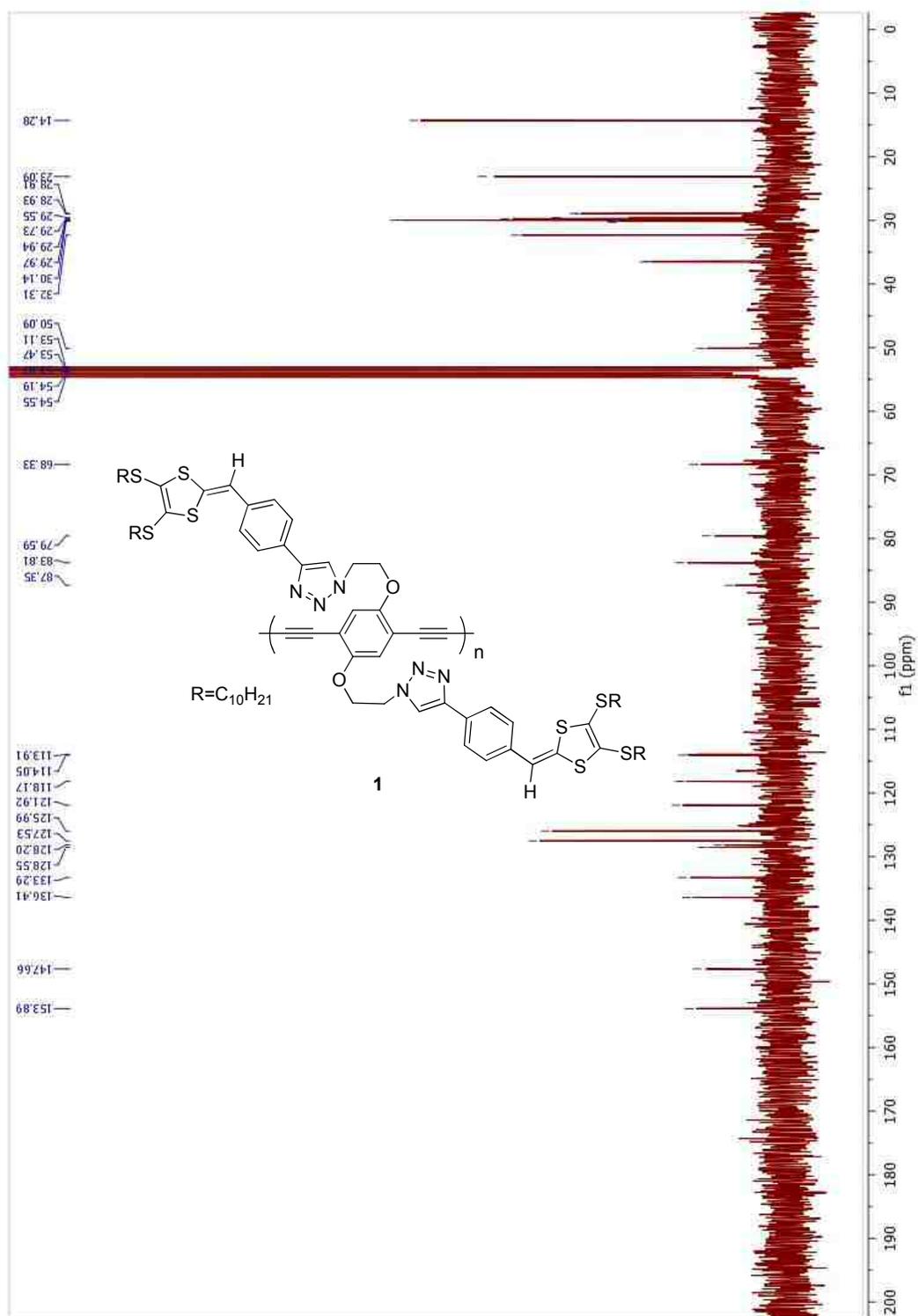


Fig. S-5 ¹H NMR (500 MHz, CDCl₃) spectrum of polymer **1**.



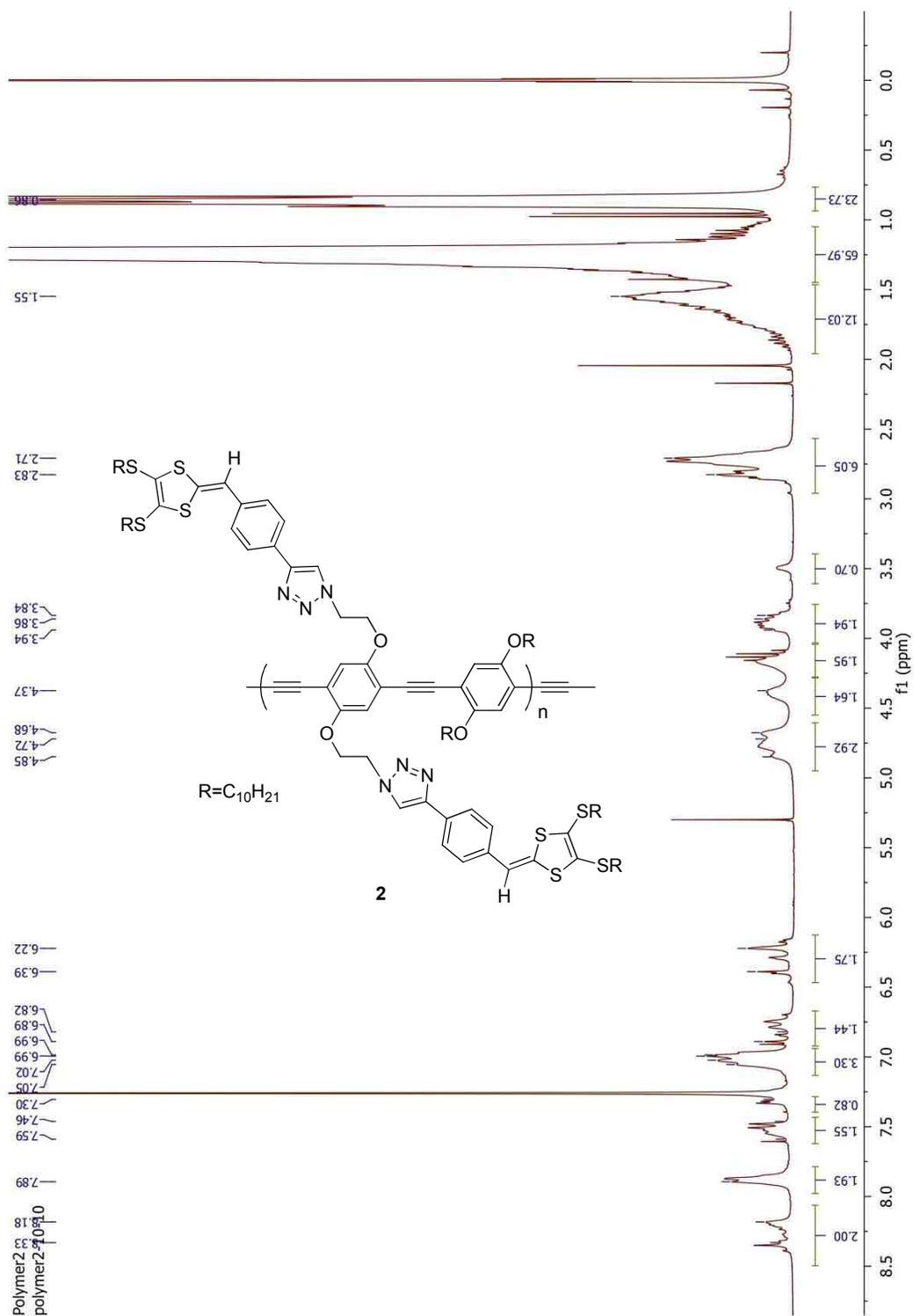


Fig. S-7 ¹H NMR (500 MHz, CDCl₃) spectrum of polymer **2**.

3. GPC Analytical Results

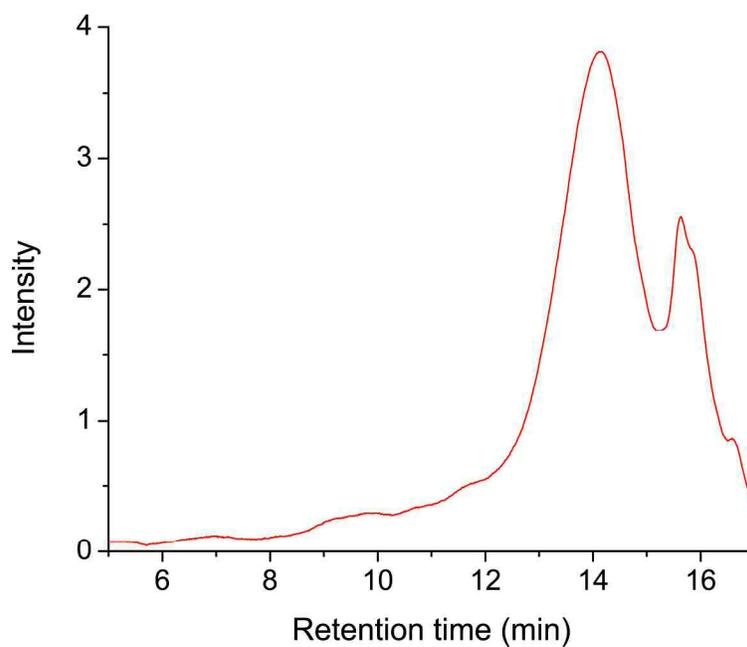


Fig. S-8 GPC profile of polymer 1.

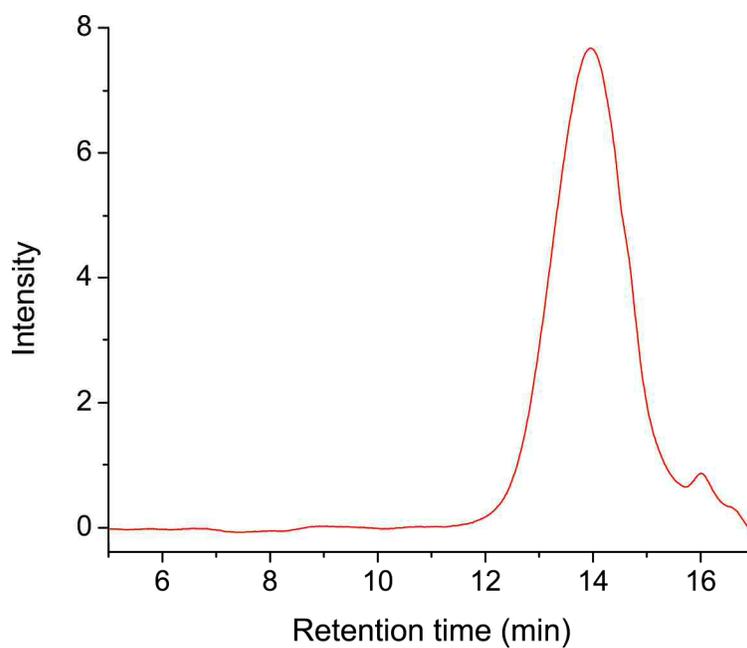


Fig. S-9 GPC profile of polymer 2.

4. UV-Vis Spectroscopic and Electrochemical Data

4.1 UV-Vis and cyclic voltammetric analysis on polymers **1** and **2**, precursor **5b**, and the complexes of polymer **1** and HiPCO SWNTs

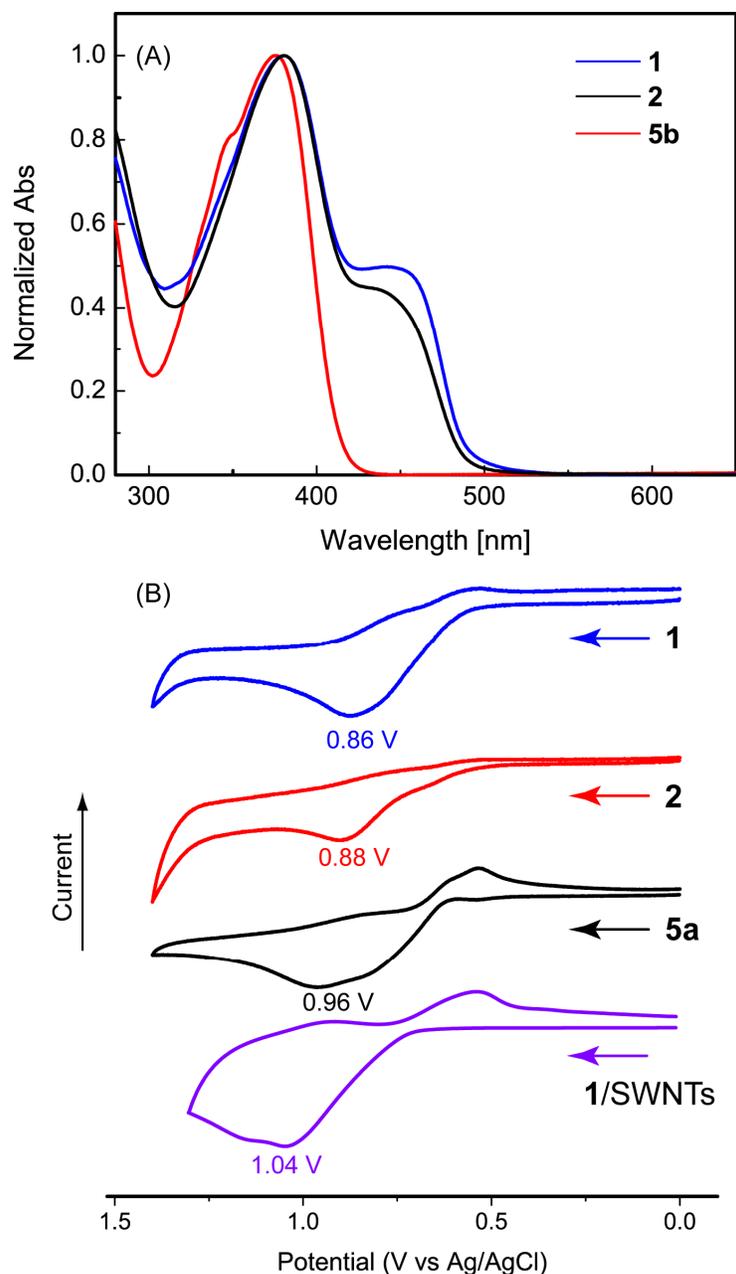


Fig. S-10 (A) UV-Vis absorption spectra of polymers **1** and **2** and DTF precursor **5b** measured in CH_2Cl_2 at room temperature. (B) Cyclic voltammograms of **1**, **2**, **5b**, and the thin film of polymer **1** and HiPCO SWNT complexes measured in CH_2Cl_2 . Electrolyte: Bu_4NBF_4 (0.1 M); working: glassy carbon; counter: Pt wire; reference: Ag/AgCl; scan rate: 200 mV s^{-1} .

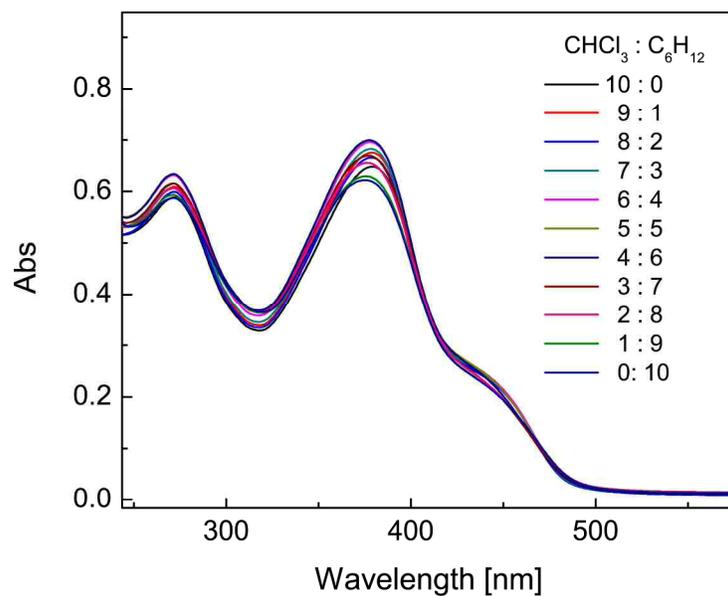
4.2 Solvent effect on UV-Vis absorption of polymer **1**

Fig. S-11 UV-Vis absorption spectra of polymer **1** measured in chloroform/hexanes at various volumetric ratios.

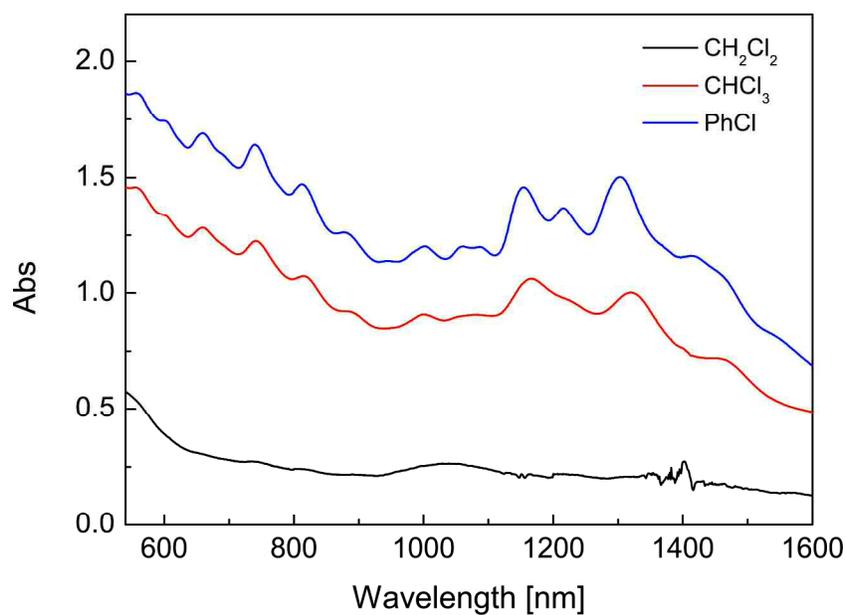
4.2 Dispersion of SWNTs with polymers **1** and **2** in different solvents

Fig. S-12 UV-Vis-NIR spectra of HiPCO SWNTs dispersed with **1** in chlorobenzene, CHCl_3 , and CH_2Cl_2 .

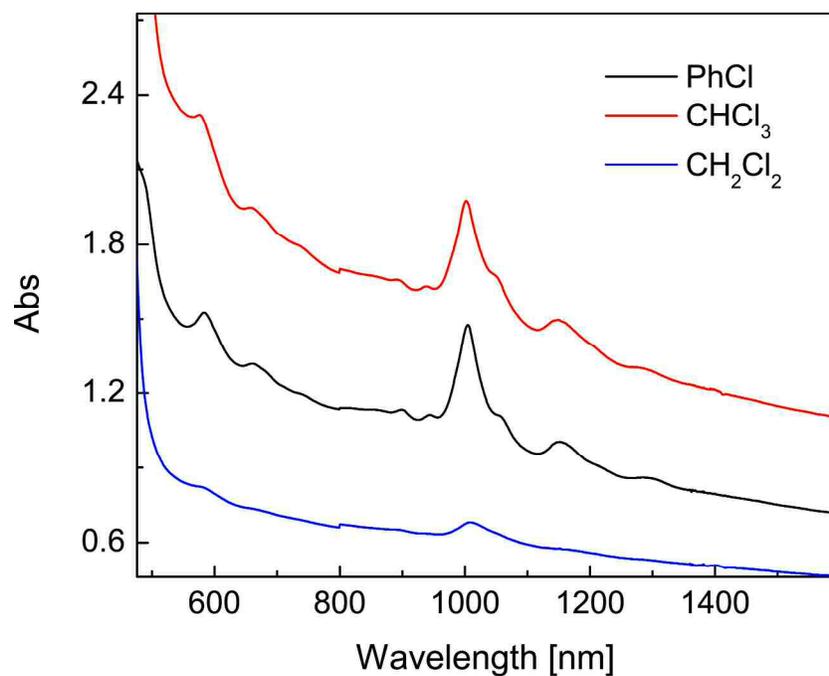


Fig. S-13. UV-Vis-NIR spectra of CoMoCAT SWNTs dispersed with polymer **1** in chlorobenzene, CHCl₃, and CH₂Cl₂.

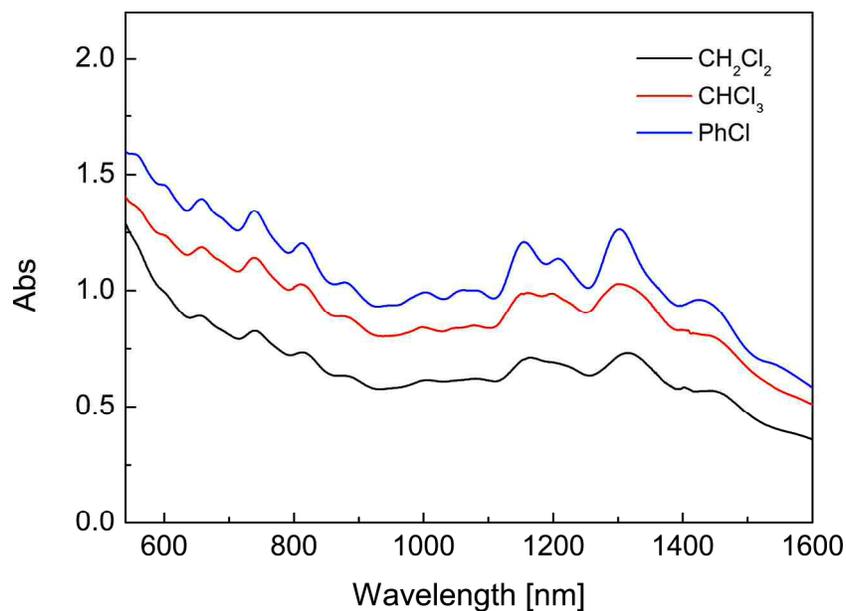


Fig. S-14 UV-Vis-NIR spectra of HiPCO SWNTs dispersed with **2** in chlorobenzene, CHCl₃, and CH₂Cl₂.

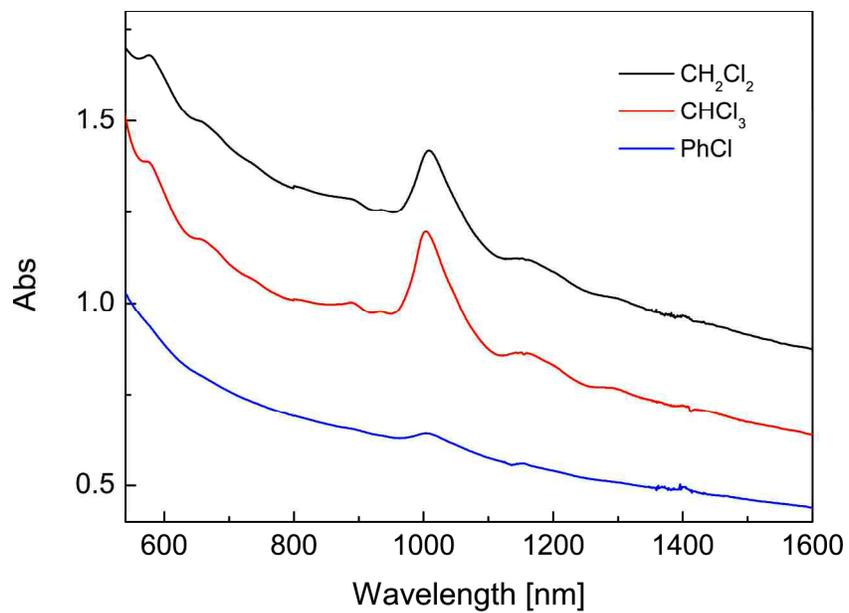


Fig. S-15 UV-Vis-NIR spectra of CoMoCAT SWNTs dispersed with polymer **2** in chlorobenzene, CHCl₃, and CH₂Cl₂.

5. Thermal Gravimetric Analysis

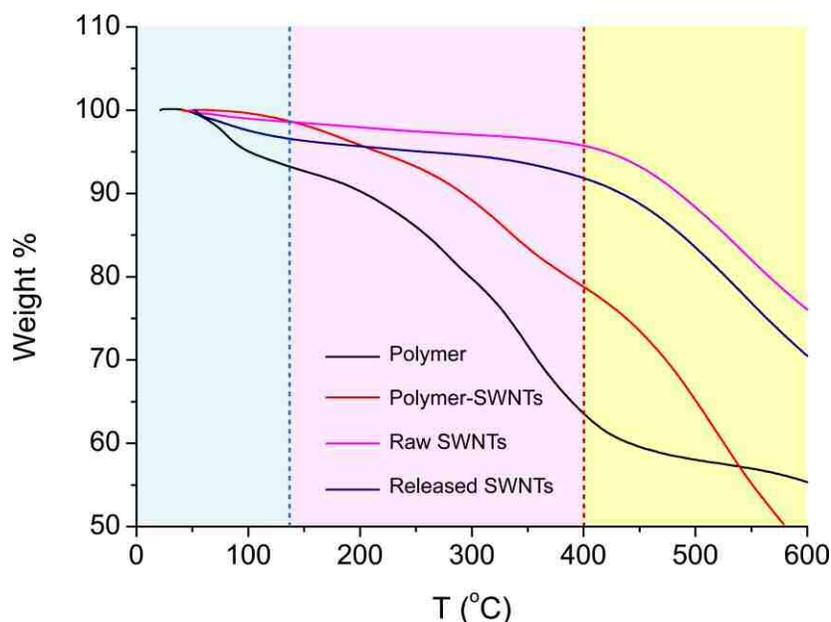


Fig. S-16 TGA profiles of polymer **1**, polymer **1**/CoMoCAT nanotube complexes, raw CoMoCAT nanotubes, and released CoMoCAT nanotubes. Scan rate: 10 °C/min.

Experimental procedures:

Polymer **1**/SWNT complexes were prepared by sonication of excess CoMoCAT nanotubes with a CHCl_3 solution of polymer **1** for 40 min. The resulting black suspension was filtered through a tightly packed cotton plug, and the filtrate was evaporated under vacuum to afford the polymer/SWNT complexes.

Released SWNTs were obtained by addition of an equal volume of hexanes to the suspension of polymer **1**/SWNTs in chloroform. The resulting mixture was subjected to centrifugation to separate the released SWNTs and polymer solution. Next, three cycles of CHCl_3 washing and centrifugation separation were performed to further remove the polymer component. Finally, the SWNTs were collected by vacuum filtration and dried in an oven at 80 °C. It was measured that 0.49 mg of HiPCO SWNTs could be recovered from every 1.00 mL of polymer **1**/ CHCl_3 solution.

TGA analysis:

From Figure S-16, a noticeable amount of weight loss can be seen in the TGA curves of polymer **1** and released SWNTs in the range from room temperature to 137 °C. The weight loss is attributable to desolvation or desorption of moisture. From 137 to 400 °C, polymer **1** shows a significant degree of weight loss as a result of decomposition reactions. Raw CoMoCAT nanotubes, on the other hand, do not show any significant weight loss below 400 °C. Given the TGA behavior observed, it is reasonable to estimate

the polymer content associated with released SWNTs by examining the weight loss occurring in the temperature range of 137-400 °C. Table S-1 lists the detailed data.

Table S-1. TGA data of polymer **1**, polymer **1**/SWNT complexes, raw SWNTs, and released SWNTs measured at 137 and 400 °C.

	Wt % (137 °C)	Wt % (400 °C)	ΔWt %	Wt % of Polymer*
Polymer 1	93.3%	63.5%	29.8%	
Raw SWNTs	98.6%	95.7%	2.9%	
Polymer 1 /SWNTs	98.6%	78.7%	19.9%	77%
Released SWNTs	96.6%	91.8%	4.8%	7.6%

*Assuming the weight of percent of polymer **1** is $x\%$ and the weight percent of SWNTs is $y\%$ in a polymer/SWNT complex, then the relationships of the measured $\Delta\text{Wt } \%$ values can be described by the following equations:

$$\Delta\text{Wt } \% (\text{polymer/SWNTs}) = \Delta\text{Wt } \% (\text{polymer}) \times x\% + \Delta\text{Wt } \% (\text{SWNTs}) \times y\%$$

$$x\% + y\% = 100\%$$

Combining these two equations, the weight percent ($y\%$) of polymer components in the polymer/SWNT complex is calculated to be 77%. For the released SWNTs, the weight percent of polymer **1** is only 7.6%.

6. AFM and SEM Imaging Results

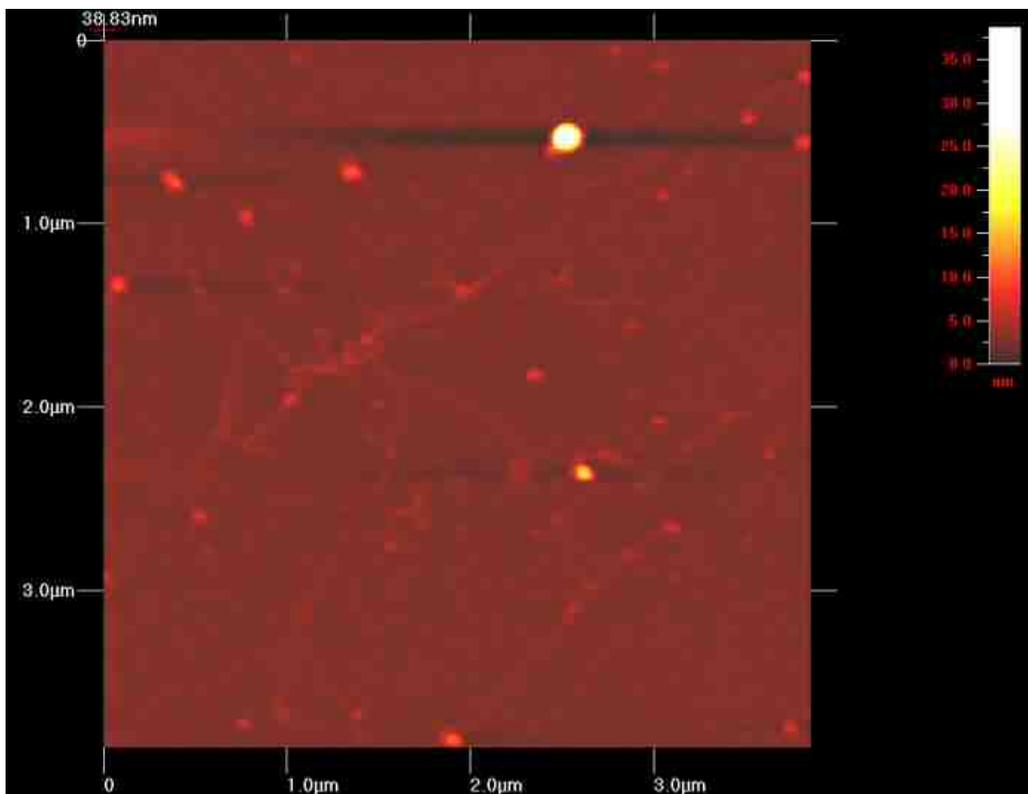


Fig. S-17 AFM image of the suspension of polymer **1** and HiPCO SWNTs drop-cast on a freshly cleaved mica substrate (tapping mode).

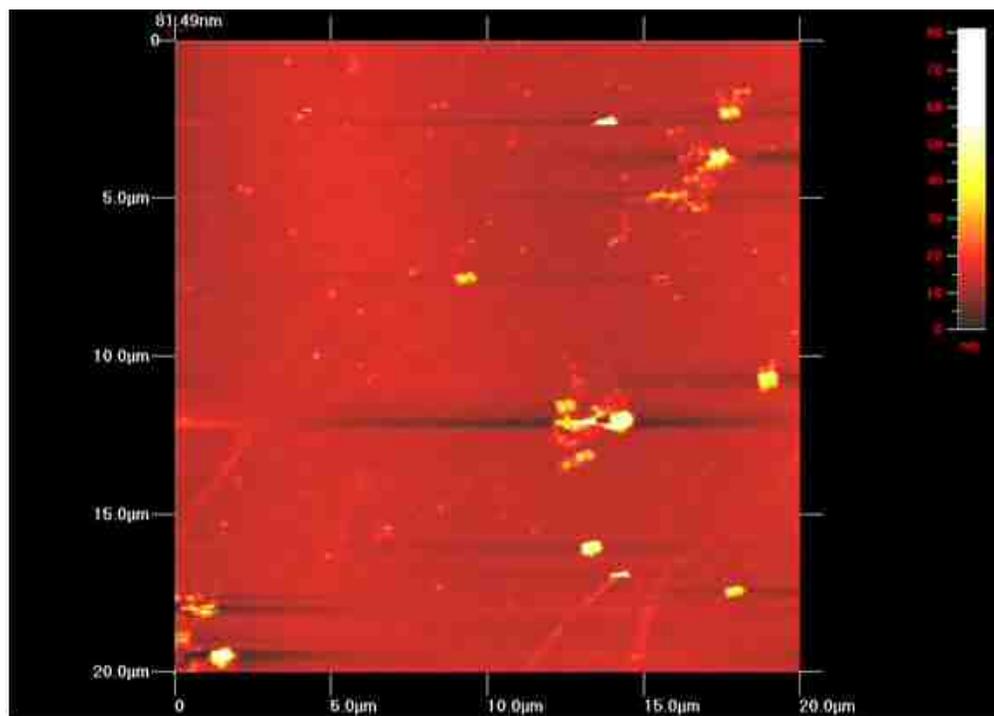


Fig. S-18 AFM image of the suspension of polymer **2** and HiPCO SWNTs drop-cast on a freshly cleaved mica substrate (tapping mode).

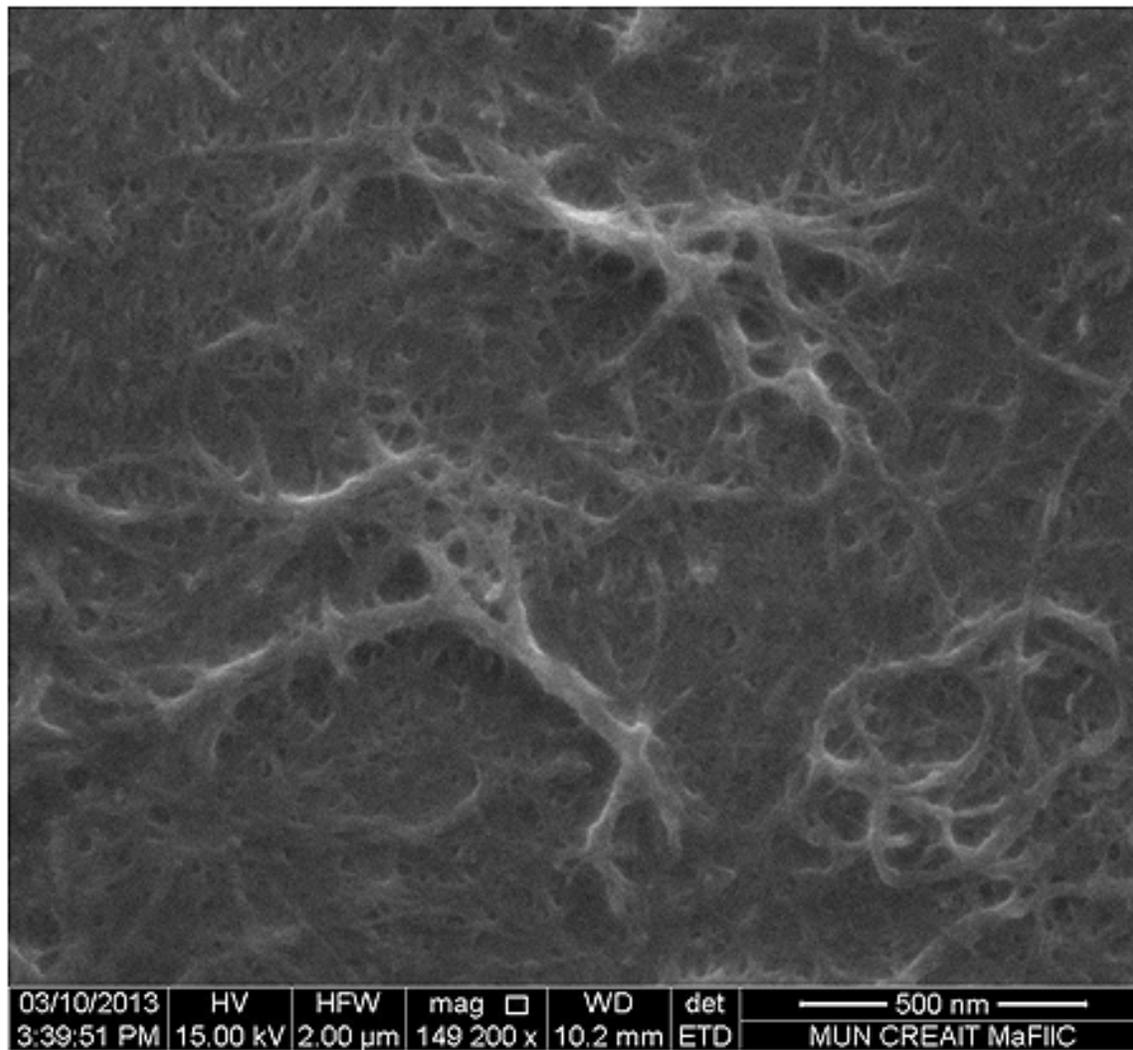


Fig. S-19 SEM image of the complex of polymer **1** and HiPCO SWNTs after solvent evaporation.

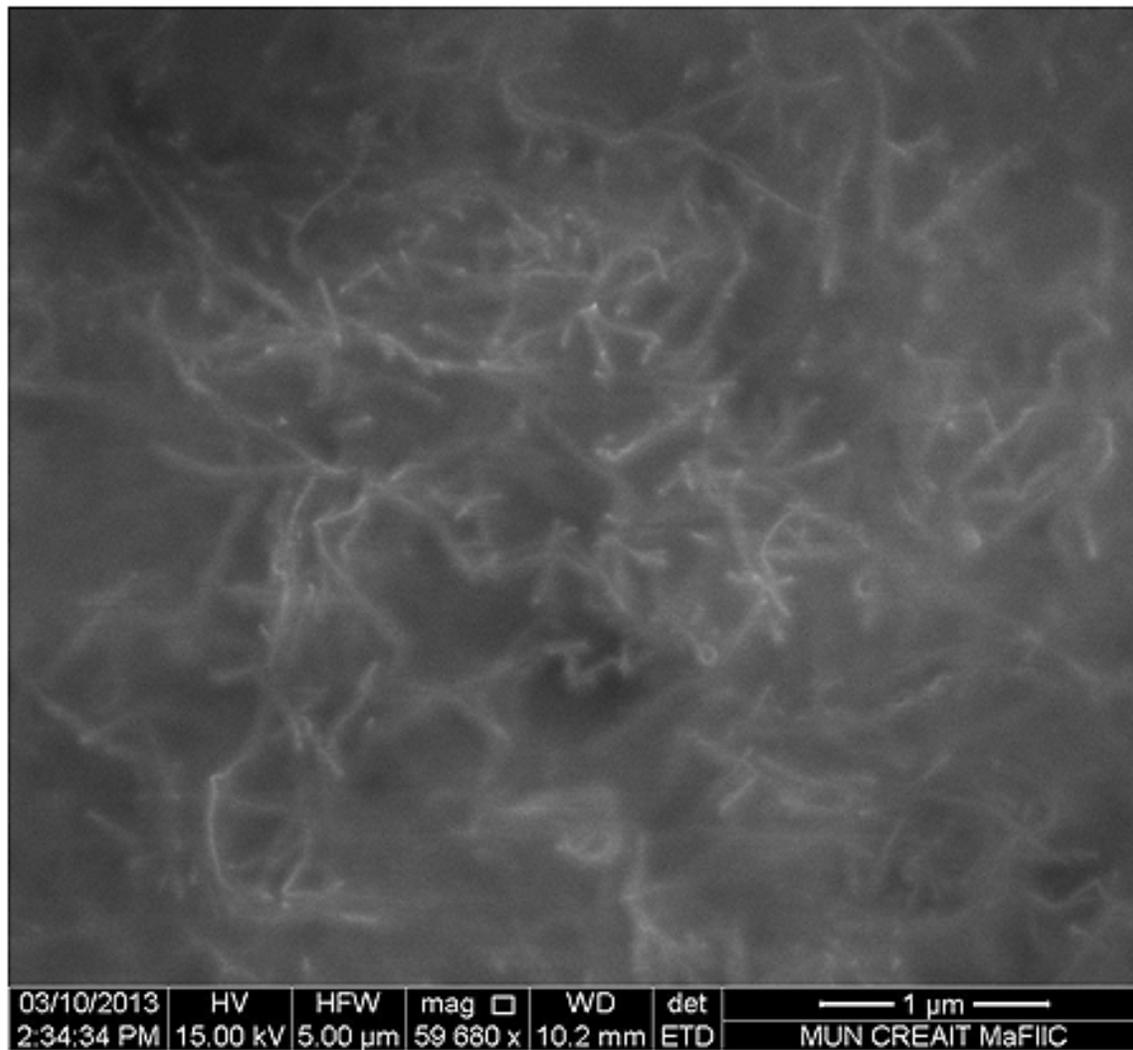


Fig. S-20 SEM image of the complex of polymer **2** and HiPCO SWNTs after solvent evaporation.

7. PLE Map of HiPCO SWNTs Dispersed with SDBS

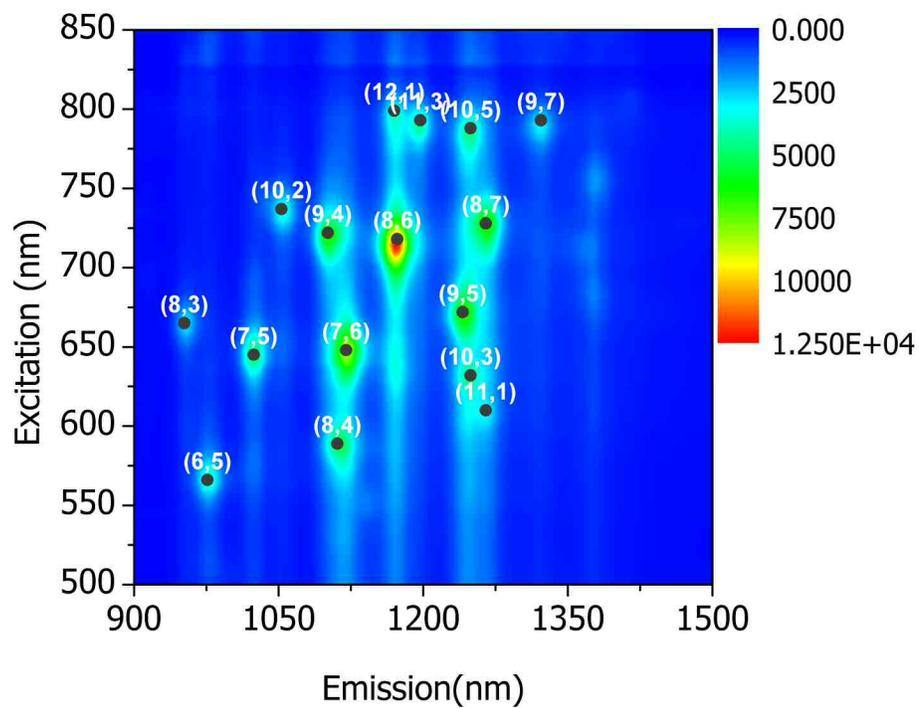


Fig. S-21 PLE map of HiPCO SWNTs dispersed with SDBS in water.

8. Spectroelectrochemical Analysis

Sample preparation: HiPCO SWNTs were dispersed in a solution of Bu_4NBF_4 (ca. 0.1 M) in CHCl_3 with the aid of ultrasonication (40 min), using polymer **2** as dispersant. The resulting black suspension was filtered through a tightly packed cotton plug and the filtrate was collected for UV-Vis spectroelectrochemical analysis. For comparison purpose, a solution of polymer **2** and Bu_4NBF_4 in CHCl_3 was prepared as well.

Measurements: samples were placed in a quartz cell with a 1 mm light path. Controlled potential electrolysis (CPE) was performed in a three-electrode setup as schematically described in Figure S-22. In the experiments, the sample solution was first subjected to electrolysis at a certain voltage for 1.5 min and then a UV-Vis-NIR absorption spectrum of the solution was measured at this voltage. The measurement was repeated at various voltages applied to the working electrode.

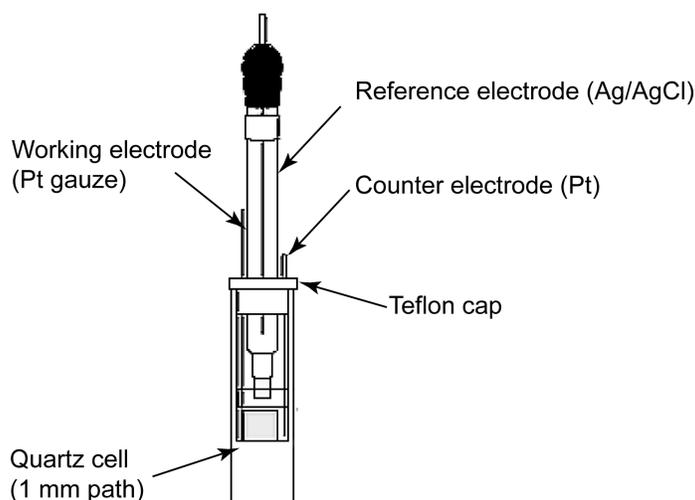


Fig. S-22 Schematic illustration of the three-electrode electrochemical cell for the spectroelectrochemical analysis.

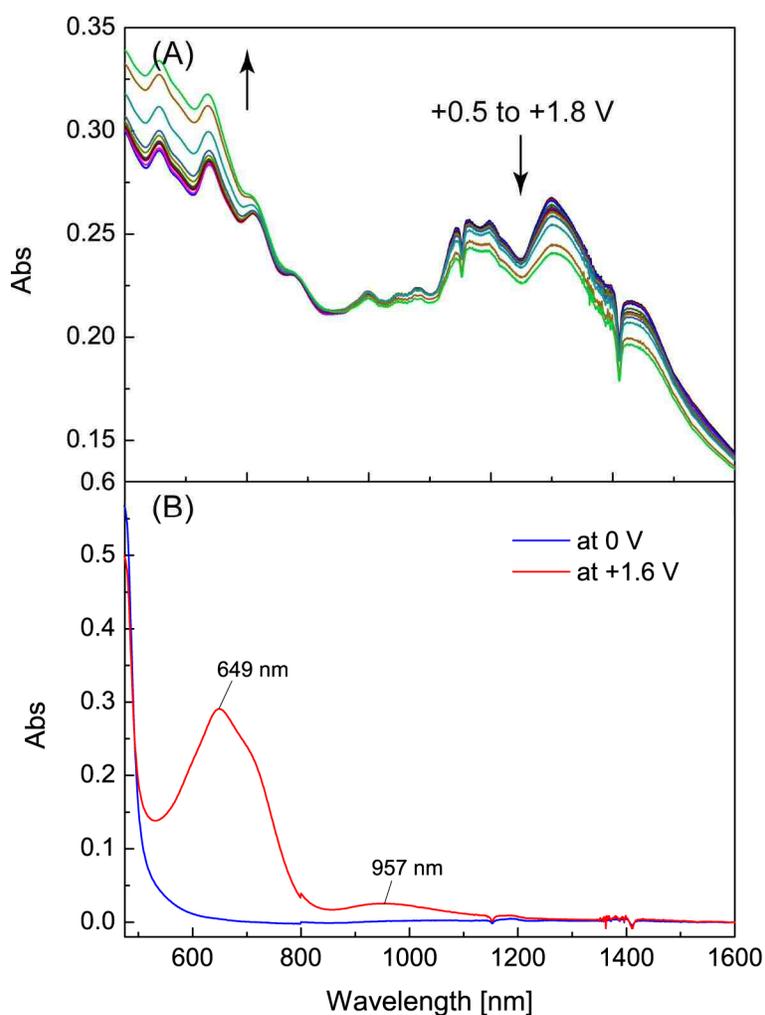


Fig. S-23 (A) Vis-NIR spectra of HiPCO SWNTs dispersed with polymer **2** in CHCl_3 measured at various applied voltages. (B) Vis-NIR spectra of polymer **2** in CHCl_3 measured at 0 V and +1.6 V.

Discussion: From Fig. S-23A, it is clearly seen that the absorption bands in the range of 1000 to 1600 nm show a trend of decrease in intensity with increasing applied voltage. In the meantime, the absorption from 570 to 800 nm shows an increasing trend. Fig. S-23B shows that polymer **2** in the neutral state does not give any significant absorption in the range from 600 to 1600 nm. After electrochemical oxidation at +1.6 V for 1.5 min, a significant absorption at 649 nm is observable, along with a weak broad band centered at 957 nm. The new absorption bands can be assigned to the DTF cations resulting from electrochemical oxidation. Overall, the spectral changes of Fig. S-23A in the range of 570 to 1000 nm are convoluted by the absorption bands of oxidized polymer **2** and SWNTs. Nevertheless, in the spectral range of 1000 to 1600 nm, the trend shown in Fig. S-23A clearly indicates that concentration of SWNTs in the solution decreases with increasing voltage (i.e. oxidation).

9. Selectivity Analysis of SWNT Dispersion Based on PLE Mapping Data

The selectivity for SWNTs with different chiral indexes is analyzed based on the PLE mapping data shown in Fig. 3. For quantitative assessment, the abundance of a particularly type of SWNT is assumed to be proportional to the fluorescence intensity it gives in the PLE map. The detailed data is summarized in Table S-2.

Table S-2. Relative abundance of SWNTs with different chiral indexes dispersed in the CH₂Cl₂ solution of polymer **1**.

	Chiral index	Fluorescence Intensity (counts)	Relative abundance
CoMoCAT tubes	(6,5)	2855.38	1.00
	(7,5)	2059.68	0.72
	(8,3)	1379.45	0.48
HiPCO tubes	(6,5)	1141.8	0.92
	(7,5)	1177.12	0.95
	(7,6)	1238.27	1.00
	(8,3)	771.99	0.62
	(8,4)	674.12	0.54
	(10,2)	741.35	0.60
	(9,4)	718.16	0.58
	(8,6)	845.65	0.68
	(8,4)	674.12	0.54
	(10,3)	530.93	0.43
	(9,5)	617.21	0.50
(8,7)	516.67	0.42	