# Supporting Information

# Reversible Dispersion and Releasing of Single-Walled Carbon Nanotubes by a Stimuli-Responsive TTFV-Phenylacetylene Polymer

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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. CoMoCAT SWNTs were purchased from Southwest NanoTechnologies Inc. Et<sub>3</sub>N and toluene were distilled from CaH<sub>2</sub>. Compounds 2, 3, and 6 were prepared according to literature procedures.<sup>1-3</sup> All reactions were performed in standard dry glassware under an inert atmosphere of N<sub>2</sub> unless otherwise noted. Evaporation and concentration was done at H<sub>2</sub>O-aspirator pressure. Flash column chromatography were 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. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker Avance 500 MHz spectrometer or a Tecmag APOLLO 300 MHz spectrometer. Chemical shifts are reported in ppm downfield from the signal of the internal reference SiMe<sub>4</sub>. 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 MS were measured on an Applied Biosystems Voyager instrument using dithranol as the matrix. The gel permeation chromatography (GPC) measurements were performed on a Waters 515 system with UV detector using polystyrene standards with THF as eluent. UV-Vis absorption spectra were obtained on a Varian diode-array spectrophotometer (model Cary 500) using 1-cm path length quartz cells. 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 measured on a Horiba Jobin Yvon confocal Raman spectrometer operated at a laser wavelength of 532nm. Cyclic voltammetric (CV) experiments were carried out in a standard three-electrode setup controlled by a BASi Epsilon workstation.

# **1.2** Synthetic Procedures





Bezaldehyde **2** (400 mg, 1.98 mmol), P(OMe)<sub>3</sub> (10 mL) and xylenes (20 mL) were mixed together, and the mixture was degassed and then heated to 120 °C. To the mixture was slowly added a solution of phosphonate **3** (448 mg, 1.98 mmol) in xylenes (4 mL) over a period of 1 h. After the addition was complete, the reaction mixture was kept stirring for another 1.5 h under heating, and then it was concentrated *in vacuo*. Filtration through a long silica plug removed the unreacted P(OMe)<sub>3</sub>. The filtrate, after concentration *in vacuo*, was subjected to silica column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/hexanes 1:9) to yield acetylenic phenyldithiafulvene **4** (480 mg, 1.26 mmol, 64%) as a yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.43 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 6.44 (s, 1H), 2.44 (s, 3H), 2.43 (s, 3H), 0.25(s, 9H). The <sup>1</sup>H NMR data is consistent with those reported in the literature.<sup>4</sup>

#### TTFV 5



To a solution of DTF **4** (393 mg, 1.04 mmol) in  $CH_2Cl_2$  (40 mL) was added I<sub>2</sub> (396 mg, 1.56 mmol). The resulting mixture, after being stirred for 4 hr, was quenched with satd Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aq. solution (50 mL). The mixture was stirred for 2 hr. Then the organic layer was separated, washed with H<sub>2</sub>O, dried over MgSO<sub>4</sub> and concentrated *in vacuo*. The residue was dissolved in CS<sub>2</sub> (2 mL) and then subjected to silica column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/ hexanes 1:9) to yield TTFV **5** (224 mg, 0.295 mmol, 57%) as a yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.38 (d, *J* 

= 8.6Hz, 4H), 7.31 (d, J = 8.6Hz, 4H), 2.42 (s, 6H), 2.37(s, 6H), 0.23 (s, 18H). The <sup>1</sup>H NMR data is consistent with those reported in the literature.<sup>4</sup>

#### TTFV 7



To a solution of TTFV 5 (83 mg, 0.11 mmol) in THF/MeOH (10 mL, 1:1) was added K<sub>2</sub>CO<sub>3</sub> (91 mg, 0.66 mmol). The mixture was stirred for 0.5 h at rt, and it was then diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with H<sub>2</sub>O, dried over MgSO<sub>4</sub>, and concentrated in vacuo. To the residue was added Et<sub>3</sub>N (30 mL) and iodoarene 6 (269 mg, 0.440 mmol). The mixture was degassed by vigorous N<sub>2</sub> bubbling. To the mixture was then added CuI (12 mg, 0.011 mmol) and Pd(PPh)<sub>4</sub> (6 mg, 0.03 mmol). The mixture was heated at 60 °C and kept stirring overnight. The resulting reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed sequentially with aq. NH<sub>4</sub>Cl and H<sub>2</sub>O, dried over MgSO<sub>4</sub>, and concentrated in vacuo. The residue was purified by silica column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/hexanes 5:95) to yield TTFV monomer 7 (116 mg, 0.0732 mmol, 67%) as a yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.45 (d, J = 8.5 Hz, 4H), 7.37 (d, J = 8.4 Hz, 4H), 6.92 (d, J = 5.1 Hz, 4H), 4.00–3.93 (m, 8H), 2.40 (d, J = 24.3 Hz, 12H), 1.84 – 1.75 (m, 8H), 1.53 - 1.46 (m, 8H), 1.39-1.19 (m, 48H), 0.86 (m, 12H), 0.25 (s, 18H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) § 154.18, 153.45, 137.91, 136.64, 131.87, 128.77, 126.30, 125.09, 123.64, 121.51, 117.28, 116.87, 114.31, 113.65, 101.20, 100.06, 95.01, 86.74, 69.58, 69.50, 31.91, 29.66, 29.62, 29.56, 29.46, 29.39, 29.36, 29.31, 26.06, 26.00, 22.71, 18.95, 18.86, 14.18, 14.14; FTIR (neat) 2922, 2854, 2152, 1503, 1465, 1475, 1378, 1277, 1213, 1019 cm<sup>-1</sup>; HR-MALDI-TOF MS *m/z* calcd for C<sub>90</sub>H<sub>126</sub>O<sub>4</sub>S<sub>8</sub>Si<sub>2</sub>1582.6960, found 1582.7006;.

#### **TTFV polymer 1**



To a solution of TTFV monomer **7** (574 mg, 0.364 mmol) in THF/MeOH (10 mL, 1:1) was added K<sub>2</sub>CO<sub>3</sub> (302 mg, 2.18 mmol). The mixture was stirred at rt for 0.5 h, and then it was diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with H<sub>2</sub>O, dried over MgSO<sub>4</sub>, and concentrated *in vacuo*. To the residue was added toluene (30 mL), CuI (20 mg, 0.11 mmol), Pd(PPh)<sub>4</sub> (25 mg, 0.036 mmol) and DBU (0.0054 mL, 0.036 mmol). The mixture was heated at 70 °C under stirring for 1 h. Then iodoarene **6** (11 mg, 0.036 mmol) was added and the mixture was stirred for 36 h. Afterwards, methanol was added and the resulting precipitates were collected by filtration to afford TTFV polymer **1** (526 mg, 90%) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.46 (d, *J* = 7.8 Hz, 20H), 7.38 (d, *J* = 7.9Hz, 20H), 6.97 (m, 20H), 4.05 – 3.90 (m, 50H), 2.43 (s, 30H), 2.38 (s, 30H), 1.81 (m, 49H), 1.51 – 1.43 (m, 55H), 1.39 – 1.19 (m, 445H), 0.90 – 0.79 (m, 128H), 0.06 (s, 18H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  155.00, 153.47, 138.08, 137.89, 136.75, 131.93, 129.05, 128.81, 128.24, 126.32, 125.31, 125.13, 123.60, 121.41, 117.71, 116.93, 115.18, 112.53, 95.69, 86.66, 79.62, 79.35, 69.82, 69.61, 31.93, 29.73, 29.64, 29.61, 29.57, 29.49, 29.38, 29.29, 29.17, 26.06, 26.01, 25.96, 22.72, 21.48, 18.97, 18.87, 14.19, 14.14. FTIR (neat) 2915, 2849, 2202, 1509, 1467, 1417, 1376, 1272, 1211, 1017 cm<sup>-1</sup>. GPC: M<sub>n</sub> = 13400 g/mol, M<sub>w</sub> = 51900 g/mol, PDI = 3.9.

# 2. NMR Spectra



Figure S-1. <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) for compound 4.



**Figure S-2**. <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) for compound **5**.



**Figure S-3**. <sup>1</sup>H NMR spectrum for compound **7**.



Figure S-4. <sup>13</sup>C NMR spectrum (75 MHz, CDCl<sub>3</sub>) for compound 7.



Figure S-5. <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) for polymer 1.



Figure S-6. <sup>13</sup>C NMR spectrum (75 MHz, CDCl<sub>3</sub>) for polymer 1.

# 3. GPC analysis of TTFV polymer 1.



Figure S-7. Gel permeation chromatogram of TTFV polymer 1. Experimental conditions: columns: 2xPolyPore; standard: polystyrene; sample concentration: 1 mg polymer in 3 mL THF.  $M_n = 13400 \text{ g/mol}, M_w = 51900 \text{ g/mol}, PDI = 3.9.$ 

# 4. Cyclic Voltammetric Properties of Compounds 1, 5, and 7



**Figure S-8**. Cyclic voltammogram of TTFV **5** ( $10^{-3}$  M), monomer **7** ( $10^{-3}$  M), and polymer **1** (2 mg/mL). Experimental conditions: Bu<sub>4</sub>NBF<sub>4</sub> (0.1 M) as the supporting electrolyte, CH<sub>2</sub>Cl<sub>2</sub> as the solvent glassy carbon as the working electrode, Pt wire as the counter electrode, Ag/AgCl as the reference electrode, and scan rate: 200 mV s<sup>-1</sup>.

# 5. Protonation Properties of TTFV Compounds by TFA

#### 5.1 UV-Vis titration experiments

The protonation behaviour of TTFV compounds 5, 7, and polymer 1 was investigated by UV-Vis titration with trifluoroacetic acid in  $CH_2Cl_2$  at room temperature. The detailed titration data are shown in the following figures.



**Figure S-9**. UV–Vis absorption spectra of TTFV **5** in CH<sub>2</sub>Cl<sub>2</sub> upon addition of TFA from.(A) 0 to  $1.6 \times 10^4$  equiv, and (B)  $1.6 \times 10^4$  to  $7.0 \times 10^4$  equiv. Arrows indicate the trends of spectral changes.

The UV-Vis titration results clearly show a two-step equilibrium. In the first step (Figure S-9A), the intensity at  $\lambda = 380$  nm steadily decreases, and those of at  $\lambda = 640$ , 710, and 950 nm increase. In the second step (Figure S-9B), the intensities at  $\lambda = 640$  and 950 nm decrease, while the intensity  $\lambda = 720$  nm increases steadily. The two steps are assigned to the following protonation reactions, which lead to the formation of thiolium and dithiolium ions respectively.<sup>5</sup>



The conformational properties of the protonated dithiolium ions are studied by density functional theory (DFT) calculations using the *Spartan'10* software. The optimized geometry was shown below.



**Figure S-10**. Molecular structure of diprotonated diphenyl-TTFV optimized at the B3LYP/6-311G\* level of theory. Left: side view; Right: front view.



**Figure S-11**. UV–Vis absorption spectra of compound **7** in  $CH_2Cl_2$  upon addition of TFA from.(A) 0 to  $6.0 \times 10^4$  equiv, and (B)  $6.0 \times 10^4$  to  $1.0 \times 10^5$  equiv. Arrows indicate the trends of spectral changes.



**Figure S-12**. UV–Vis absorption spectra of polymer **1** in  $CH_2Cl_2$  upon addition of TFA from.(A) 0 to  $2.0 \times 10^4$  equiv, and (B)  $2.0 \times 10^4$  to  $6.0 \times 10^4$  equiv (molar equiv was calculated based on the average molecular weight of polymer determined by GPC). Arrows indicate the trends of spectral changes.

# 6. Multi-Cycle Dispersion-Releasing of SWNTs

# 6.1 Multi-cycle dispersion-releasing of CoMoCAT SWNTs

# Cycle 1

To a toluene solution of polymer **1** (8.0 mL, 4.5 mg/mL) was added CoMoCAT SWNTs (40 mg). The mixture was ultrasonicated for 30 min, left still for 2 h, and then filtered through a tightly packed cotton plug to remove insoluble components. A clear black SWNT solution was obtained which was characterized by UV-Vis spectral analysis.

To the solution was added an excess amount of trifluoroacetic acid (TFA, 2.0 mL). Precipitation of SWNTs was observed. The mixture was subjected to centrifugation for 15 min to afford a clear yellow solution and SWNT precipitates on the bottom. The top organic layer was carefully transferred to an Erlenmeyer flask by a pipette, washed with aq. Na<sub>2</sub>CO<sub>3</sub> solution, and dried over MgSO<sub>4</sub> to afford the recovered polymer solution. UV-Vis and <sup>1</sup>H NMR analyses on the recovered polymer showed that the recovered polymer does not undergo any changes in molecular structure. The bottom precipitates was collected and washed sequentially with toluene (20 mL) and acetonitrile (20 mL), and air-dried overnight in the fumehood to afford the released SWNTs (16 mg).

# Cycle 2

To the released SWNTs (16 mg) was added a toluene solution of polymer 1 (3.2 mL, 4.5 mg/mL). The mixture was treated with the same procedure in cycle 1 to afford a SWNT solution, which was characterized by UV-Vis analysis.

To the solution was added an excess amount of TFA (1.0 mL). The mixture was treated with the same procedure in cycle 1 to afford the released SWNTs (3 mg) and the recovered polymer solution.

## Cycle 3

To the released SWNTs (3 mg) was added a toluene solution of polymer (0.6 mL). The mixture was treated with the same procedure in cycle 1 to afford a SWNT solution, which was characterized by UV-Vis analysis.

Then to the solution was added an excess amount of TFA (0.1 mL). The mixture was treated with the same procedure in cycle 1 to give recovered polymer solution and the released SWNTs, the weight of which was not determined due to the small amount.

	Cycle 1	Cycle 2	Cycle 3
Starting CoMoCAT NTs	40 mg	16 mg	3 mg
Polymer 1 (4.5 mg/mL)	8.0 mL	3.2 mL	0.6 mL
TFA	2.0 mL	1.0 mL	0.1 mL
Recovered CoMoCAT NTs	16 mg	$3 \text{ mg}^*$	-

**Table S-1.** Quantities of starting and recovered CoMoCAT SWNTs, polymer solution, and TFA used in the multi-cycle dispersion-releasing of SWNTs.

\*Low recovery is due to partially protonation of SWNTs and significant mechanical loss during small-quantity sample handling.

# 6.2 Multi-cycle dispersion-releasing of HiPCO SWNTs

## Cycle 1

To a toluene solution of polymer (32.0 mL, 2.3 mg/mL) was added HiPCO SWNTs (48 mg). The mixture was ultrasonicated for 30 min, left to stand still for 2 h, and filtered through a tightly packed cotton plug to remove insoluble components. A clear black SWNT solution was obtained, which was characterized by UV-Vis spectral analysis.

To the solution was added an excess amount of TFA (3.0 mL), which led to the release of SWNTs as precipitates. The mixture was subjected to centrifugation for 15 min to afford a clear yellow solution and SWNT precipitates on the bottom. The top organic layer was carefully transferred to an Erlenmeyer flask by a pipette, washed with aq.  $Na_2CO_3$  solution, and dried over MgSO<sub>4</sub> to afford the recovered polymer solution. The bottom precipitates was washed sequentially with toluene (20 mL) and acetonitrile (20 mL), and air-dried overnight in the fumehood to afford the released SWNTs (10 mg).

## Cycle 2

To the released SWNTs (10 mg) was added a toluene solution of polymer (6.0 ml, 2.3 mg/mL). The mixture was treated with the same procedure in cycle 1 to afford a SWNT solution, which was characterized by UV-Vis analysis.

To the solution was added an excess amount of TFA (0.6 mL). The mixture was treated with the same procedure in cycle 1 to afford the released SWNTs (0.5 mg) and the recovered polymer solution.

## Cycle 3

To the released SWNTs (0.5 mg) was added a toluene solution of polymer (0.3 mL, 2.3 mg/mL). The mixture was treated with the same procedure in cycle 1 to afford a SWNT solution, which was characterized by UV-Vis analysis.

To the solution was added an excess amount of TFA (0.03 mL). The mixture was treated with the same procedure in cycle 1 to give recovered polymer solution and the released SWNTs (trace).

**Table S-2.** Quantities of starting and recovered HiPCO SWNTs, polymer solution, and TFA used in the multi-cycle dispersion-releasing of SWNTs.

	Cycle 1	Cycle 2	Cycle 3
Starting HiPCO NTs	48 mg	10 mg	0.5 mg
Polymer (2.3 mg/mL)	32 mL	6.0 mL	0.3 mL
TFA	3.0 mL	0.6 mL	0.03 mL
Recovered HiPCO NTs	10 mg	$0.5 \text{ mg}^*$	-

\*Low recovery is due to partially protonation of SWNTs and significant mechanical loss during small-quantity sample handling.

# 6. References

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