

## Supplementary data

### High-Performance Semiconductors for Thin-Film Transistors Based on 2,6-bis(2-thienylvinyl)anthracene

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#### 1. Measurements

<sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> and DMSO on a 300 MHz Bruker Spectrospin 300 with tetramethylsilane as an internal standard. TGA analyses were performed on a TGA Q50 TA instrument at 10 °Cmin<sup>-1</sup> under a nitrogen atmosphere. DSC analyses were performed on a DSC2910 TA instrument at 10 °Cmin<sup>-1</sup> under nitrogen flow. UV-vis absorption spectra were recorded on a BECKMAN COULTER DU 800 spectrophotometer using 2.5 cm path-length quartz cells. For solid-state measurements, oligomers were thermally evaporated in a vacuum chamber on quartz plates to form 300 Å thick films at the deposition rate of 0.5 Å s<sup>-1</sup>. XRD analyses were carried out at room temperature with a Mac Science (M18XHF-22) diffraction meter using CuKα radiation as the X-ray source at 50 kV and 100 mA. Data were collected in the conventional  $\theta$ -2 $\theta$  configuration (2.5–30°) from thin films thermally evaporated in a vacuum chamber on SiO<sub>2</sub>/Si substrates at 0.5 Å s<sup>-1</sup> for 300 Å. AFM images of the same vacuum-deposited thin film were taken using a PSIA XE-100 Advanced Scanning Microscope. The voltammetric apparatus used was a CH Instruments model 700C electrochemical workstation. Cyclic voltammograms (CVs) were obtained at room temperature in a three-electrode cell with a working electrode (Au), a reference electrode (Ag/AgCl), and a counter electrode (Pt) in dichlorobenzene containing tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup>, 0.1 M) as supporting

electrolyte at a scan rate of 100 mV/s. All the potentials were calibrated with the standard ferrocene/ferrocenium redox couple ( $E = +0.41$  V measured). The field-effect measurements were carried out using top-contact FETs. TFT devices with 50  $\mu\text{m}$  channel length ( $L$ ) and 500  $\mu\text{m}$  channel widths ( $W$ ) were fabricated on thermally oxidized, highly n-doped silicon substrates. The  $\text{SiO}_2$  gate dielectric was 300 nm thick. The organic semiconductor (300 Å) was evaporated ( $0.1 \text{ \AA s}^{-1}$ , at  $1 \times 10^{-6}$  torr) onto a non-pretreated or OTS-pretreated oxide surface. Gold source and drain electrodes were evaporated on top of the films through a shadow mask. All measurement were performed at room temperature using a 4155C Agilent semiconductor parameter analyzer, and mobilities ( $\mu$ ) were calculated in the saturation regime by using the relationship:  $\mu_{\text{sat}} = (2I_{\text{DS}}L) / (WC(V_{\text{G}} - V_{\text{th}})^2)$ , where  $I_{\text{DS}}$  is the source-drain saturation current;  $C$  ( $1.18 \times 10^{-8}$  F) is the oxide capacitance,  $V_{\text{G}}$  is the gate voltage, and  $V_{\text{th}}$  is the threshold voltage.

## 2. Synthetic Details

All chemicals were purchased from Aldrich and Lancaster.

**5-Hexyl-2-thiophenecarboxaldehyde:** To a stirred THF solution (20 mL) containing 2-hexylthiophene (Lancaster) (2.4 g, 13.26 mmol) was slowly added 6.8 mL of n-BuLi (2.5 M in hexanes, 25 mmol) at 0 °C under a  $\text{N}_2$  atmosphere, and the solution was stirred for 15 min. DMF (1.56g, 21.39 mmol) was added, and the mixture was allowed to warm to room temperature. The mixture was poured into an aqueous solution of ammonium chloride (1 N) and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with water, dried over  $\text{MgSO}_4$ , and evaporated. The residue was purified by column chromatography to give 2.7 g (97%) of a yellow oil.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.82 (s, 1H), 7.55 (d, 1H,  $J = 4$  Hz), 6.83 (d, 1H,  $J = 4$  Hz), 2.85 (t, 1H,  $J = 7.5$  Hz), 1.0-1.28 (m, 8H), 0.87 (t, 3H,  $J = 6.5$ Hz).

**2,6-Bis(cholormethyl)anthraquinone:** A mixture of 2,6-dimethylantraquinone (3.8 g, 16.09 mmol),  $\text{SO}_2\text{Cl}_2$  (50 mL), and 2,2'-azobis(2-methyl propionitrile) (0.16 g, 0.96 mmol) was refluxed for 24 h. The excess  $\text{SO}_2\text{Cl}_2$  was removed by distillation in vacuo. The solid residue was collected by filtration, washed several times with petroleum ether, dried, and recrystallized from DMF to yield 3.8 g (78%) of 2,6-bis(cholormethyl)

anthraquinone.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  8.41 (m, 4H), 7.98 (s, 2H), 5.00 (s, 4H). High-resolution mass spectrometry (HRMS): Calcd. for  $\text{C}_{16}\text{H}_{10}\text{Cl}_2\text{O}_2$  304.0057. Found: 304.0034.

**2,6-Bis(hydroxymethyl)anthraquinone:** A suspension of 2,6-bis(chloromethyl)anthraquinone (3.5 g, 11.47 mmol) in 300 mL of water and 400 mL of DMSO was refluxed with vigorous stirring. Upon heating for 4 h, a clear solution was obtained. The reaction mixture was refluxed for 38 h and then cooled to room temperature. The crystalline product was collected by filtration and recrystallized from DMF to give 3.0 g (98%) of 2,6-bis(hydroxymethyl)anthraquinone.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  8.17 (m, 4H), 7.85 (d, 2H,  $J = 10.7$  Hz), 5.57 (s, 2H), 4.70 (s, 4H). High-resolution mass spectrometry (HRMS): Calcd. for  $\text{C}_{16}\text{H}_{12}\text{O}_4$  268.0735. Found: 268.0749.

**2,6-Bis(hydroxymethyl)anthracene:** To a solution of 2,6-bis(hydroxymethyl)anthraquinone (2.8 g 10.43 mmol) in concentrated ammonium hydroxide (70 mL) was added zinc powder (6.0 g). The reaction mixture was refluxed overnight. The insoluble material was removed by filtration and washed with hot DMSO. The solution was precipitated in 200 mL of 1 N HCl. The product was collected by filtration to give 1.86 g (75%) of 2,6-bis(hydroxymethyl)anthracene.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  8.49 (s, 2H), 8.04 (d, 2H,  $J = 8.7$  Hz), 7.94 (s, 2H), 7.46 (d, 2H,  $J = 8.7$  Hz), 5.40 (t, 2H,  $J = 5.6$  Hz), 4.69 (d, 4H,  $J = 5.6$  Hz). High-resolution mass spectrometry (HRMS): Calcd. for  $\text{C}_{16}\text{H}_{14}\text{O}_2$  238.0994. Found: 238.1003.

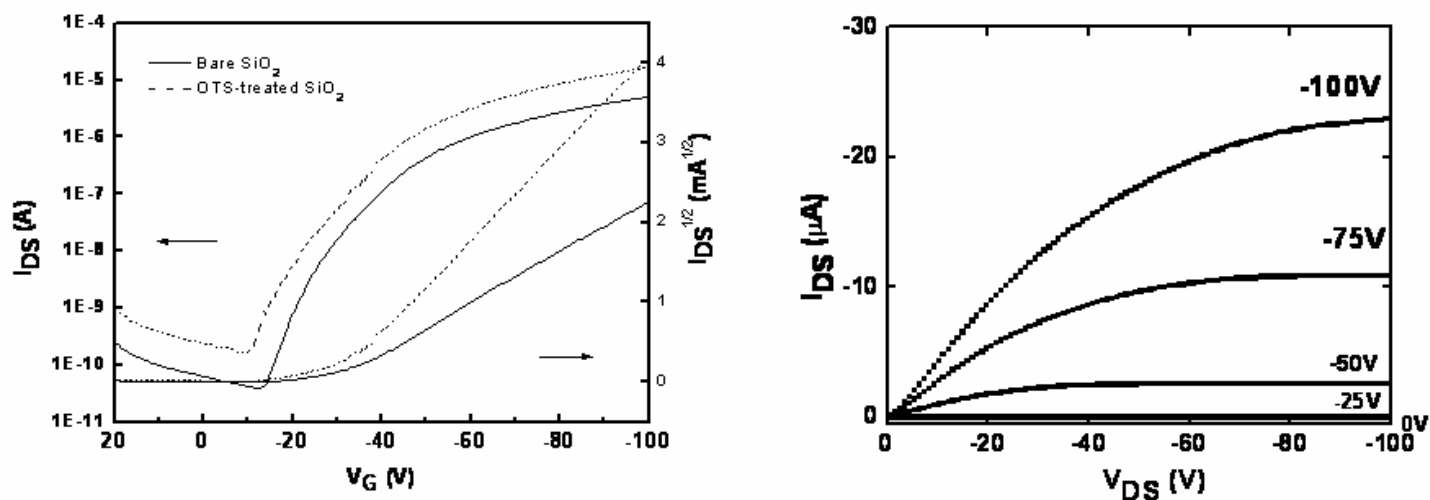
**2,6-Bis(bromomethyl)anthracene:** Phosphorus tribromide (4.4 g, 16.30 mmol) was added dropwise to a suspension of 2,6-bis(hydroxymethyl)anthracene (1.5 g, 6.29 mmol) in DMF (30 mL) at 0 °C. Upon formation of yellow precipitation, the mixture was warmed to room temperature and stirred for 4h. The solids were collected by filtration and were washed water and hexane to give rise to 2,6-bis(bromomethyl)anthracene as a yellow solid (2.2 g, 98%). The product was further purified by recrystallization from DMF.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  8.56 (s, 2H), 8.15 (s, 2H), 8.12 (d, 2H,  $J = 11.5$  Hz), 4.93 (s, 4H). High-resolution mass spectrometry (HRMS): Calcd. for  $\text{C}_{16}\text{H}_{12}\text{Br}_2$  361.9306. Found: 361.9277.

**2,6-Bis(diethylphosphorylmethyl)anthracene:** 2,6-bis(bromomethyl)anthracene (2.2 g, 6.04 mmol) was

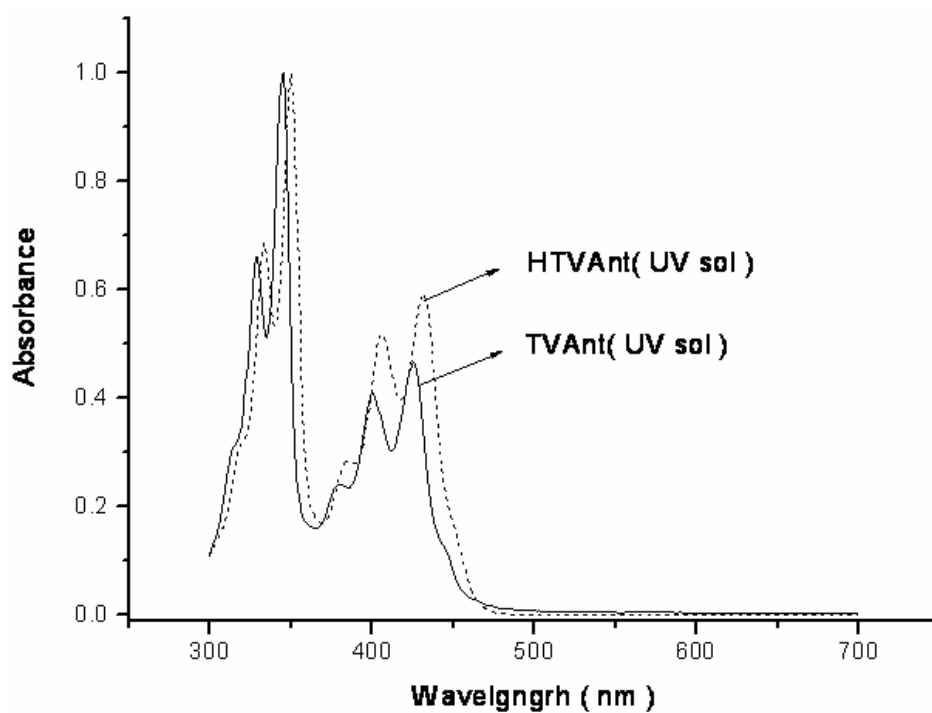
added to triethyl phosphite (50 mL), and the resulting solution was refluxed for 12 h. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel using ethyl acetate/dichloromethane (2:1) as the eluent. Yield (90%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.49 (s, 2H), 8.04 (d, 2H, J = 8.7 Hz), 7.94 (s, 2H), 7.46 (d, 2H, J = 8.7 Hz), 5.40 (t, 2H, J = 5.6 Hz), 4.69 (d, 4H, J = 5.6 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 131.54, 130.83, 128.75, 128.61, 128.39, 127.84, 125.67, (62.26, 62.16), (35.10, 33.27), (16.44, 16.30). MS (EI) *m/z*: (M<sup>+</sup>) calcd for C<sub>24</sub>H<sub>32</sub>O<sub>6</sub>P<sub>2</sub> 478.16; found 478.

**2,6-bis(2-thienylvinyl)anthracene (TVAnt):** LDA (1.5 M in cyclohexane, 2.9 mL, 5.22 mmol) was added dropwise to a stirred solution of 2,6-bis(diethylphosphorylmethyl)anthracene (1.0 g, 2.09 mmol) in anhydrous THF (50 mL) at -78 °C under nitrogen. The mixture was stirred for 1 h and then thiophene-2-carbaldehyde (0.58 g, 5.22 mmol) in THF (10 mL) was added dropwise over a period of 10 min. After the mixture was stirred for 2 h at -78 °C and for 12 h at room temperature, 5 mL of water was added and the solvent was evaporated. The residue was washed with water and MeOH. The desired product was separated by sublimation. High-resolution mass spectrometry (HRMS): Calcd. for C<sub>16</sub>H<sub>10</sub>Cl<sub>2</sub> O<sub>2</sub> 394.0850. Found: 394.0852, Anal. Calcd for CHS: C, 79.15; H, 4.60; S, 16.25; Found : C, 79.24 ; H, 4.56; S, 16.21.

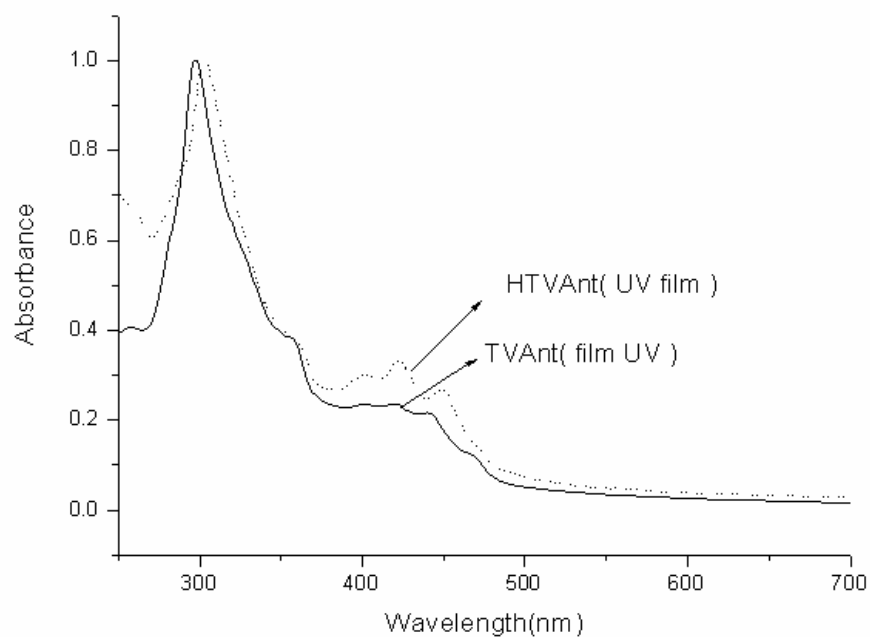
**2,6-Bis[2-(5-hexylthienyl)vinyl]anthracene (HTVAnt):** LDA (1.5 M in cyclohexane, 3.2 mL, 5.75 mmol) was added dropwise to a stirred solution of 2,6-bis(diethylphosphorylmethyl)anthracene (1.2 g, 2.50 mmol) in anhydrous THF (50 mL) at -78 °C under nitrogen. The mixture was stirred for 1 h and then 5-hexylthiophene-2-carbaldehyde (1.47 g, 7.50 mmol) in THF (20 mL) was added dropwise over a period of 10 min. After the mixture was stirred for 2 h at -78 °C and for 12 h at room temperature, 5 mL of water was added and the solvent was evaporated. The residue was washed with water and MeOH. The desired product was separated by sublimation. High-resolution mass spectrometry (HRMS): Calcd. for C<sub>38</sub>H<sub>42</sub>S<sub>2</sub> 562.2728. Found: 562.2728. Anal. Calcd.: C, 81.09; H, 7.52; S, 11.39; Found: C, 80.99; H, 7.03; S, 11.63.



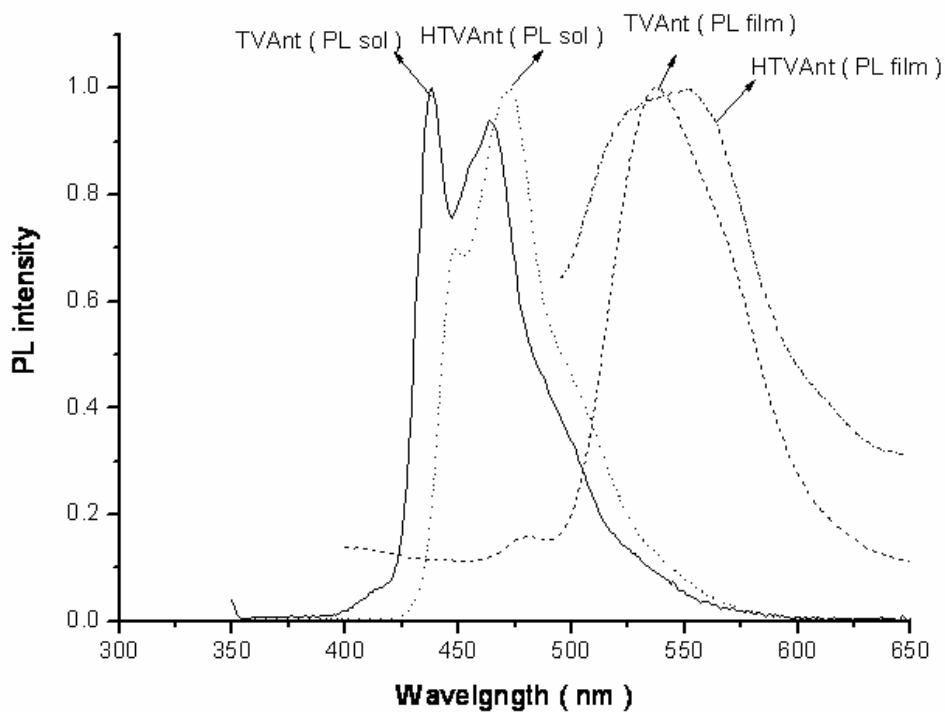
**Figure S1.** Source-drain current ( $I_{DS}$ ) versus source-drain voltage ( $V_{DS}$ ) at various gate voltage ( $V_G$ ) for top-contact field-effect transistor using HTVAnt deposited at  $T_{\text{sub}} = 75^\circ\text{C}$  on OTS-treated  $\text{SiO}_2$ . The transfer characteristics in the saturation regime at a constant source-drain voltage ( $V_{DS} = -100\text{ V}$ ) are also included.



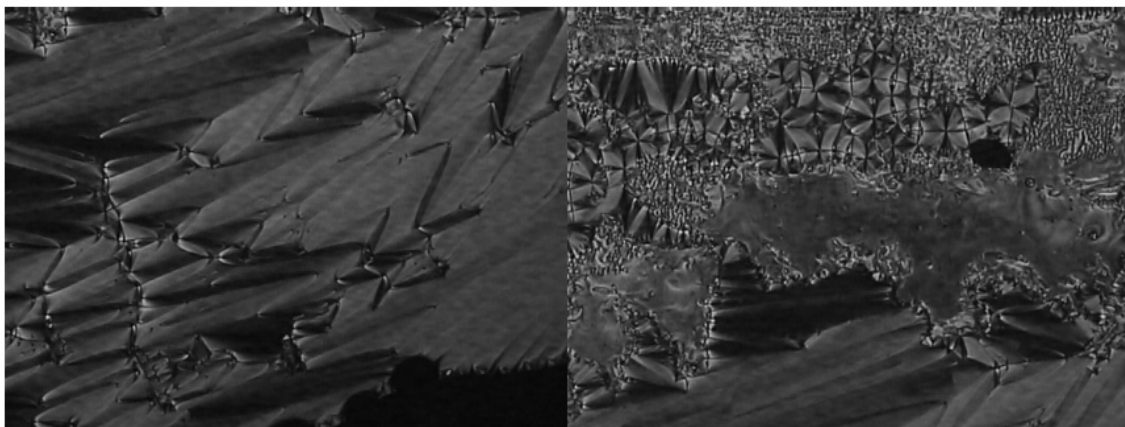
**Figure S2.** UV-vis absorption spectra of TVAnt and HTVAnt in toluene.



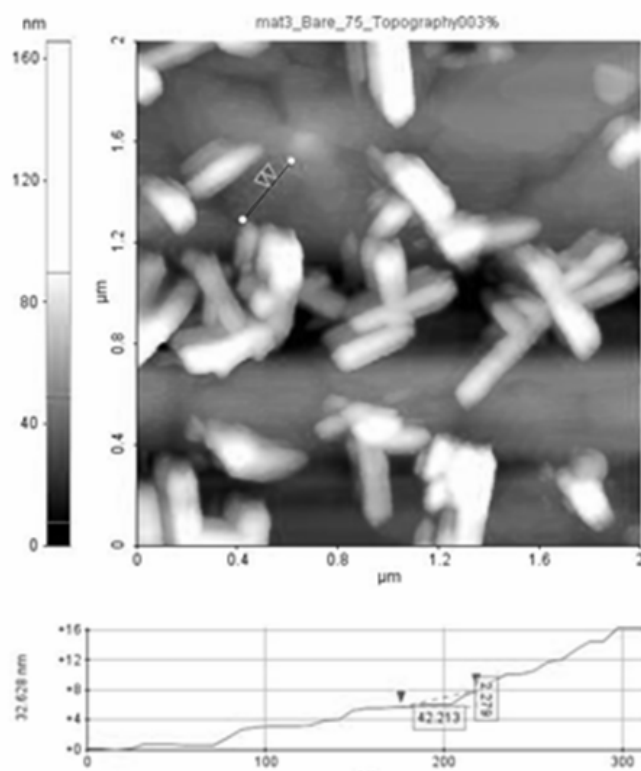
**Figure S3.** UV-vis absorption spectra of TVAnt and HTVAnt (film).



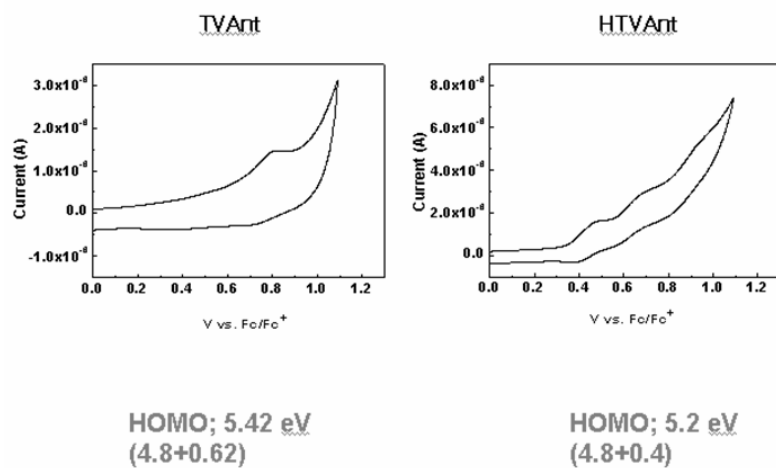
**Figure S4.** PL emission spectra of TVAnt and HTVAnt in toluene and film.



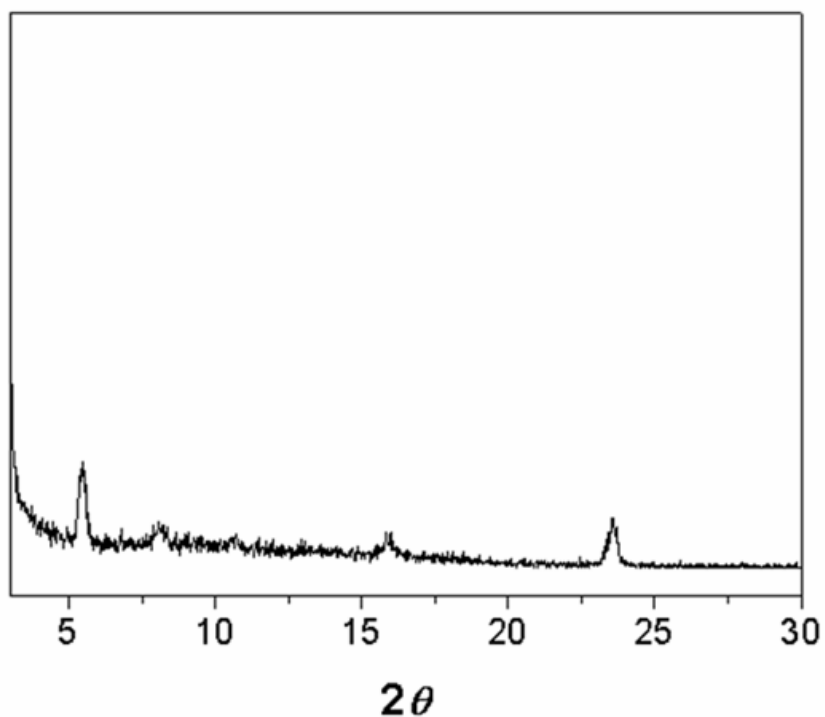
**Figure S5.** Polarized optical micrograph (POM) of the HTVAnt phase at 265 °C during cooling process.



**Figure S6.** AFM images of thin films on the bare substrates of TVAnt at 75 °C



**Figure S7.** Cyclic voltammograms of TVAnt and HTVAnt.



**Figure S8.** XRD pattern of HTVAnt thin films vacuum-deposited on OTS-treated SiO<sub>2</sub>/Si at T<sub>sub</sub> = 50 °C.



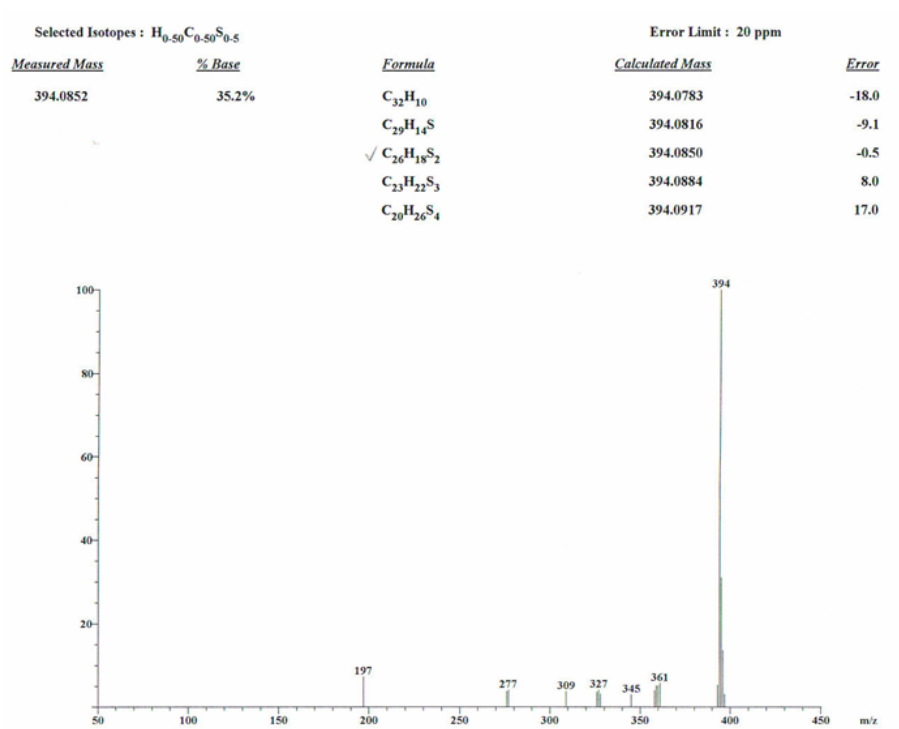


Figure S9. High-resolution mass spectral data of TVAnt.

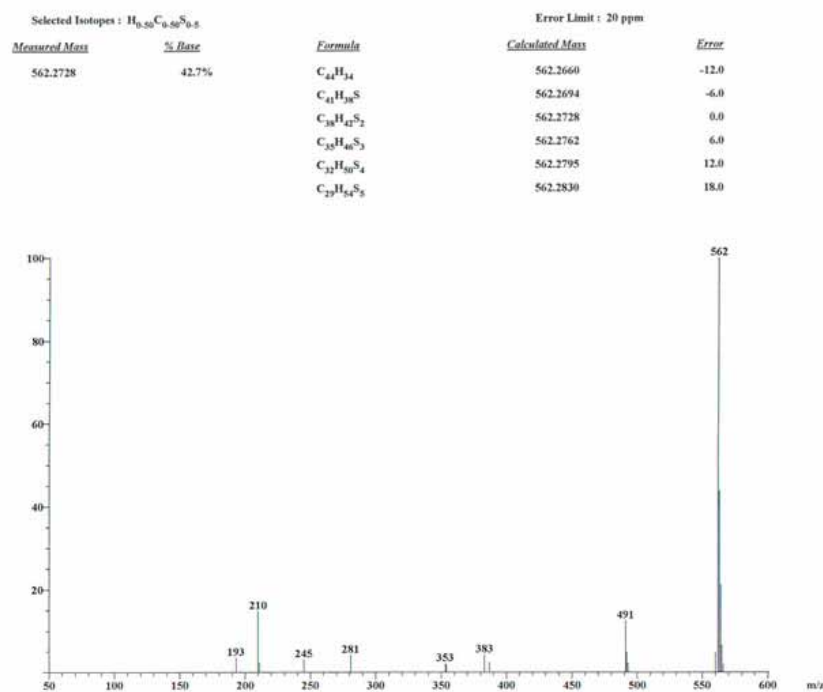


Figure S10. High-resolution mass spectral data of HTVAnt.