

Supplementary data

High-Performance Organic Semiconductors for Thin-Film Transistors Based on 2,7-

Divinyll[1]benzothieno[3,2-b]benzothiophene

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1. Measurements

The ¹H and ¹³C NMR spectra were recorded in CDCl₃ and DMSO-*d*₆ using an Advance 300 MHz Bruker spectrometer. The ¹H NMR and ¹³C NMR chemical shifts in CDCl₃ were reported relative to those in CHCl₃ (7.27 ppm and 77.23 ppm, respectively). The TGA analyses were performed on a TGA Q50 TA instrument at 10 °C min⁻¹ under a nitrogen atmosphere. The DSC analyses were performed on a DSC2910 TA instrument at 10 °C min⁻¹ under nitrogen flow. The UV-vis absorption spectra were recorded on a Beckman Coulter DU 800 spectrophotometer using quartz cells with path lengths of 2.5 cm. For solid-state measurements, the oligomers were thermally evaporated in a vacuum chamber on quartz plates to form 300-Å-thick films at a deposition rate of 0.5 Å s⁻¹. The 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. The data were collected in the conventional θ -2 θ configuration (2.5–30°) from thin films thermally evaporated on SiO₂/Si substrates in a vacuum chamber to form 300-Å-thick films at a rate of 0.5 Å s⁻¹. The AFM images of the vacuum-deposited thin films were recorded using a PSIA XE-100 Advanced Scanning Microscope. The voltammetric apparatus used was a CH Instruments model 700C electrochemical workstation. The cyclic voltammograms (CVs) were obtained at room temperature in a three-electrode cell equipped with a working electrode (Au), a reference electrode (Ag/AgCl), and a counter electrode (Pt) in dichlorobenzene containing tetrabutylammonium

hexafluorophosphate ($\text{Bu}_4\text{N}^+\text{PF}_6^-$, 0.1 M) as the 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 a channel length (L) of 50 μm and a channel width (W) of 1000 μm were fabricated on thermally oxidized highly n-doped silicon substrates. The SiO_2 gate dielectric was 300 nm in thickness. The organic semiconductor (300 Å) was evaporated (0.1 \AA s^{-1} at 1×10^{-6} torr) onto a non-pretreated or octadecyltrichlorosilane (OTS)-pretreated oxide surface. Gold source/drain electrodes were evaporated on top of the films through a shadow mask. All the measurements were performed at room temperature using a 4155C Agilent semiconductor parameter analyzer, and the mobilities (μ) 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_{DS} is the source-drain saturation current; C (1.18×10^{-8} F), the oxide capacitance; V_{g} , the gate voltage; V_{th} , the threshold voltage.

2. Synthetic Details

All chemicals were purchased from Aldrich and Lancaster.

2,7-Dihydroxymethyl[1]benzothieno[3,2-b]benzothiophene

To a solution of [1]benzothieno[3,2-b]benzothiophene-2,7-dicarboxylates (1.50 g, 3.9 mmol) in THF (40 mL) was added LiAlH_4 (0.74 g, 19.5 mmol). The reaction mixture was stirred overnight. The insoluble material was removed by filtration and washed with hot DMSO. The filtrate and washings were collected, and the product was precipitated by adding 50 mL of 1 N HCl. The product was collected by filtration to afford 1.86 g (75%) of pure 2,7-dihydroxymethyl[1]benzothieno[3,2-b]benzothiophene. ^1H NMR (300 MHz, DMSO): δ 8.05 (s, 2H), 7.98 (d, 2H, $J = 8.1$ Hz), 7.48 (d, 2H, $J = 8.2$ Hz), 5.38 (t, 2H, $J = 5.6$ Hz), 4.69 (d, 4H, $J = 5.3$ Hz).

2,7-Dibromomethyl[1]benzothieno[3,2-b]benzothiophene

Phosphorus tribromide (3.24 g, 11.9 mmol) was added dropwise to a suspension of 2,7-dihydroxymethyl [1]benzothieno[3,2-b]benzothiophene (0.9 g, 2.99 mmol) in DMF (20 mL) at 0 °C. Upon the formation of a yellow precipitate, the mixture was warmed to room temperature and stirred for 4 h. The solids were

collected by filtration and were washed with water and hexane to afford 2,7-bis(dibromomethyl)[1]benzothieno[3,2-b]benzothiophene as a yellow solid (1.1 g, 78%). The product was further purified by recrystallization from DMF. ^1H NMR (300 MHz, DMSO): δ 8.24 (s, 2H), 8.08 (d, 2H, $J = 8.2$ Hz), 7.63 (d, 2H, $J = 8.1$ Hz), 4.91 (s, 4H).

2,7-Bis(diethylphosphorylmethyl)[1]benzothieno[3,2-b] benzothiophene

2,7-dibromomethyl[1]benzothieno[3,2-b]benzothiophene (1.1 g, 2.58 mmol) was added to triethylphosphite (30 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 to obtain the product in 90% yield. ^1H NMR (300 MHz, CDCl_3): δ 7.87 (s, 2H), 7.84 (d, 2H, $J = 8.2$ Hz), 7.42 (d, 2H, $J = 8.1$ Hz), 4.05 (m, 8H), 3.36 (d, 4H, $J = 21.5$ Hz), 1.27 (t, 12H, $J = 7.0$ Hz). ^{13}C NMR (75 MHz, CDCl_3): (142.62, 142.58), 133.18, 131.90, (128.79, 128.67), (126.92, 126.84), (124.98, 124.88), 121.40, (62.33, 62.24), (34.81, 32.97), (16.45, 16.37).

2,7-Bis(2-cyclohexylvinyl)[1]benzothieno[3,2-b]benzothiophene (DCV-BTBT)

LDA (1.5 M in cyclohexane, 4.0 mL, 6.0 mmol) was added dropwise to a stirred solution of 2,7-bis(diethylphosphorylmethyl)[1]benzothieno[3,2-b] benzothiophene (1.3 g, 2.41 mmol) in anhydrous THF (50 mL) at -78 °C under a nitrogen atmosphere. The mixture was stirred for 1 h, and then, cyclohexanecarbaldehyde (0.67 g, 6.02 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 $\text{C}_{30}\text{H}_{32}\text{S}_2$: 456.1945. Found: 456.1951. Anal. Calcd for CHS: C, 78.90; H, 7.06; S, 14.04. Found: C, 78.48; H, 7.14; S, 14.36.

2,7-Distyryl[1]benzothieno[3,2-b]benzothiophene (DPV-BTBT)

LDA (1.5 M in cyclohexane, 4.0 mL, 6.0 mmol) was added dropwise to a stirred solution of 2,7-bis(diethylphosphorylmethyl)[1]benzothieno[3,2-b] benzothiophene (1.3 g, 2.41 mmol) in anhydrous THF (50

mL) at $-78\text{ }^{\circ}\text{C}$ under a nitrogen atmosphere. The mixture was stirred for 1 h, and then, benzaldehyde (0.67 g, 6.0 mmol) in THF (20 mL) was added dropwise over a period of 10 min. After the mixture was stirred for 2 h at $-78\text{ }^{\circ}\text{C}$ 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. HRMS: Calcd. for $\text{C}_{30}\text{H}_{20}\text{S}_2$: 444.1006. Found: 444.1008. Anal. Calcd. For CHS: C, 81.04; H, 4.53; S, 14.42. Found: C, 81.04; H, 4.55; S, 14.40.

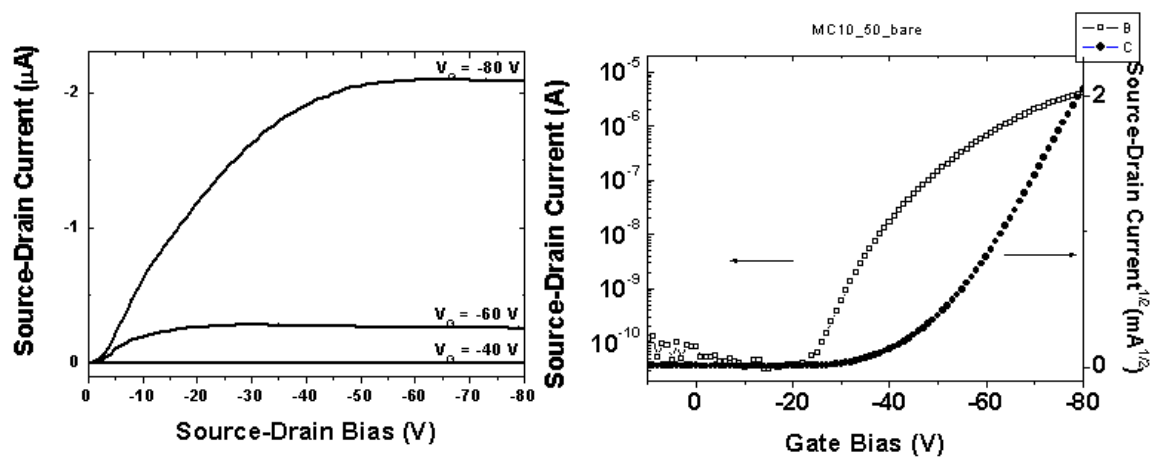


Figure S1. Source-drain current (I_{DS}) versus source-drain voltage (V_{DS}) at various gate voltage (V_G) for top-contact field-effect transistor using DCV-BTBT deposited at $T_{\text{sub}} = 50\text{ }^\circ\text{C}$ on SiO_2 . The transfer characteristics in the saturation regime at a constant source-drain voltage ($V_{\text{DS}} = -100\text{ V}$) are also included (fresh device).

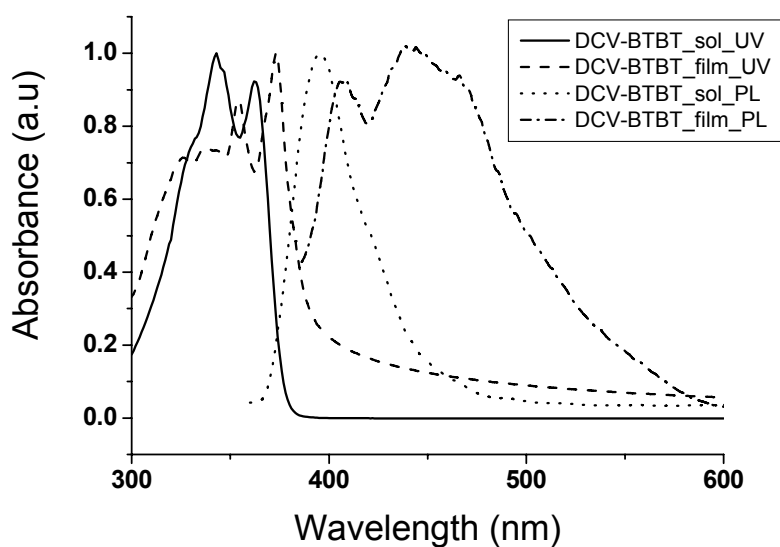


Figure S2. UV-vis absorption spectra of DCV-BTBT in xylene.

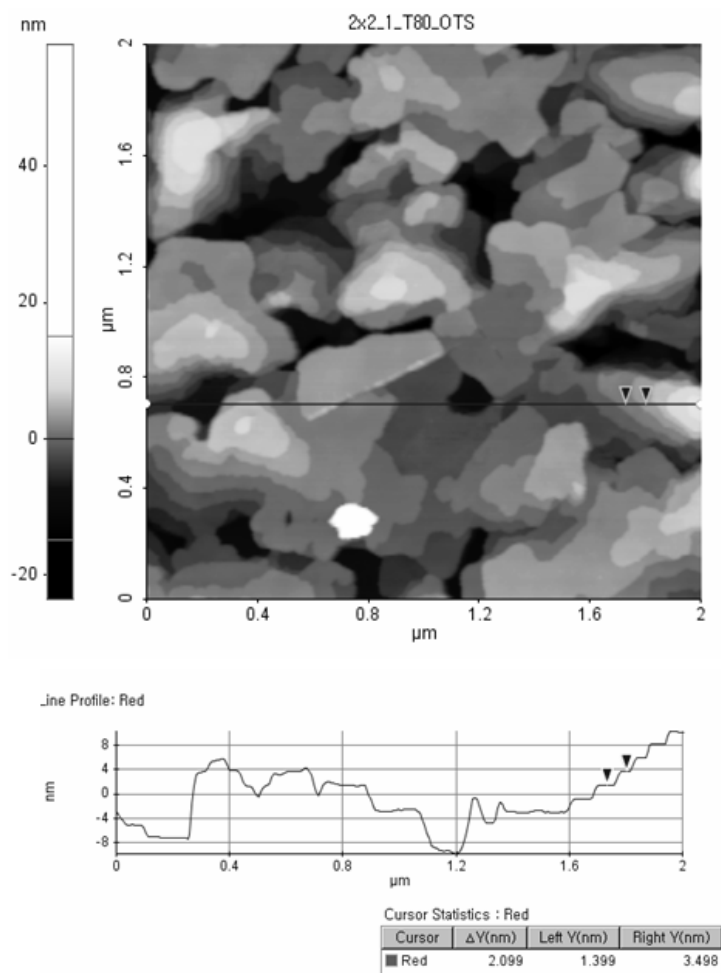


Figure S3. AFM images of thin films on the OTS-treated SiO₂ substrates of DPV-BTBT at 80 °C.

DCV-BTBT

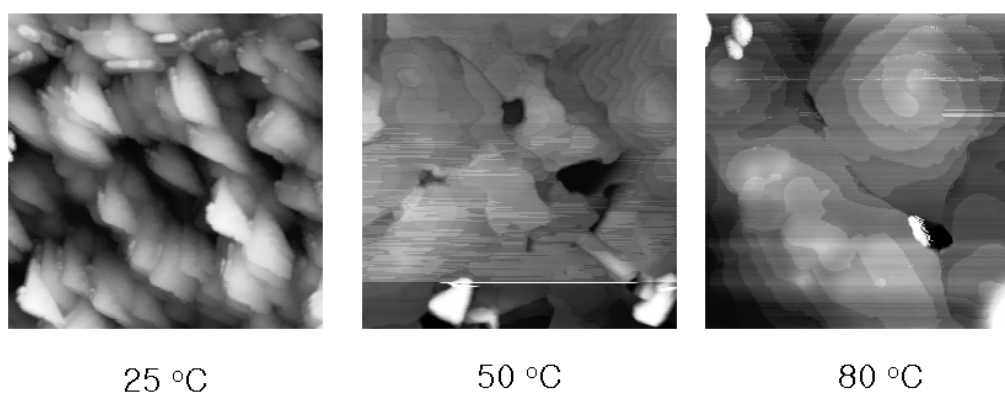
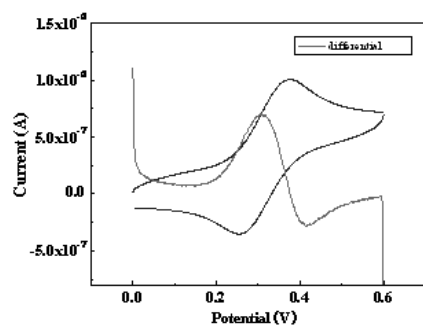


Figure S4. AFM images of thin films on the OTS-treated SiO₂ substrates of DCV-BTBT at 25, 50, 80 °C.



Cyclic Voltammogram of FOC(0.31)

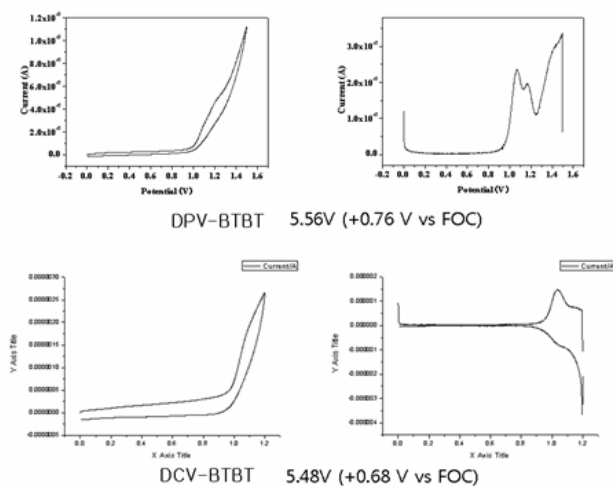


Figure S5. Cyclic voltammograms of DPV-BTBT and DCV-BTBT.

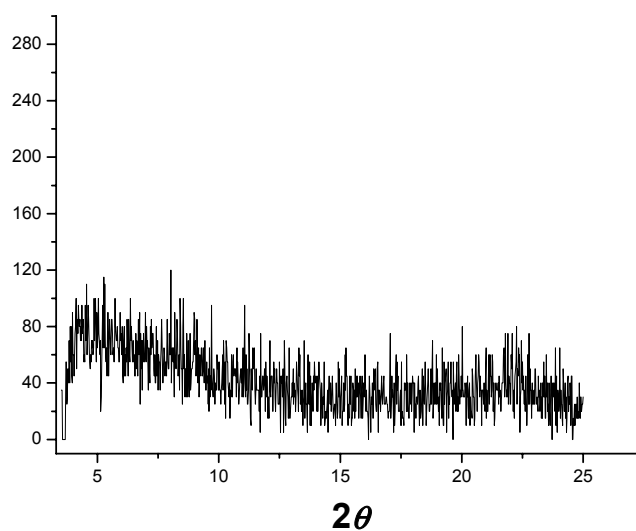


Figure S6. XRD pattern of DCV-BTBT thin films vacuum-deposited on OTS-treated SiO_2/Si at $T_{\text{sub}} = 80^\circ\text{C}$.

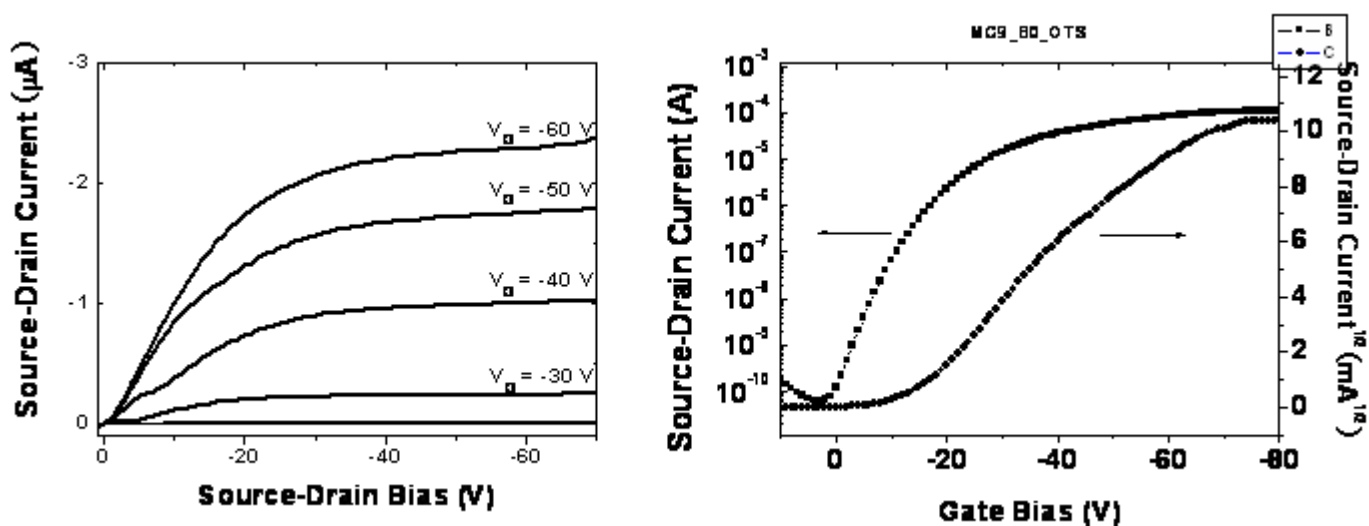


Figure S7 Source-drain current (I_{DS}) versus source-drain voltage (V_{DS}) at various gate voltages (V_G) for top-contact field-effect transistor using DPV-BTBT deposited at $T_{sub} = 80\text{ }^\circ\text{C}$ on OTS-treated SiO_2 . The transfer characteristics in the saturation regime at a constant source-drain voltage ($V_{DS} = -100\text{ V}$) are also included (fresh device).

Table S1 Field-effect mobility (μ_{TFT}), on/off current ratio (I_{on}/I_{off}), and threshold voltage (V_{th}) of DCV-BTBT vacuum-deposited on differently treated SiO_2 surfaces and at different substrate temperature (T_{sub})

		T_{sub}	μ_{TFT} [cm^2/Vs]	I_{on}/I_{off}	V_{th} [V]
DCV-BTBT	Bare	25	0.00013	10^3	-24
		50	0.0248	10^5	-40
	OTS	80	0.00013	10^3	-20
		25	0.0031	10^4	-22
		50	0.00139	10^4	-60
		80	0.00015	10^3	-10