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Functionalized Benzothieno[3,2-b]thiophenes (BTTs) for High Performance Organic Thin-Film Transistors (OTFTs)

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Table S1. Summary of crystal structure data for Bp-BTT[a]

Empirical formula	**$C_{20}H_{14}S_2$**
Formula weight	**342.45**
Temperature (K)[b]	**100(2)**
Crystal system	**Monoclinic**
Space group	**Pn**
Unit cell dimensions (Å)	**a = 5.8953(7)** **b = 7.5358(9)** **c = 35.049(4)** **α = 90.00°** **β = 90.563(7)°** **γ = 90.00°**
V, Å^3	**1557.0(3)**
Z	**4**
d (calc), g/cm^3	**1.461**
Absorption coefficient (mm^{-1})	**3.064**
F(000)	**712**
Crystal size (mm)	**0.43 × 0.34 ×0.01**
Reflections collected	**6992**
Independent reflections	**3644**
R_{int}	**0.0509**
Final R indices [I>2sigma(I)][c]	**R1 = 0.0493** **wR2 = 0.1166**
R indices (all data)	**R1 = 0.0670** **wR2 = 0.1341**

[a] CCD area detector diffractometer; Mo Kα radiation; λ = 1.54178 Å. [b] Temperature for data collection. [c] Refinement method: Full-matrix least-squares on F^2.

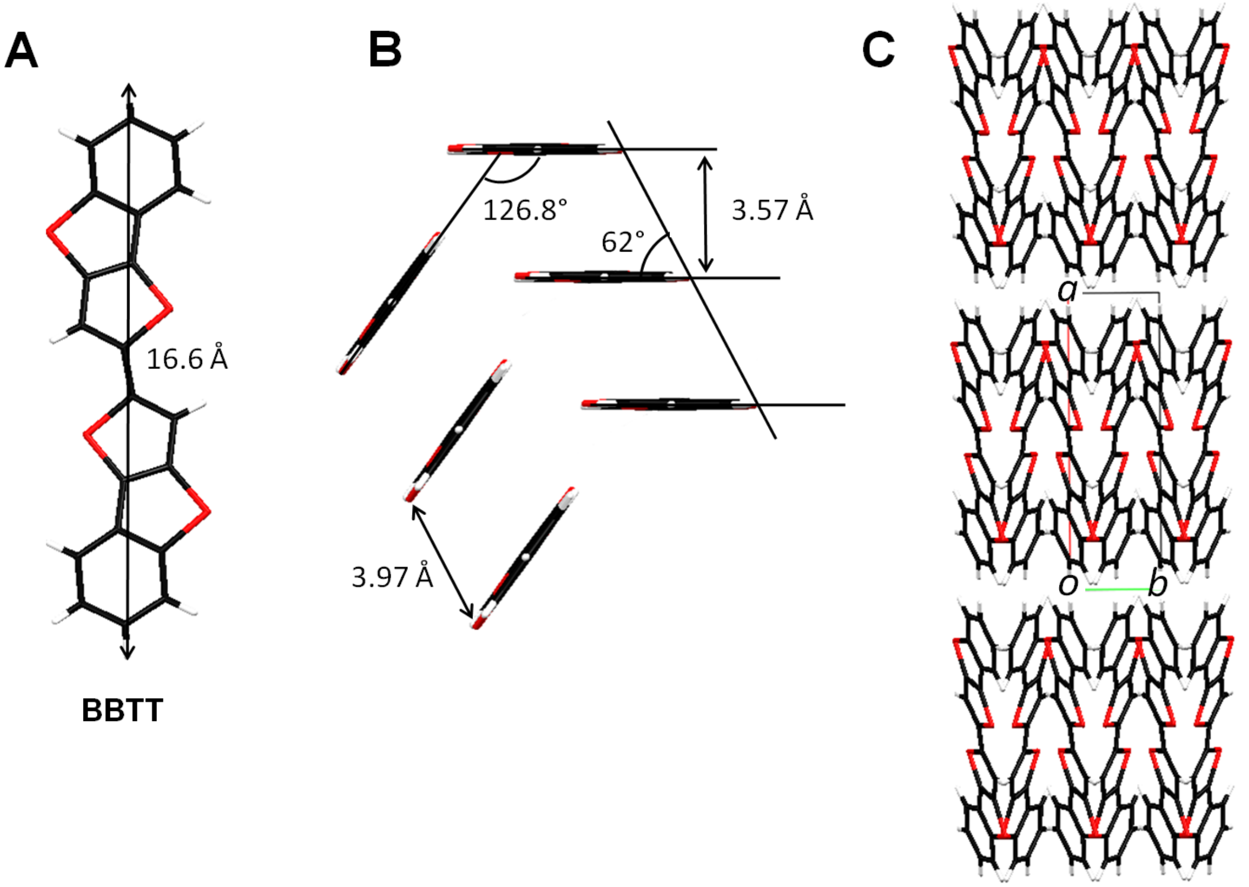

Figure S1. Single crystal structure of BBTT. (A) molecular length of BBTT = 16.6 Å, (B) unit cell packing viewed along π plane disection, herringbone packing, herringbone angle between BTT cores = 126.8°, distance between BTT cores = 3.57Å, tilting angle between BTT cores in the molecule = 0 °, slipping angle between adjacent molecules to the direction of the short molecular axis = 62°, thus, the roll angle is 90 - 62 = 28°, the shortest sulfur to sulfur distance = 3.97Å (C) unit cell packing viewed along *b*-axis exhibits no shift between adjacent molecules in the direction of the long molecular axis.

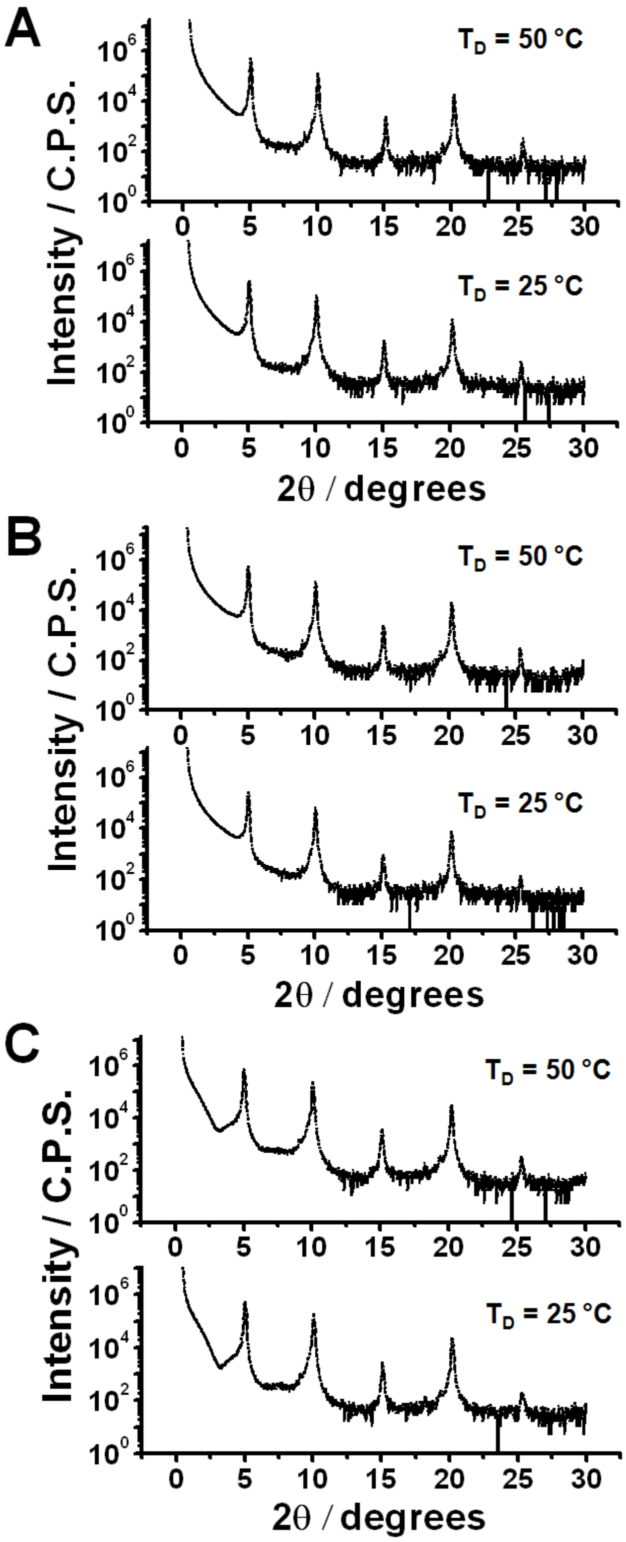

Figure S2. Representative θ/2θ X-ray diffraction scans of A. Bp-BTT on bare SiO_2, B. Bp-BTT on HMDS C. Bp-BTT on OTS deposited at the indicated T_D values.

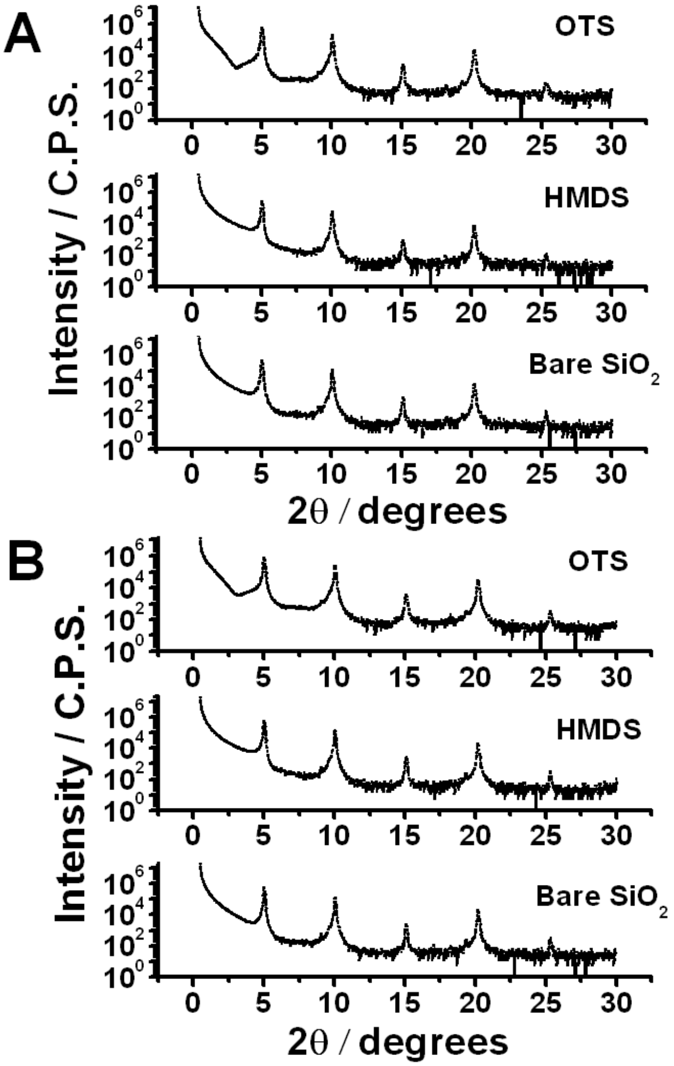

Figure S3. Representative θ/2θ X-ray diffraction scans of A. Bp-BTT at T_D = 25 °C, B. Bp-BTT at T_D = 50 °C deposited on the indicated coated or bare Si/SiO_2 substrates.

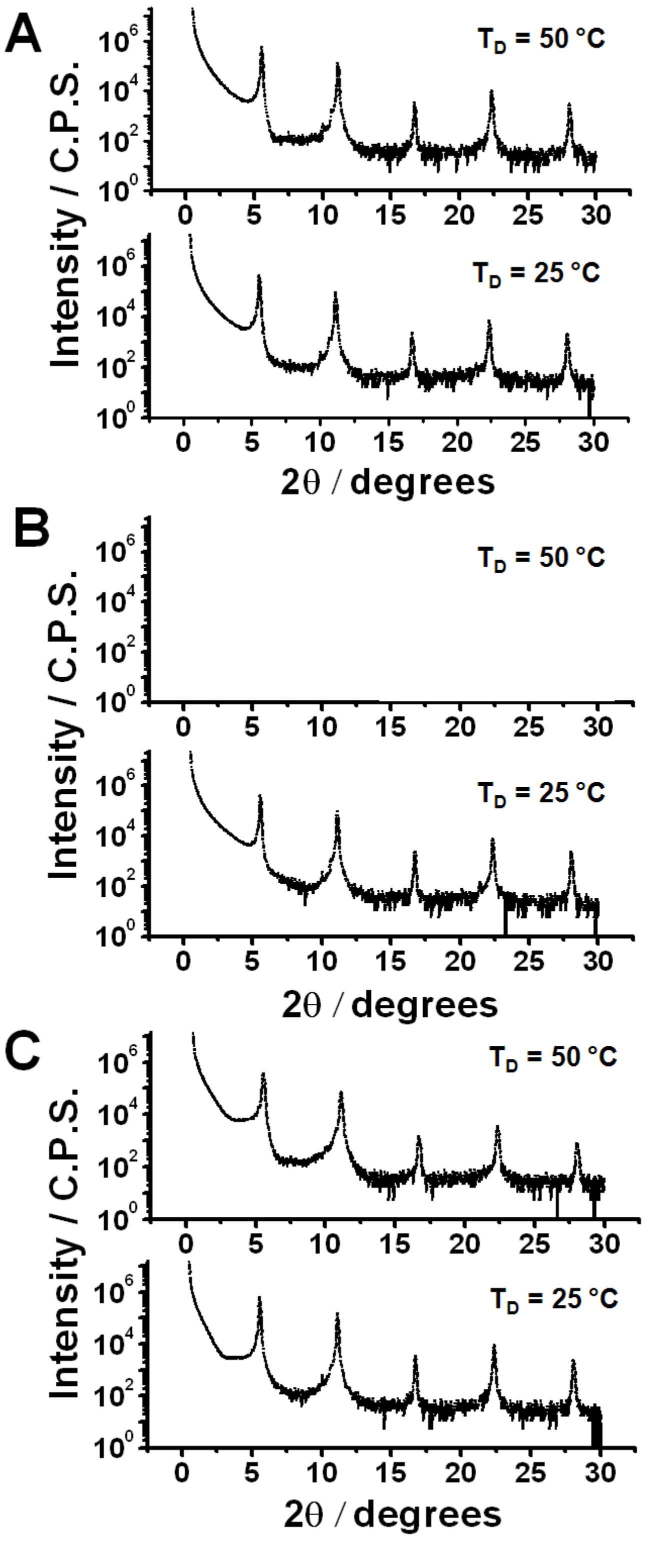

Figure S4. Representative θ/2θ X-ray diffraction scans of A. Np-BTT on bare SiO_2, B.Np-BTT on HMDS, C.Np-BTT on OTS deposited at the indicated T_D values.

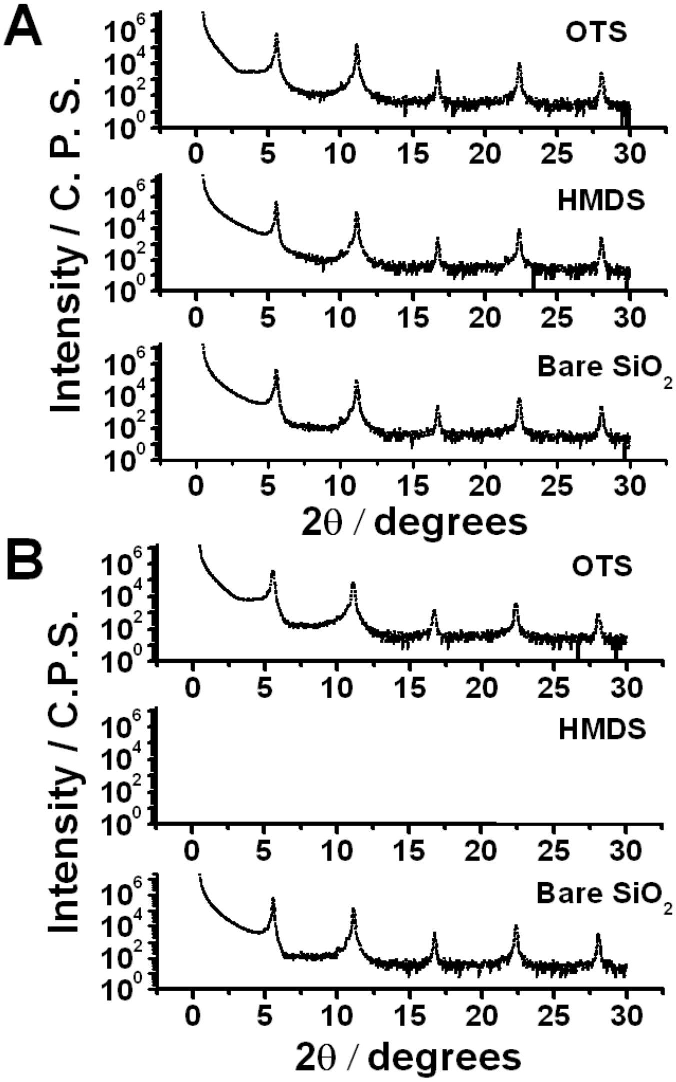

Figure S5. Representative θ/2θ X-ray diffraction scans of A. Np-BTT at T_D = 25 °C, B. Np-BTT at T_D = 50 °C deposited on the indicated coated or bare Si/SiO$_2$ substrates.

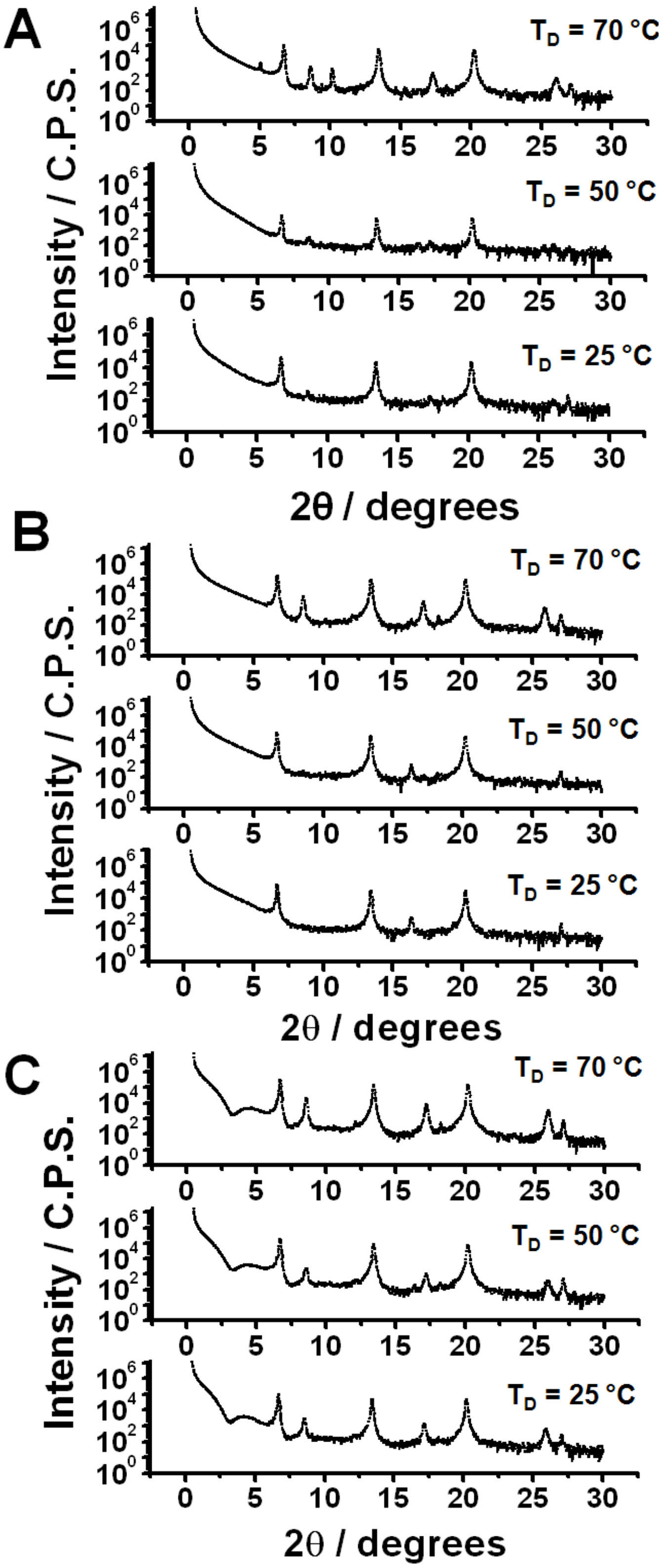

Figure S6. Representative θ/2θ X-ray diffraction scans of A. BBTT on bare SiO_2, B.BBTT on HMDS, C.BBTT on OTS deposited at the indicated T_D values.

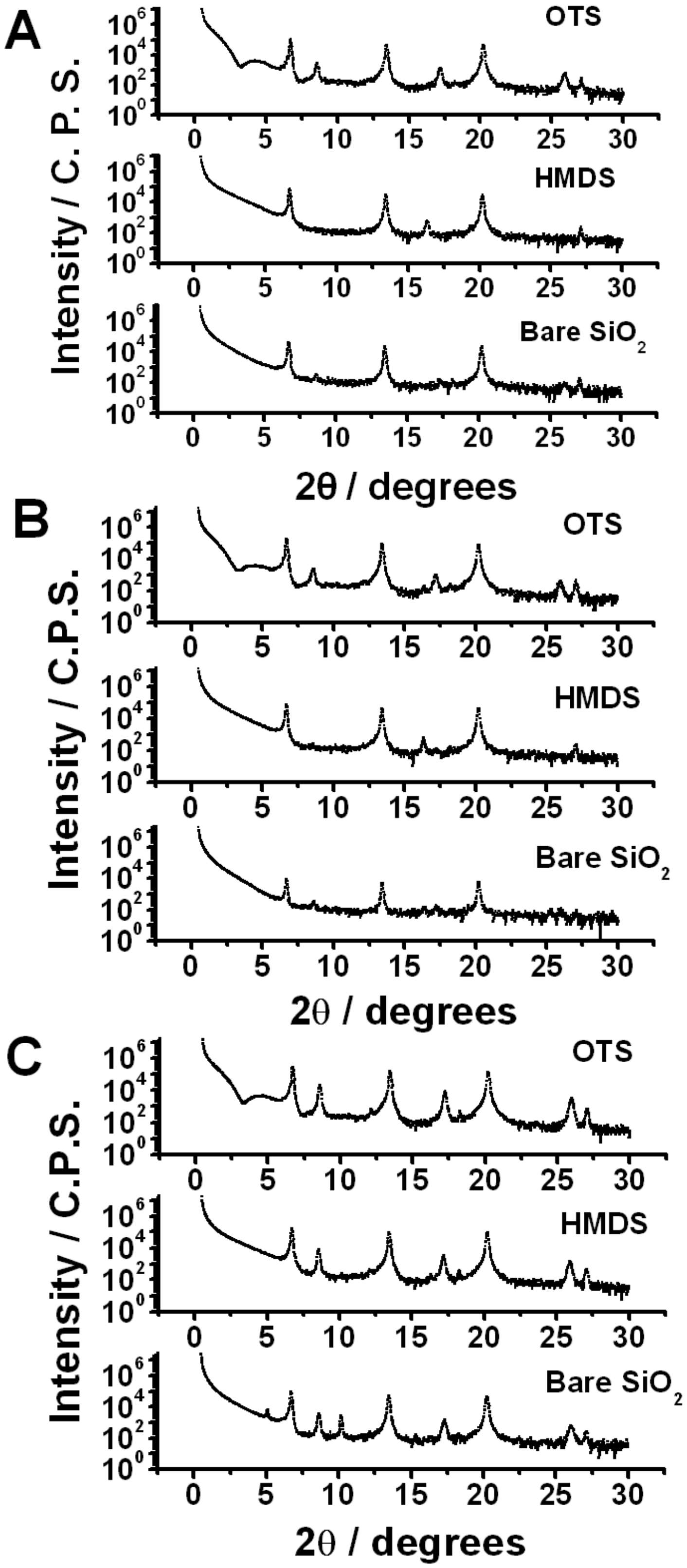

Figure S7. Representative θ/2θ X-ray diffraction scans of A. BBTT at T_D = 25 °C, B. BBTT at T_D = 50 °C, C. BBTT at T_D = 70 °C deposited on the indicated coated or bare Si/SiO_2 substrates.

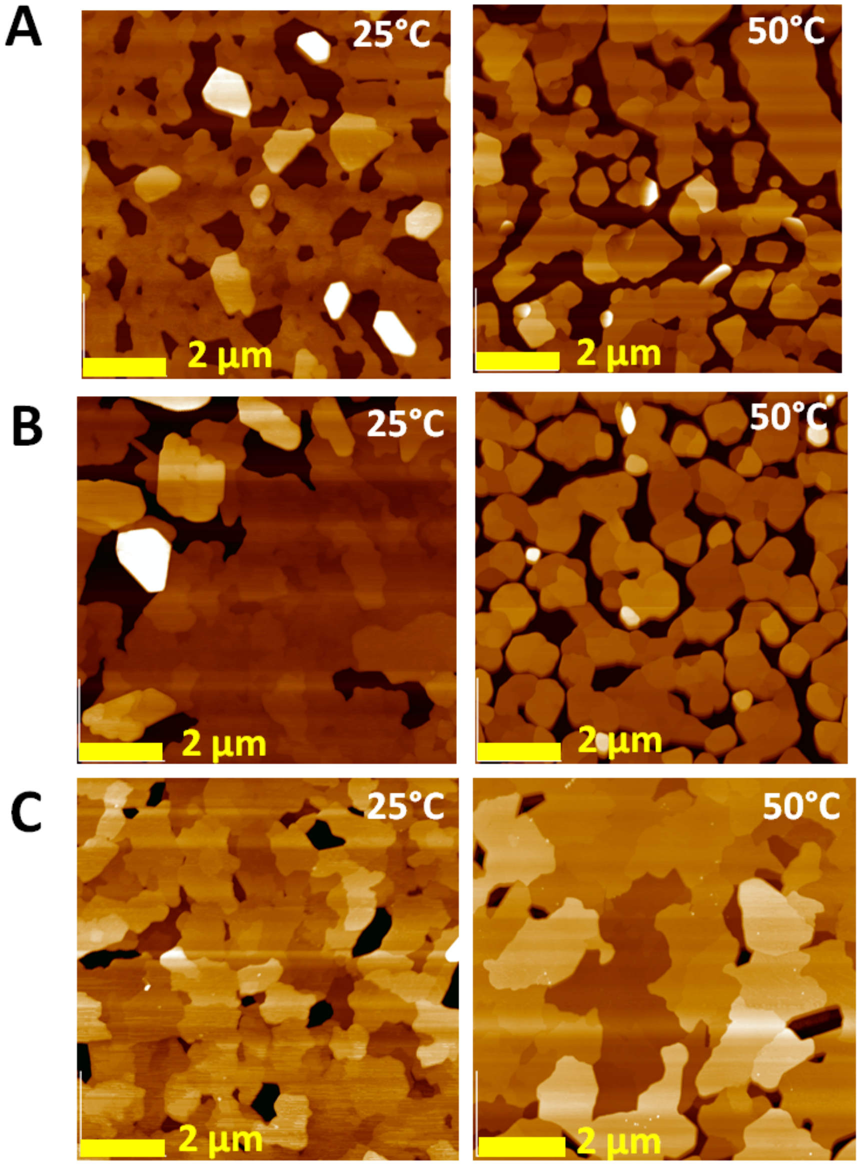

Figure S8. AFM images of 50 nm thick Bp-BTT films grown on specified substrates and at specified temperatures: (A) bare SiO_2 (B) SiO_2 with HMDS SAM treatment, and (C) SiO_2 with OTS SAM treatment (tapping mode, topography, 9 µm X 9 µm)

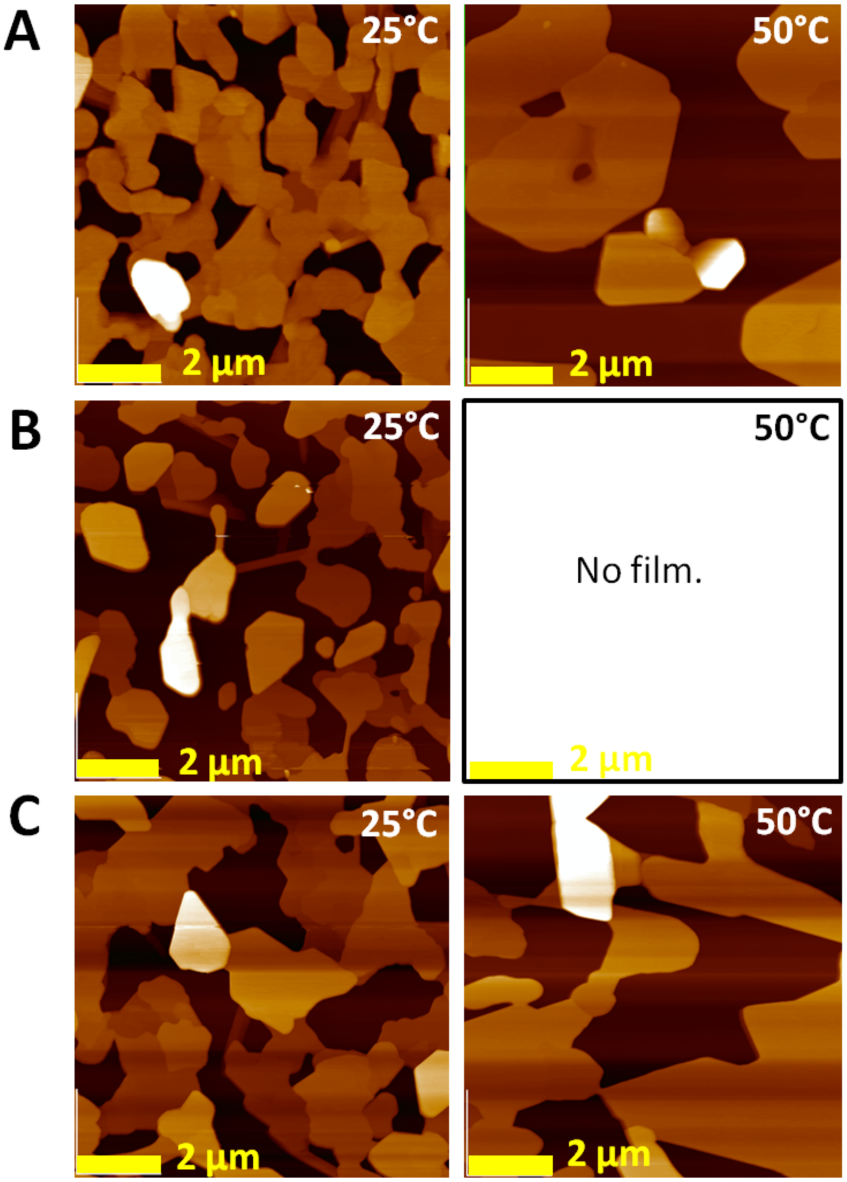

Figure S9. AFM images of 50 nm thick Np-BTT films grown on specified substrates and at specified temperatures: (A) bare SiO_2 (B) SiO_2 with HMDS SAM treatment, and (C) SiO_2 with OTS SAM treatment (tapping mode, topography, 9 µm X 9 µm)

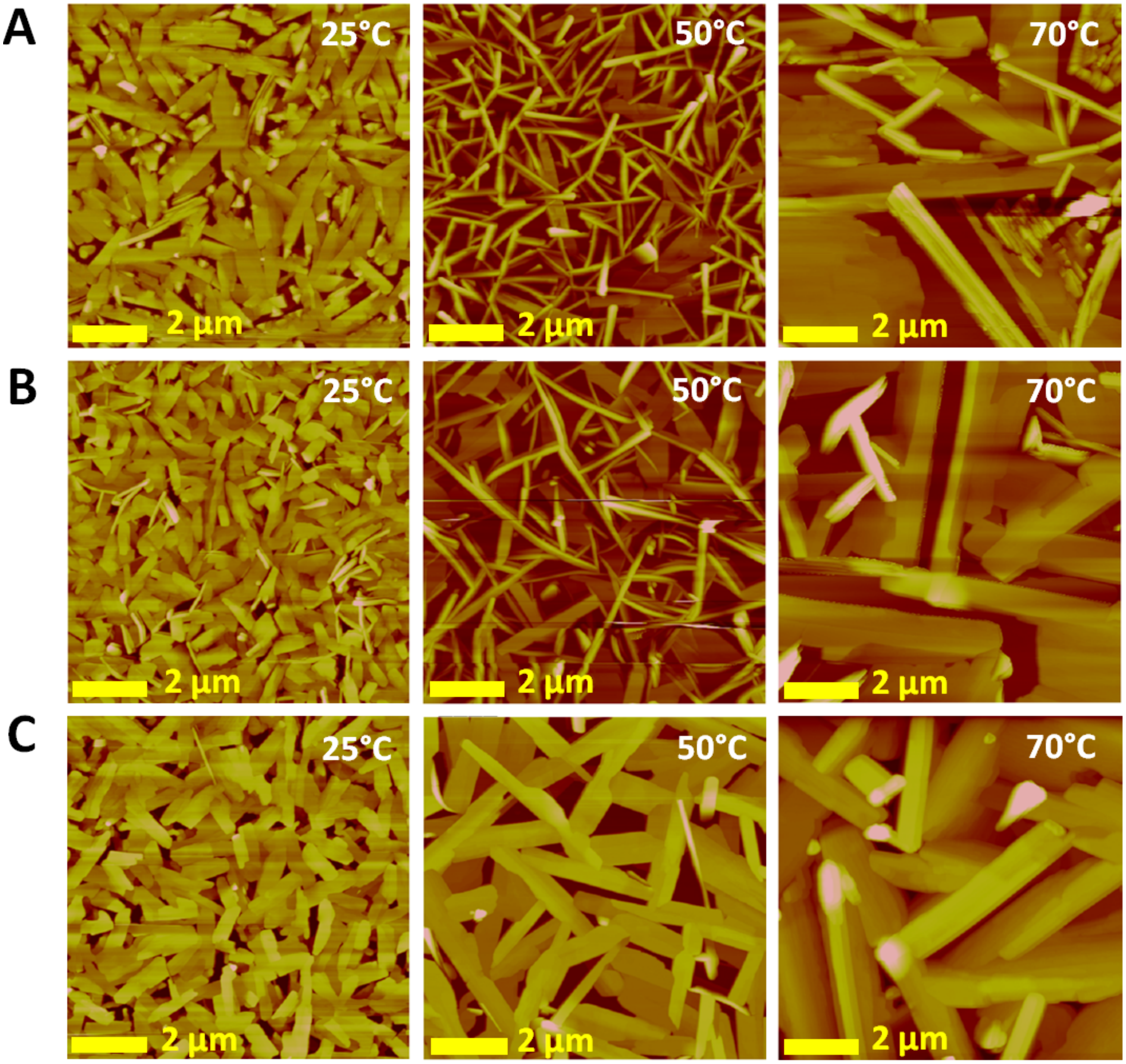

Figure S10. AFM images of 50 nm thick BBTT films grown on specified substrates and at specified temperatures: (A) bare SiO_2 (B) SiO_2 with HMDS SAM treatment, and (C) SiO_2 with OTS SAM treatment (tapping mode, topography, 10 µm X 10 µm)

Experimental Section

Materials and Methods: All chemicals and solvents were of reagent grade and were obtained from Aldrich, Arco, or TCI Chemical Co. Reaction Solvents (toluene, benzene, ether, and THF) were distilled under nitrogen from sodium/benzophenone ketyl, and halogenated solvents were distilled from CaH_2. ^1H and ^{13}C NMR spectra were recorded on a Bruker 500 or a 300 instrument. Chemical shifts for ^1H and ^{13}C NMR spectra were referenced to solvent signals. Differential scanning calorimetry (DSC) was carried out on a Mettler DSC 822 instrument, calibrated with a pure indium sample at a scan rate of 10 K/min. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer TGA-7 thermal analysis system using dry nitrogen as the carrier gas at a flow rate of 40 mL/min. The UV–Vis absorption and fluorescence spectra were obtained using JASCO V-530 and Hitachi F-4500 spectrometers, respectively, and all spectra were measured in the indicated solvents at room temperature. IR spectra were obtained using a JASCO FT/IR-4100 spectrometer. Differential pulse voltammetry (DPV) experiments[1] were performed with a CH Instruments model CHI621C Electrochemical Analyzer. Under N_2, semiconductor material was dissolved in anhydrous 0.1 M o-$C_6H_4Cl_2$ solution to prepare a 10^{-3} M test solution. In each DPV experiment, 5 mL of the test solution is scanned together with Fc^+/Fc (10^{-3} M; as internal standard) under N_2. All measurements were carried out at the temperature indicated with a conventional three-electrode configuration consisting of a platinum disk working electrode, an auxiliary platinum wire electrode, and a non-aqueous Ag reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in a specified dry solvent. All potentials reported are referenced to an Fc^+/Fc internal standard (at +0.6 V). Elemental analyses were performed on a Heraeus CHN-O-Rapid elemental analyzer. Mass spectrometric data were obtained with a JMS-700 HRMS instrument. Prime grade silicon wafers (p^+-Si) with ~ 300 nm (±5%) thermally grown oxide (from WRS Materials) were used as device substrates. 3-bromobenzo[b]thiophene[2] was prepared according to the literature.

Synthesis of benzothieno[3,2-b]thiophene (**BTT**). Under nitrogen and anhydrous condition at 0 °C, 2.0 M LDA (24.9 mL in hexanes, 0.050 mol) was slowly added to an 100 mL THF solution of 3-bromobenzo[*b*]thiophene (7.56 g, 0.036 mol), and the mixture was stirred for 1 h. Dry *N*-formylpiperidine (4.33 mL, 0.040 mol) was then added into this reaction mixture and stirred for 1 h, which was then warmed to room temperature and stirred for 8 h. THF was removed and 6M HCl aqueous solution was added, then saturated NaCl aqueous solution was loaded. The organic fraction was extracted with ethyl acetate and dried with anhydrous $MgSO_4$. The product was chromatographed (silica gel; 10% EA/hexanes as the eluent) to give 6.85 g of golden yellow solid in a yield of 80%.[3,4] ^{1}H NMR ($CDCl_3$**;** 300 MHz): δ 10.29 (s, 1H), 8.02 (d, J = 8.7 Hz, 1H), 7.88 (d, J = 8.7 Hz, 1H), 7.55 (m, 2H). At 0 °C, ethyl 2-sulfanylacetate (5.3 g, 0.04 mol) was slowly added into a 250 mL DMF solution of 3-bromobenzo[*b*]thiophene-2-carbaldehyde (10.0 g, 0.04 mol) and K_2CO_3 (11.5g, 0.08 mol), and the reaction mixture was then stirred at room temperature for 3 days. Dilute HCl aqueous solution was added and then saturated NaCl aqueous solution was loaded. The organic fraction was extracted with ethyl acetate and dried with anhydrous $MgSO_4$. The product was chromatographed (silica gel; 10% EA/hexanes as the eluent) to give 10.6 g of golden yellow solid in a yield of 98%.[63] ^{1}H NMR ($CDCl_3$**;** 300 MHz): δ 8.02 (s, 1H), 7.88 (m, 2H), 7.43 (m, 2H), 4.43 (d, J = 6.9 Hz, 1H), 4.39 (d, J = 7.2 Hz, 1H), 1.44 (s, 1H), 1.42 (s, 1H), 1.39 (s, 1H). A 250 mL THF solution of benzothieno[3,2-*b*]thiophene-2-carboxylicacid ethyl ester (10 g, 0.04) and 53 mL of 10% NaOH aqueous solution was refluxed for 8 h. THF was removed and then dilute HCl aqueous solution was added. The precipitate was collected by filtration, which was washed with water and hexanes to give 8.8 g of white solid in a yield of 98%.[5] ^{1}H NMR (CDCl$_3$; 300 MHz): δ 8.12 (s, 1H), 7.92 (m, 2H), 7.46 (m, 2H). A 250 mL dry quinoline solution of benzothieno[3,2-*b*]thiophene-2-carboxylic acid (4 g, 0.02 mol) and Cu (1.1 g, 0.02 mol) was refluxed at 250 °C for 8 h. Cu was filtered out first, dilute HCl aquesous solution was added, then saturated NaCl aqueous solution was added. The organic fraction was extracted with ether and dried with anhydrous MgSO$_4$. BTT was chromatographed (silica gel; 10% EA/hexanes as the eluent) to give 2.79 g of white solid in a yield of 86%. ^{1}H NMR (CDCl$_3$; 300 MHz): δ 7.87 (d, *J* = 1.5 Hz, 1H), 7.84 (d, *J* = 1.5 Hz, 1H), 7.51 (d, *J* = 5.1 Hz, 1H), 7.38 (m, 3H).

Synthesis of 2-biphenylbenzothieno[3,2-*b*]thiophene (Bp-BTT): Under anhydrous condition at 0 °C, 2.5 M *n*-BuLi (0.57 mL in hexanes, 1.45 mmol) was slowly added to a 30 mL THF solution of BTT (250 mg, 1.31 mmol) and the mixture was stirred for 1 h. Next, tri-*n*-butyltin chloride (0.39 mL, 1.45 mmol) was added and the mixture was stirred for 1 hat this temperature, then warmed to room temperature and stirred for 8 h. After simple filtration under nitrogen, THF was removed under vacuum and 20 mL toluene was loaded. The toluene solution was then transferred into a (4-bromophenyl)benzene (338 mg, 1.45 mmol) and tetrakis(triphenylphosphine)palladium (61 mg, 0.05 mmol) toluene (30 mL) solution was refluxed at 140 °C for 2 days. After cooling back to room tempertaure, the desired solid product was collected by filtration and washed with hexanes and ether to give crude product in a yield of 70%. The product was then purified by gradient sublimation at pressures of ~ 10^{-5} Torr at 245 °C, giving a bright-yellow solid, 269 mg; yield, 55%. Mp: 261 °C. ^{1}H NMR (CDCl$_3$; 300 MHz): δ 7.86 (m, 2H), 7.76 (m, 2H), 7.66 (m, 4H), 7.59 (s, 1H), 7.41 (m, 5H).

This material was insufficiently soluble to obtain a useful ^{13}C NMR spectrum. Anal. Calcd for $C_{22}H_{14}S_2$: C, 77.15; H, 4.12; Found: C, 77.09; H, 4.21; HRMS (EI, m/z) calcd.: 342.0530 (M^+). Found: 342.0537.

Synthesis of 2-Naphthalenebenzothieno[3,2-*b*]thiophene (Np-BTT): Similar to synthetic procedure of Bp-BTT, 2-bromonaphthalene (300 mg, 1.45 mmol) was used instead of (4-bromophenyl)benzene. After simliar work up, the desired product (crude yield 75%) was purified by gradient sublimation at pressures of ~ 10^{-5} Torr at 240 °C, giving a bright-yellow solid, 199 mg; yield, 48%. Mp: 221 °C. ^{1}H NMR ($CDCl_3$; 300 MHz): δ 8.12 (s, 1H), 7.85 (m, 6H), 7.67 (s, 1H), 7.44 (m, 4H). This material was insufficiently soluble to obtain a useful ^{13}C NMR spectrum. Anal. Calcd for $C_{20}H_{12}S_2$: C, 75.91; H, 3.82; Found: C, 75.84; H, 3.77. HRMS (EI, m/z) calcd.: 316.0371 (M^+). Found: 316.0380.

Synthesis of bisbenzothieno[3,2-*b*]thiophene (BBTT): 175 mL THF solution of BTT (5.3 g, 0.028 mol) and NBS (5.45 g, 0.031 mol) was stirred for 30 min, then warmed back to room temperature and stirred for 12 h. $NaHSO_4$ was added first and then saturated NaCl aqueous solution was loaded. The organic fraction was extracted with ether and dried with anhydrous $MgSO_4$. 2-bromobenzothieno[3,2-*b*]thiophene was chromatographed (silica gel; hexanes as the eluent) to give 7.24 g of white solid in a yield of 96%. The product was used in the next step without further purification. ^{1}H NMR ($CDCl_3$; 300 MHz): δ 7.84 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 6.3 Hz, 1H), 7.44~7.33 (m, 2H), 7.32 (s, 1H). Similar to synthetic procedure of Bp-BTT, 2-bromobenzothieno[3,2-*b*]thiophene (390 mg, 1.45 mmol) was used instead of (4-bromophenyl)benzene. After simliar work up, the desired product (crude yield 72%) was purified by gradient sublimation at pressures of ~ 10^{-5} Torr at 255 °C, giving a bright-yellow solid, 254 mg; yield, 51%. Mp: 342 °C. This material was insufficiently soluble to obtain a useful ^{1}H or ^{13}C NMR spectrum. Anal. Calcd for $C_{20}H_{10}S_4$: C, 63.46; H, 2.66; Found: C, 63.40; H, 2.73. HRMS (EI, m/z) calcd.: 377.9655 (M^+). Found: 377.9665.

X-ray Crystal Structure Determination of Bp-BTT: Yellow crystals suitable for X-ray diffraction were crystallized from a hot toluene solution of Bp-BTT. The chosen crystals were mounted on a glass fiber. Data collection of Bp-BTT crystal was carried out on a Bruker Smart Apex2 CCD diffractometer with Cu Kα radiation (λ = 1.54178 Å) at 293(2) K. After data collection, the frames were integrated and absorption corrections were applied. The initial crystal structure was solved by direct methods, the structure solution was expanded through successive least-squares cycles, and the final solution was determined. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon atoms were fixed at calculated positions and refined using a riding mode. Crystal data, data collection, and refinement parameters are summarized in Table S1.

OTFT Fabrication: Thin film transistors were fabricated in bottom-gate/top-contact configuration. Highly doped p-type (100) silicon wafers (<0.004 Ωcm) were used as gate electrodes as well as substrates, and 300 nm SiO_2 thermally grown on Si was used as the gate insulator. The areal capacitance was 11.4 nF/cm^2. The substrate surface was treated with octadecatrichlorosilane (OTS) or hexamethyldisilazane (HMDS) purchased from Sigma-Aldrich Chemical Co. A few drops of HMDS were loaded inside a self-assembly chamber filled with N_2 gas. The SiO_2/Si substrates were exposed to this atmosphere for 7 days to give a hydrophobic surface. After HMDS deposition, the advancing aqueous contact angle was 95°. OTS SAMs were fabricated by immersing SiO_2/Si substrates in 3.0 mM hexane solutions of the silane agent for 1 h after leaving the solution in air under 55 – 60 % humidity for 10 h. After OTS deposition, the advancing aqueous contact angle of a water drop was 104°. Semiconductor thin films (50 nm) were next vapor-deposited onto the SiO_2/Si held at predetermined temperatures of 25˚C and 50˚C for Bp-BTT and Np-BTT, 25˚C, 50˚C, and 70 °C for BBTT with a deposition rate of 0.1 Å/s at 6×10^{-6} Torr, employing a high-vacuum deposition chamber (Denton Vacuum, Inc., USA). Gold source and drain electrodes (50 nm) were vapor-deposited at 2×10^{-6} Torr through a shadow mask in the vacuum deposition chamber. Devices were fabricated with a typical channel length of 100 μm and a channel width of 5000 μm.

OTFT Characterization: I-V plots of device performance were measured under vacuum, and transfer and output plots were recorded for each device. The current-voltage (*I-V*) characteristics of the devices were measured using a Keithley 6430 subfemtoammeter and a Keithly 2400 source meter, operated by a local Labview program and GPIB communication. Key device parameters, such as charge carrier mobility (μ) and on-to-off current ratio (I_{on}/I_{off}), were extracted from the source-drain current (I_{SD}) versus source-gate voltage (V_{SG}) characteristics employing standard procedures.[6] Mobilities were obtained from the formula defined by the saturation regime in transfer plots, $\mu = 2I_{SD}L/[C_iW(V_{SG}-V_T)^2]$, where I_{SD} is the source-drain current, V_{SG} is source-gate voltage, V_T is the threshold voltage. Threshold voltage was obtained from x intercept of V_{SG} vs $I_{SD}^{1/2}$ plots. AFM measurements were performed by using a JEOL-Microscope (JEOL Ltd. Japan) and Dimension Icon Scanning Probe Microscope (Veeco, USA) in the tapping mode. The surface roughness as evaluated by tapping mode AFM showed a root-mean square (RMS) roughness of 0.15 nm for SiO_2, 0.20 nm for HMDS, 0.35 nm for OTS.

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