Supporting Information

High charge carrier mobility, low bandgap D-A benzothiadiazole oligo-thiophene based polymeric semiconductors

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Materials and Methods

All solvents (chloroform, toluene, ethanol, THF, 1,2-dichloroethane, DMF, dichloroethane (EDC), chlorobenzene, 1,2-dichorobenzene (DCB), 1,2,4-trichlorobenzene) were purchased as anhydrous grade solvents from Sigma-Aldrich. THF and toluene were distilled over sodium with benzophenone as the indicator. bis(triphenylphosphine)palladium(II) dichloride ($Pd(PPh_3)_2Cl_2$), 4,7-dibromobenzo[c]-1,2,5-thiadiazole, hexamethyldisilazane (HMDS), 2-(tributylstannyl)thiophene, tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$), tri(o-tolyl)phosphine ($P(o\text{-}tolyl)_3$), bis(cyclopentadienyl)cobalt(III) hexafluorophosphate ($CcPF_6$), were purchased from Sigma-Aldrich. 5-formylthiophene-2-boronic acid was purchased from Frontier Scientific, Inc., 3-dodecylthiophene was purchased from either Sigma-Aldrich or Rieke Metals, n-octadecyltrichlorosilane (OTS-18) was purchased from Acros Organics, 1H,1H,2H,2H-perfluorodecyltriethoxysilane (FDTS) was purchased from Gelest, Inc., and tetra-n-butylammonium hexafluorophosphate ($[nBu_4N]^+[PF_6]^-$) was purcahsed from TCI America. Silica gel was purchased from Sorbent Technologies (Premium Rf™, porosity: 60Å; particle size: 40-75 μm).

^1H NMR and ^{13}C NMR spectra were recorded using a Varian Mercury Vx 400 (400 MHz) nuclear magnetic resonance spectrometer. Compounds were dissolved in deteurated solvents at room temperature; spectra of polymers were recorded in 1,1,2,2-tetrachloroethane-d_2, $C_2D_2Cl_4$, at 80 °C or 95 °C. Electron ionization mass spectra (EI-MS) were recorded using a Waters AutoSpec; while matrix-assisted laser desorption/ionization mass spectral (MALDI-MS) mesurements were conducted on a

Bruker Autoflex III Smartbeam instrument. Molecular weights of **PBT4**, **PBT6**, **PBT6(L)** and **PBT6V2'** were measured using a PL-GPC 220 instrument (courtesy of the Prof. Richard F. Jordan Research Group in the Department of Chemistry at the University of Chicago) using TCB as the mobile phase (stabilized with 125 ppm butylated hydroxytoluene) at 135 °C; the molecular weight of **PBT6V2** was measured on a Waters Associates GPC V2000 liquid chromatography system using an internal differential refractive index detector at 40 °C and HPLC grade THF as the eluent. UV-Vis absorption spectra and fluorescence spectra were recorded on an Agilent 8453 UV-Visible Spectrophotometer and Shimadzu RF-5301PC Fluorescence Spectrometer, respectively. Electrochemical redox potentials of polymer films (drop cast onto the platinum button working electrode from hot $CHCl_3$ solution) were carried out in a three-electrode cell consisting of a platinum button working electrode, a platinum wire counter electrode, and a Ag/Ag^+ reference electrode in a 0.1 M solution of $[nBu_4N]^+[PF_6]^-$ in acetonitrile. The $CcPF_6$ redox couple was used as the internal standard, to prevent overlap with the oxidation wave of the polymers. **Figure S7a** shows the redox wave of $CcPF_6$, which is 1.33 eV lower than that of $FcPF_6$ (-4.80 eV versus vacuum). Accordingly, $CcPF_6$ has an absolute energy of -3.47 eV versus vacuum. A cyclic voltammetry (CV) was performed on a CHI Instruments 620D Electrochemical Analyzer/Workstation with a scan rate of 50 mV/s. The thermal decomposition temperature of polymer powders were investigated with a Perkin-Elmer Pyris 1 thermogravimetric analyzer (TGA) in a nitrogen atmosphere (25 mL/min) with a heating rate of 10 °C/min. Thermal transitions of polymers were measured with a TA Q200 Differential Scanning Calorimeter (DSC) in a nitrogen atmosphere (50 mL/min) with a

heating/cooling rate of 10 °C/min. 1D-XRD measurements were performed on a PANalytical X-ray diffractometer and reflectometer (operating voltage of 45 kV and current of 40 mA) equipped with a Cu K_α X-ray irradiation source (λ = 1.541 Å), and at a fixed incidence angle of 1°. 2D-GIXS measurements were carried out using a Bruker-AXS Microdiffractometer (operating voltage of 45 kV and current of 40 mA) with a 0.8 mm collimator, K_α monochromator, Hi-Star area detector, and Eulerian cradle sample holder, at a fixed incidence angle (0.2° for **PBT6** and 1.2° for **PBT4**), and a 90° or 30° out-plane tilt angle, γ. 2D-WAXD measurements were conducted using a Rigaku MicroMax 002 X-ray source (operating voltage of 45 kV and current of 0.65 mA) CuK_α radiation filtered by confocal optic system (λ = 1.5418 Å) and equipped with a Rigaku R-axis IV++ detector. Polymer films for XRD characterization were prepared by drop casting chloroform solutions of the polymers onto octadecyltrichlorosilane (OTS-18) pre-treated SiO_2 dielectric (300 nm)/n-doped Si substrates. The morphology of polymer thin films deposited on FET devices were measured with a Veeco Digital Instruments Dimension 3100 scanning probe microscope in the tapping mode with a silicon etched probe tip.

Table S1. λ_{abs} and λ_{em} of **PBT6** in solvents possessing distinct polarities and polarizabilities

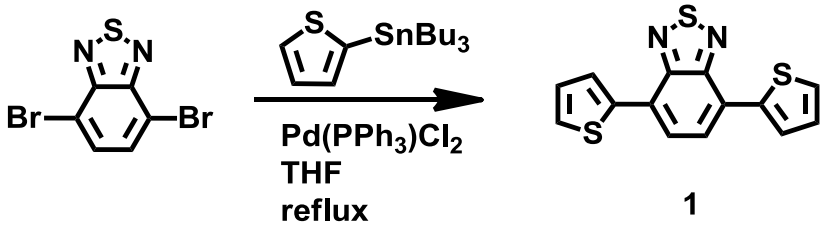
	λ_{abs} (nm) [a]	**λ_{em} (nm)** [b]	**ε** [c]	**n_D** [d]	**polarity** [e]	**polarizability** [f]
$CHCl_3$	536	666	4.81	1.4458	0.36	0.2105
CB	550	696	5.62	1.5248	0.38	0.2345
DCB	557	710	9.93	1.5514	0.43	0.2420
TCB	566	692	2.24	1.5717	0.23	0.2475

[a] peak with maximal intensity in absorption spectra (ca. 3.8×10^{-5} M) of **PBT6** (Figure 3b); [b] peak with maximal intensity in fluorescence spectra (ca. 2×10^{-6} M) of **PBT6** (Figure 3a); [c] dielectric constant; [d] refractive index; [e] calculated from $(\varepsilon - 1) / (2\varepsilon + 1)^1$; [f] calculated from $(n^2 - 1) / (2n^2 + 1)^1$

Positive solvatochromism is displayed in both absorption and fluorescence spectra from $CHCl_3$, to CB, and to DCB (λ_{abs} and λ_{em} are red shifted along with the increase in solvent polarity). Interestingly, λ_{abs} is also red shifted along with the increase in electronic polarizabilities of the solvents.

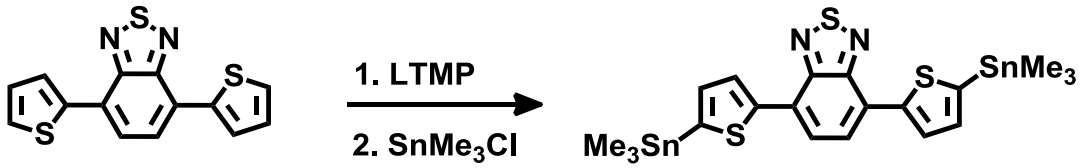
Synthetic Details

All reactions were carried out under an argon atmosphere using a standard Schlenk line technique. The compounds 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**1**),[2] 4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**M1**),[3] 2-bromo-3-dodecylthiophene (**2**),[4] 4,4'-didodecyl-2,2'-bithiophene (**3**),[4b,5] 5,5'-dibromo-4,4'-didodecyl-2,2'-bithiophene (**M4**),[6] 4,7-bis(5-formyl-2-thiophenyl)-2,1,3-benzothiadiazole (**4**),[7] 4,7-bis(3-bis(methylenediethyl phosphonate)-thiophen-2-yl)-2,1,3-benzothiadiazole (**M6**),[8] 2-tributylstannyl-4-dodecylthiophene (**7**),[9] 7-bis(4-n-dodecylthiophen-2-yl)-2,1,3-benzothiadiazole (**8**)[10] were prepared following published procedures.



4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (1): 4,7-dibromobenzo[c]-1,2,5-thiadiazole (5.0 g, 17 mmol, 1.0 eq.), 2-(tributylstannyl)thiophene (14.6 g, 39 mmol, 2.3 eq.) and $Pd(PPh_3)_2Cl_2$ (1.194 g, 1.7 mmol, 0.1 eq.) were dissolved into THF (125 mL) under argon. After purged by argon for 30 min, the reaction mixture was heated to 75 °C and heated at reflux for 19 h, before cooling to room temperature. D.I. H_2O (100 mL) was added and the mixture was extracted into CH_2Cl_2 (3 x 30 mL). The combined organic solution was washed with brine (3 x 100 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure after filtration. The resulting dark brown residue

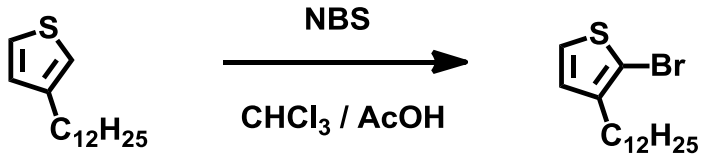
was purified by column chromatography (silica gel, hexane/CH_2Cl_2, 4:1, v/v). The final product was recrystallized from ethanol to afford orange needle-like crystals (yield: 65 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, J = 3.7, 1.1 Hz, 2H), 7.89 (s, 2H), 7.46 (dd, J = 5.1, 1.1 Hz, 2H), 7.22 (dd, J = 5.1, 3.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.75, 139.51, 128.17, 127.66, 126.96, 126.09, 125.88. EI-MS (m/z): 299.9 [M^+]; HRMS: [M^+] calcd for $C_{14}H_8N_2S_3$, 299.9846; found, 299.9850, Δ = 1.3 ppm.



1 M1

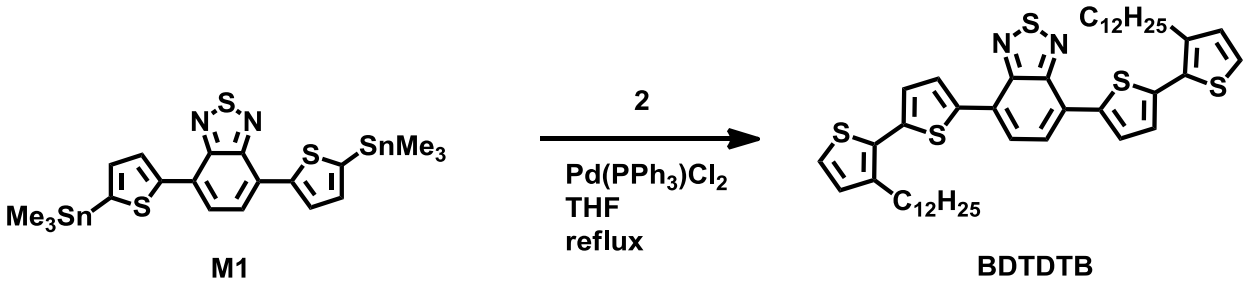
4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (M1): 2,2,6,6-tetramethylpiperdine (1.46 mL, 8.66 mmol, 2.6 eq.) was dissolved into dry THF (20 mL) under argon. n-butyllithium (3.46 mL of a 2.5 M solution in hexane, 8.66 mmol, 2.6 eq.) was added into the solution rapidly at -78 °C. The resulting solution was stirred at -78 °C for 30 min, and was warmed to room temperature and stirred for 10 min, to afford lithium 2,2,6,6-tetramethylpiperidide (LTMP). The solution was cooled to -78 °C and **1** (1.0 g, 3.33 mmol, 1.0 eq.) in THF (15 mL) was added in a dropwise manner, during which time the colorless solution turned purple. The resulting solution was stirred at -78 °C for 45 min; and trimethyltin chloride (8.32 mL of a 1.0 M solution in THF, 8.33 mmol, 2.5 eq) was then added in a dropwise manner, during which time the solution turned from purple to orange. The solution was then warmed to room temperature and was stirred for 12 h. Brine (20 mL) was added and the mixture was extracted into

CH_2Cl_2 (3 x 30 mL), washed with brine (3 x 60 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure after filtration. The residue was recrystallized from ethanol to give orange needle-like crystals (yield: 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 3.5 Hz, 2H), 7.88 (s, 2H), 7.30 (d, J = 3.4 Hz, 2H), 0.43 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.86, 145.25, 140.45, 136.30, 128.59, 126.03, 126.01, -7.93. EI-MS (m/z): 625.9 [M^+]; HRMS: [M^+] calcd for $C_{20}H_{24}N_2S_3Sn_2$, 627.9163; found, 627.9146, Δ = 2.7 ppm.

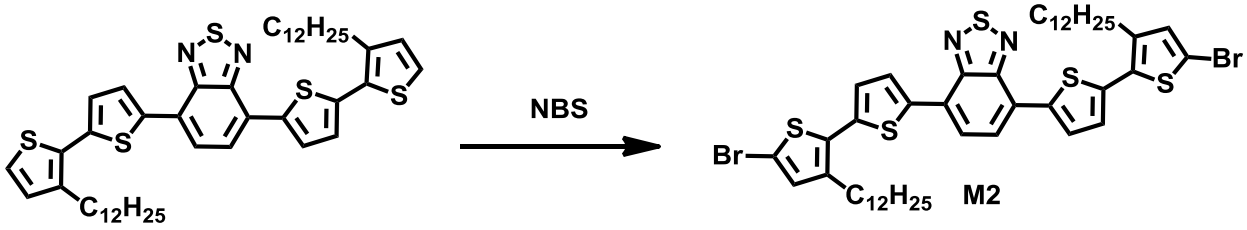


2

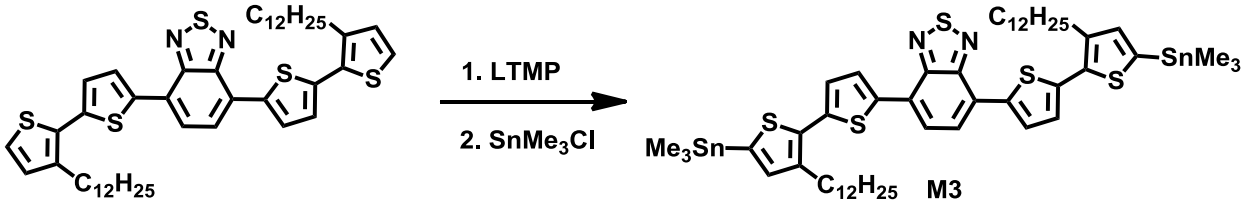
2-bromo-3-dodecylthiophene (2): NBS (3.53 g, 19.8 mmol, 1 eq.) was dissolved in $CHCl_3$/acetic acid (70 ml, 1:1, v/v) and the solution was added dropwise to 3-dodecylthiophene at 0 °C (5.0 g, 19.8 mmol, 1.0 eq.) using an addition funnel. The solution was stirred at room temperature in the dark, for 15 h, under argon. D.I. H_2O (50 mL) was added and the mixture was extracted into Et_2O (3 x 30 mL). The combined organic solution was washed with brine (3 x 50 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure after filtration. An orange oil was used in the next step without further purification (yield: ~90 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, J = 5.6 Hz, 1H), 6.79 (d, J = 5.6 Hz, 1H), 2.56 (t, J = 8 Hz, 2H), 1.57 (p, J = 8 Hz, 2H), 1.37 – 1.20 (m, 18H), 0.88 (t, J = 6.8 Hz, 3H).



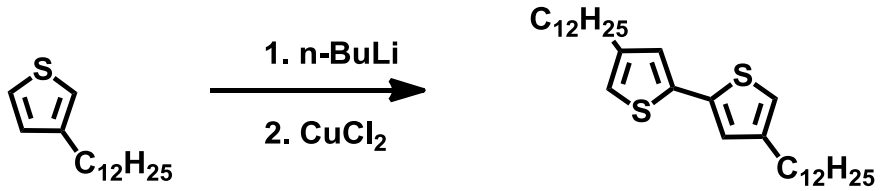
4,7-bis(3'-dodecyl-[2,2'-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole (BDTDTB): **M1** (1.0 g, 1.6 mmol, 1.0 eq.), **2** (1.19 g, 3.59 mmol, 2.25 eq.) and $Pd(PPh_3)Cl_2$ (70 mg, 9.6 μmol, 0.06 eq.) were dissolved into THF (38 mL) under argon. After purged by argon for 30 min, the mixture was heated to 75 °C and heated at reflux for 24 h. D.I. H_2O (100 mL) was added and the mixture was extracted into CH_2Cl_2 (3 x 30 mL). The combined organic solution was washed with brine (3 x 100 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure after filtration. The resulting dark purple residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2, 7:2, v/v), and further purified by column chromatography (silica gel, hexane/CH_2Cl_2, 100:20, v/v), to afford a purple solid (yield: 35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 3.9 Hz, 2H), 7.87 (s, 2H), 7.22 (d, J = 3.9 Hz, 5.2 Hz, 4H), 6.98 (d, J = 5.2 Hz, 2H), 2.85 (t, J = 8 Hz, 4H), 1.68 (p, J = 8 Hz, 4H), 1.45 - 1.16 (m, 36 Hz), 0.86 (t, J = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.76, 140.38, 139.14, 138.05, 130.76, 130.42, 128.27, 126.96, 125.83, 125.52, 124.32, 32.15, 30.92, 29.93, 29.92, 29.89, 29.86, 29.78, 29.70, 29.60, 29.59, 22.92, 14.35. MALDI-MS (m/z): 800.3 [M^+]; HRMS: [M^+] calcd for $C_{46}H_{60}N_2S_5$, 800.3339; found, 800.3360, Δ = 2.6 ppm.



4,7-bis(5'-bromo-3'-dodecyl-[2,2'-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole (M2): NBS (92 mg, 0.51 mmol, 2.05 eq.) was dissolved into $CHCl_3$/acetic acid (20 mL, 1:1, v/v) and dropwise added into **BDTDTB** (200 mg, 0.25 mmol, 1.0 eq.) in anhydrous $CHCl_3$/acetic acid (20 mL, 1:1, v/v) at 0 ˚C using an addition funnel. The resulting mixture was stirred in the dark at 0 ˚C for 3 h, followed by stirring at room temperature for 12 h. The mixture was then poured into D.I. H_2O (50 mL), and was extracted into CH_2Cl_2 (3 x 30 mL). The combined organic solution was washed with brine (3 x 50 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure after filtration. The product was washed with methanol (3 x 20 mL) and isolated as a purple solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 3.9 Hz, 2H), 7.86 (s, 2H), 7.16 (d, J = 3.9 Hz, 2H), 6.93 (s, 2H), 2.78 (t, J = 7.6 Hz, 4H), 1.64 (p, J = 7.6 Hz, 4H), 1.43 – 1.16 (m, 36H), 0.86 (t, J = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.68, 140.93, 139.57, 136.68, 133.04, 132.22, 128.21, 127.28, 125.76, 125.53, 111.09, 32.15, 30.77, 29.92, 29.91, 29.89, 29.82, 29.66, 29.65, 29.59, 29.55, 22.92, 14.35. MALDI-MS (m/z): 958.2 [M^+]; HRMS: [M^+] calcd for $C_{46}H_{58}Br_2N_2S_5$, 956.1558; found, 956.1570, Δ = 1.3 ppm.



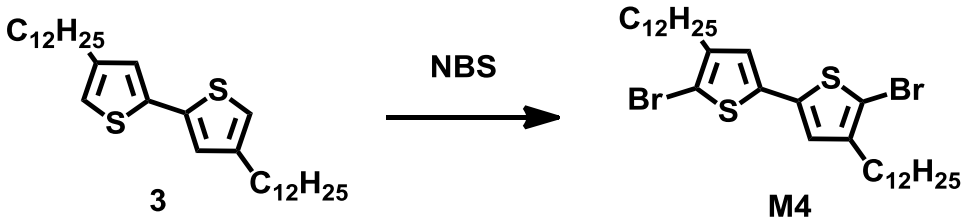
4,7-bis(3'-dodecyl-5'-(trimethylstannyl)-[2,2'-bithiophen]-5yl)benzo[c][1,2,5]thiadiazole (M3): 2,2,6,6-tetramethylpiperidine (47 mg, 0.33 mmol, 2.67 eq.) in THF (1 mL) was cooled to -78 ˚C under argon, followed by the addition of n-butyllithium (0.13 mL of a 2.5 M solution in hexane, 0.33 mmol, 2.6 eq.). The resulting solution was stirred at -78 °C for 30 min, and was warmed to room temperature and stirred for 10 min, to afford lithium 2,2,6,6-tetramethylpiperidide (LTMP). It was subsequently cooled down to -78 ˚C and **BDTDTB** (100 mg, 0.13 mmol, 1.0 eq.) in THF (3.2 mL) was added in a dropwise manner. After stirring at -78 ˚C for 1 h, $SnMe_3Cl$ (0.34 mL of a 1.0 M solution in THF, 0.33 mmol, 2.67 eq.) was added in a dropwise manner. The resulting solution was then warmed to room temperature and stirred for 12 h. After poured into D.I. H_2O (50 mL), the mixture was extracted into CH_2Cl_2 (3 x 15 mL), washed with brine (3 x 30 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure after filtration. The final product was washed with methanol (3 x 20 mL) and isolated as a purple solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 3.9 Hz, 2H), 7.86 (s, 2H), 7.20 (d, J = 3.5 Hz, 2H), 7.04 (s, 2H), 2.79 (t, J = 8 Hz, 4H), 1.65 – 1.74 (m, 4H), 1.40 – 1.16 (s, 36H), 0.86 (t, J = 6.8 Hz, 6H), 0.40 (s, 18H).



3

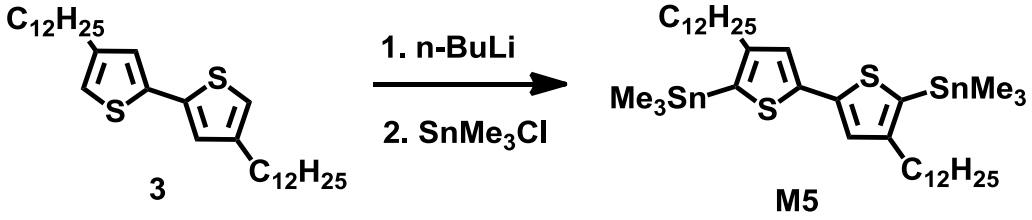
4,4'-didodecyl-2,2'-bithiophene (3): n-butyllithium (19.0 mL of a 2.5 M solution in hexane, 47.52 mmol, 1.2 eq.) was added dropwise into 3-dodecylthiophene (10.0 g,

39.6 mmol, 1.0 eq.) and tetramethylethylenediamine (TMEDA, 7.1 mL, 47.52 mmol, 1.2 eq.) in Et_2O (80 mL) at -78 ˚C under argon. The resulting solution was warmed to room temperature within 20 min, and heated to 40 ˚C for 1 h, followed by cooling down to -78 ˚C. The anhydrous $CuCl_2$ (6.39 g, 47.52 mmol, 1.2 eq.) was rapidly added into the solution at -78 °C. The resulting slurry was stirred at room temperature for 15 h. The crude product was extracted into hexane (5 x 50 mL), washed with brine (3 x 100 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure after filtration. The resulting residue was purified by column chromatography (silica gel, hexane). The final product was recrystallized from EtOH/acetone (1:1, v/v) to afford a light-yellow solid (yield: 45 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, J = 1.4 Hz, 2H), 6.76 (d, J = 1.4 Hz, 2H), 2.56 (t, J = 7.6 Hz, 4H), 1.61 (p, J = 7.6 Hz, 4H), 1.43 – 1.19 (m, 36H), 0.88 (t, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.20, 137.58, 125.02, 118.91, 32.15, 30.75, 30.62, 29.90, 29.89, 29.87, 29.82, 29.69, 29.59, 29.54, 22.92, 14.35. EI-MS (m/z): 502.4 [M^+]; HRMS: [M^+] calcd for $C_{32}H_{54}S_2$, 502.3667; found, 502.3667, Δ = 0 ppm.



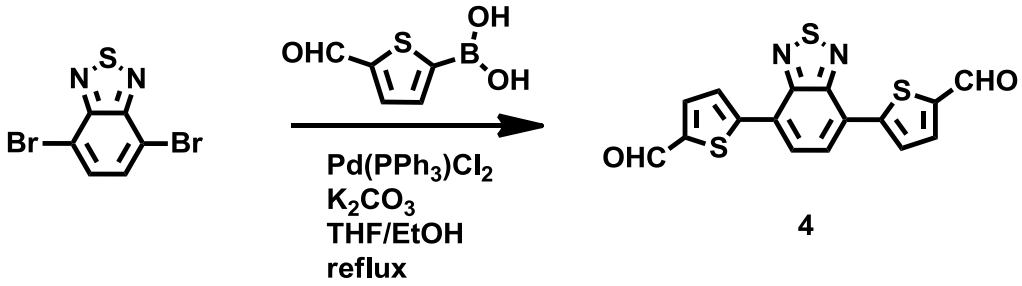
5,5'-dibromo-4,4'-didodecyl-2,2'-bithiophene (M4): NBS (726 mg, 4.08 mmol, 2.05 eq.) in $CHCl_3$/AcOH (50 mL, 1:1, v/v) was dropwise added into **3** (1.0 g, 1.99 mmol, 1.0 eq.) in $CHCl_3$/AcOH (20 mL, 1:1, v/v) at 0 ˚C using an addition funnel. The resulting mixture was stirred at room temperature under dark for 12 h, and was then poured into

D.I. H_2O (50 mL). The mixture was extracted into CH_2Cl_2 (3 x 50 mL), washed with brine (3 x 50 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure after filtration. The product was washed with methanol (3 x 20 mL) and isolated as a yellow powder (yield: 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (s, 2H), 2.51 (t, J = 8 Hz, 4H), 1.57 (p, J = 7.6 Hz, 4H), 1.43 – 1.19 (m, 36H), 0.88 (t, J = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.18, 136.36, 124.67, 108.06, 32.15, 29.90, 29.87, 29.84, 29.77, 29.61, 29.59, 29.42, 22.92, 14.36 (Note: some peaks in ^{13}C NMR spectrum overlap). EI-MS (m/z): 660.2 [M^+]; HRMS: [M^+] calcd for $C_{32}H_{52}Br_2S_2$, 658.1857; found, 658.1877, Δ = 3.0 ppm.



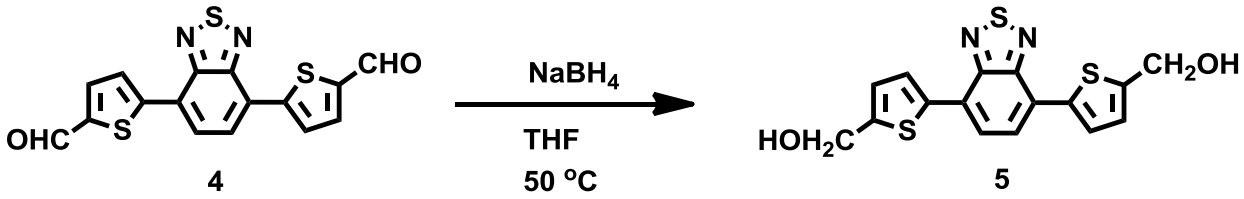
(4,4'-didodecyl-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane) (M5): n-butyllithium (0.62 mL of a 2.5 M solution in hexane, 1.55 mmol, 2.6 eq.) was added dropwise into **3** (300 mg, 0.60 mmol, 1.0 eq.) in THF (5 mL) at -78 ˚C. The solution was stirred at -78 ˚C for 30 min, at room temperature for 1 h, and cooled down to -78 ˚C, followed by the dropwise addition of $SnMe_3Cl$ (1.8 mL of 1.0 M solution in THF, 1.79 mmol, 3.0 eq.). The resulting solution was stirred at room temperature for 10 h, and was then poured into D.I. H_2O (30 mL). The mixture was extracted into hexane (3 x 20 mL), washed with brine (3 x 50 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure after filtration. The resulting brown-yellow oil was recrystallized from

hexane at -78 ˚C to afford yellow oil containing 84.5 wt% of **M5** and 15.6 wt% of **(4,4'-didodecyl-[2,2'-bithiophen]-5-yl)trimethylstannane (M5')**. ^{1}H NMR (400 MHz, $CDCl_3$) of **M5** δ 7.10 (s, 2H), 2.54 (t, J = 7.6 Hz, 4H), 1.59 (p, J = 8 Hz, 4H), 1.37 – 1.20 (m, 36 H), 0.88 (t, J = 6.8 Hz, 6H), 0.37 (s, J = 18H). ^{1}H NMR (400 MHz, $CDCl_3$) of **M5'** δ 7.11 (s, 1H), 6.97 (d, J = 1.6 Hz, 1H), 6.75 (d, J = 1.6 Hz, 1H), 2.54 (t, J = 7.6 Hz, 4H), 1.59 (p, J = 8 Hz, 4H), 1.37 – 1.20 (m, 36 H), 0.88 (t, J = 6.8 Hz, 6H), 0.38 (s, J = 9H).



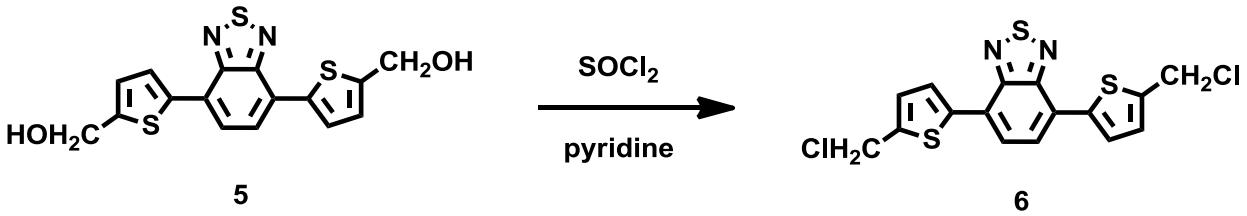
4,7-bis(5-formyl-2-thiophenyl)-2,1,3-benzothiadiazole (4): Na_2CO_3 (19.47 g, 183.6 mmol, 12.0 eq.) was dissolved into D.I. H_2O (92 mL) to make a 2.0 M aq. solution of Na_2CO_3. 5-formylthiophene-2-boronic acid (6.0 g, 38.3 mmol, 2.5 eq.) was dissolved into ethanol (50 mL). The two solutions were then bubbled with argon for 2 h. Degassed Na_2CO_3 aq. solution and 5-formylthiophene-2-boronic acid solution were added to the solution of 4,7-dibromobenzo[c]-1,2,5-thiadiazole (4.5 g, 15.3 mmol, 1.0 eq.) and $Pd(PPh_3)_2Cl_2$ (1.0 g, 1.42 mmol, 0.09 eq.) in toluene (60 mL) under argon. After purged by argon for 30 min, the solution was stirred at 50 °C for 18 h, during which time the organe solution turned to a red slurry. D.I. water (100 mL) was added at room temperature and the red residue was collected by filtration, washed with methanol (3 x 20 mL) followed by $CHCl_3$ (3 x 20 mL). The pure product was recrystallized from $CHCl_3$

to afford a red solid (yield: 35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 2H), 8.26 (d, J = 4.0 Hz, 2H), 8.06 (s, 2H), 7.87 (d, J = 4.0 Hz, 2H). FT-IR (KBr, cm-1): v = 3088 (m), 2839 (w), 2815 (w), 1646 (s), 1523 (w), 1450 (s), 1233 (s), 820 (m). EI-MS (m/z (%)): 355.9 (100) [M^+], 354.9 (50) [M^+ − H]; HRMS: [M^+] calcd for $C_{16}H_8N_2O_2S_3$, 355.9740; found, 355.9748, Δ = 2.2 ppm.



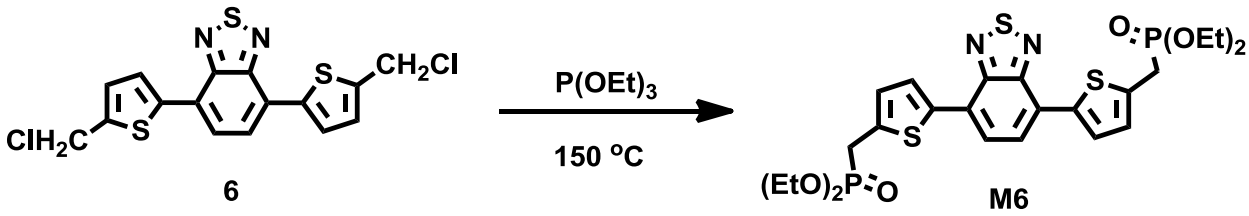
4 5

4,7-bis(5-hydroxylmethyl-thiophen-2-yl)-2,1,3-benzothiadiazole (5): $NaBH_4$ (102 mg, 2.7 mmol, 3.0 eq.) was added to **4** (0.32 g, 0.9 mmol, 1.0 eq.) in THF (25 mL) under argon. The mixture was heated to 50 °C for 12 h, before cooling to room temperature. D. I. H_2O (50 mL) was added and the resulting mixture was stirred at room temperature for 30 min. The mixture was collected by filtration, washed with brine (3 x 20 mL), followed by methanol (3 x 20 mL), to afford red solid that was used in the next step without further purification (yield: 70 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.01 (s, 2H), 7.99 (d, J = 3.8 Hz, 2H), 7.07 (d, J = 3.7 Hz, 2H), 5.62 (s, 2H), 4.69 (s, 4H). EI-MS (m/z): 360.0 [M^+]; HRMS: [M^+] calcd for $C_{16}H_{12}N_2O_2S_3$, 360.0074; found, 360.0061, Δ = 3.6 ppm.



5 6

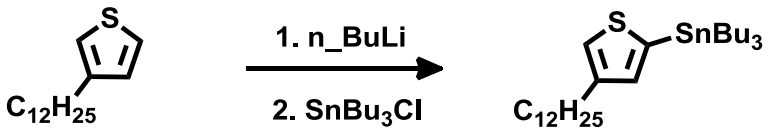
4,7-bis(5-chloromethyl-thiophen-2-yl)-2,1,3-benzothiadiazole (6): diol **5** (650 mg, 1.8 mmol, 1.0 eq.) and anhydrous pyridine (0.9 mL, 10.8 mmol, 6.0 eq.) were dissolved into toluene (45 mL) at 0 °C. Thionyl chloride (1.2 mL, 15.8 mmol, 8.8 eq.) was then added in a dropwise manner at 0 °C. The resulting mixture was stirred at 0 °C for 1h followed by stirring at room temperature for 10 h, under argon. The excess thionyl chloride and toluene was removed under reduce pressure. The residue was washed with methanol (3 x 20 mL) and isolated as a dark-red solid, which was employed to the next step without further purification (yield: 65 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 3.8 Hz, 2H), 7.85 (s, 2H), 7.18 (dt, J = 3.8, 0.7 Hz, 1H), 4.87 (d, J = 0.5 Hz, 2H). EI-MS (m/z): 395.9 [M^+]; HRMS: [M^+] calcd for $C_{16}H_{10}Cl_2N_2S_3$, 395.9395; found, 395.9383, Δ = 3.0 ppm.



6 M6

4,7-bis(3-bis(methylenediethylphosphonate)-thiophen-2-yl)-2,1,3-benzothiadiazole (M6): bis(chloromethyl) compound **6** (627 mg, 1.58 mmol, 1.0 eq.) was mixed with $P(OEt)_3$ (4.1 mL, 23.7 mmol, 15.0 eq.). The resulting mixture was stirred at 148 °C for 8 h under argon. The excess $P(OEt)_3$ was removed by vacuum distillation (*ca.* 10^{-4} torr) at

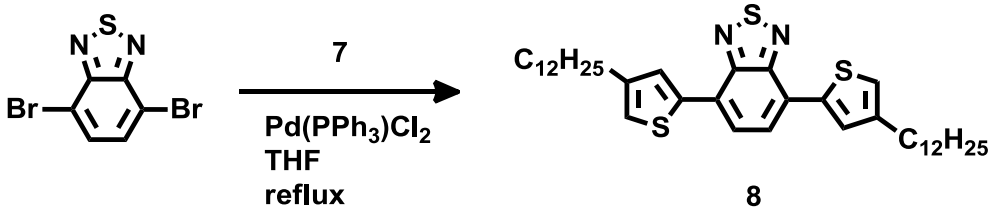
60 °C. The dark red crude product was purified by column chromatography (silica gel, EtOAc/MeOH, 105:10, v/v) and isolated as a dark-red gel-like solid (yield: 34 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 3.7 Hz, 2H), 7.79 (s, 2H), 7.07 (t, J = 3.6 Hz, 2H), 4.16 – 4.07 (m, 8H), 3.45 (d, J = 24 Hz, 4H), 1.31 (t, J = 8 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.69, 138.93 (138.88), 134.50 (134.40), 128.68 (128.59), 127.84 (127.80), 125.87, 125.56, 62.82 (62.75), 29.30 (27.87), 16.67 (16.61). (Note: values inside brackets refer to coupled peaks due to heteronuclear coupling of carbon-13 to phosphorus-31) EI-MS (m/z): 600.0 [M^+], 463.0 (55) [$M^+ - C_4H_{10}O_3P$], 325.9 (43) [$M^+ - C_8H_{20}O_6P_2$]; HRMS: [M^+] calcd for $C_{24}H_{30}N_2O_6P_2S_3$, 600.0742; found, 600.0741, Δ = 0.2 ppm.



7

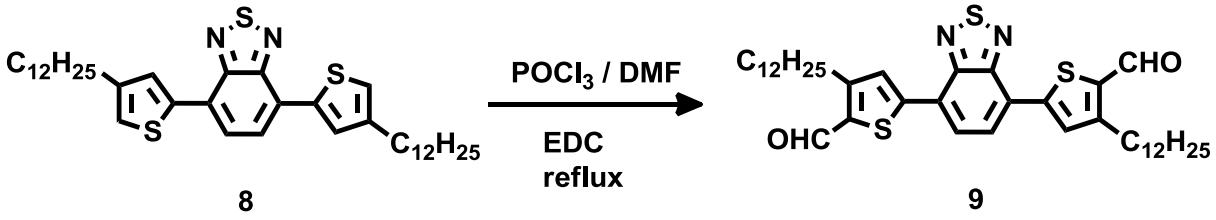
2-tributylstannyl-4-dodecylthiophene (7): 3-dodecylthiophene (3.0 g, 15.3 mmol, 1.0 eq.) and tetramethylethylenediamine, TMEDA, (2.75 mL, 18.5 mmol, 1.2 eq.) were dissolved into THF (35 mL) under argon. n-butyllithium (7.33 mL of a 2.5 M solution in hexane, 18.5 mmol, 1.2 eq.) was dropwise added at -78 °C. The resulting solution was stirred at -78 °C for 40 min followed by warming to room temperature and stirred for an additional 1.5 h. The resulting light-yellow solution was again cooled to -78 °C and tributyltin chloride (5.18 mL, 19.1 mmol, 1.25 eq.) was added in a dropwise manner. The solution was stirred at room temperature for 8 h, and was poured into D.I. H_2O (50 mL). The mixture was extracted into CH_2Cl_2 (3 x 30 mL), washed with brine (3 x 30 mL),

dried over anhydrous $MgSO_4$, and concentrated under reduced pressure after filtration, to afford a yellow color oil, which was employed to the subsequent step without further purification (yield: ~90 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 1H), 6.97 (s, 1H), 2.65 (t, J = 8 Hz, 2H), 1.65 – 1.61 (m, 2H), 1.59 – 1.50 (m, 6H) 1.41 – 1.20 (m, 24H), 1.14 – 1.05 (m, 6H), 0.91 – 0.88 (m, 12H).



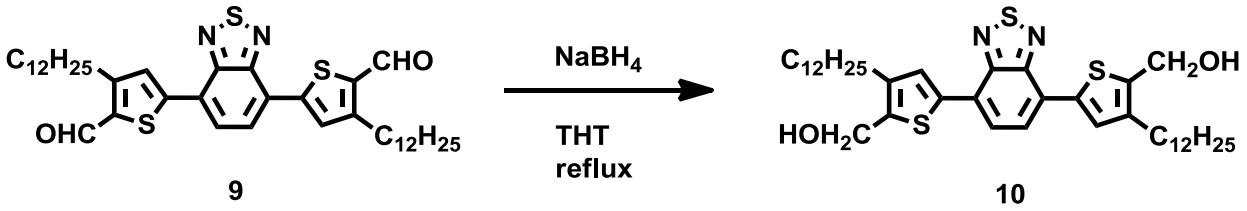
4,7-bis(4-n-dodecylthiophen-2-yl)-2,1,3-benzothiadiazole (8): 4,7-dibromobenzo[c]-1,2,5-thiadiazole (1.39 g, 4.75 mmol, 1.0 eq.), **7** (6.42 g, 11.9 mmol, 2.5 eq.) and $Pd(PPh_3)_2Cl_2$ (0.33 g, 0.48 mmol, 0.1 eq.) were dissolved into THF (45 mL) under argon. After purged by argon for 30 min, the solution was heated to 73 °C and heated at reflux for 36 hours, before cooling to room temperature. D.I. H_2O (60 mL) was added and the mixture was extracted into CH_2Cl_2 (3 x 30 mL). The combined organic solution was washed with brine (3 x 50 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure after filtration. The dark red residue was purified by column chromatography (silica gel, hexane/DCM, 100:15 to 100:30, v/v) and was isolated as a red solid (yield: 82 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 1.4 Hz, 2H), 7.83 (s, 2H), 7.04 (d, J = 1.3 Hz, 2H), 2.69 (t, J = 8 Hz, 4H), 1.65 – 1.74 (m, 4H) 1.43 – 1.19 (m, 36H), 0.88 (t, J = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.86, 144.59, 139.22, 129.22, 126.25, 125.75, 121.74, 32.15, 30.88, 30.74, 29.91, 29.90, 29.88, 29.85, 29.72,

29.60, 29.59, 22.92, 14.35. EI-MS (m/z): 636.3 [M^+]; HRMS: [M^+] calcd for $C_{38}H_{56}N_2S_3$, 636.3602; found, 636.3606, Δ = 0.6 ppm.

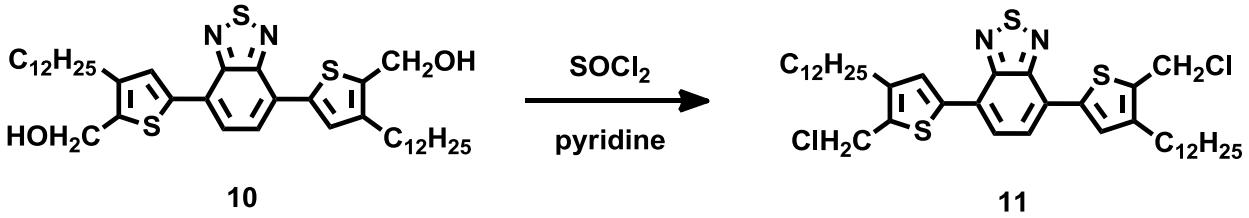


4,7-bis(4-n-dodecylthiophen-5-formyl-2-yl)-2,1,3-benzothiadiazole (9): compound **8** (2.26 g, 3.55 mmol, 1.0 eq.) was dissolved into EDC (60 mL) under argon. The solution was cooled to 0 °C, followed by the addition of DMF (5.5 mL, 70.96 mmol, 20.0 eq.) and subsequently the dropwise addition of phosphoryl chloride, $POCl_3$, (5.62 mL, 60.32 mmol, 17.0 eq.). The resulting mixture was heated to 90 °C and heated at reflux for 12 h, before cooling to room temperature. Sodium acetate aqueous solution (1.0 M in D.I. H_2O, 200 mL) was added. The resulting mixture was stirred vigorously for 1.5 h, and was neutralized by addition of a NaOH aqueous solution. The mixture was extracted into CH_2Cl_2 (3 x 50 mL). The combined organic solution was washed with brine (3 x 50 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure after filtration. The brown residue was purified by column chromatography (silica gel, CH_2Cl_2) to afford an orange solid, which was then recrystallized from ethanol to afford an orange, cotton-like solid (yield: 90 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.11 (s, 2H), 8.10 (s, 2H), 8.01 (s, 2H), 3.04 (t, J = 8 Hz, 4H), 1.78 (p, J = 4Hz, 4H), 1.40 – 1.25 (m, 36H), 0.87 (t, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.19, 153.37, 152.38, 146.72, 138.10, 131.23, 126.97, 126.40, 31.89, 31.50, 29.64, 29.61, 29.54, 29.53, 29.39, 29.35, 29.33,

28.67, 22.67, 14.10. EI-MS (m/z): 692.3 [M^+]; HRMS: [M^+] calcd for $C_{40}H_{56}N_2O_2S_3$, 692.3488; found, 692.3504, Δ = 2.3 ppm.

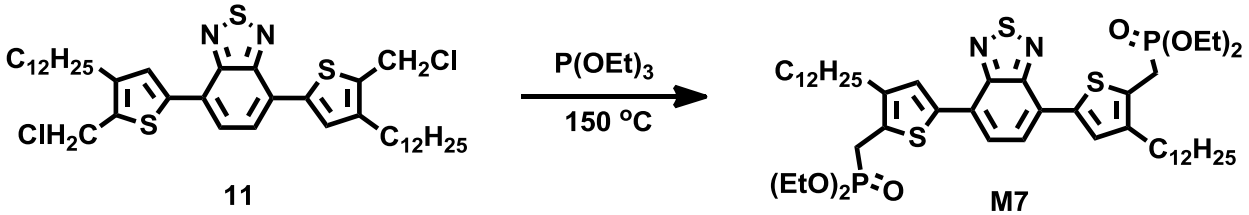


4,7-bis(4-n-dodecylthiophen-5-hydroxylmethyl-2-yl)-2,1,3-benzothiadiazole (10): sodium borohydride, $NaBH_4$ (84 mg, 2.25 mmol, 3.0 eq.) (*note: too much $NaBH_4$ could reduce benzothiadiazole to 1,2-phenylene-diamine*) was added to **9** (0.52 g, 0.75 mmol, 1.0 eq.) in THF (35 mL) under argon. The mixture was heated to 73 °C and heated of reflux for 8 h, before cooling to room temperature. D. I. water (45 mL) was added and the resulting mixture was stirred at room temperature for 2 h. The mixture was extracted into $CHCl_3$ (3 x 20 mL). The combined organic solution was washed with brine (3 x 20 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure after filtration. The resulting red precipitate was washed with methanol (3 x 20 mL) to afford target product (yield: 76 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.97 (s, 2H), 7.92 (s, 2H), 5.47 (s, 2H), 4.63 (d, J = 5.4 Hz, 4H), 1.60 – 1.55 (m, 4H), 1.36 – 1.15 (m, 36H), 0.84 – 0.78 (t, 6H). (Note: 4 protons in the region of about 2 to 3 ppm corresponding to Th–CH_2– were obscured by a large proton peak from water in the DMSO-d_6 solvent. (Th: thiophene)).



10 11

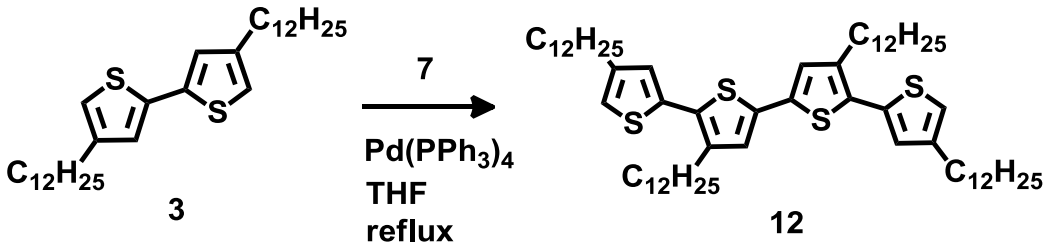
4,7-bis(4-n-dodecylthiophen-5-chloromethyl-2-yl)-2,1,3-benzothiadiazole (11): diol **10** (0.5 g, 0.72 mmol, 1.0 eq.) and anhydrous pyridine (0.35 ml, 4.3 mmol, 6.0 eq.) were dissolved into toluene (35 mL). Thionyl chloride (0.52 mL, 7.2 mmol, 10.0 eq.) was added in a dropwise manner at 0 °C. The resulting mixture was stirred at room temperature for 15 h under argon. The excess thionyl chloride and toluene were removed under reduced pressure. The mixture was extracted into CH_2Cl_2 (3 x 30 mL). The combined organic solution was washed with brine (3 x 30 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure after filtration. The resulting dark-red precipitate was washed with methanol (3 x 20 mL) and was employed in the next step without further purification (yield: 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 2H), 7.82 (s, 2H), 4.83 (s, 4H), 2.69 (t, J = 8 Hz, 4H), 1.75 – 1.65 (m, 4H), 1.30 - 1.20 (m, 36H), 0.87 (t, J = 6.8 Hz, 6H).



11 M7

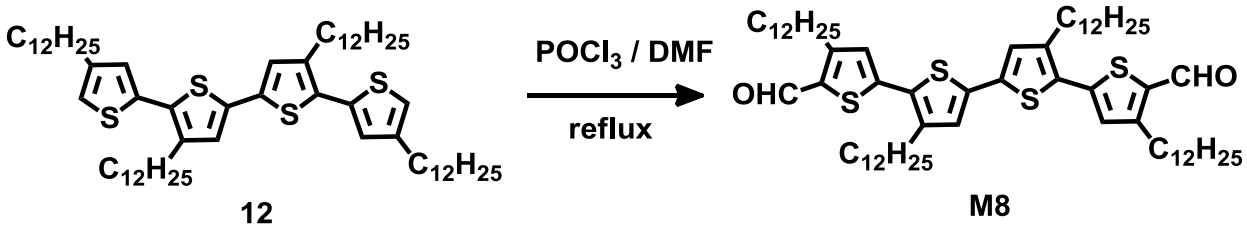
4,7-bis(3-bis(methylenediethyl phosphonate)-4-n-dodecylthiophen-2-yl)-2,1,3-benzothiadiazole (M7): bis(chloromethyl) compound **11** (418 mg, 0.57 mmol, 1.0 eq.) was

blended with triethyl phosphate, $P(OEt)_3$ (2 mL, 11.38 mmol, 20.0 eq.). The resulting mixture was stirred at 140 °C for 12 h under argon. The excess $P(OEt)_3$ was removed by vacuum distillation (10^{-4} torr) at 60 °C. The dark red crude product was purified by column chromatography (silica gel, EtOAc) and isolated as dark-red solid (yield: 47 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 2H), 7.77 (s, 2H), 4.11 (dq, J = 14.1, 7.1 Hz, 8H), 3.37 (d, J = 21.0 Hz, 4H), 2.63 (t, J = 6.9 Hz, 4H), 1.66 (p, J = 7.8 Hz, 4H), 1.44 – 1.21 (m, 48H), 0.87 (t, J = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.66, 142.24 (142.14), 137.14 (137.10), 129.44 (129.40), 127.78 (127.66), 125.67, 125.34, 62.65 (62.59), 32.06, 30.69, 30.67, 29.83, 29.82, 29.79, 29.77, 29.72, 29.50, 28.69, 28.68, 27.44 (26.00), 22.83, 16.63 (16.57), 14.27 (Note: values inside brackets refer to coupled peaks due to heteronuclear coupling of carbon-13 to phosphorus-31). MALDI-MS (m/z (%)): 936.5 (50) [M^+], 799.4 (100) [$M^+ - C_4H_{10}O_3P$]; HRMS: [M^+] calcd for $C_{48}H_{78}N_2O_6P_2S_3$, 936.4464; found, 936.4497, Δ = 3.5 ppm.



3',4,4'',4'''-tetradodecyl-2,2':5',2'':5'',2'''-quaterthiophene (12): **3** (1.23 g, 1.86 mmol, 1.0 eq.), **7** of (3.42 g, 4.47 mmol, 2.4 eq.), and $Pd(PPh_3)_4$ (0.43 g, 0.37 mmol, 0.2 eq.) were dissolved into toluene (35 mL) under argon. After purged with argon for 30 min, the solution was heated to 120 °C and heated of reflux for 24 h, before cooling to room

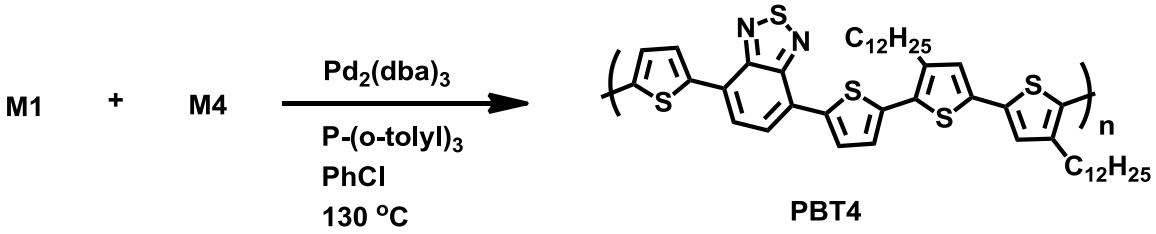
temperature. D.I. H_2O (50 mL) was added and the mixture was extracted into CH_2Cl_2 (3 x 30 mL). The combined organic solution was washed with brine (3 x 30 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure after filtration. The brown residue was purified by column chromatography (silica gel, hexane/DCM, 100:5, v/v), to afford an orange solid (yield: 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 2H), 6.95 (d, J = 1.4 Hz, 2H), 6.88 (d, J = 1.4 Hz, 2H), 2.71 (t, J = 7.6 Hz, 4H), 2.60 (t, J = 7.4 Hz, 4H), 1.68 – 1.60 (m, 8H), 1.42 - 1.18 (m, 72H), 0.88 (t, J = 6.7 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.87, 140.23, 135.82, 134.83, 130.18, 127.30, 126.51, 120.15, 32.16, 30.72, 30.65, 29.92, 29.89, 29.85, 29.77, 29.68, 29.60, 29.58, 22.93, 14.35. MALDI-MS (m/z): 1002.7 [M^+]; HRMS: [M^+] calcd for $C_{64}H_{106}S_4$, 1002.7171; found, 1002.7177, Δ = 0.6 ppm.



12 M8

3',4,4'',4'''-tetradodecyl-[2,2':5',2'':5'',2'''-quaterthiophene]-5,5'''-dicarbaldehyde (M8): DMF (2 mL, 24.9 mmol, 25.0 eq.) was added to **12** (1.0 g, 1.0 mmol, 1.0 eq.) in EDC (40 mL) at 0 °C under argon, followed by the addition of phosphoryl chloride, $POCl_3$, (1.9 mL, 19.9 mmol, 20.0 eq.) in a dropwise manner. The resulting solution was heated to 90 °C and heated of reflux for 12 h, before cooling to room temperature. The sodium acetate aqueous solution (100 mL of 1.0 M solution) was added for hydrolysis and the mixture was further stirred for 1 h at room temperature. The mixture was

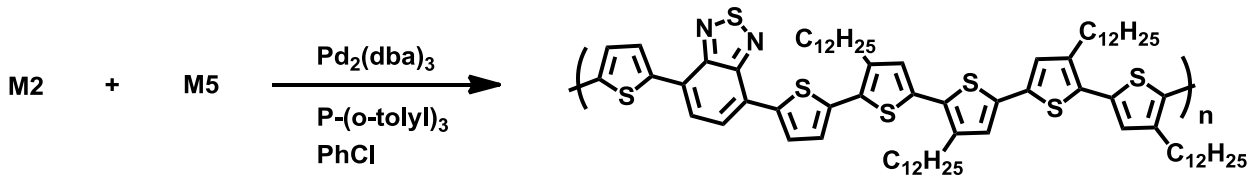
extracted into CH_2Cl_2 (3 x 30 mL). The combined organic solution was washed with brine (3 x 30 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure after filtration. The residue was washed with methanol (3 x 50 mL) and isolated as a red powder (yield: 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 2H), 7.05 (s, 2H), 7.04 (s, 2H), 2.94 (t, J = 7.8 Hz, 4H), 2.79 (t, J = 7.8 Hz, 4H), 1.74 – 1.64 (m, 8H), 1.44 – 1.15 (m, 72H), 0.87 (t, J = 6.8 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.84, 153.53, 144.95, 143.26, 136.66, 136.27, 129.64, 128.55, 127.71, 32.14, 31.64, 30.44, 29.87, 29.85, 29.75, 29.69, 29.58, 29.57, 28.70, 22.91, 14.34. MALDI-MS (m/z): 1058.7 [M^+]; HRMS: [M^+] calcd for $C_{66}H_{106}O_2S_4$, 1058.7071; found, 1058.7076, Δ = 0.5 ppm.



PBT4

Poly(benzothiadiazole-quaterthiophene) (PBT4): **M1** (95 mg, 0.15 mmol, 1.0 eq.), **M4** (100 mg, 0.15 mmol, 1.0 eq.), $Pd_2(dba)_3$ (15 mg, 15 μmol, 0.1 eq.), and P(o-tolyl)$_3$ (20 mg, 60 μmol, 0.4 eq.) into chlorobenzene (10 mL) under argon. The resulting mixture was stirred at 130 ˚C for 3 days and was then poured into methanol (300 mL) to quench the polymerization. The precipitated powders were collected by filtration and then washed by Soxhlet extraction sequentially using methanol (12 h), acetone (12 h), hexane (12 h), and $CHCl_3$ (4 h). The $CHCl_3$ solution was collected and then concentrated under reduced pressure. The concentrated solution was added in a

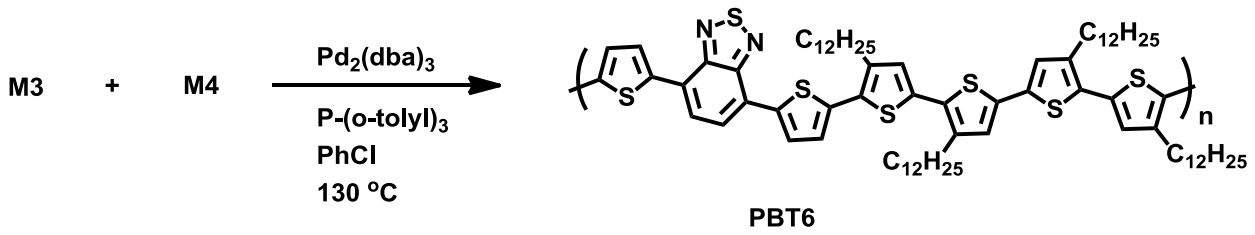
dropwise manner to methanol (200 mL). The precipitate was collected by filtration from methanol followed by drying under vacuum at room temperature for 12 h to afford a black polymer powder (50 mg, yield: 42%). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$ at 80 °C) δ 8.21 – 8.16 (br, 2H), 7.93 (d, 2H), 7.32 (d, 2H), 7.14 (s, 2H), 2.95 – 2.86 (m, 4H), 1.84 – 1.75 (m, 4H), 1.42 – 1.14 (m, 36H), 0.92 (t, J = 6.7 Hz, 6H). GPC (TCB, 135 °C): M_n = 5.8 kDa, M_w = 9.7 kDa, PDI = 1.67, DP = ca. 7.3.



PBT6L

Poly(benzothiadiazole-sexithiophene) (PBT6(L)): **M2** (100 mg, 0.10 mmol, 1.0 eq.), **M5** mixture (109 mg, including 0.10 mmol of **M5**, 1.0 eq.; 0.02 mmol of **M5'**, 0.2 eq.), $Pd_2(dba)_3$ (5 mg, 5 μmol, 0.05 eq.), and P(o-tolyl)$_3$ (6.4 mg, 20.8 μmol, 0.2 eq.) into chlorobenzene (6.9 mL) under argon. The resulting mixture was stirred at 130 ˚C for 3 days, after which it was poured into methanol (300 mL) to quench the polymerization. The precipitated powders were collected by filtration and then washed by Soxhlet extraction sequentially using methanol (12 h), acetone (12 h), hexane (12 h), and $CHCl_3$ (2 h). The $CHCl_3$ solution was collected and then concentrated under reduced pressure. The concentrated solution was added in a dropwise manner to methanol (200 mL). The precipitate was collected by filtration from methanol followed by drying under vacuum at room temperature for 12 h to afford a black fine powder (95 mg, yield: 71%). ^{1}H NMR

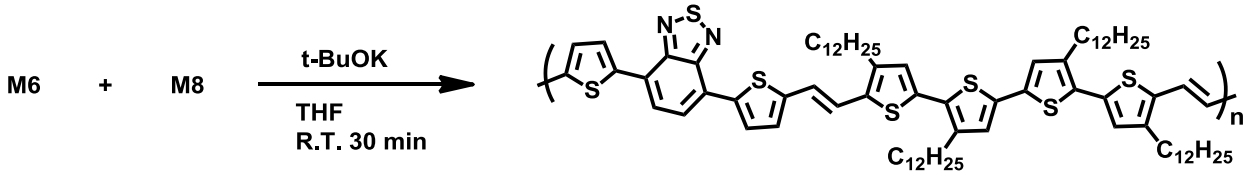
(400 MHz, $C_2D_2Cl_4$ at 95 °C) δ 8.19 (d, J = 2.4 Hz, 2H), 7.94 (s, 2H), 7.32 (d, J = 2.8 Hz, 2H), 7.15 – 7.04 (br, 4H), 2.98 – 2.90 (m, 4H), 2.90 – 2.79 (m, 4H), 1.87 – 1.73 (m, 8H), 1.42 – 1.11 (m, 72 H), 0.93 (t, J = 6.2 Hz, 12H). GPC (TCB, 135 °C): M_n = 8.6 kDa, M_w = 14.8 kDa, PDI = 1.72, DP = ca. 6.6.



PBT6

poly(benzothiadiazole-sexithiophene) (PBT6): **M3** (112 mg, 0.1 mmol, 1.0 eq.), **M4** (66 mg, 0.1 mmol, 1.0 eq.), $Pd_2(dba)_3$ (5 mg, 5 μmol, 0.05 eq.), and P(o-tolyl)$_3$ (13 mg, 40 μmol, 0.4 eq.) were dissolved into chlorobenzene (6.6 mL) under argon. The resulting mixture was stirred at 130 ˚C for 5 days and was then poured into methanol (300 mL) to quench the polymerization. The precipitated powders were collected by filtration and then washed by Soxhlet extraction sequentially using methanol (12 h), acetone (12 h), hexane (12 h), and $CHCl_3$ (1 h). The $CHCl_3$ solution was collected and then concentrated under reduced pressure. The concentrated solution was added in a dropwise manner to methanol (200 mL). The precipitate was collected by filtration from methanol followed by drying under vacuum at room temperature for 12 h to afford the black polymer powder (94 mg, yield: 72%). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$ at 95 °C) δ 8.20 (s, 2H), 7.94 (s, 2H), 7.32 (s, 2H), 7.09 (s, 4H), 2.98 – 2.90 (m, 4H), 2.90 – 2.81 (m, 4H),

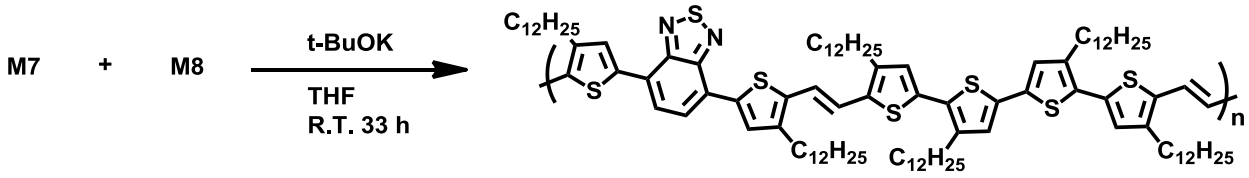
1.88 – 1.73 (m, 8H), 1.42 – 1.12 (m, 72H), 0.93 (t, J = 6.8 Hz, 12H). GPC (TCB, 135 °C): M_n = 18.1 kDa, M_w = 36.5 kDa, PDI = 2.02, DP = ca. 13.9



PBT6V2

Poly(dithieno-benzothiadiazole-vinylene-quaterthiophene) (PBT6V2): **M6** (50 mg, 83 μmol, 1.0 eq.) in THF (1.5 mL) was added to **M8** (90 mg, 83 μmol, 1.0 eq.) in THF (2 mL). Potassium *tert*-butoxide (0.33 mL of a 1.0 M solution in THF, 332 μmol, 4.0 eq.) was added in a dropwise manner to the solution at room temperature. The resulting mixture was immediately turned from red-orange to dark-purple with an enhancement in viscosity. The polymerization was quenched after 30 min by pouring the mixture into methanol (300 mL). The precipitated powders were collected by filtration and then washed by Soxhlet extraction sequentially using methanol (12 h), acetone (12 h), hexane (12 h), and $CHCl_3$ (6 h). The $CHCl_3$ solution was collected and then concentrated under reduced pressure. The concentrated solution was added in a dropwise manner to methanol (200 mL). The precipitate was collected by filtration from methanol followed by drying under vacuum at room temperature for 12 h to afford the black polymer powder (15 mg, yield: 13%). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$ at 95 °C) δ 8.15 (s, Th-H), 7.91 (s, BT-H), 7.34 – 7.31 (br, =CH-), 7.22 (s, Th-H), 7.07 (s, Th-H), 7.00 (s, Th-H), 6.97 – 6.95 (br, =CH-), 2.85 (s, Th-CH_2-), 2.78 (s, Th-CH_2-), 1.82 – 1.69 (br, -

CH_2-), 1.42 – 1.11 (m, -CH_2-), 0.94 (s, -CH_3). (Th: thiophene, BT: benzothiadiazole). GPC (THF, 40 °C): M_n = 11.3 kDa, M_w = 35.5 kDa, PDI = 3.13, DP = ca. 8.4.



PBT6V2'

Poly(didodecylthieno-benzothiadiazole-vinylene-quaterthiophene) (PBT6V2'): **M7** (70 mg, 75 μmol, 1.0 eq.) in THF (1.5 mL) was added into **M8** (80 mg, 75 μmol, 1.0 eq.) in THF (2 mL). Potassium *tert*-butoxide (0.3 ml of a 1.0 M solution in THF, 0.3 mmol, 4.0 eq.) was then added in a dropwise manner to the solution at room temperature. The mixture was immediately turned from red-orange to dark-purple with an enhancement in viscosity. The polymerization was quenched after 33 h at room temperature by pouring the mixture into methanol (300 mL). The precipitated powders were collected by filtration and then washed by Soxhlet extraction sequentially using methanol (12 h), acetone (12 h), hexane (12 h), and $CHCl_3$ (6 h). The $CHCl_3$ solution was collected and then concentrated under reduced pressure. The concentrated solution was added in a dropwise manner to methanol (200 mL). The precipitate was collected by filtration from methanol followed by drying under vacuum at room temperature for 12 h to afford the black polymer powder (20 mg, yield: 16%). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$ at 95 °C) δ 8.04 (s, Th-H), 7.88 (s, BT-H), 7.17 – 7.00 (br, Th-H, =CH-), 2.89 – 2.81 (br, Th-CH_2-), 2.81 – 2.72 (br, Th-CH_2-), 1.86 – 1.67 (m, -CH_2-), 1.43 – 1.11 (m, -CH_2-), 0.93 (s, -CH_3). GPC (TCB, 135 °C): M_n = 14.3 kDa, M_w = 42.5 kDa, PDI = 2.98, DP = ca. 8.5.

(Note that during Soxhlet extraction, almost all **PBT4** and all **PBT6** residues, after washing sequentially with methanol, acetone and hexane, were soluble in $CHCl_3$, while only 20~30 wt% of the purified **PBT6V2** and **PBDT6V2'** polymers could be solubilized, suggesting that HWE polymerization may facilitate development of high MW, but also insoluble material.)

OFET Device Fabrication and Measurement

The bottom contact, bottom gate FET devices were fabricated on a heavily doped silicon wafer <100> as the gate electrode with a 300 nm thick layer of thermally grown SiO_2 as the gate dielectric which has a capacitance of approximately 1.15 x 10^{-4} F/m^2. Au source and drain contacts with a fixed channel size (50 μm in length and 2 mm in width) were deposited onto the SiO_2 layer using a conventional photolithography lift-off process followed by E-beam evaporation of 50 nm Au contacts with 3 nm of Cr as the adhesion layer. Prior to deposition of semiconducting polymer film, the devices were cleaned by sonication in acetone for 30 min and subsequently rinsed sequentially with acetone, methanol and isopropanol, followed by drying under a flow of nitrogen. The SiO_2 surface was pretreated by exposing the devices under UV/ozone for 15 min followed by immersion into a 2.54 x 10^{-3} M (1 μL/mL) solution of OTS-18 in anhydrous toluene for 10 min, in nitrogen rich environment. The devices were then cleaned by sonication in toluene for 10 min, followed by rinsing with acetone, methanol and isopropanol, and drying under a flow of nitrogen. For the spin-coating process, a hot polymer solution (8 mg/mL in DCB) was spin-coated onto OTS-18 pretreated FET

substrates at 1000 rpm for 1 min in air. The resulting OFET devices were annealed in a vacuum oven (66.19 torr) at 200 °C (**PBT6** at 115 °C) for 1 h and subsequently cooled to room temperature under vacuum over a period of 8 h.

In the study of the relationship between **PBT6** mobility and annealing temperature (**Figure S18**), the OFET devices having a spin-coated **PBT6** film were dried at room temperature inside a nitrogen-filled glovebox, and annealed at the given temperature on a hotplate for 2 h, followed by rapidly cooling to room temperature within 2 min inside a glovebox.

For drop-cast processing, a hot solution (8 mg/mL of **PBT6** solution in DCB) was drop-cast onto OTS-18 pretreated FET substrates inside a glovebox. The resulting OFET devices were dried inside the glovebox at room temperaure for 17 h. The device characteristics of these as-cast thin-film OFETs were initially measured; and then the devices were annealed at 80 °C on a hotplate for 24 h followed by rapidly cooling to room temperature within 2 min inside a glovebox.

FET devices with HMDS modified dielectric were prepared by inserting the UV/ozone cleaned devices into a vacuum oven filled with HMDS vapor at room temperature for 10 min, followed by rinsing with acetone, methanol and isopropanol, and drying in a flow of nitrogen. FET devices with FDTS modified dielectric were prepared by immersing the UV/ozone cleaned devices into 22.76 x 10^{-3} M (10 μL/mL) FDTS in anhydrous toluene for 1 h, in nitrogen rich environment. The devices were then cleaned by sonication in toluene for 10 min followed by rinsing with acetone, methanol and isopropanol, and finally drying under a flow of nitrogen.

All OFET characterization was performed using a probe station inside a nitrogen filled glovebox using an Agilent 4155C semiconductor parameter analyzer. The FET mobilities were calculated from the saturation regime (V_{SD} = - 80 V, V_{SD} = - 100 V for **PBT6V**) in the transfer plots of V_G vs. I_{SD} by extracting the slope of the linear range of V_G vs. $I_{SD}^{1/2}$ plot and using the following equation:

$$\left.\frac{\partial I_{SD}^{1/2}}{\partial V_G}\right|_{V_{SD}} = \left(\mu_h C_{ox}(\frac{W}{2L})\right)^{1/2}$$

where I_{SD} and V_{SD} are the source-drain current (A) and source-drain voltage (V), respectively; V_G is the gate voltage (V) scanning from 20 to -80 V (20 to -60 V to **PBT6(L)** and **PBT6V**) in the transfer plot; C_{ox} is the capacitance per unit area of the gate dielectric layer, 1.15 x 10^{-4} F/m^2; W and L refer to the channel length (50 μm) and width (2 mm); μ_h represents the hole mobility in the saturation regime (cm^2/Vs).

In the following equation:

$$I_{SD} = \mu_h C_{ox}(\frac{W}{2L})(V_G - V_T)^2$$

the threshold voltage, V_T, was calculated by extrapolating $V_T = V_G$ at $I_{SD} = 0$ in the V_G vs. $I_{SD}^{1/2}$ curve in the saturation regime (V_{SD} = - 80 V). Current on and off ratio, $I_{ON/OFF}$, was determined through dividing I_{SD} at V_G = -80 V (I_{ON}) by the minimum I_{SD} at around V_G = 0~20 V (I_{OFF}).

Devices maintained in a nitrogen filled glovebox have exhibited stability in excess of 3 months. Upon storage in an ambient air environment, device performance begins to degrade after 3 to 5 days.

The mobilities of **PBT6** on HMDS and FDTS-treated substrates were 0.15 cm^2/Vs and 0.092 cm^2/Vs, respectively, after annealing at 80 °C for 24 h (**Table S2**). The lower mobility of **PBT6** on these self-assembled monolayers compared with that on OTS-18 might emanate from the long aliphatic chain of OTS-18 relative to HMDS that may promote an edge-on orientation of the polymer chain thus benefiting field effect hole transport between the source and drain electrodes; the strong hydrophobilicity of FDTS likely inhibits favorable polymer chain orientation.

Table S2. Effect of self-assembled monolayers and drop-casting process on the hole transport property of **PBT6** based on OFETs annealed at 80 °C for 24 h (channel size: 50 μm of long x 2 mm of wide)

SAMs	Spin-coated film			Drop-casted film		
	μ_h (cm^2/Vs)	$I_{ON/OFF}$	$_T$ (V)	μ_h ($cm^2/V.s$)	$I_{ON/OFF}$	V_T (V)
HMDS	0.15	10^5	-7.5	0.055	10^5	-6.4
FDTS	-[b]	-	-	0.092	10^5	-3.4

[a] values in parentheses are maximal mobilities attained; [b] no uniform film was developed on FDTS pre-coated device due to high contact angle.

Figures

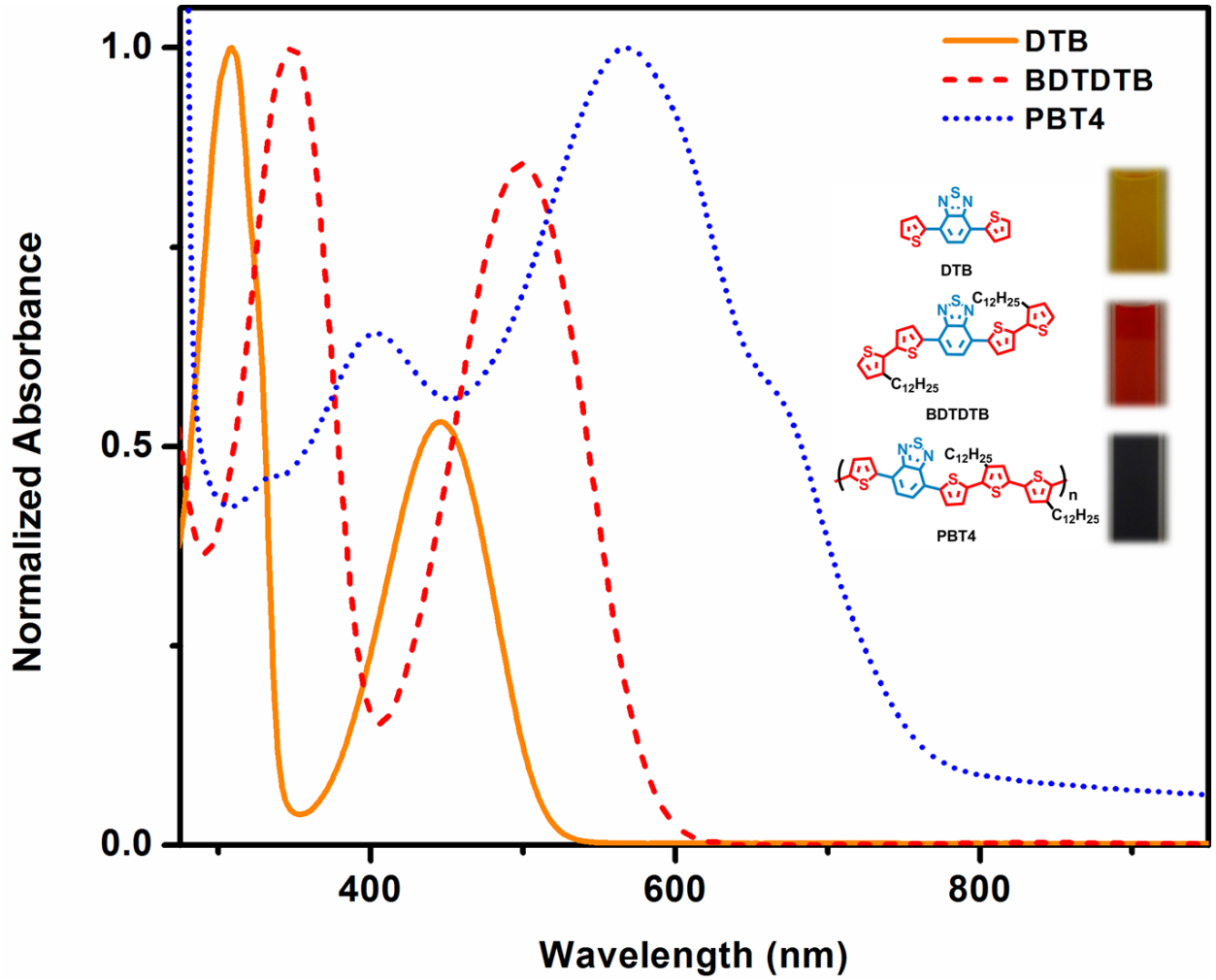


Figure S1. The shift of absorption band upon extending from the small molecule (**DTB**) to the oligomer (**BDTDTB**), and polymer (**PBT4**)

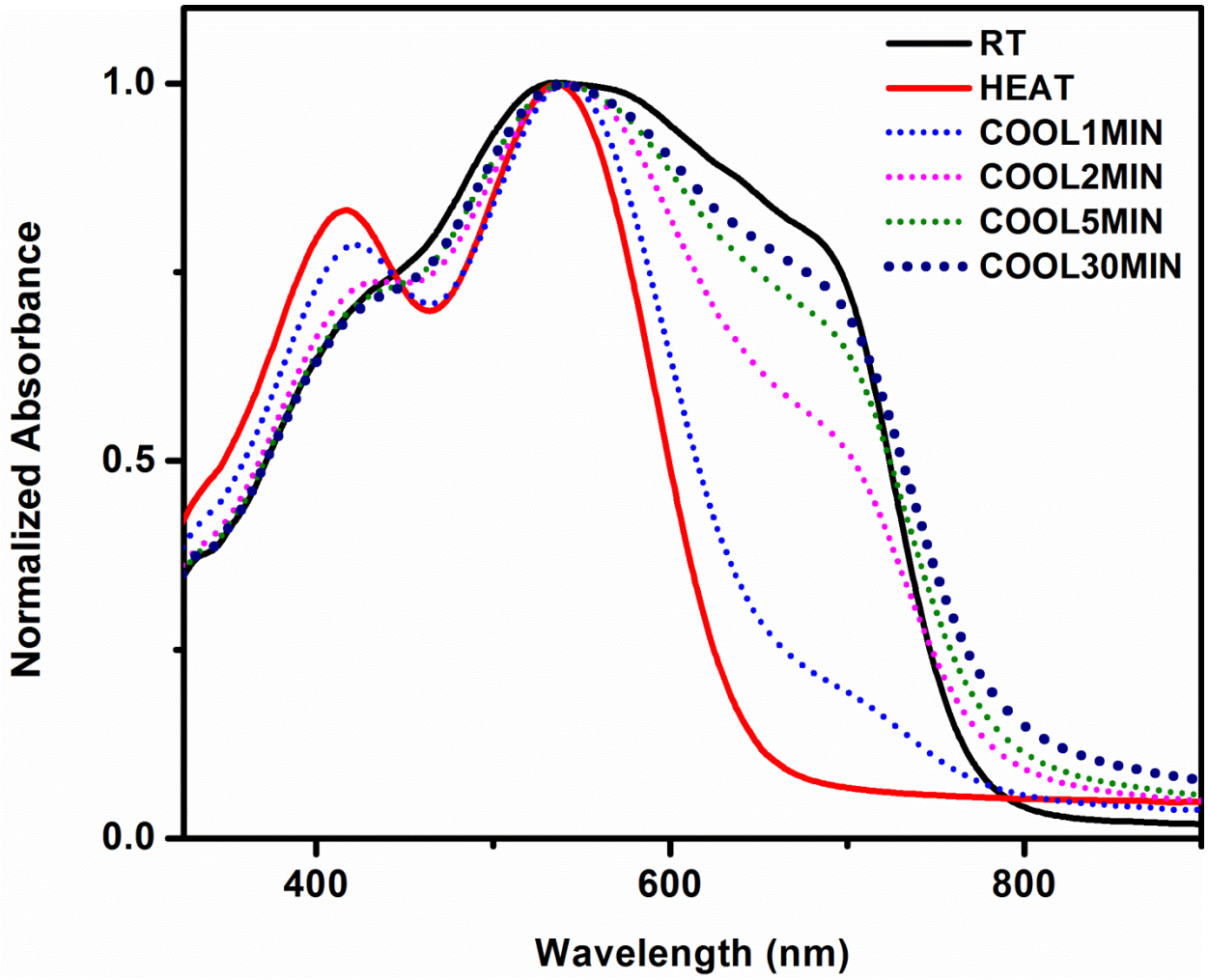


Figure S2a. Thermochromism of **PBT6** in $CHCl_3$ solution (3.8×10^{-5} M): (i) room temperature; (ii) after heating (under heat gun for 1 min); (iii) additional 1 min of cooling after heating; (iv) additional 2 min of cooling; (v) additional 5 min of cooling; (vi) additional 30 min of cooling

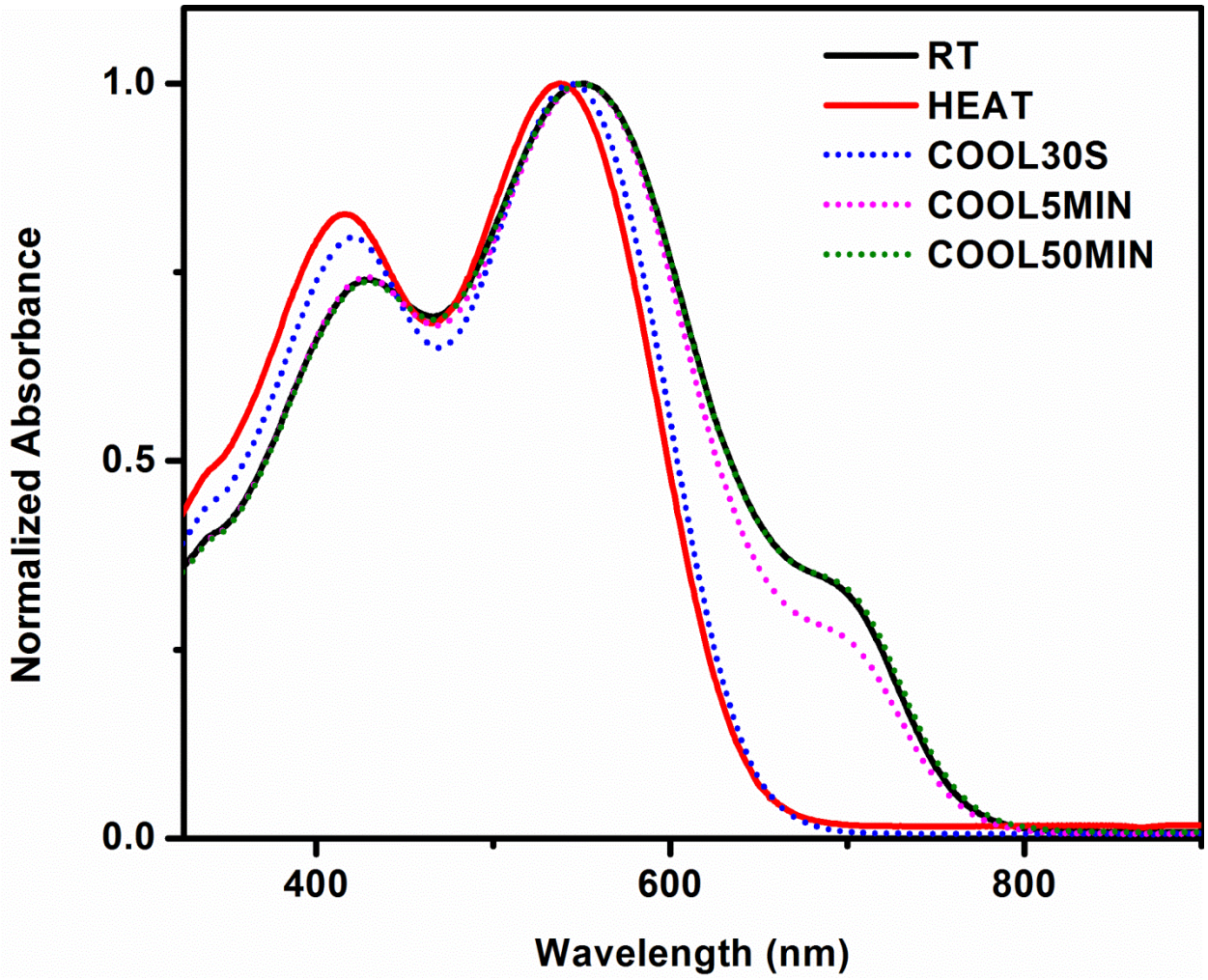


Figure S2b. Thermochromism of **PBT6** in CB solution (3.8 x 10^{-5} M): (i) room temperature; (ii) after heating (under heat gun for 1 min); (iii) additional 30s of cooling after heating; (iv) additional 5 min of cooling; (v) additional 50 min of cooling

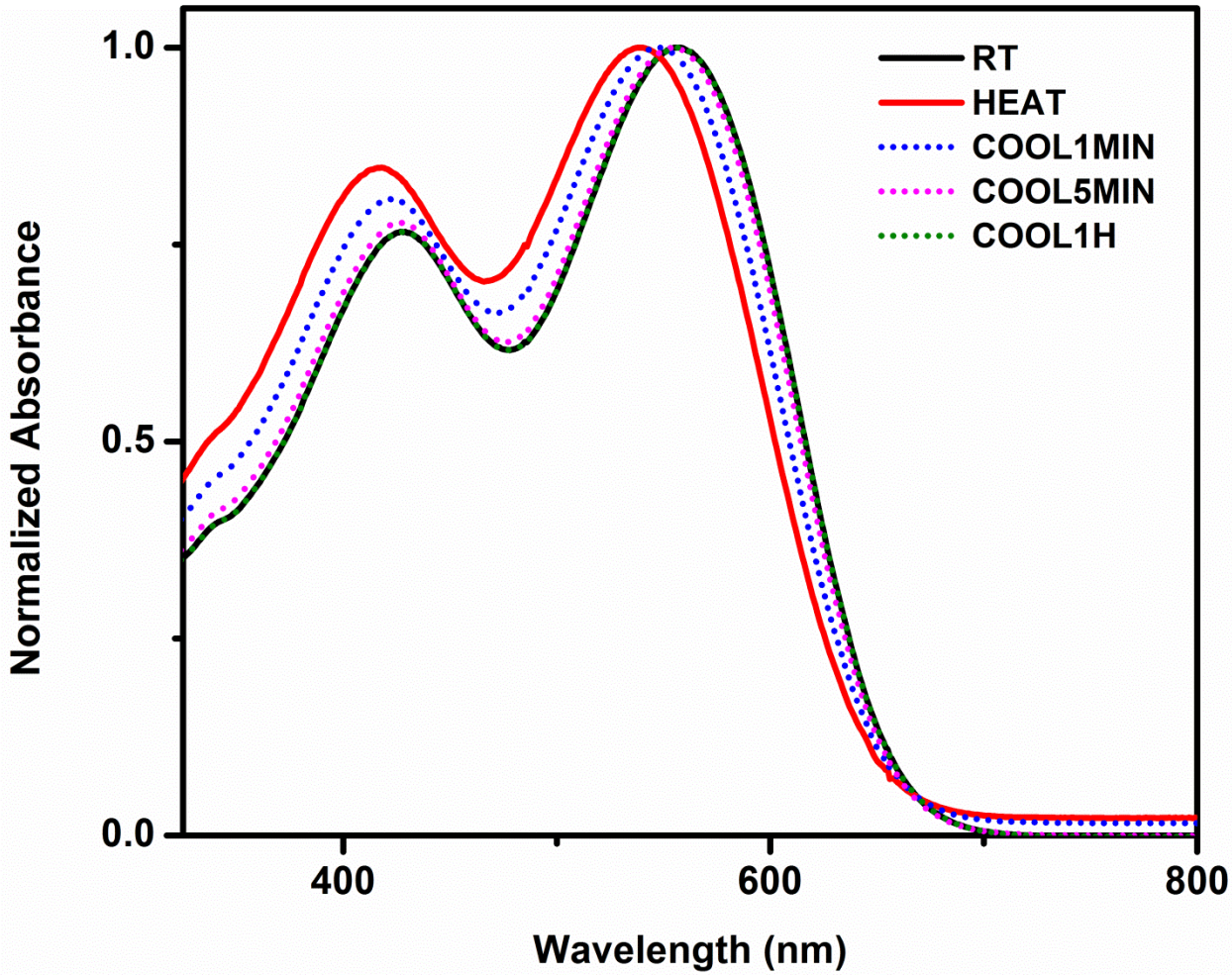


Figure S3. Thermochromism of **PBT6** in DCB solution (1 x 10^{-5} M): (i) room temperature; (ii) after heating (under heat gun for 3 min); (iii) additional 1 min of cooling after heating; (iv) additional 5 min of cooling; (v) additional 1 h of cooling

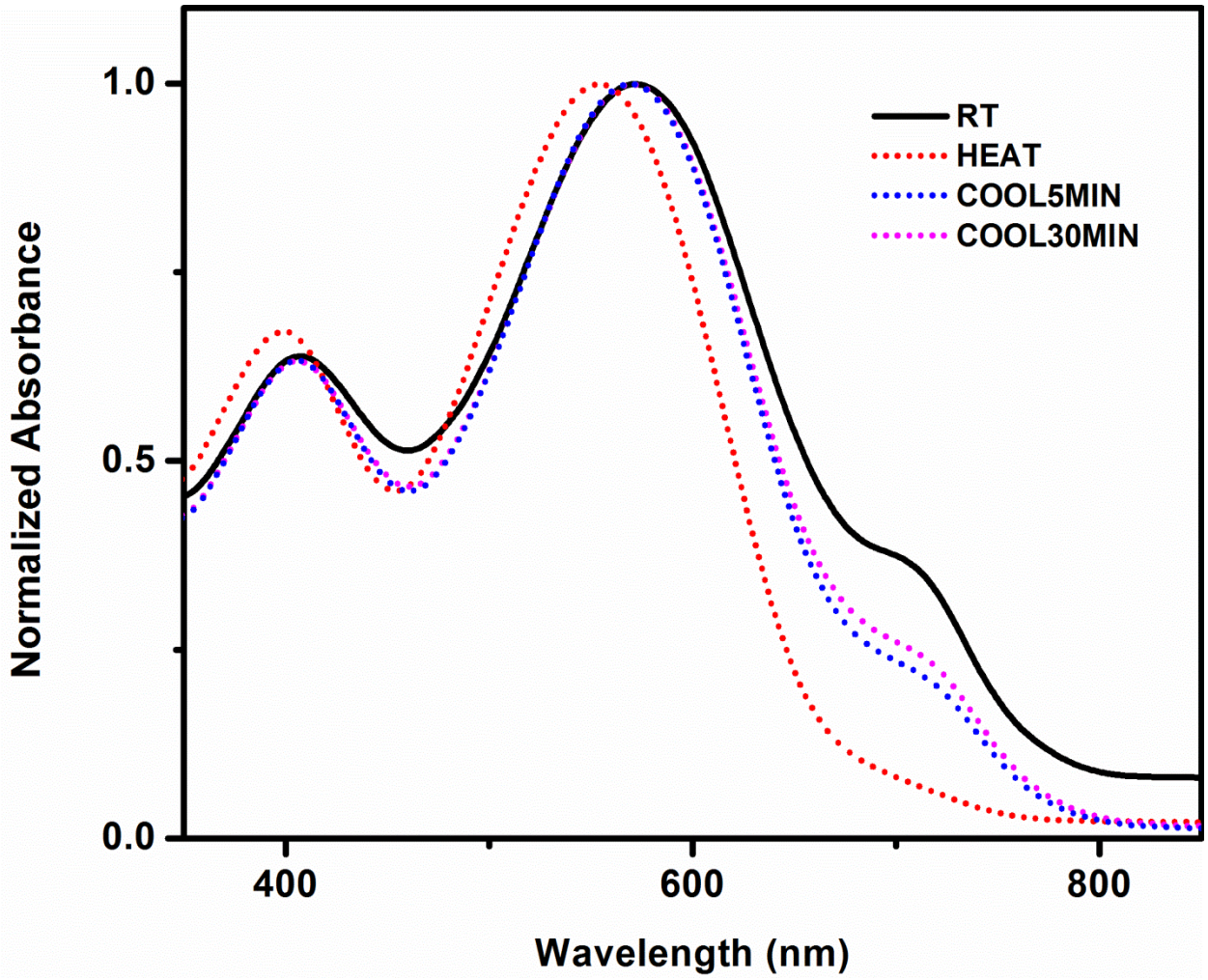


Figure S4. Thermochromism of **PBT4** in CB solution (2 x 10^{-5} M): (i) room temperature; (ii) after heating (heat gun for 1 min); (iii) additional 5 min of cooling after heating; (iv) additional 30 min of cooling

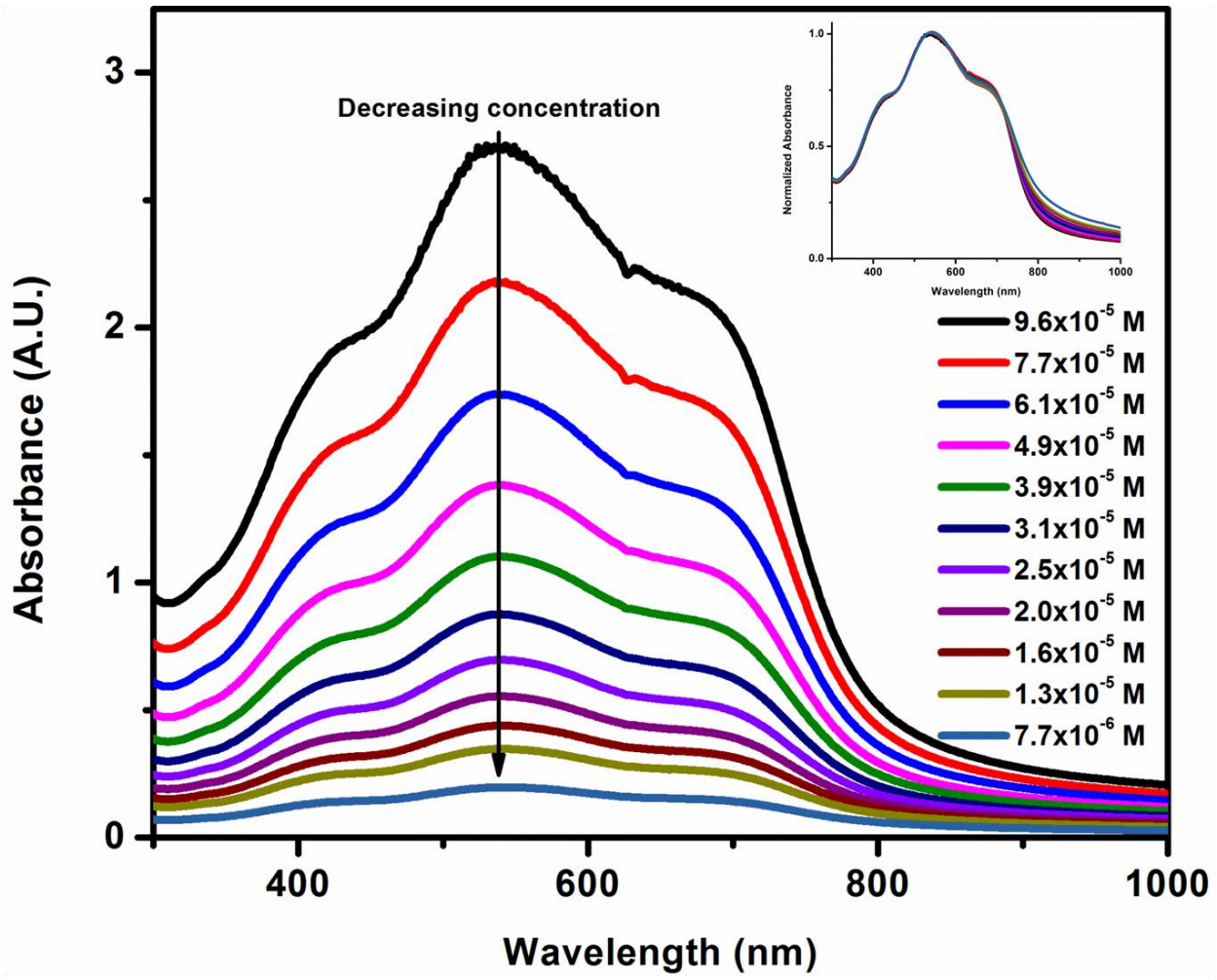


Figure S5. The change of absorbance in **PBT6** in $CHCl_3$ solution upon stepwise dilution from 9.6 x 10^{-5} M to 7.7 x 10^{-6} M. The inset is the figure of normalized absorbance versus wavelength setting the absorbance at 539 nm as 1.0, signifying the relative absorbance of the shoulder at λ = 689 nm compared to the primary bands remains constant.

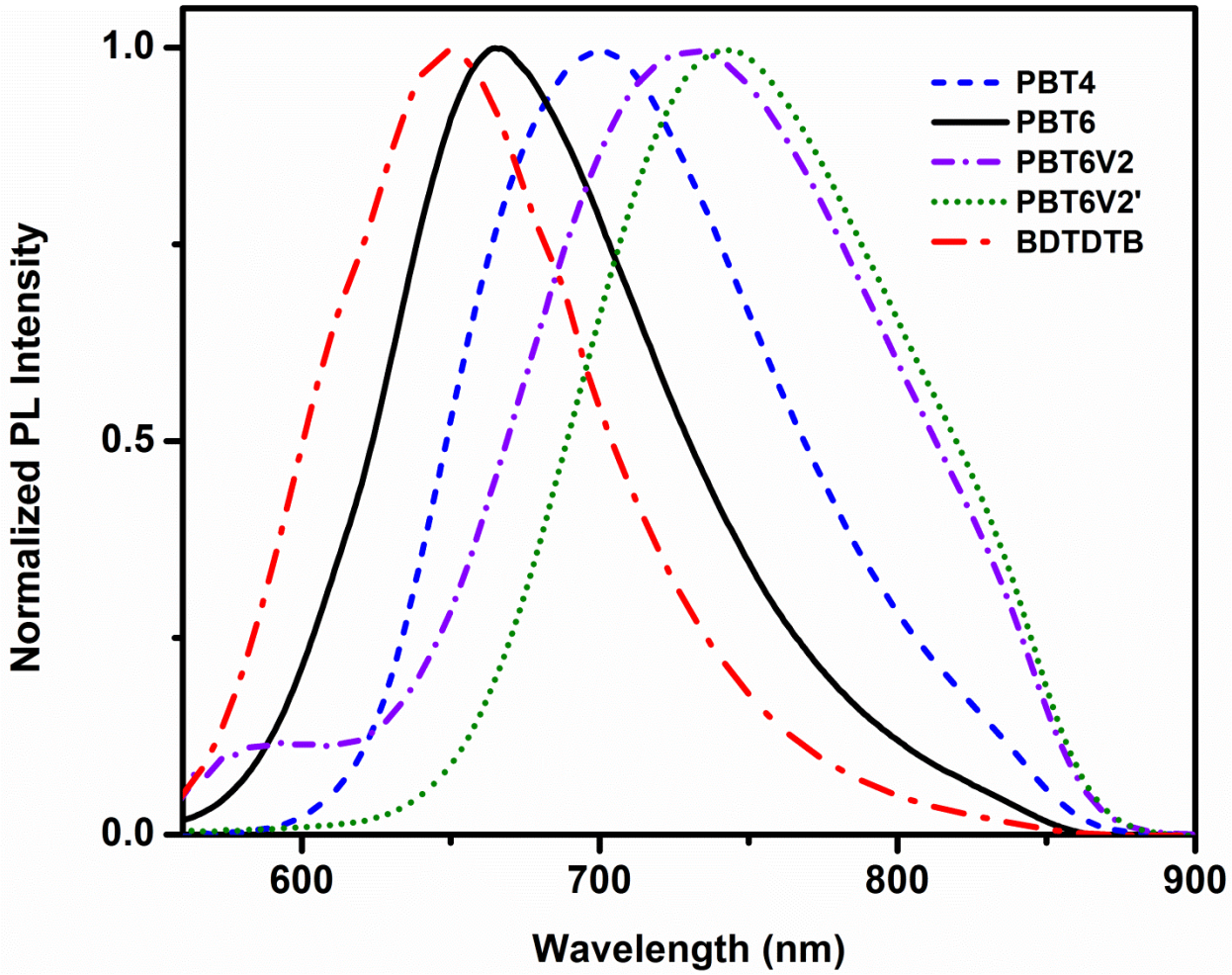


Figure S6. Normalized photoluminescence spectra (excitation wavelength, λ_{ex} = 450 nm) of **PBT4**, **PBT6**, **PBT6V**, **PBT6VD** and **BDTDTB** in $CHCl_3$ solution

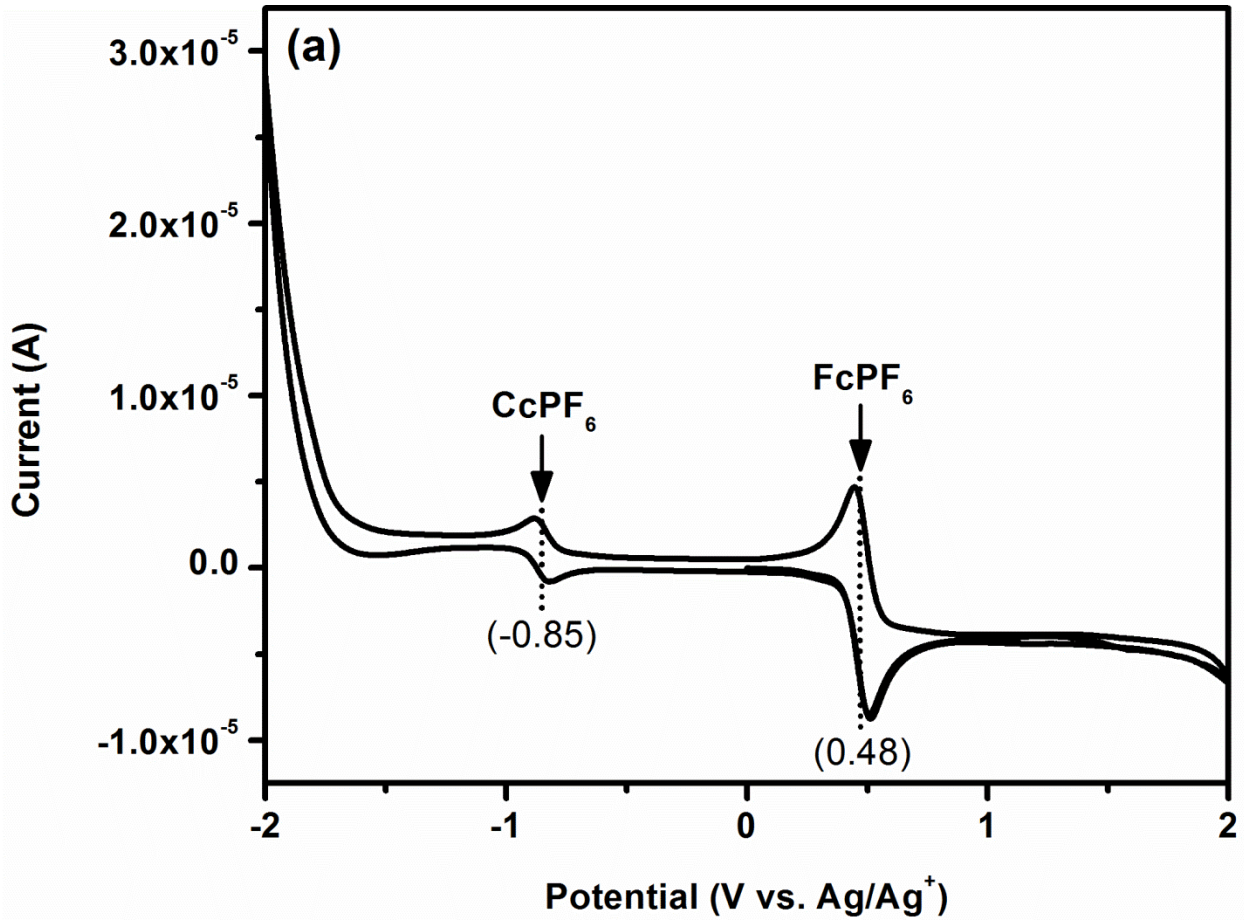


Figure S7a. Cyclic voltammogram of bis(cyclopentadienyl)cobalt(III) hexafluorophosphate (cobaltocenium hexafluorophosphate, $CcPF_6$) and ferrocenium hexafluorophosphate ($FcPF_6$) in a 0.1 M solution of $[n\text{-}Bu_4N]^+[PF_6]^-$ in acetonitrile.

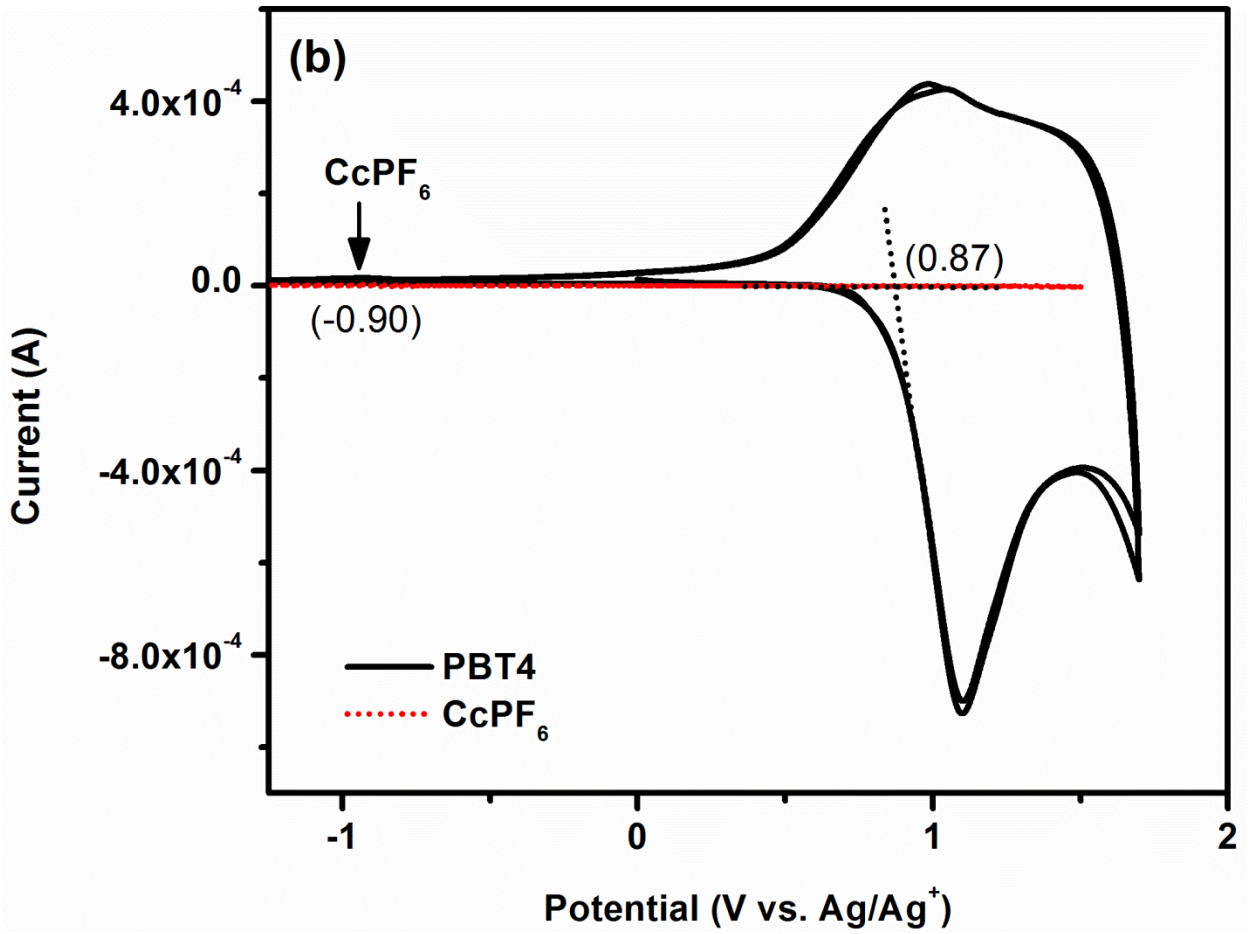


Figure S7b. Cyclic voltammogram of **PBT4** with CcPF6 as internal reference in a 0.1 M solution of $[n\text{-}Bu_4N]^+[PF_6]^-$ in acetonitrile.

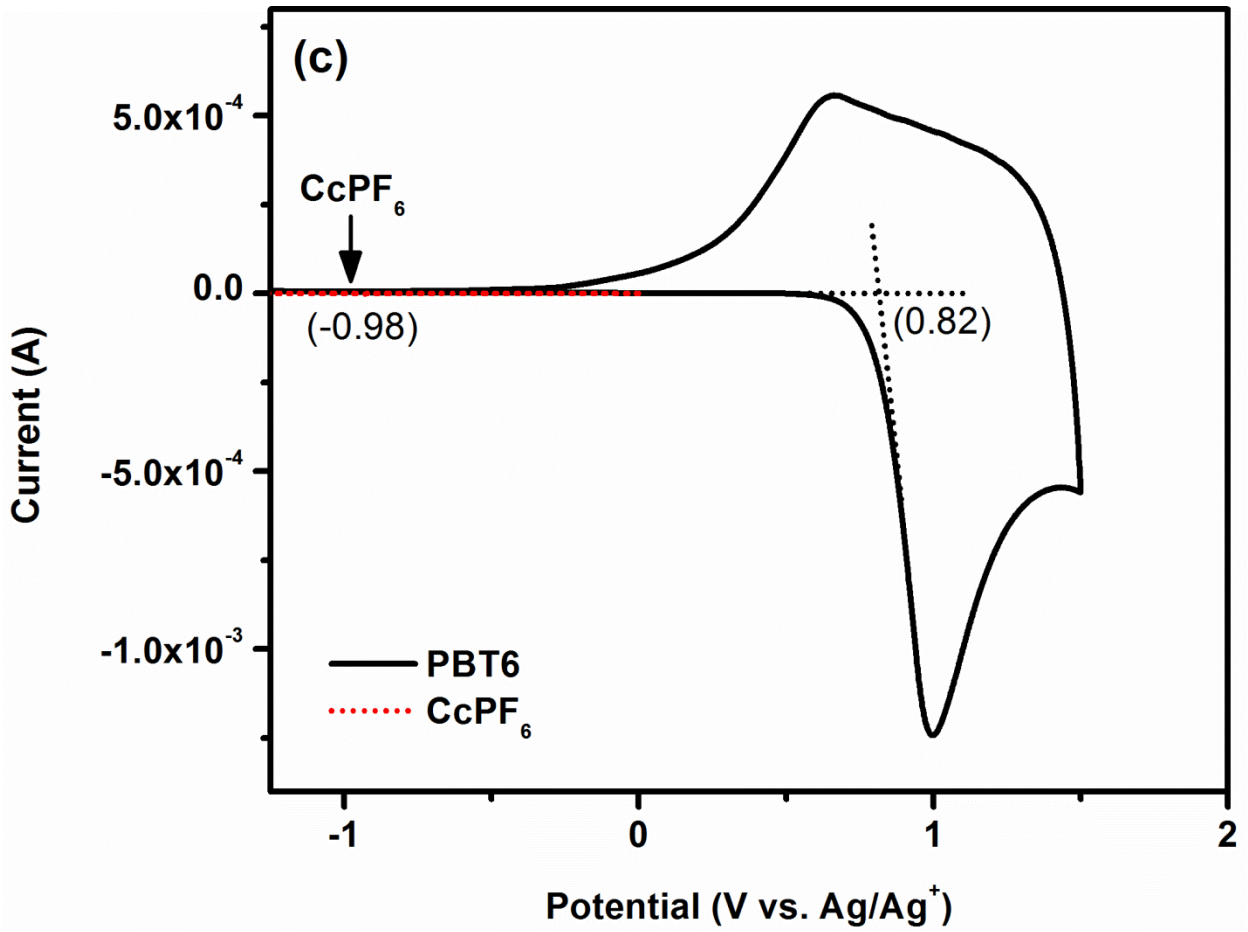


Figure S7c. Cyclic voltammogram of **PBT6** with $CcPF_6$ as internal reference in a 0.1 M solution of $[n\text{-}Bu_4N]^+[PF_6]^-$ in acetonitrile.

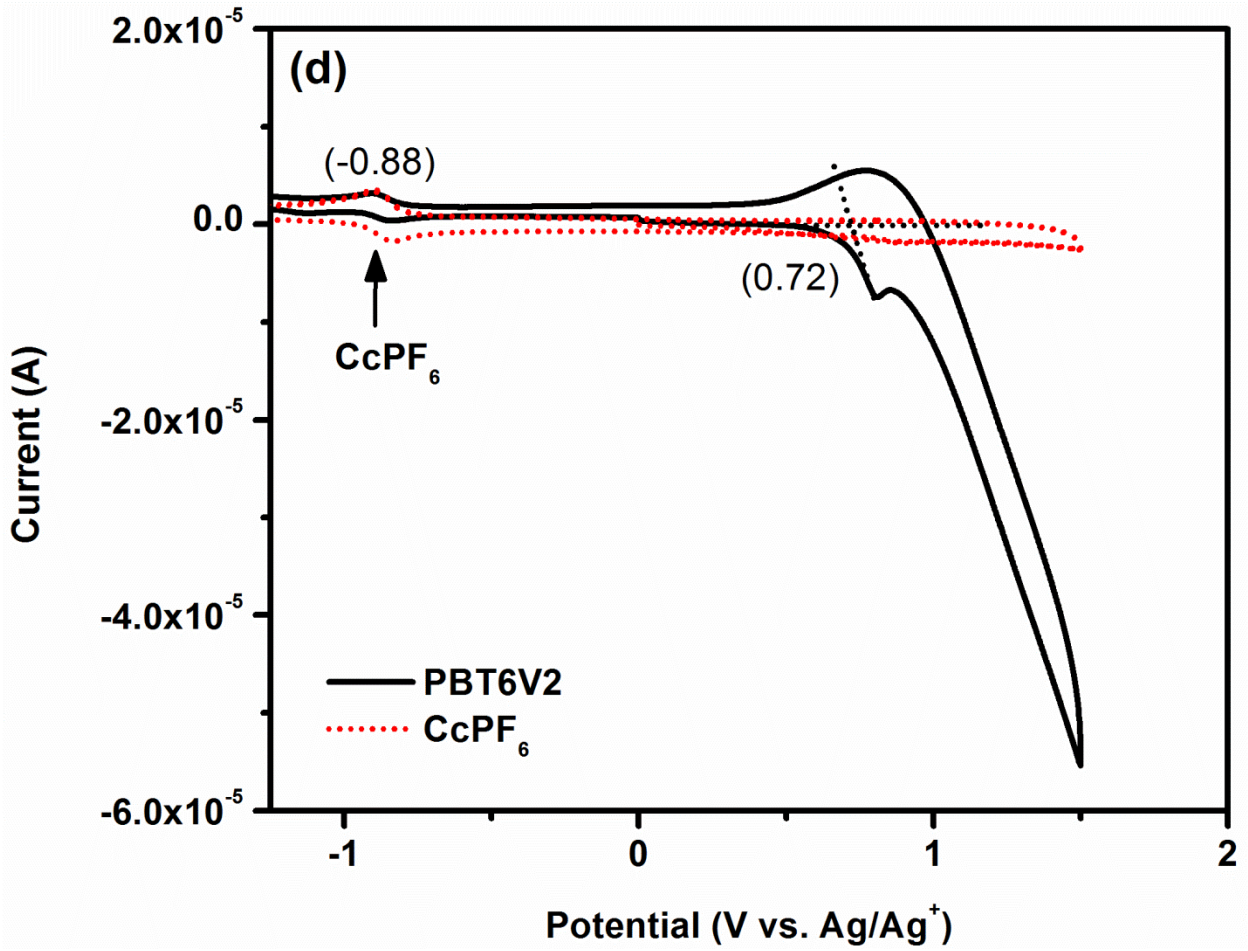


Figure S7d. Cyclic voltammogram of **PBT6V2** with $CcPF_6$ as internal reference in a 0.1 M solution of $[n\text{-}Bu_4N]^+[PF_6]^-$ in acetonitrile.

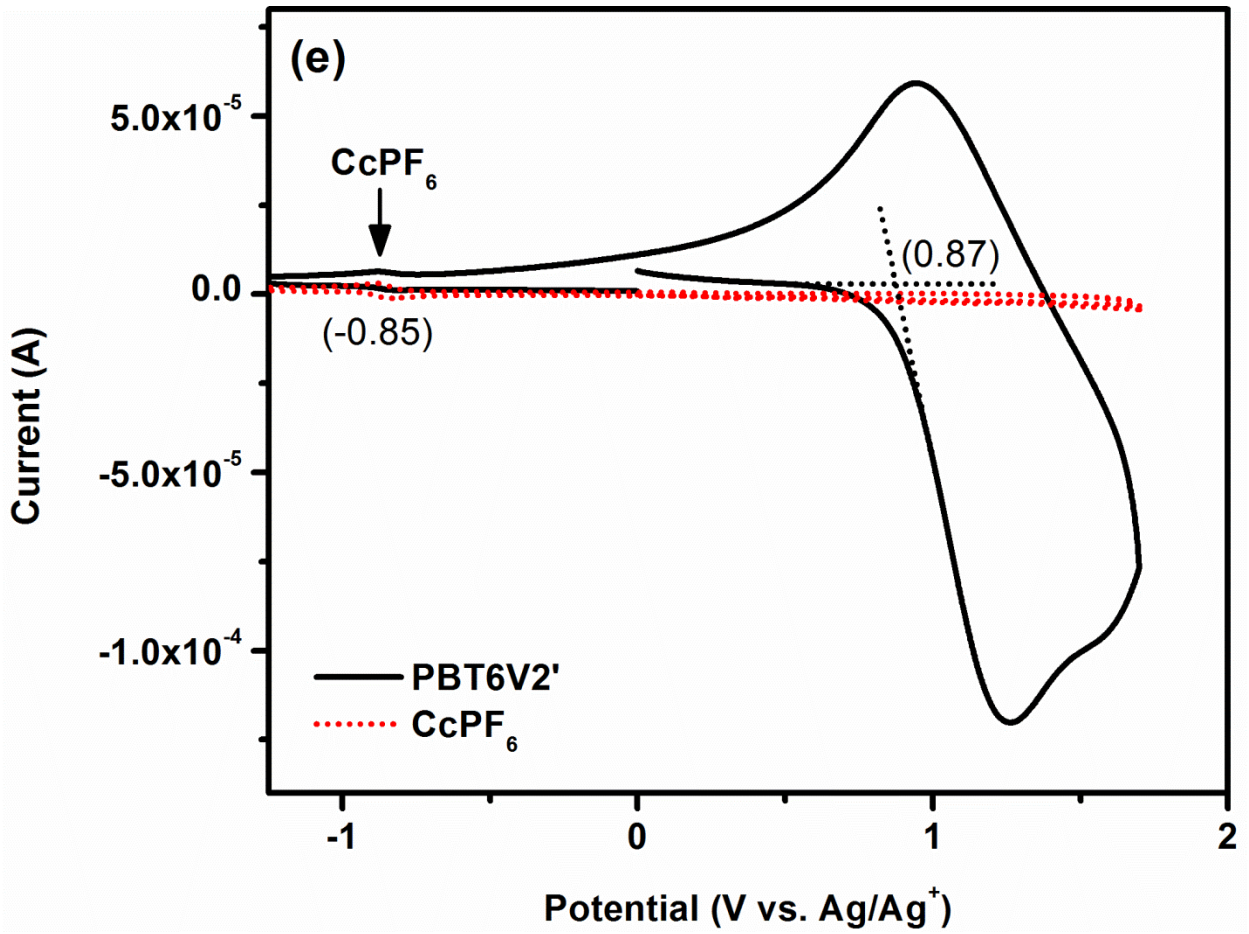


Figure S7e. Cyclic voltammogram of **PBT6V2'** with $CcPF_6$ as internal reference in a 0.1 M solution of $[n\text{-}Bu_4N]^+[PF_6]^-$ in acetonitrile.

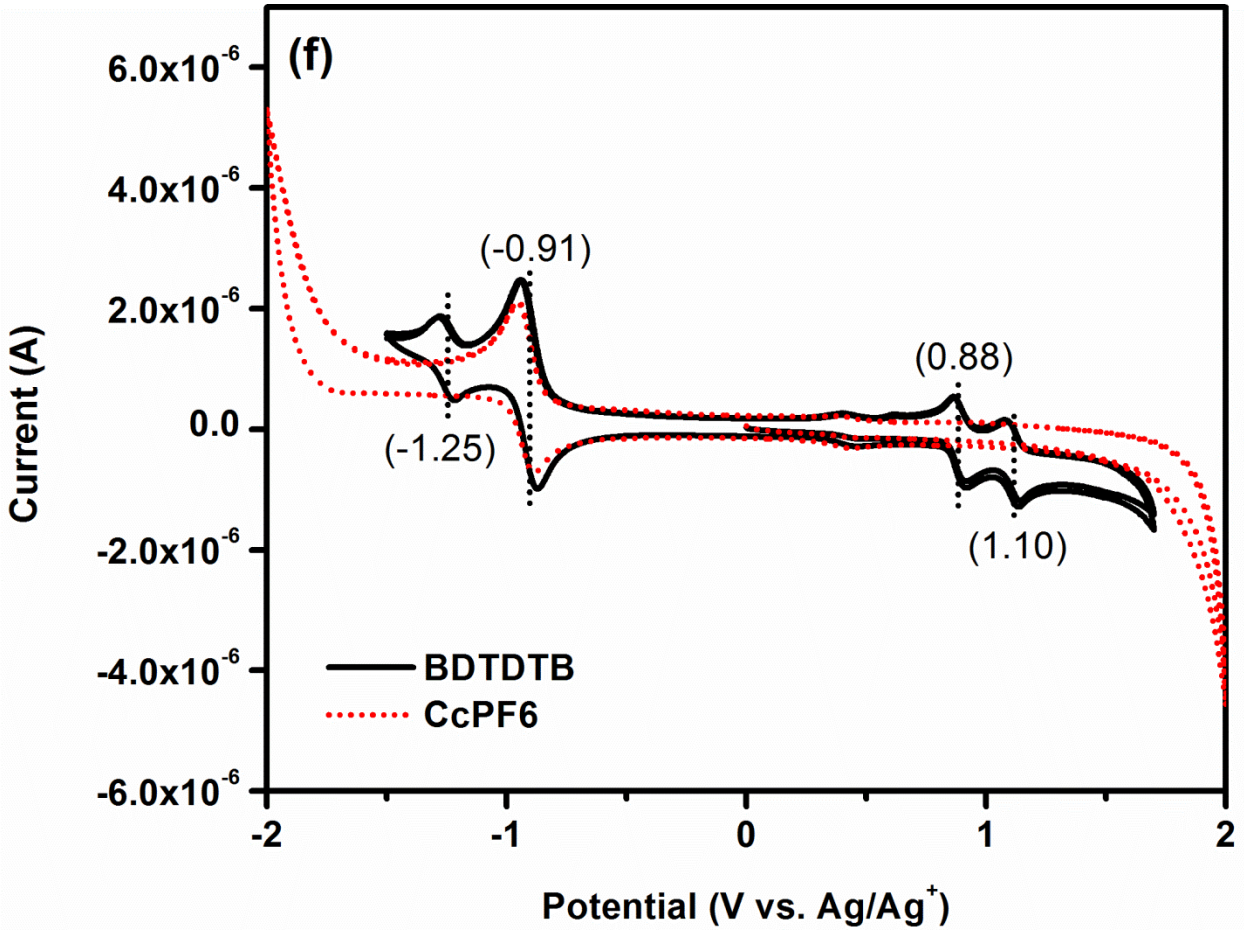


Figure S7f. Cyclic voltammogram of **BDTDTB** with $CcPF_6$ as internal reference in a 0.1 M solution of $[n\text{-}Bu_4N]^+[PF_6]^-$ in acetonitrile.

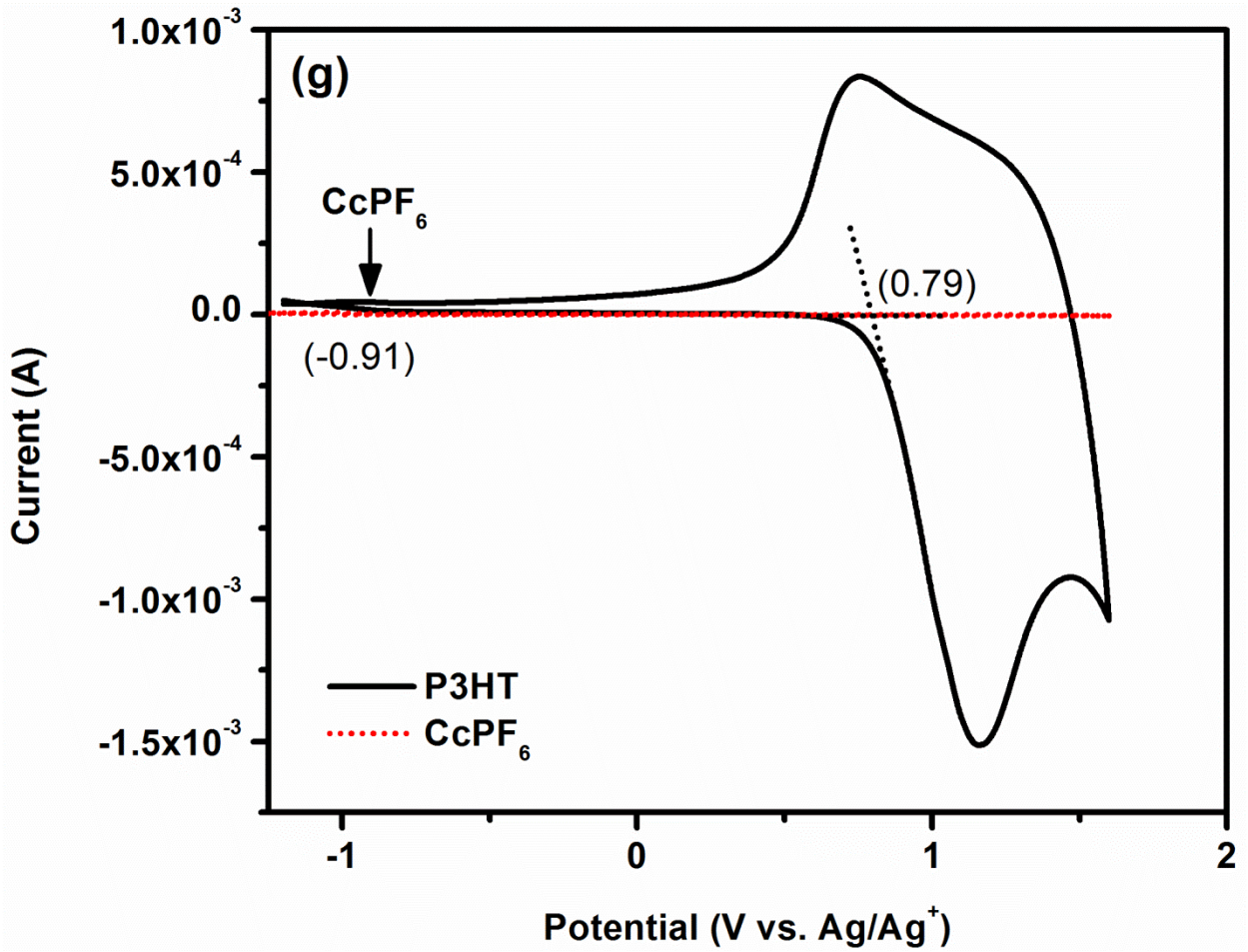


Figure S7g. Cyclic voltammogram of **P3HT** with $CcPF_6$ as internal reference in a 0.1 M solution of $[n\text{-}Bu_4N]^+[PF_6]^-$ in acetonitrile.

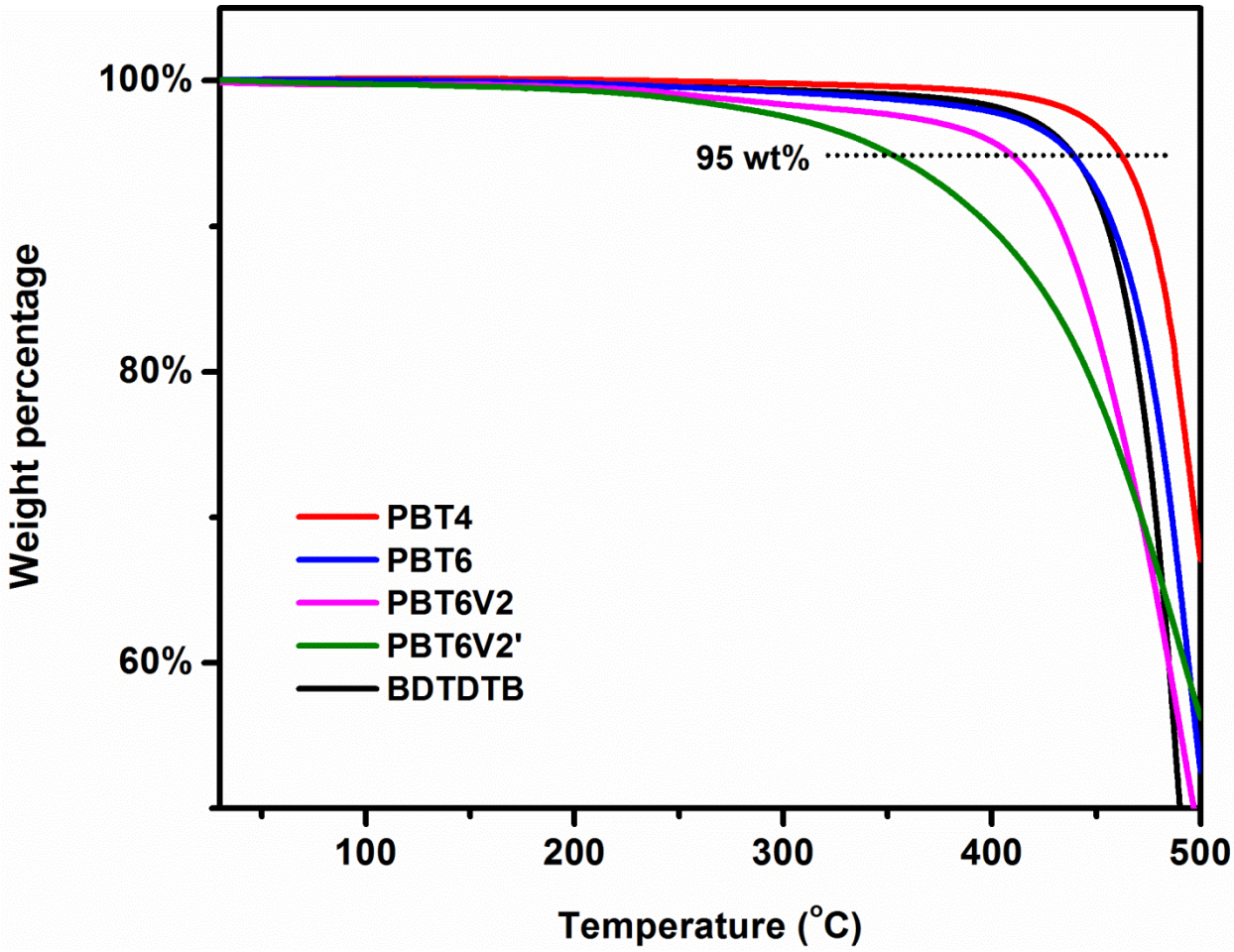


Figure S8. Thermo gravimetric analysis of polymers and oligomer (thermal decomposition temperature defined as the temperature of 5% weight-loss).

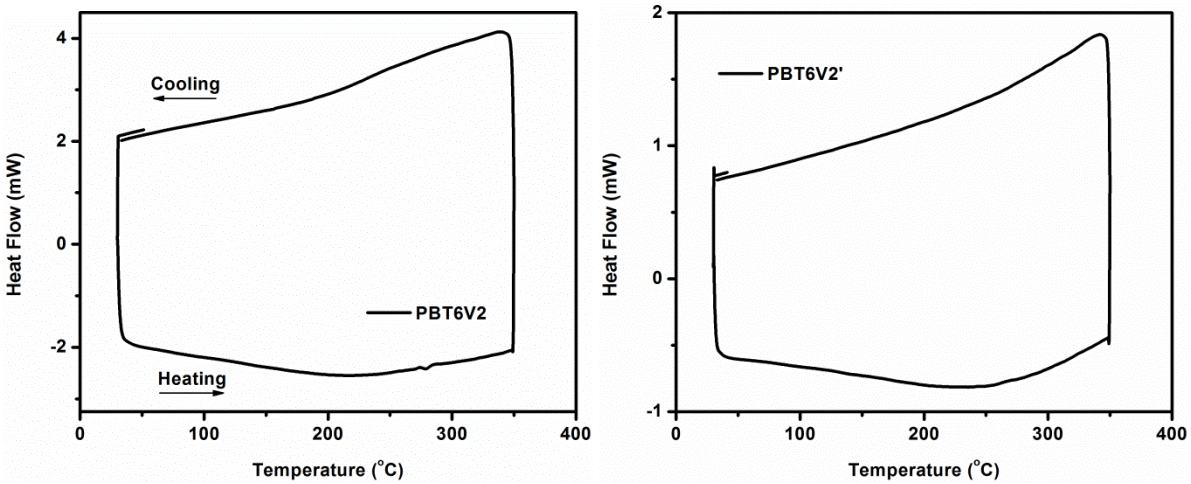


Figure S9. Differential scanning calorimetry diagrams of **PBT6V2** (left) and **PBT6V2'** (right) display no thermal transitions in the second heating / cooling scan at 10 °C / min.

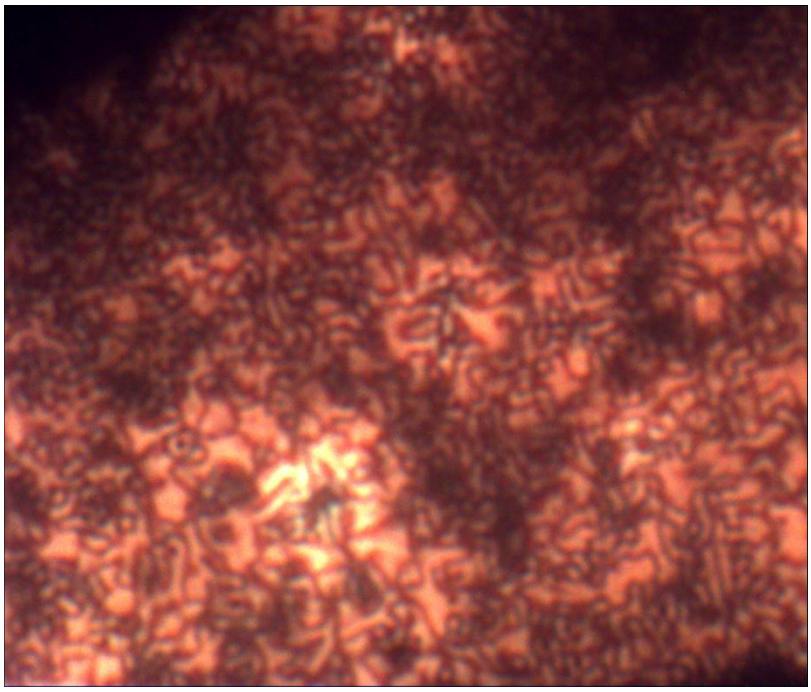


Figure S10. Thin film morphology of **PBT6(L)** under POM at room temperature (**PBT6(L)** film was prepared by spin-coating a 8 mg/ mL solution of **PBT6(L)** in DCB followed by annealing at 200 °C for 1 h)

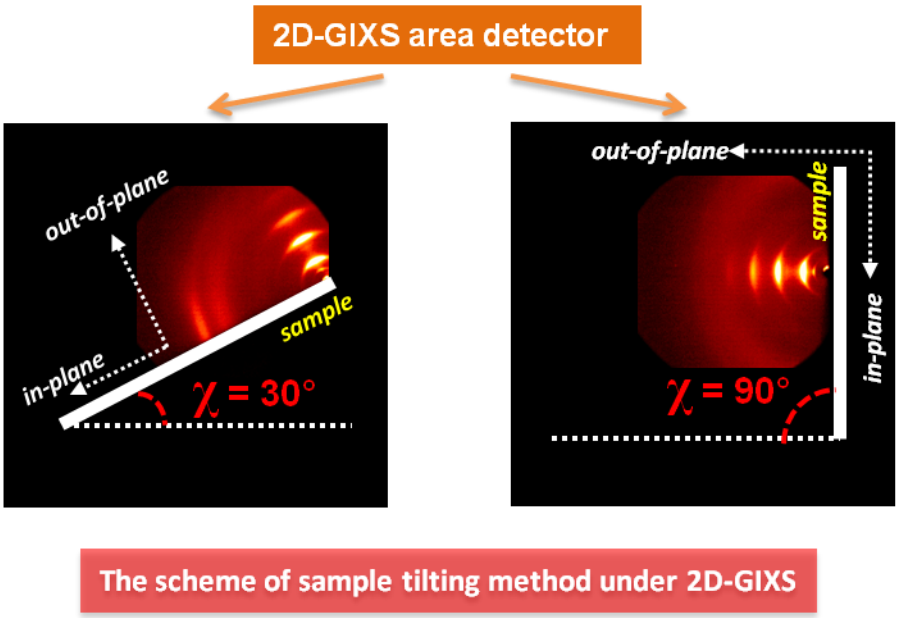


Figure S11a. The scheme of sample tilting under 2D-GIXS measurement. The direction of X-ray incidence beam is perpendicular to the 2D_GIXS area detector.

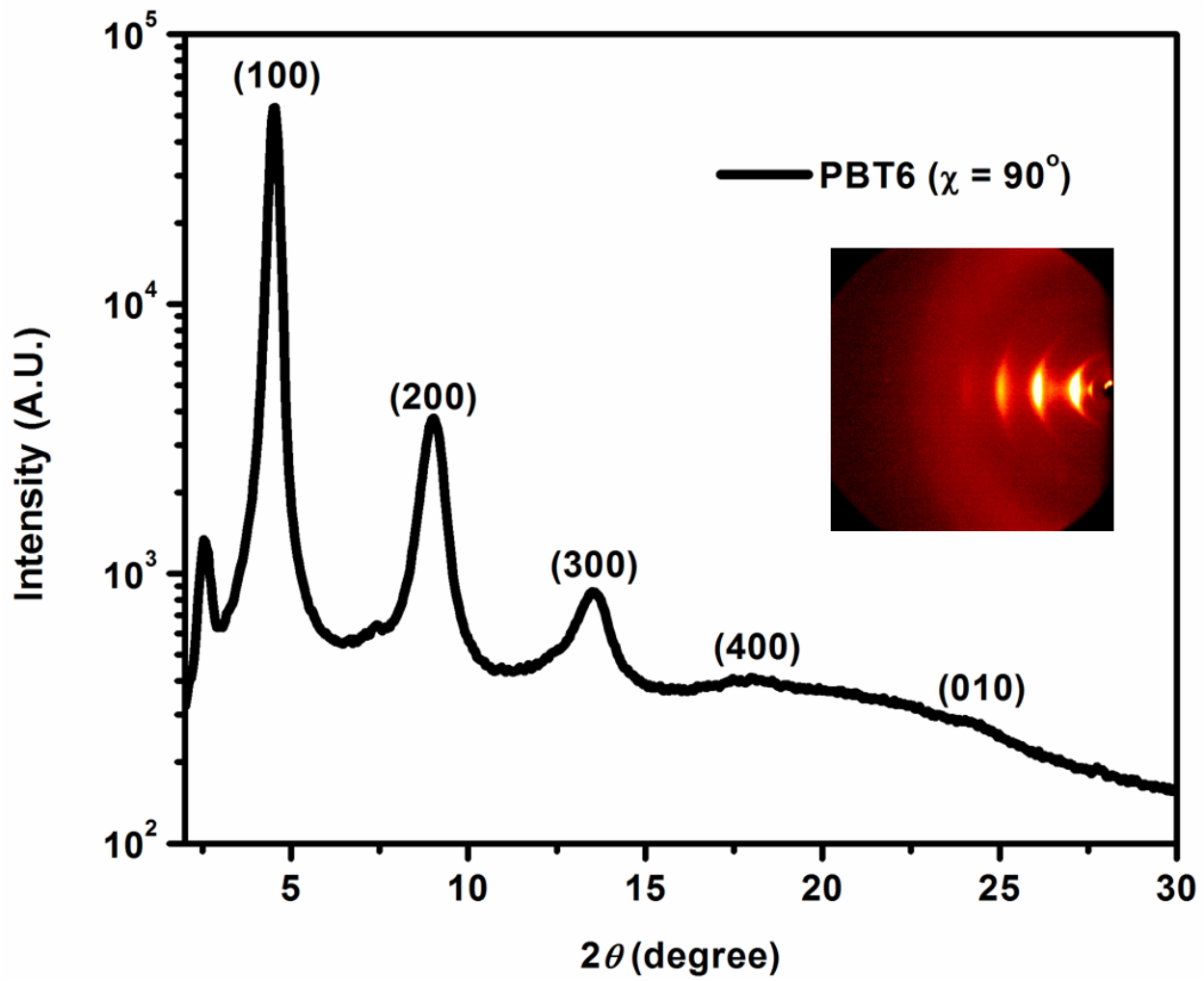


Figure S11b. 2D-GIXS area detector image of a **PBT6** drop-cast film tilted at χ = 90° (inset) and the corresponding integrated intensity diffraction pattern.

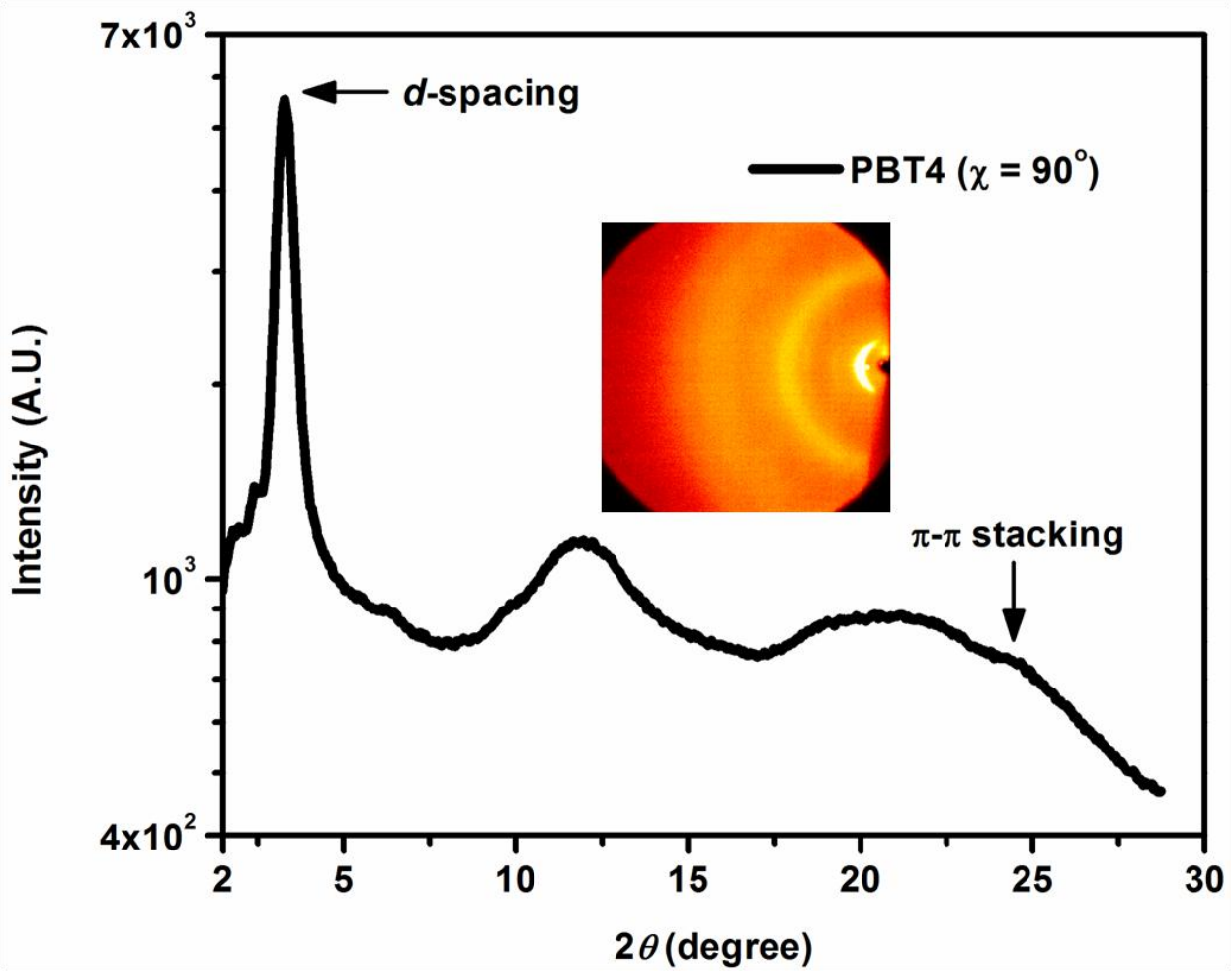


Figure S11c. 2D-GIXS area detector image of a **PBT4** drop-cast films tilted at χ = 90° (inset) and the corresponding integrated intensity diffraction pattern.

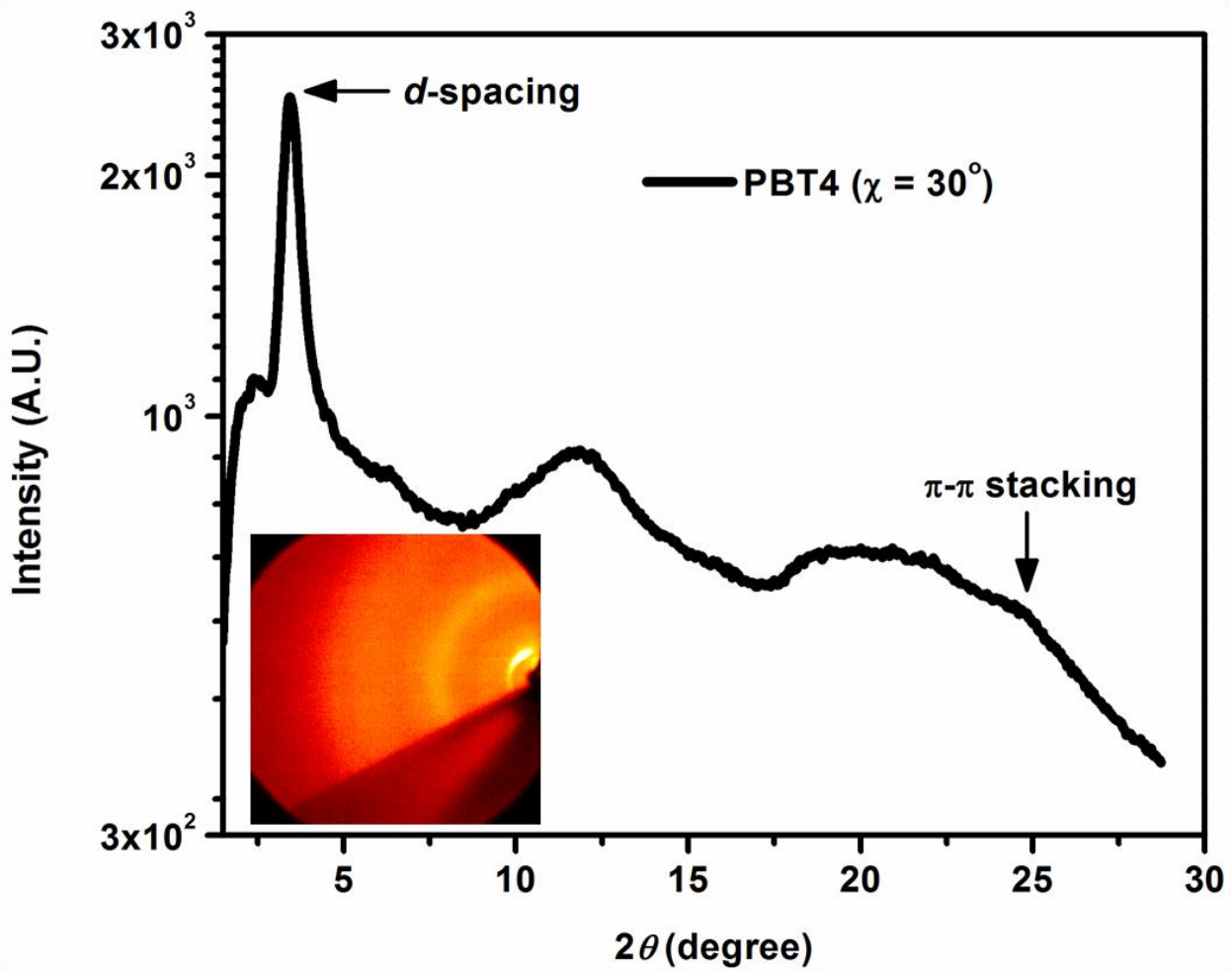


Figure S11d. 2D-GIXS area detector image of a **PBT4** drop-cast films tilted at χ = 30° (inset) and the corresponding integrated intensity diffraction pattern.

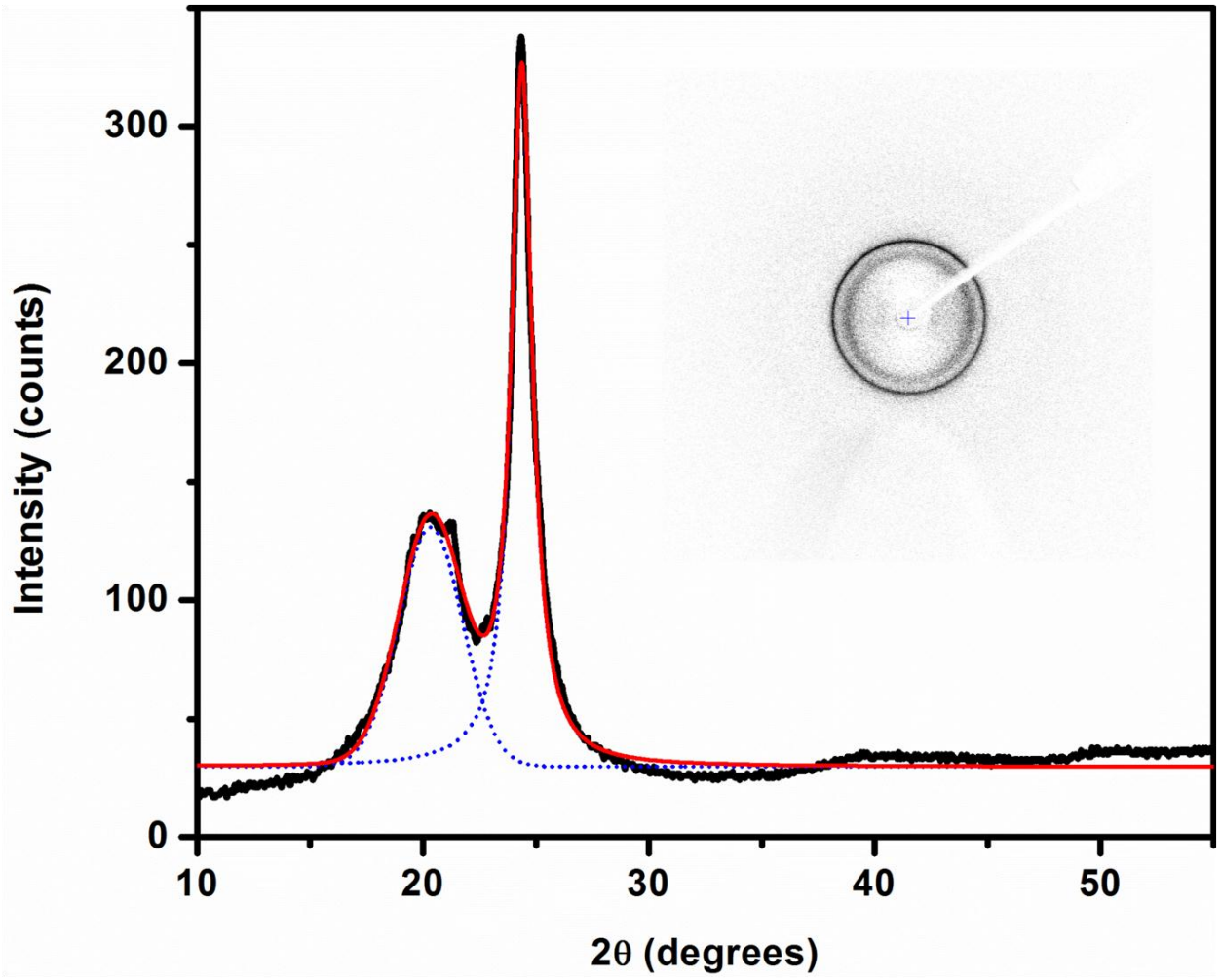


Figure S12. The integrated intensity diffraction patterns of **PBT6** drop-cast film measured by transmission 2D-WAXD. The inset is the corresponding area detector image.

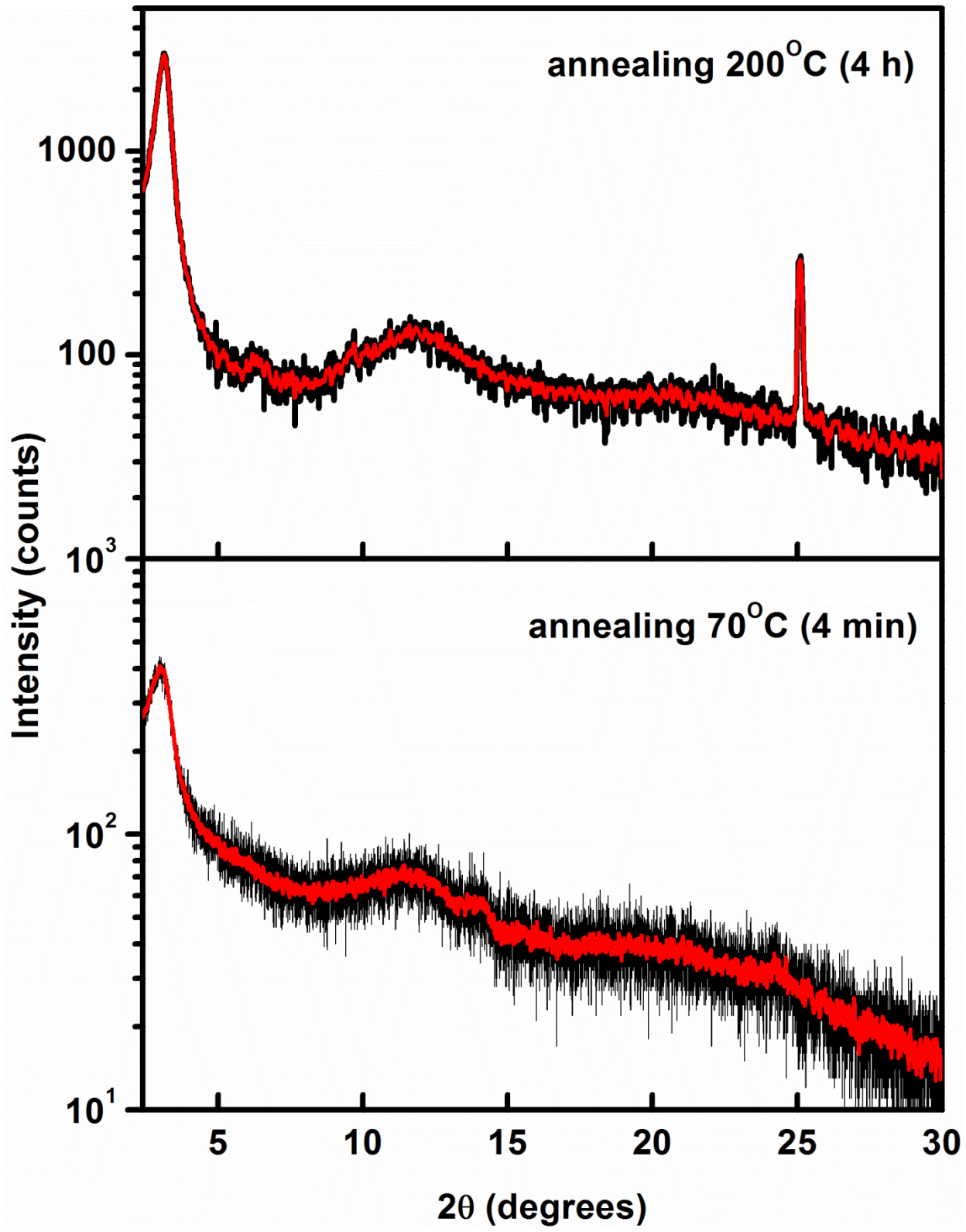

annealing 200°C (4 h)
annealing 70°C (4 min)
Intensity (counts)
1000
100
10³
10²
10¹
5
10
15
20
25
30
2θ (degrees)

Figure S13. 1D-XRD (out-of-plane) diffraction patterns of **PBT4** drop-cast film at room temperature and after annealing at 200 °C for 4 h

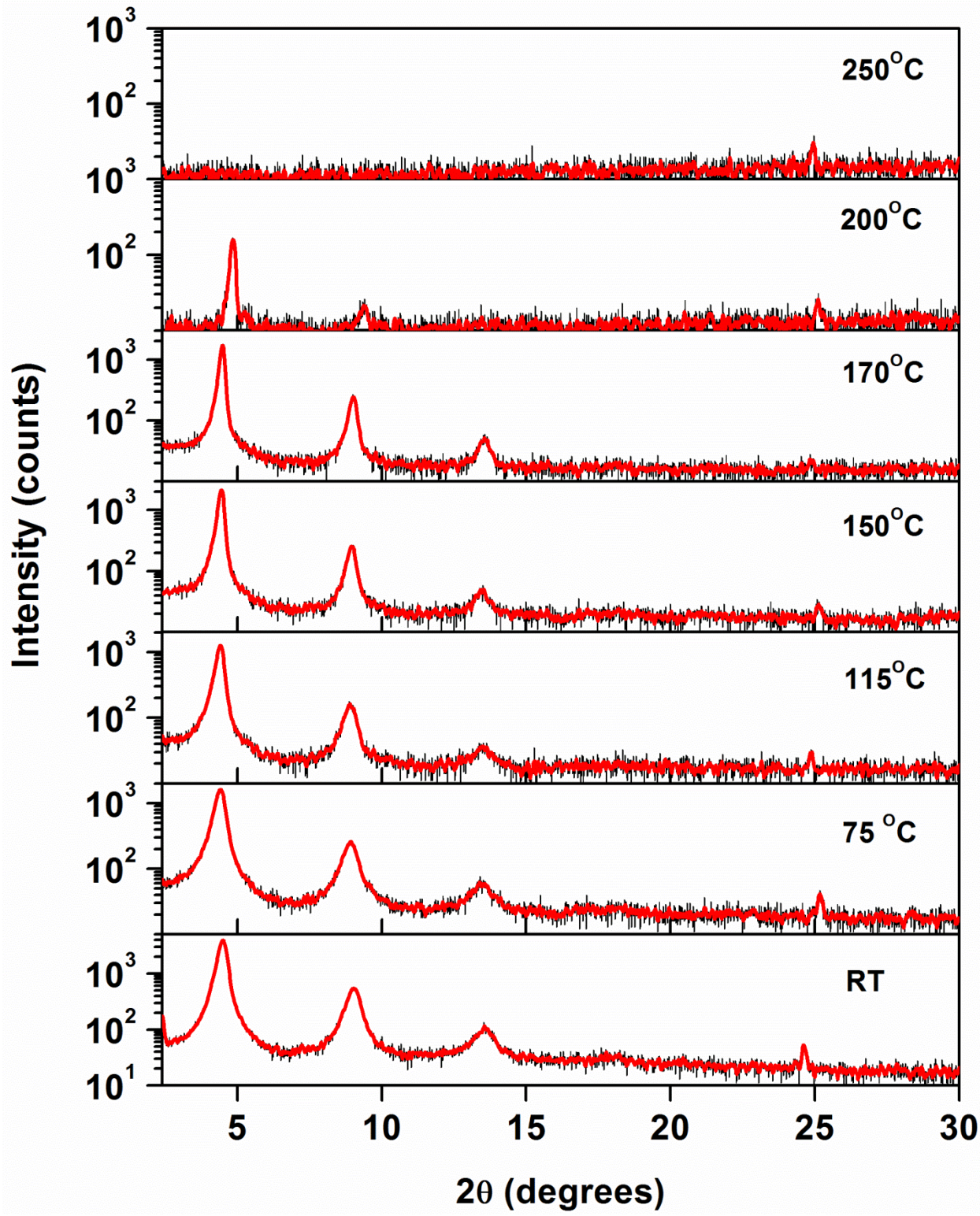


Figure S14. 1D-XRD (out-of-plane) patterns of **PBT6** drop-cast film at room temperature; after annealing at 75 °C for 1 h; after annealing at 115 °C for 1 h; after

annealing at 150 °C for 1 h; after annealing at 170 °C for 1 h; after annealing at 200 °C for 1 h; after annealing at 250 °C for 1 h

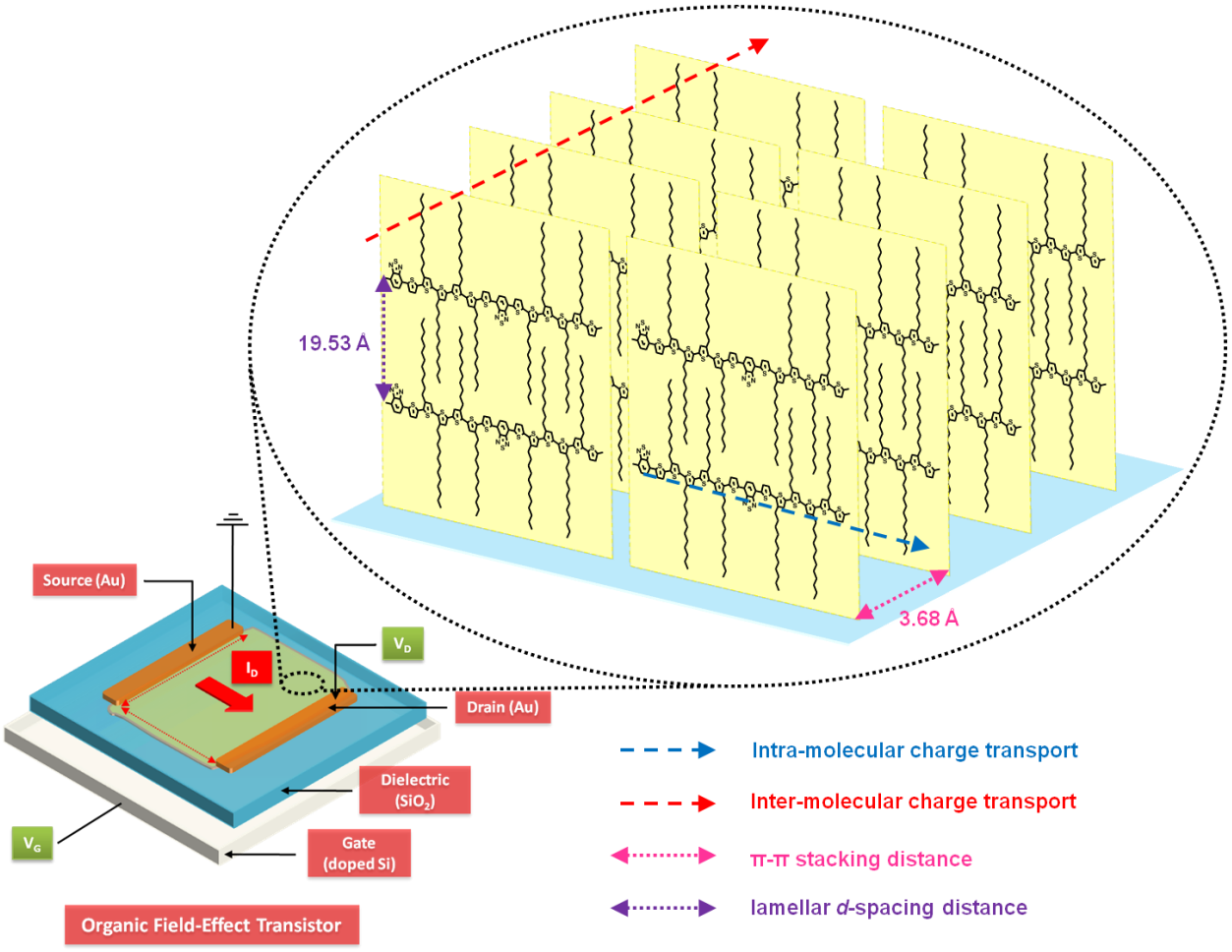


Figure S15. Idealized, lamellar π stacking edge-on orientation of **PBT6** thin film onto the bottom contact, bottom gate OFET substrate.

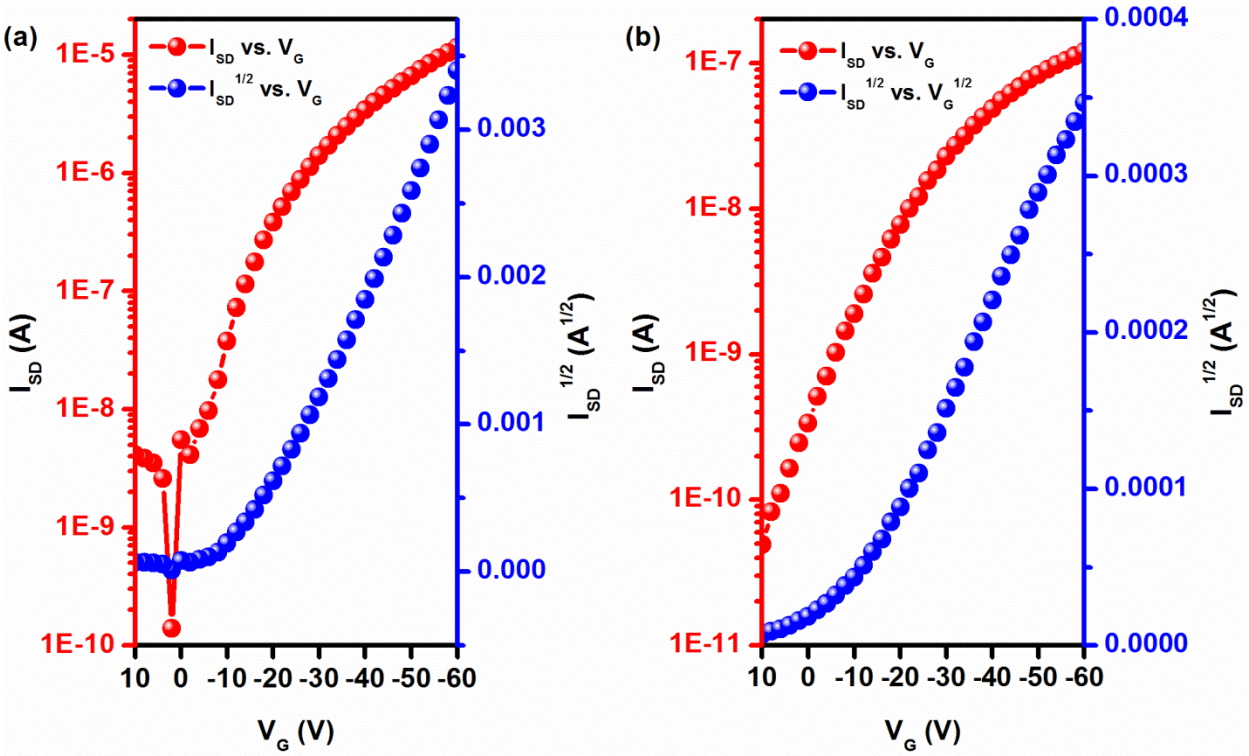


Figure S16. Transfer characterization of OFETs (V_{SD} = -80 V, channel size: 50 μm long x 2 mm wide): (a) spin-coated **PBT6(L)** film, and (b) spin-coated **PBT6V2** film.

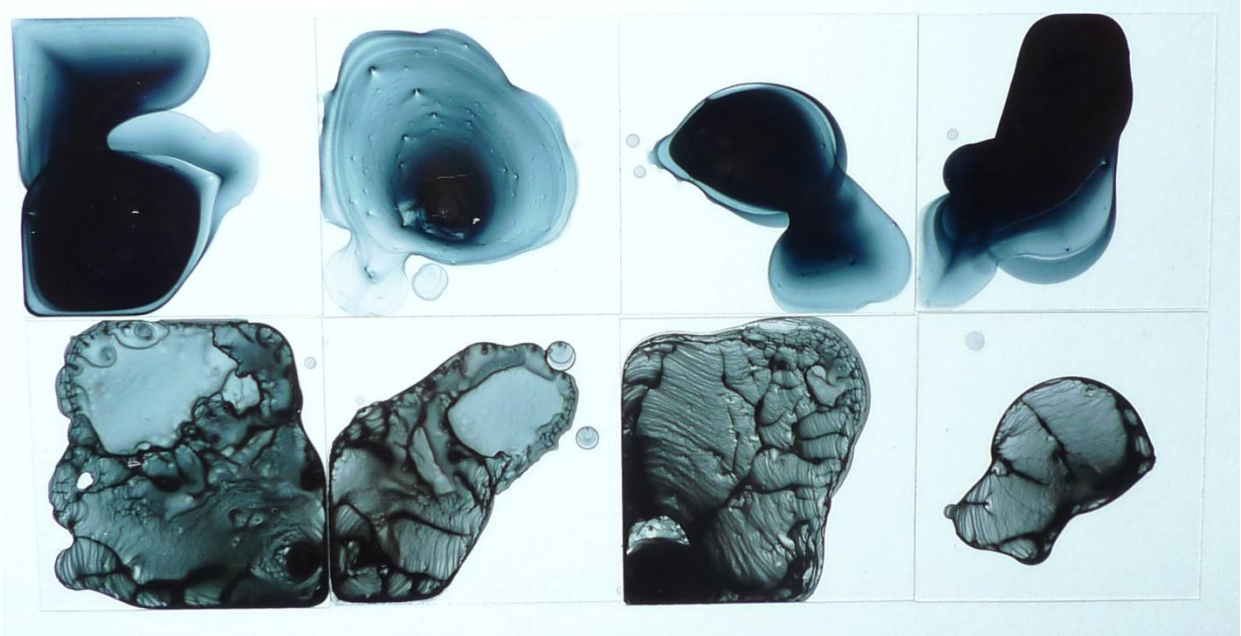


Figure S17. Photographs of drop cast films from 8 mg/ml of **PBT6** (upper row) and **PBT6(L)** in DCB on glass microcovers

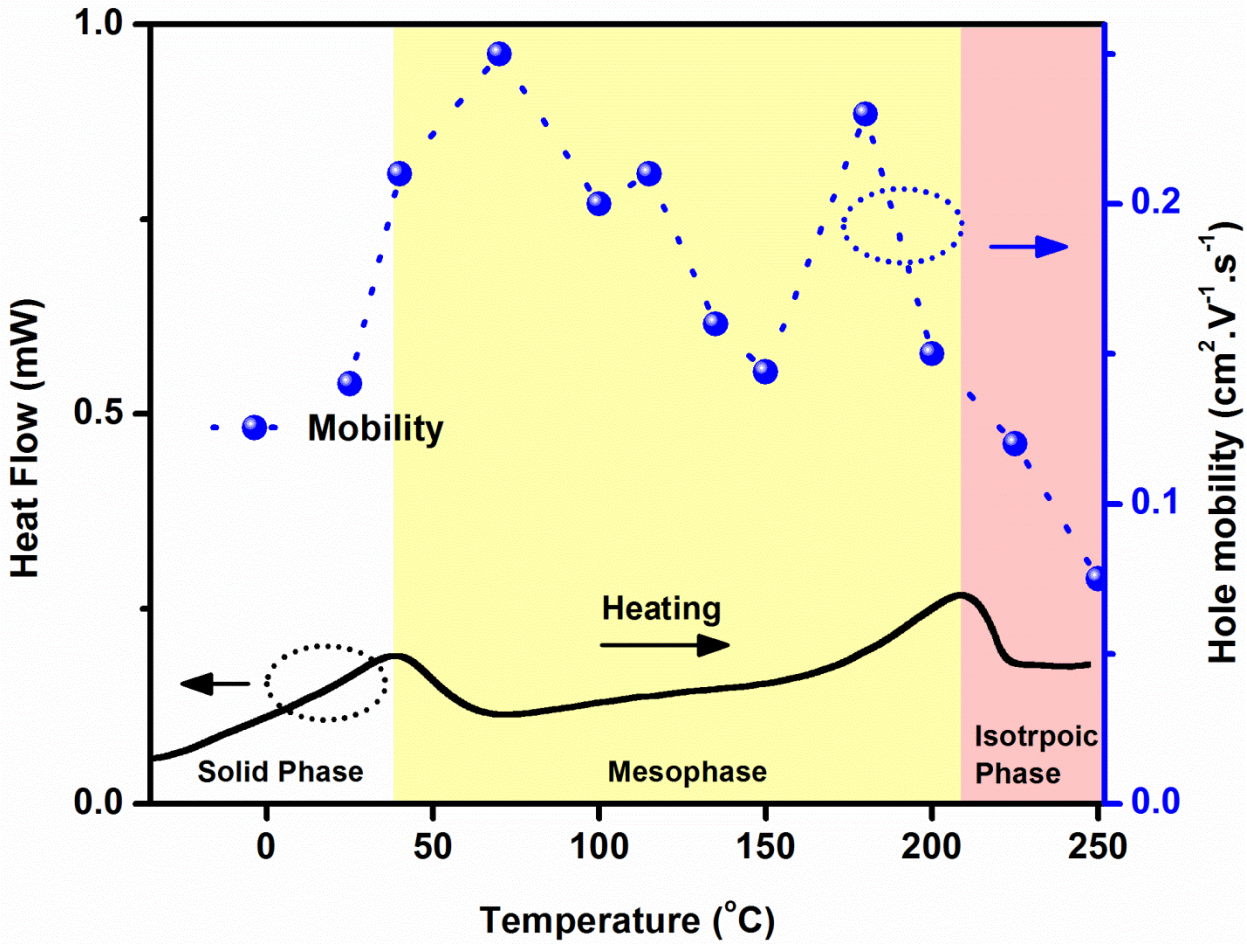
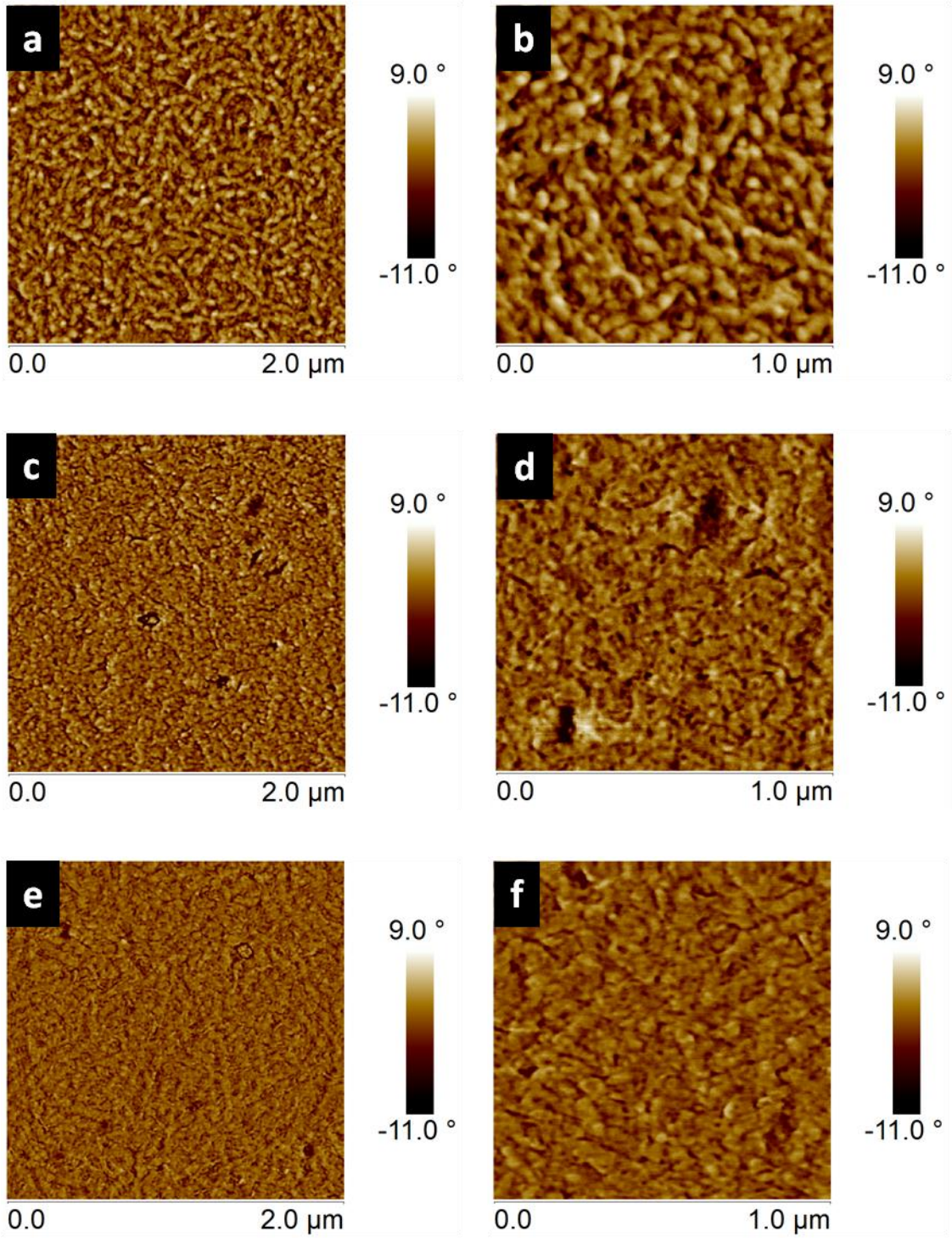


Figure S18. Hole mobility of **PBT6** from OFET measurements subjected to annealing in solid phase (room temperature), mesophase (40 °C, 70 °C, 100 °C, 115 °C, 135 °C, 150 °C and 180 °C) and isotropic phase (200 °C, 225 °C and 250 °C). The DSC trace at the bottom indicates the temperature of thermal transition.


a
9.0 °
-11.0 °
0.0
2.0 µm
b
9.0 °
-11.0 °
0.0
1.0 µm
c
9.0 °
-11.0 °
0.0
2.0 µm
d
9.0 °
-11.0 °
0.0
1.0 µm
e
9.0 °
-11.0 °
0.0
2.0 µm
f
9.0 °
-11.0 °
0.0
1.0 µm

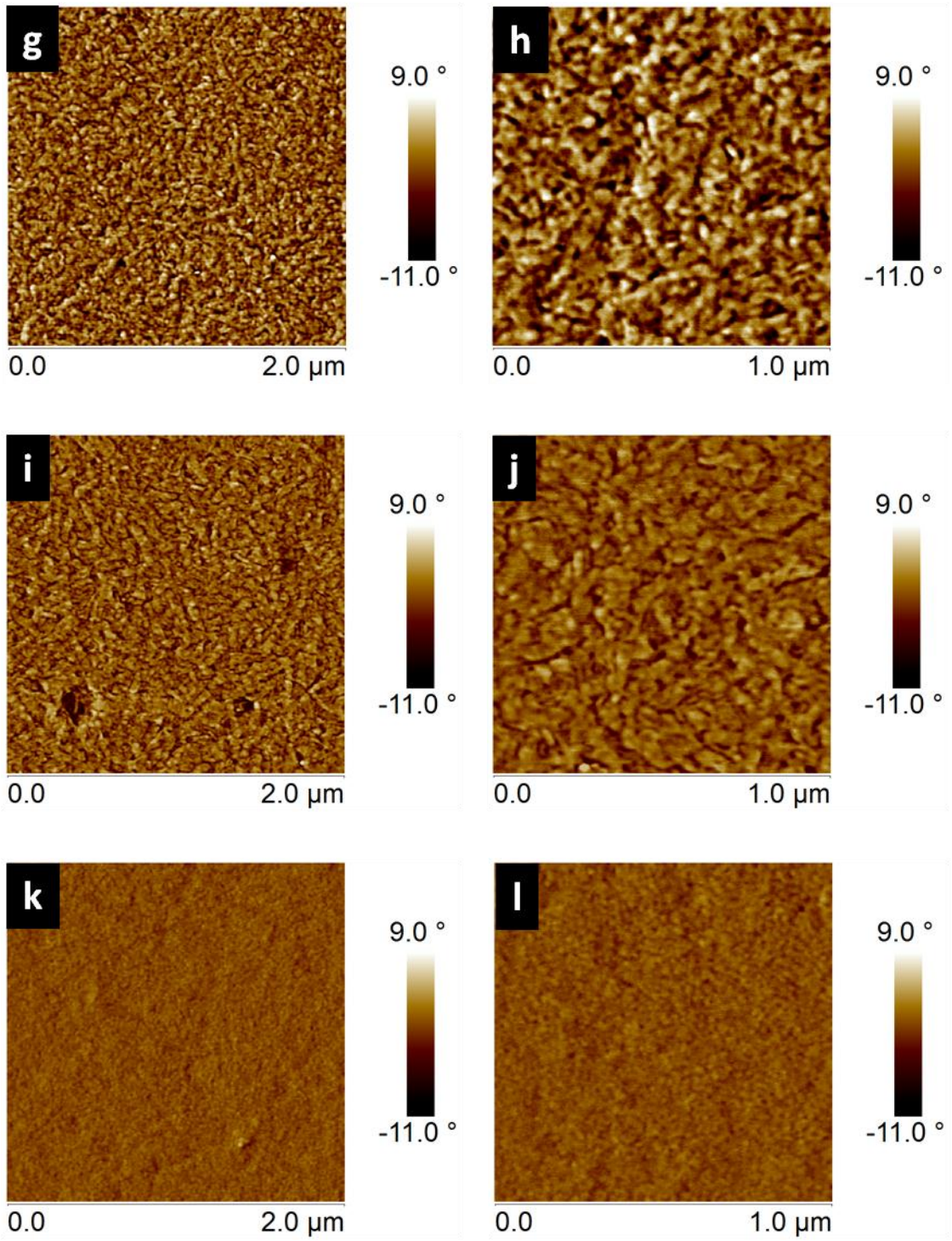


Figure S19. Tapping mode AFM phase images of **PBT6** films prepared by spin-coating 8 mg /mL polymer solutions in DCB onto OTS-18 pre-treated OFETs: (a, b) as spun, (c,

d) after annealed at 39 °C for 2h, (e, f) annealed at 70 °C for 2h, (g, h) annealed at 100 °C for 2h, (i, j) annealed at 115 °C for 2h, and (k, l) annealed at 250 °C for 2h.

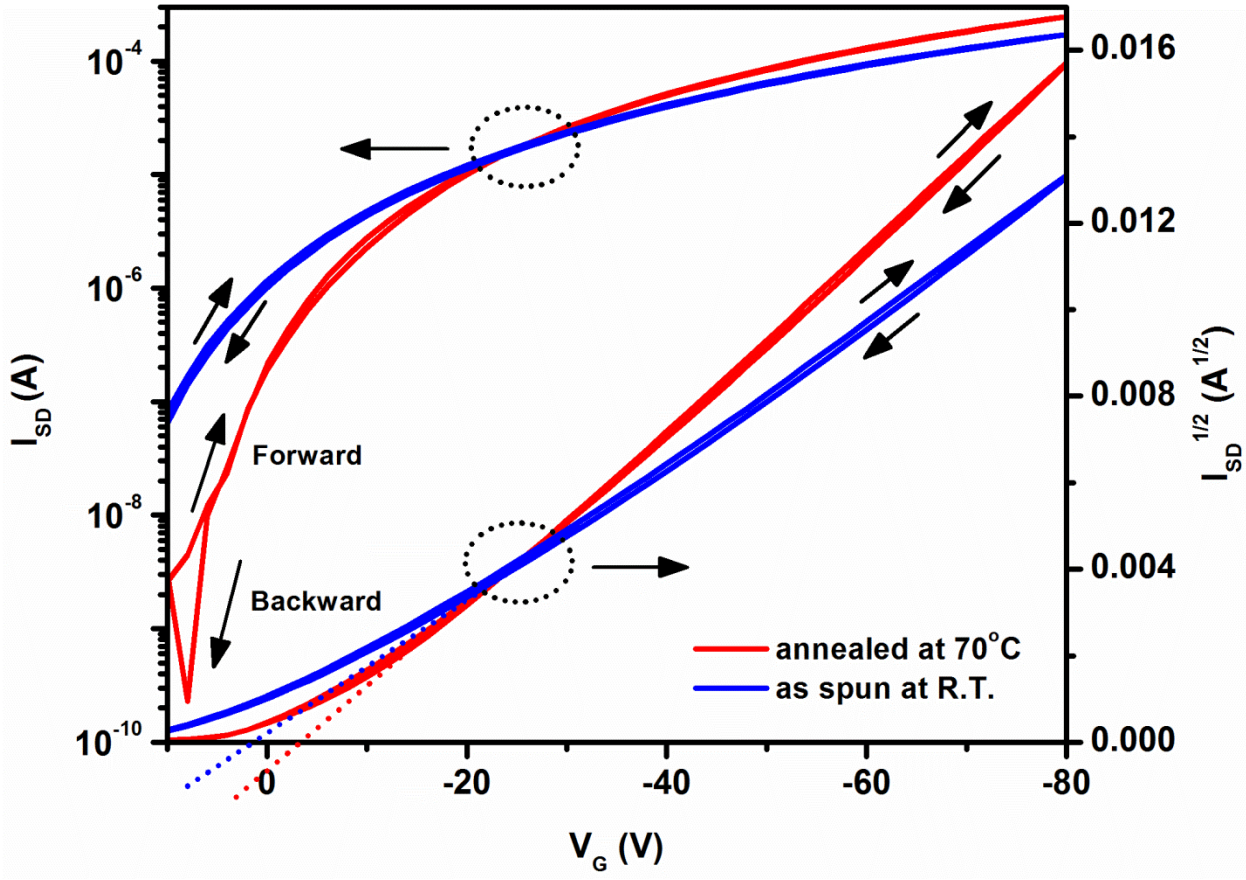


Figure S20. Transfer characterizations of OFETs at V_{SD} = -80 V (channel size: 50 μm long x 2 mm wide) based on a spin-coated **PBT6** film as spun at room temperature and annealed at 70 °C for 2 h, in sweeping mode. Arrows signify the sweeping directions (forward: 10 to -80 V; backward: -80 to 10 V) of gate voltage, V_G.

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