Supplementary Information

Synthesis and characterization of thiazolo[5,4-d]thiazole-based copolymer for high performance polymer solar cells

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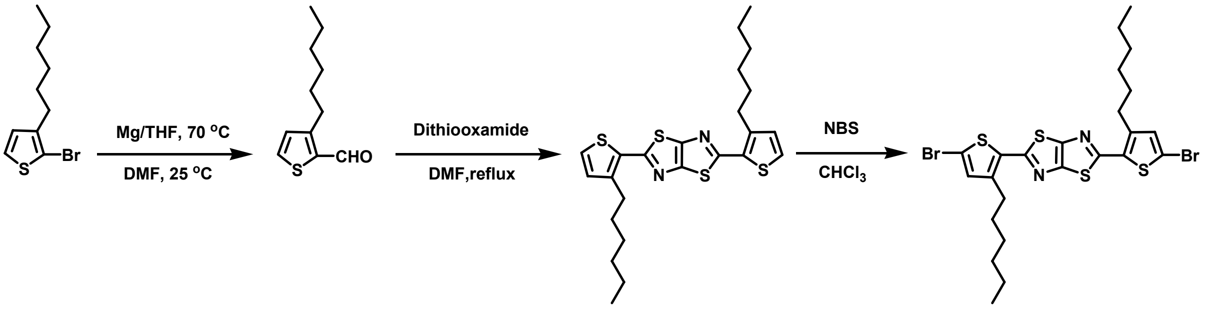
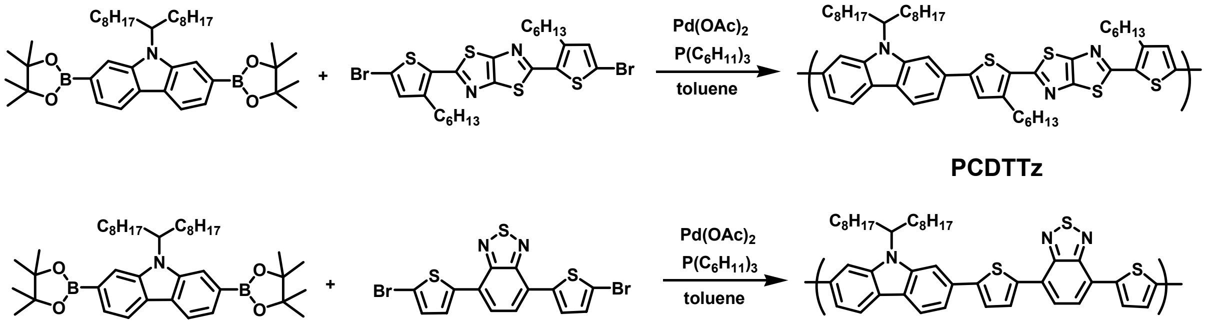
Scheme S1. Synthetic route to the monomer.



1 **2** **3** **4**

Scheme S2. Synthetic routes to the polymers.



PCDTBT

General: The synthesized compounds were characterized with ^{1}H NMR spectra obtained using a Bruker DPX-300 NMR Spectrometer. UV-visible analysis was performed with a Lambda 20 (Perkin Elmer) diode array spectrophotometer. The number- and weight-average molecular weights of the polymers were determined by gel permeation chromatography (GPC; Viscotek) equipped with TDA 302 detector and PL-gel (Varian) column, using chloroform as the eluent and polystyrene as the standard. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed under a nitrogen atmosphere at a heating rate of 10 ^{o}C/min with a Dupont 9900 analyzer.

Materials: 2-Bromo-3-hexylthiophene, dithiooxamide, phenol, *N*-bromosuccinimide (NBS), dimethylformamide (DMF), tricyclohexyl phosphine, and toluene (99.8%, anhydrous) were purchased from Aldrich. Palladium (II) acetate was purchased from Strem Chemicals Co.. All chemicals were used without further purification. The monomer 2,7-bis(4’,4’,5’,5’-tetramethyl-1’,3’,2’-dioxaborolan-2’-yl)-N-9”-hepta-decanylcarbazole was prepared according to reported procedures.[1]

3-Hexylthiophene-2-carboxaldehyde (2). 2-Bromo-3-hexylthiophene (5.0 g, 20 mmol) and a catalytic amount of iodine were added to a dry THF (50 mL) suspension of Mg turnings (0.62 g, 26 mmol) under an argon atmosphere. The mixture was allowed to stir vigorously and was heated to reflux for 5 hrs and then the solution was cannulated to a dried flask. Anhydrous DMF (3 mL) was added dropwise to this solution at room temperature, and the mixture was allowed to stir overnight. The reaction was quenched with 200 mL of 5% HCl, and THF was removed on a rotary evaporator. The mixture was extracted with ether. The organic layer was dried with anhydrous $MgSO_4$ and then concentrated under reduced pressure. The crude product was purified by column chromatography with hexane/ethyl acetate (20:1) as eluent to give **2**: 3.1 g, yield 78%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) : 10.02 (s, 1H), 7.62 (d, 1H), 6.98 (d, 1H), 2.94 (t, 2H), 1.67-1.62 (m, 3H), 1.36-1.25 (m, 5H), 0.86 (t, 3H). Anal. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.22; S, 16.33. Found: C, 67.25; H, 8.17; S, 16.31.

2,5-Bis(3-hexylthiophen-2-yl)-thiazolo[5,4-d]thiazole (3). A solution of dithiooxamide (0.35 g, 2.93 mmol), **2** (2.30 g, 11.7 mmol), and DMF was heated to reflux for 5 hrs. The crude product was purified by column chromatography with hexane/ethylacetate (20:1) as eluent to give **3**: 0.57 g, yield 40%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) : 7.38 (d, 2H), 7.02 (d, 2H), 2.95 (t, 4H), 1.73-1.65 (m, 4H), 1.45-1.25 (m, 12H), 0.89 (t, 6H). Anal. Calcd for $C_{24}H_{30}N_2S_4$: C, 60.72; H, 6.37; N, 5.90; S, 27.02. Found: C, 60.70; H, 6.36; N, 5.87; S, 27.05.

2,5-Bis(5-bromo-3-hexylthiophene-2-yl)-thiazolo[5,4-d]thiazole (4). A solution of **3** (0.34 g, 0.74 mmol) NBS (0.29 g, 1.63 mmol), and chloroform (10 ml) was heasted to reflux for 3 hr. Then the reaction solution was cooled to room temperature and washed with water. The organic layer was dried with anhydrous $MgSO_4$ and then concentrated under reduced pressure. The resulting brown-yellow solid was washed with 10 mL of hexane at room temperature for 1hr to afford yellow product: 0.30 g, yield 66%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) : 6.94 (s, 2H), 2.95 (t, 4H), 1.70-1.60 (m, 4H), 1.49-1.31 (m, 12H), 0.89 (t, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) : 160.2, 150.0, 143.4, 133.5, 133.3, 115.5, 31.6, 30.2, 29.8, 29.3, 22.6, 14.1. Anal. Calcd for $C_{24}H_{28}Br_2N_2S_4$: C, 45.57; H, 4.46; N, 4.43; S, 20.28. Found: C, 45.59; H, 4.41; N, 4.43; S, 20.26.

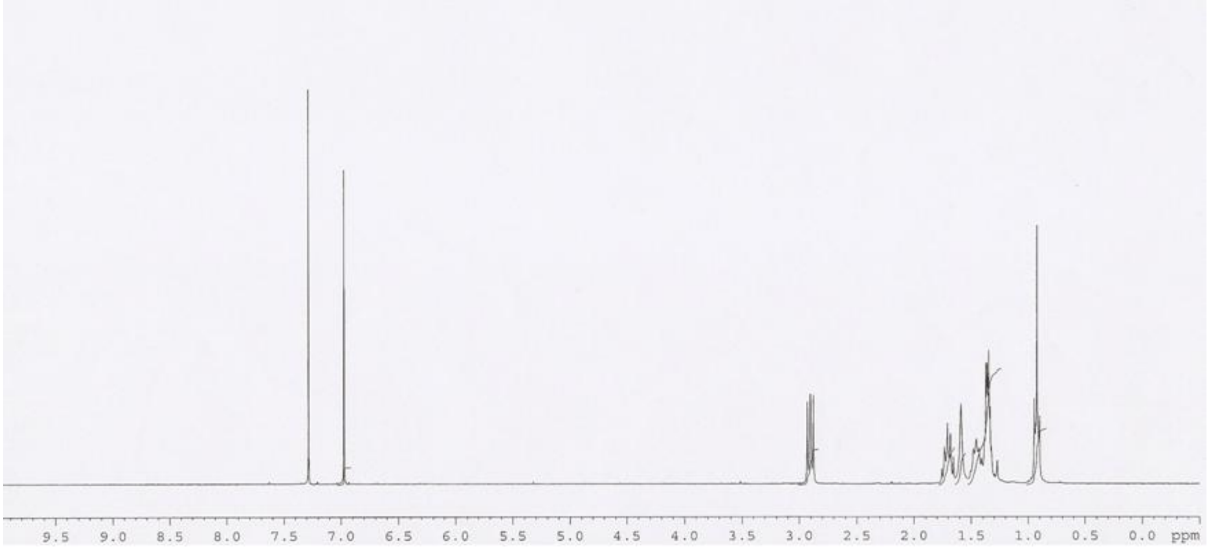


Figure S1. ^{1}H NMR spectrum of the monomer **4**.

Poly([N-9'heptadecanyl-2,7-carbazole-alt-5,5-(2,5-bis(3-hexylthiophene-2-yl)-thiazolo[5,4-d]thiazole)] (**PCDTTz**). 2,7-bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-N-9"-hepta-decanylcarbazole (0.263 g, 0.400 mmol), 2,5-bis(5-bromo-3-hexylthiophene-2-yl)-thiazolo[5,4-d]thiazole (0.253 g, 0.400 mmol), palladium (II) acetate (5.4 mg, 0.0080 mmol), and tricyclohexyl phosphine (3.4 mg, 0.0120 mmol) were dissolved in 4 mL of anhydrous toluene. To the solution, tetraethylammonium hydroxide solution (1.30 g) degassed by sonicator was added under argon flow. After 24 hr, the reaction mixture was cooled to about 50 °C and added slowly to a vigorously stirred mixture consisting of 230 mL of methanol and 13 mL of 1 N aqueous HCl. The polymer fibers were collected by filtration and reprecipitation from methanol. The polymer was purified by washing for 2 days in a soxhlet apparatus with acetone to remove oligomers and catalyst residues, and column chromatographed with a chloroform/toluene solution of the polymer. The reprecipitation procedure in toluene/methanol was then repeated several times. The final product was obtained after drying in vacuo at 40 °C (0.252 g, yield 72 %). Solubility parameter for PCDTTz using the Van Krevelen method (Synthia program) is 20.84 $(\mathrm{J/cm^3})^{1/2}$. ^{1}H NMR

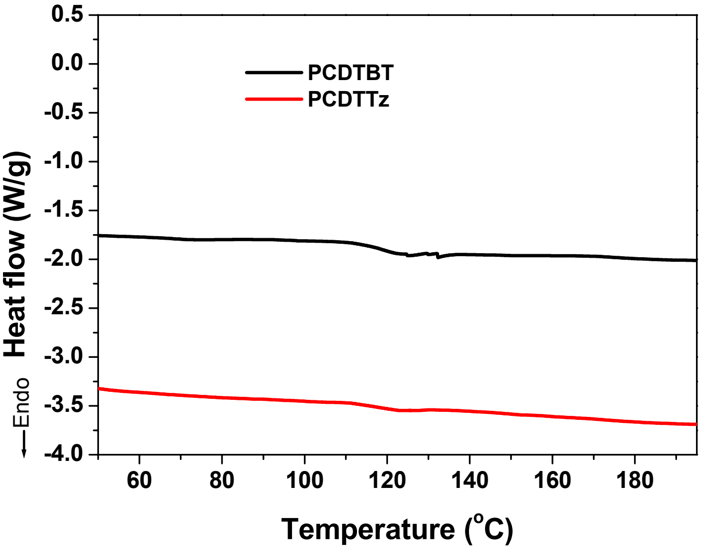
(300 MHz, CD_2Cl_2) δ (ppm): 8.06 (br, 2H), 7.55 (br, 2H), 7.50 (br, 2H), 6.96 (br, 2H), 4.61 (br, 1H), 2.98 (br, 6H), 2.38 (br, 2H), 2.2 -1.10 (m, 40H), 0.94 (br, 6H), 0.79 (br, 6H). (Multiple peaks are due to the phenomenon of atropisomerism.[1]) Anal. Calcd: C, 72.63; H, 7.94; N, 4.79; S, 14.63. Found: C, 72.59; H, 7.91; N, 4.71; S, 14.51.

Poly([N-9'heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (**PCDTBT**). PCDTBT was synthesized with the procedure described for **PCDTTz**. The copolymerization of the monomers 2,7-bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-N-9''-hepta-decanylcarbazole (0.263 g, 0.400 mmol), 4,7-di(2-bromothien-5-yl)-2,1,3-benzothiadiazole (0.183 g, 0.400 mmol) gave PCDTBT (0.196 g, yield 70 %). Solubility parameter for PCDTBT using the Van Krevelen method (Synthia program) is 21.51 $(J/cm^3)^{1/2}$. ^1H NMR (300 MHz, CD_2Cl_2) δ (ppm): 8.18 (br, 2H), 8.09 (br, 2H), 7.94 (br, 2H), 7.69 (br, 2H), 7.59 (br, 2H), 7.50 (br, 2H), 4.66 (br, 1H), 2.39 (br, 2H), 2.02 (br, 2H), 1.14 (br, 24H), 0.77 (br, 6H). (Multiple peaks are due to the phenomenon of atropisomerism.[1]) Anal. Calcd: C, 73.56; H, 6.75; N, 5.99; S, 13.70. Found: C, 73.67; H, 6.69; N, 5.82; S, 13.61.

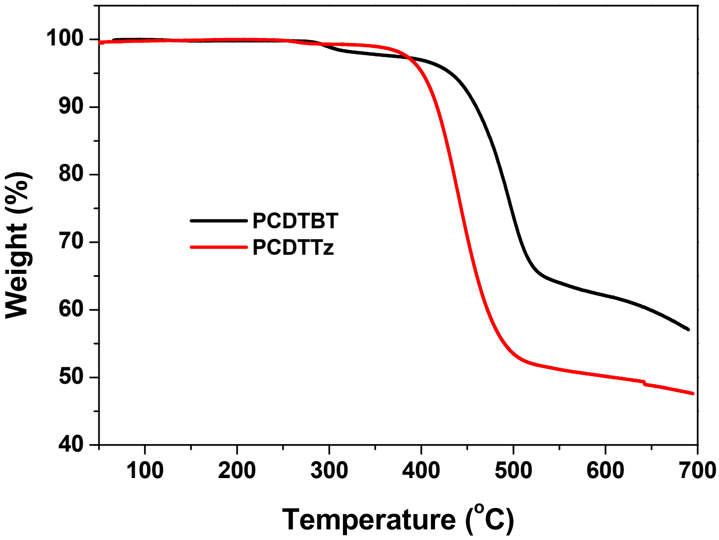
Fabrication of the organic thin film transistors (OTFTs): OTFT devices were fabricated in a bottom-contact geometry (channel length = 6 μm, width = 120 μm). The source and drain contacts consisted of gold (100 nm), and the dielectric was silicon oxide (SiO_2) with a thickness of 300 nm. The SiO_2 surface was cleaned, dried, and pretreated with a solution of 1.0 mM octyltrichlorosilane (OTS-8) in toluene at room temperature for 2 h under nitrogen to produce apolar and smooth surfaces onto which the polymers could be spin-coated. The polymers were dissolved to a concentration of 0.5 wt-% in chlorobenzene. Films of the organic semiconductors were spin-coated at 1500 rpm for 50 s to a thickness of 50 nm, followed by an annealing process. All device fabrication procedures and measurements were carried out in air at room temperature.

Fabrication of the polymer solar cells (PSCs): In this study, the devices were fabricated with the structure ITO/PEDOT:PSS/polymer:$PC_{71}BM$/LiF/Al. The procedure for cleaning the ITO surface included sonication and rinsing in deionized water, methanol, and acetone. The hole-transporting PEDOT:PSS layer was spin-coated onto each ITO anode from a solution purchased from H. C. Starck and baked for 20 min at 140 ^{o}C in glove box. Each polymer:$PC_{71}BM$ solution was then spin-coated onto the PEDOT:PSS layer. The polymer solution for spin-coating was prepared by dissolving the polymer (1 wt%) in o-dichlorobenzene. Pre-annealing was not carried out. LiF and aluminum contacts were formed by vacuum deposition at pressures below 3 x 10^{-6} Torr, providing an active area of 0.09 cm^2. Solar cell efficiencies were characterized under simulated 100 mW/cm^2 AM 1.5G irradiation from a Xe arc lamp with an AM 1.5 global filter. Simulator irradiance was characterized using a calibrated spectrometer, and the illumination intensity was set using an NREL-certified silicon diode with an integrated KG1 optical filter: short-circuit currents were found to be within 11% of the values calculated using the integrated external quantum efficiency (EQE) spectra and the solar spectrum. The EQE was measured by underfilling the device area using a reflective microscope objective to focus the light output from a 100 W halogen lamp outfitted with a monochromator and optical chopper; the photocurrent was measured using a lock-in amplifier, and the absolute photon flux was determined using a calibrated silicon photodiode. All device fabrication procedures and measurements were carried out in air at room temperature.

2. Physical Properties.



(a)



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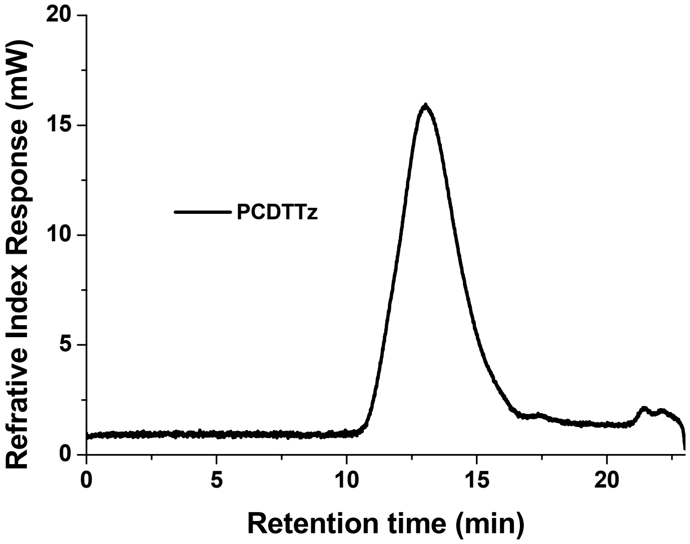
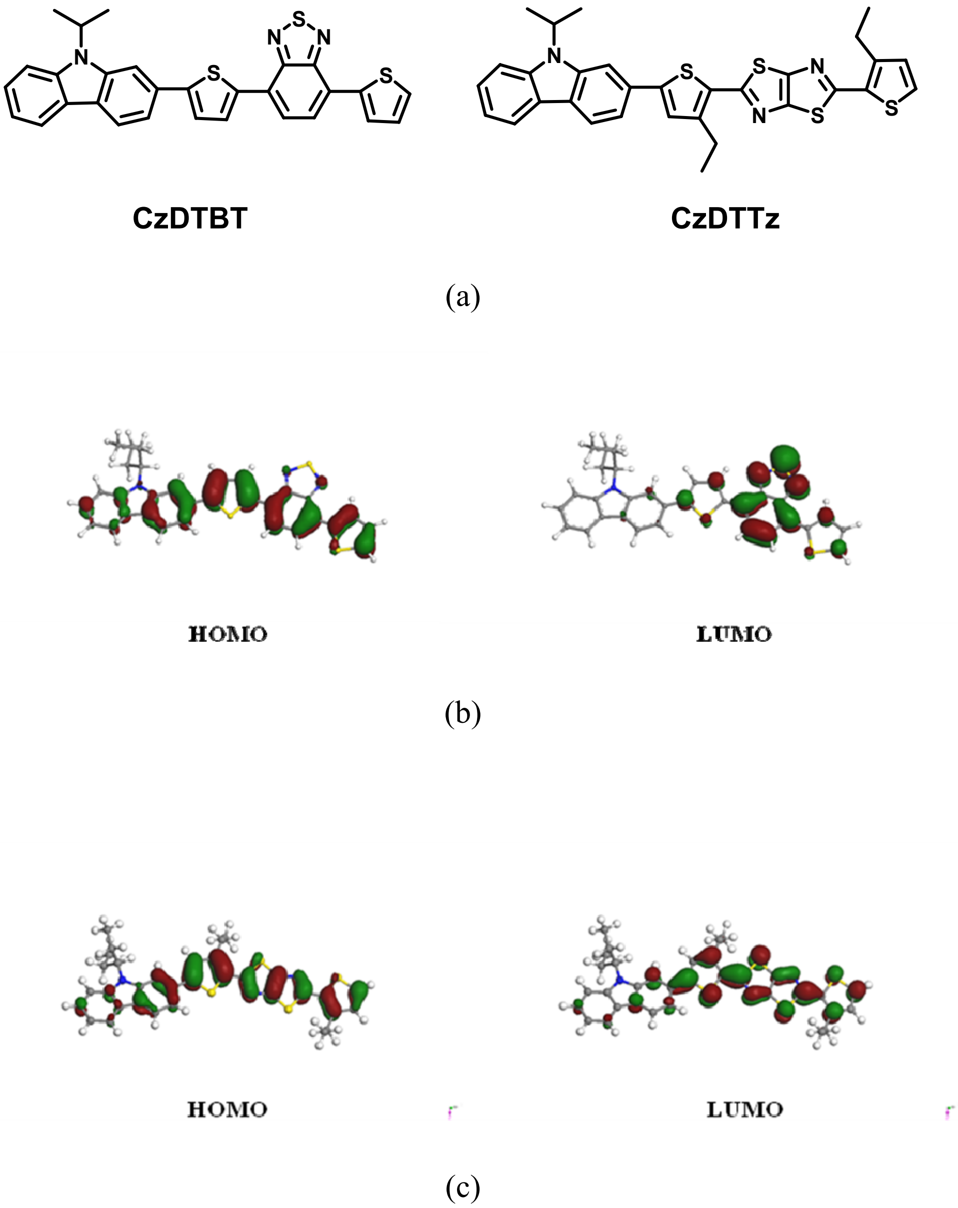


(c)

Figure S2. DSC spectra (a), TGA traces (b), and GPC curves (c) of the polymers.

3. Computational methodology: the charge-density isosurface of model compounds.

To obtain further information about ICT electronic structure of the polymers, density-functional theory (DFT) calculation for the model compound were carried out using the DMol 3. Figure S3 reproduces the calculated molecular orbitals of model compounds.



Fiure S3. Structure of model compounds (a) and the charge-density isosurfaces for HOMO and LUMO levels of the model compounds: CzDTBT (b) and CzDTTz (c).

4. Electrochemical Properties.

To investigate the redox behavior of the copolymers and determine the energy levels of their highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO), the electrochemical properties of the polymers were investigated by using cyclic voltammetry (CV). A copolymer-coated platinum electrode was used as the working electrode, a platinum wire was used as the counter electrode, and an Ag/AgNO$_3$ (0.10 M) electrode was used as the reference electrode. The electrochemical properties of the copolymers were investigated in an electrolyte consisting of a solution of 0.1 M tetrabutylammonium tetrafluoroborate (TBABF$_4$) in acetonitrile at room temperature under nitrogen with a scan rate of 50 mV/s. The HOMO energy levels of the copolymers can be deduced from the onset potentials of p-doping waves with the assumption that the energy level of ferrocene (Fc) is 4.8 eV below vacuum level.

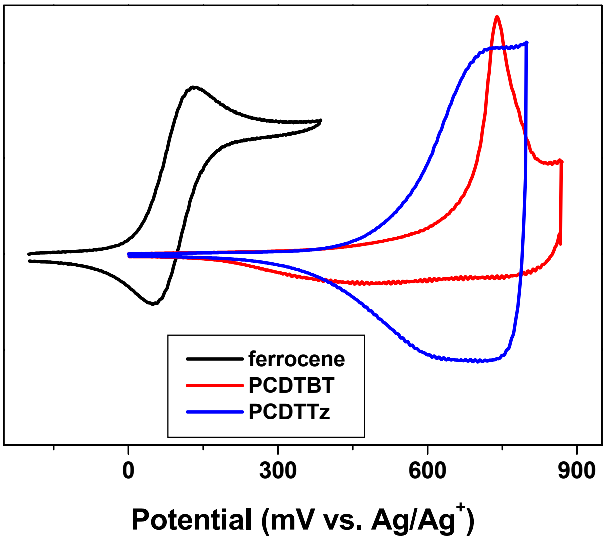
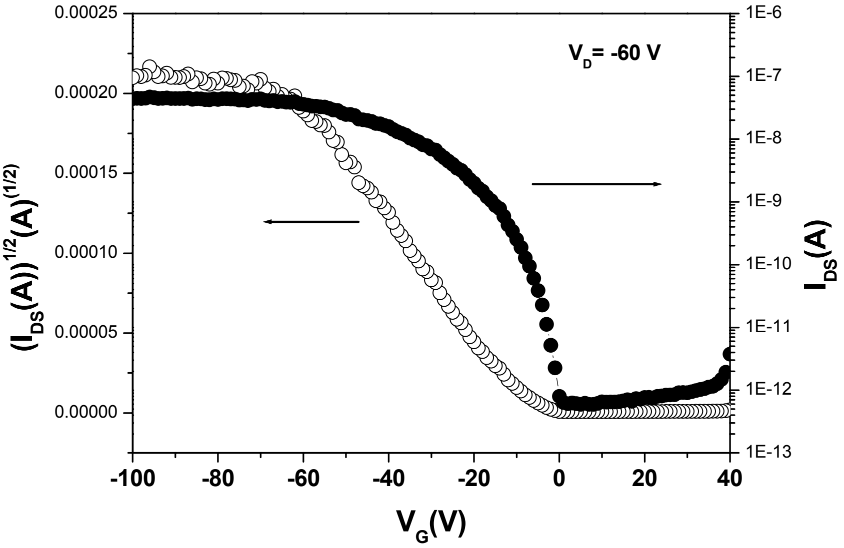
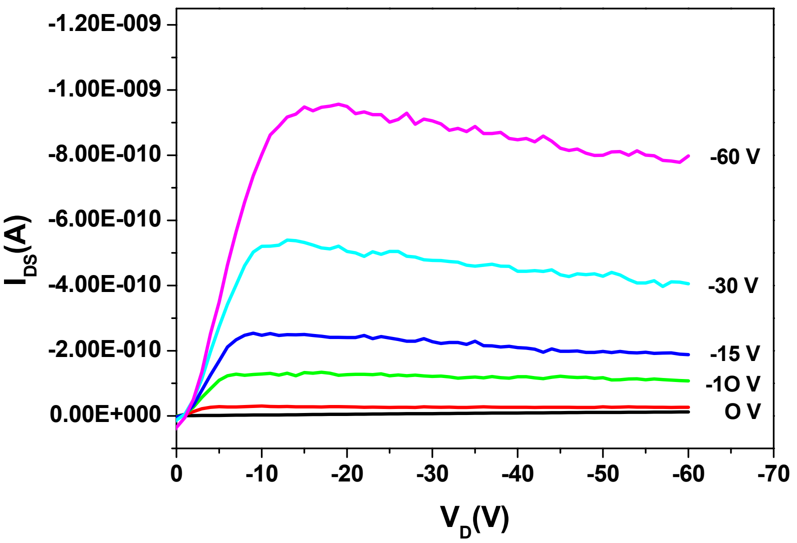


Figure S4. Cyclic voltammograms of the polymers.

5. Transfer characteristics of FET fabricated using PCDTBT.



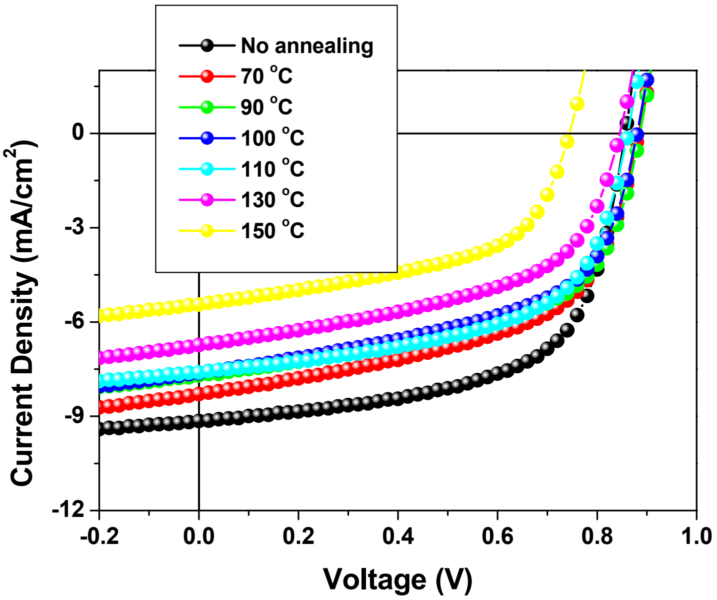
(a)



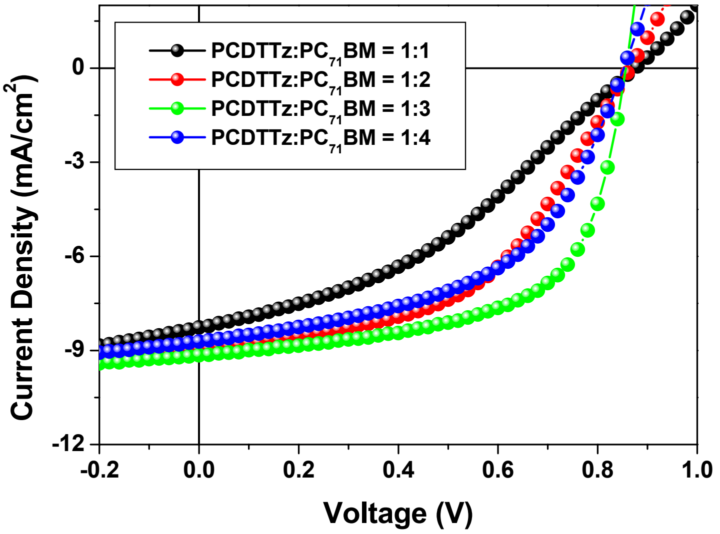
(b)

Figure S5. (a) Transfer curves in saturated regime for PCDTBT. (b) The output curves at different gate voltages for PCDTBT.

6. The performance of the PSCs under variety of conditions.



(a)



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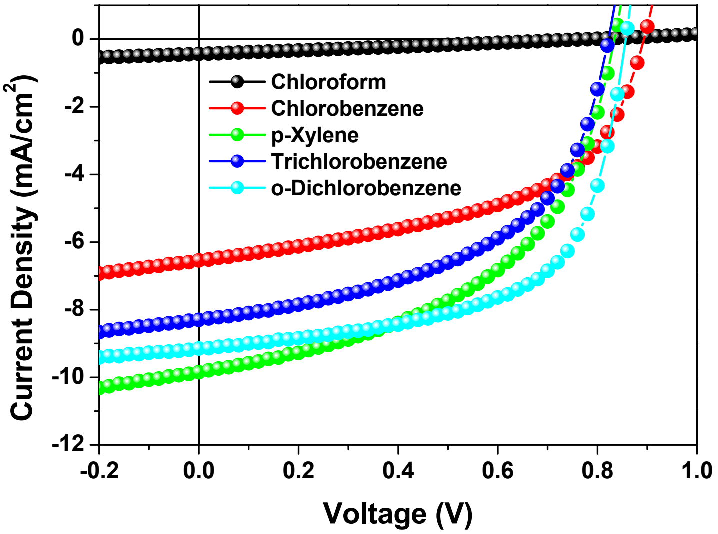

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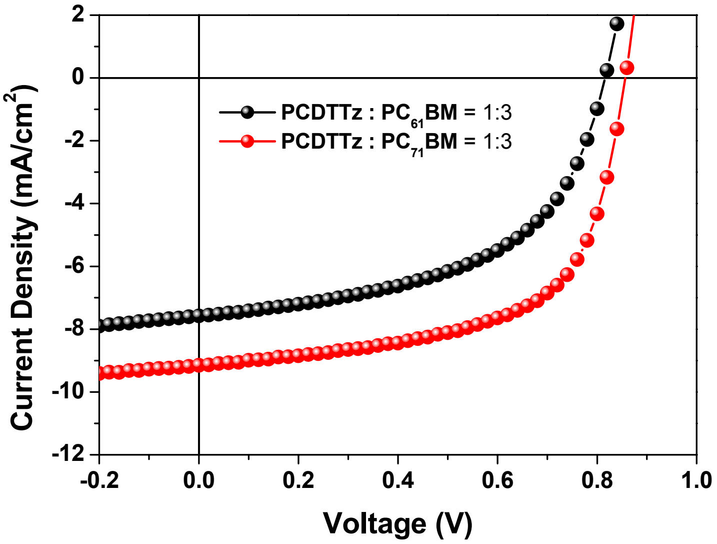
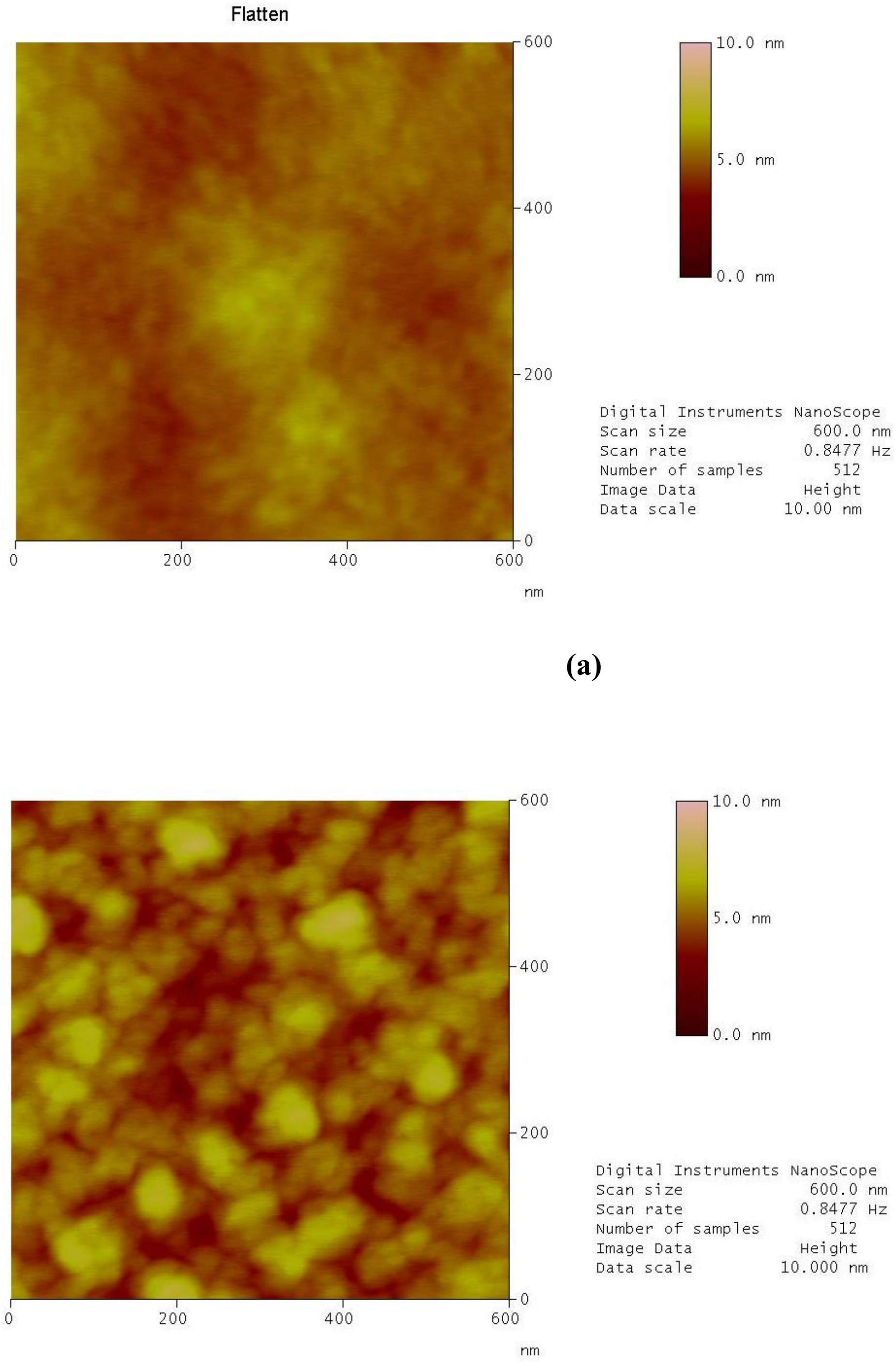


(d)

Figure S6. The performance of the PSC materials under variety of conditions. (a) the annealing temperatures; (b) the blend ratio of polymer to PC$_{71}$BM; (c) type of solvents; (d) the type of PCBMs.

7. Morphology characterization



(a)

(b)

Figure S7. AFM topography of films spin coated from PCDTBT/PC$_{71}$BM (a) and PCDTTz/PC$_{71}$BM (b).

8. Reference.

1. Blouin, N.; Michaud, A.; Leclerc, M. *Adv. Mater.* **2007**, *19*, 2295-2300.