Electronic Supplementary Information for:

Cyanothiophene-based low band-gap polymer for organic solar cells

J. Arul Clement,‡ Heung Gyu Kim,‡ Myungsun Sim,‡ Boseok Kang and Kilwon Cho*

Department of Chemical Engineering, Pohang University of Science and Technology, Pohang, 790-784, Korea

Synthesis

Materials

All reagents were purchased from Aldrich, TCI and Acros, and used without further purification. All anhydrous organic solvents for synthesis and device fabrication such as tetrahydrofuran (THF), chloroform, dichloromethane, toluene, *N,N*-dimethylformamide (DMF), chlorobenzene (CB), 1,2-dichlorobenzene (DCB) were purchased from Aldrich.

Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 operating at 400 MHz and 100 MHz in chloroform-d solutions with TMS as the internal standard. Number-average (M_n) and weight-average (M_w) molecular weights were measured by gel permeation chromatography (GPC) using a Shimadzu LC solution with chloroform as the eluent and a calibration curve of polystyrene standards at 40 °C. UV-Visible absorption spectra were measured by a Varian CARY-5000 UV/Visible Spectrophotometer. Differential scanning calorimetric (DSC) and thermogravimetric analysis (TGA) measurements of the polymers were performed using a DSC 2910 (TA instruments) and a TGA 2050 (TA instruments) under a nitrogen atmosphere at a heating and cooling rate of 10 °C min^{-1}. Cyclic voltammogram was recorded using a PowerLab/AD instrument model system. A 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) solution in acetonitrile was used as the electrolyte solution. A three electrode system was used consisting of an Ag/AgCl reference electrode, a glassy carbon working electrode, and a platinum counter electrode. Polymer thin films were formed by drop casting of polymer solutions in chloroform on the working electrode. The potential of Ag/AgCl reference electrode was internally calibrated by using the ferrocene/ferrocenium redox couple (Fc/Fc$^+$). The energy levels were estimated using the equations: HOMO= $-(4.80 + E_{\text{onset, ox}})$, and LUMO= $-(4.80 + E_{\text{onset, red}})$.

Synthesis of 4-dodecyloxy-2,5-dihydrothiophene-3-carbonitrile (2)

To a solution of 4-cyano-3-tetrahydrothiophene (1 g, 7.87 mmol) in 10 mL of DMF, Cs_2CO_3 (2.81 g, 1.1 equiv) and dodecyl methanesulfonate (2.49 g, 1.2 equiv) were added. The solution was irradiated in CEM microwave oven (T = 80 °C) for 5 min. After the completion of the reaction (checked by TLC) the reaction mixture was poured into water, neutralized with dilute HCl (2 M) and extracted with dichloromethane (3 × 50 mL). The combined organic layer was washed several times with water and dried with $MgSO_4$. After evaporation of the solvent, the residue was purified through column chromatography using hexane and ethyl acetate (10:1) as the eluent to afford 1.75 g of compound **2** (75% yield) as a pale yellow oily liquid. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ: 4.30 (t, 2H, J = 6.4 Hz), 3.76 (s, 4H), 1.74-1.67 (m, 2H), 1.29-1.23 (m, 18H), 0.86 (t, 3H, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 168.9, 115.7, 80.6, 72.3, 36.0, 34.1, 31.9, 29.6(2C), 29.5, 29.4, 29.3, 29.2, 25.6, 22.7, 14.1.

Synthesis of 4-cyano-3-dodecyloxythiophene (3)

Under nitrogen atmosphere, a solution of compound **2** (1.5 g 5.08 mmol) in dichloromethane (50 mL) was stirred at 50 °C then a solution of DDQ (1.38 g, 1.2 equiv) in THF (20 mL) was slowly added from an additional funnel. After addition, the reaction mixture was allowed to stir for 12 h. After addition of water (100 mL), the mixture was extracted with dichloromethane (3 × 20 mL). The organic phase was dried over $MgSO_4$ and evaporated under reduced pressure. The resulting oil was purified by column chromatography on silica gel using hexane and ethyl acetate (10:1) as the eluent to afford 1.13 g of compound **3** (76% yield) as a colorless solid. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.77 (s, 1H, ArH), 6.27(s, 1H, ArH), 4.0 (t, 2H, J = 6.6 Hz), 1.86-1.79 (m, 2H), 1.48-1.43 (m, 2H), 1.28 (m, 16H), 0.89 (t, 3H, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 157.6, 134.1, 113.4, 104.1, 97.9, 71.3, 31.9, 29.6 (2C), 29.5, 29.4, 29.3, 28.9, 25.9, 22.7, 14.1. Elemental analysis: calc. for $C_{17}H_{27}NOS$: C, 69.58; H, 9.27; N, 4.77; S, 10.93. Found: C, 69.81; H, 9.09; N, 4.52; S, 10.31%.

Synthesis of 2-bromo-3-dodecyloxy-4-cyanothiophene (4)

NBS (0.73 g, 1.2 equiv) was slowly added to a solution of compound **3** (1.0 g, 3.41 mmol) in chloroform (10 mL) under nitrogen atmosphere. The reaction mixture was heated at 50 °C for 10 h in dark. After addition of water (30 ml), the mixture was extracted with dichloromethane (2 × 20 mL). The organic phase was dried over $MgSO_4$ and evaporated under reduced pressure. The resulting oil was purified by column chromatography on silica gel using hexane and ethyl acetate (10:1) as the eluent to afford 1.02 g of compound **4** (80% yield) as a pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.79 (s, 1H, ArH), 4.24 (t, 2H, J = 6.6 Hz), 1.84-1.77 (m, 2H), 1.53-1.48 (m, 2H), 1.33- 1.28 (m, 16 H), 0.896 (t, 3H, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 154.5, 133.8, 112.9, 106.6, 98.2, 75.0, 31.9, 29.9, 29.7, 29.6(2C), 29.5, 29.4, 29.3, 25.7, 22.7, 14.1.

Synthesis of 5,5'-dibromo-4,4'-didodecyloxy-2,2'-bithiophene-3,3'-dicarbonitrile (5)

The mixture of a palladium catalyst (0.03 g, 0.080 mmol), 8 mL of DMSO, and compound **4** (1 g, 2.68 mmol) was stirred. To the resulting mixture, silver (I) fluoride (0.68 g, 2 equiv) was added and heated at 60 °C for 7 h. Then, the mixture was cooled to room temperature and passed through a Celite pad, which was successively washed with chloroform. The filtrate was washed with water and the aqueous layer was extracted with chloroform. The combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to give a crude solid. Recrystallization of crude product using dichloromethane and methanol gave 0.57 g of compound **5** (57% yield) as a red solid. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ: 4.28 (t, 4H, J = 6.6 Hz), 1.86-1.79 (m, 4H), 1.55-1.47 (m, 4H), 1.28 (m, 32 H), 0.90 (t, 6H, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 155.4, 138.2, 112.3, 105.2, 100.3, 75.5, 31.9, 29.9, 29.7, 29.6 (2C), 29.5, 29.4, 29.3, 25.6, 22.7, 14.1. Elemental analysis: calc. for $C_{34}H_{50}Br_2N_2O_2S_2$: C, 54.98; H, 6.79; N, 3.77; S 8.63. Found: C, 54.78; H, 6.69; N, 3.78; S, 8.78%.

Synthesis of PBDT-CT

Compound **5** (0.32 g, 0.43 mmol), monomer **6** (0.33 g, 0.43 mmol), and $Pd(PPh_3)_4$ (10 mg) were dissolved in a mixture of toluene (15 mL) and DMF (2 mL). The reaction flask was purged with nitrogen for 2 h. The solution was refluxed for 3 days at 120 °C, and then cooled to RT. The polymer solution was poured into methanol (200 mL). The resulting blue-black solid was filtered and Soxhlet extracted with methanol, acetone, hexane, and chloroform until the wash solution of each extraction was colorless. The chloroform fraction was concentrated and poured into methanol, filtered, and dried under vacuum to afford 0.43 g (89% yield) of blue black solid. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.70-6.71 (m, 2H), 4.68-3.79 (br, 8H), 1.97-0.74 (br, 76H). GPC ($CHCl_3$, 40 °C): M_n = 54 kg mol^{-1}, M_w = 152 kg mol^{-1}, PDI = 2.81. Elemental analysis: calc. for $C_{60}H_{86}N_2O_4S_4$: C, 70.13; H, 8.44; N, 2.73; S 12.48. Found: C, 70.17; H, 8.44; N, 2.62; S, 12.59%.

Fabrication and characterization of the polymer solar cells

Polymer solar cells were fabricated on top of ITO-coated substrates. The ITO substrates were cleaned by detergent, water, acetone and ethanol and treated with UV-ozone for 20 min. The conventional device structure consists of an ITO substrate coated with a thin layer of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Baytron, PTP 4083, Bayer AG) as the anode; LiF (0.6 nm) and Al (100 nm) were thermally-evaporated as the cathode. For the inverted structure, 10 wt% ZnO nanoparticles were dispersed in 1-butanol and spin-coated on ITO substrates at 4000 rpm to function as the cathode. MoO_3 (9 nm) and Ag (100 nm) were thermally evaporated as the anode. PBDT-CT and PCBM blend solutions (1:2) were prepared in chlorobenzene at PBDT-CT concentration of 6.7 mg ml^{-1}. The blend solutions with 2 vol% 1,8-diiodoctane (DIO) as additive were spin-coated on the substrates and dried at 70 °C for 10 min. The current density-voltage (*J-V*) characteristics were measured by using Keithley 4200 source under AM 1.5 solar illumination (Oriel 1 kW solar simulator) with respect to the reference cell PVM 132 (calibrated at the National Renewable Energy Laboratory).

Fabrication and characterization of organic thin film transistor (OTFT)

For the fabrication of the OTFTs, a highly doped p-Si wafer was used as a gate metal and substrate. 300 nm thick thermally grown oxide layer was employed as gate dielectric. Prior to spin-casting of semiconducting polymer solution, hexamethyldisilazane (HMDS) was treated on the gate oxide. 10 mg ml^{-1} of PBDT-CT in CB was spin-casted at 1500 rpm for 60 s, and annealed at 150 °C for 30 min under nitrongen atmosphere. The devices were completed by evaporating gold through a shadow mask to define the source and drain with 100 nm thick. The channel length and width were 150 and 1500 μm, respectively. Electrical property of these devices was measured by using Kithley 2636A, semiconductor analyzer in air.

Space charge limited current (SCLC) hole-mobility measurements

The hole mobility of the **PBDT-CT**/ PCBM blend (w/w, 1:2) was measured by the space charge limited current (SCLC) method which is based on field-dependent Poole-Frenkel Law with a device structure of ITO/PEDOT:PSS/**PBDT-CT**:PCBM/Pd. The hole mobility was calculated by equation:

$$J_{SCLC} = (9/8)\varepsilon_r \varepsilon_0 \mu (V^2 / L^3)$$

Which ε_r is the dielectric constant of the material, ε_0 is the permittivity of free space, L is the distance between the cathode and anode, which is equivalent to the film thickness, and V is the applied voltage. Fig. S7 displays the SCLC curves from the hole only devices.

Device performance of solar cells processed without and with DIO

The J-V curves of the inverted solar devices processed without and with DIO solvent additive are shown in Fig. S10. With the introduction of DIO, the V_{oc} decreased slightly from 0.92 V to 0.90 V, the J_{sc} increased slightly from 5.03 mA cm^{-2} to 5.55 mA cm^{-2}, the FF increased significantly from 0.52 to 0.67, and thus power conversion efficiency increased from 2.41 % to 3.36 %.

Grazing incidence X-ray diffraction

Grazing incidence X-ray diffraction (GIXRD) experiments were performed using the 5A beamline (incident angle: 0.12°, 1D out of plane) at the Pohang Accelerator Laboratory (PAL). The GIXRD measurements were obtained in a scanning interval of 2θ between 3° and 27° with the monochromatic radiation of the X-ray wavelength of 1.07 Å.

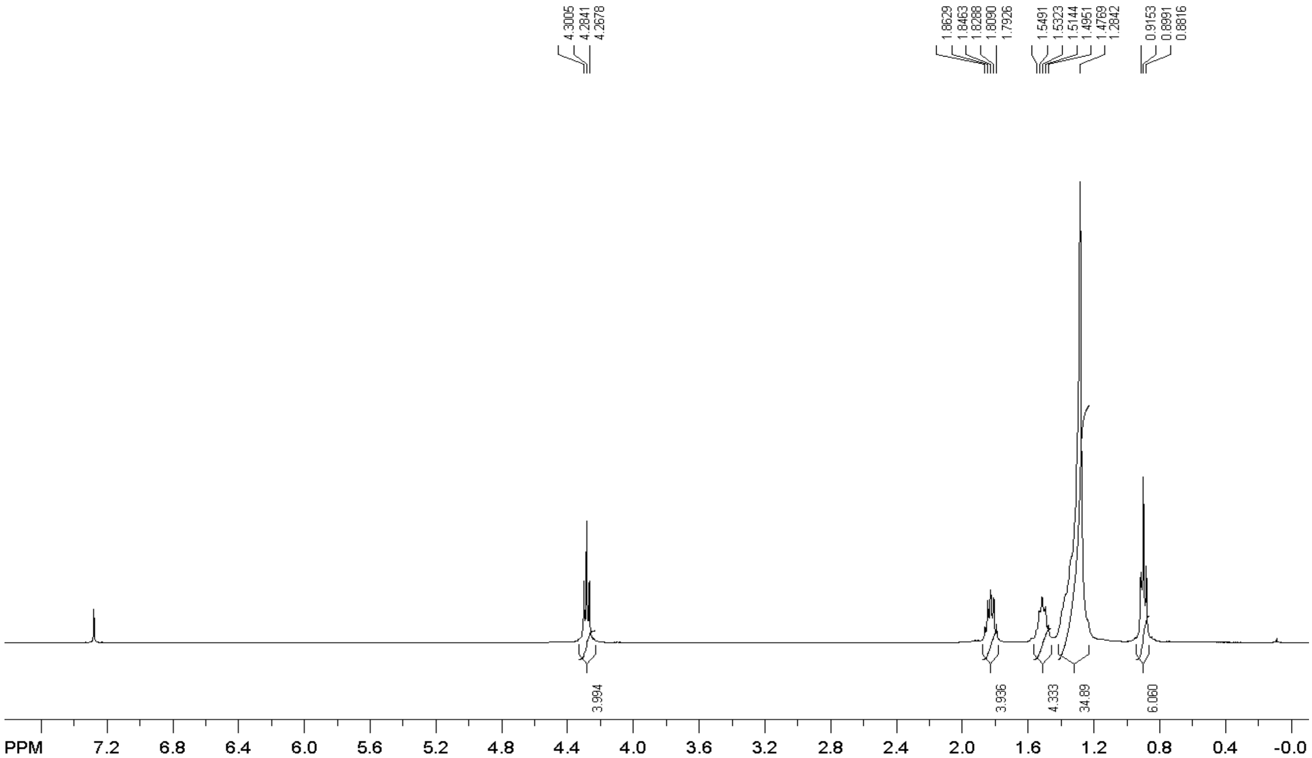

Fig. S1 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 6.

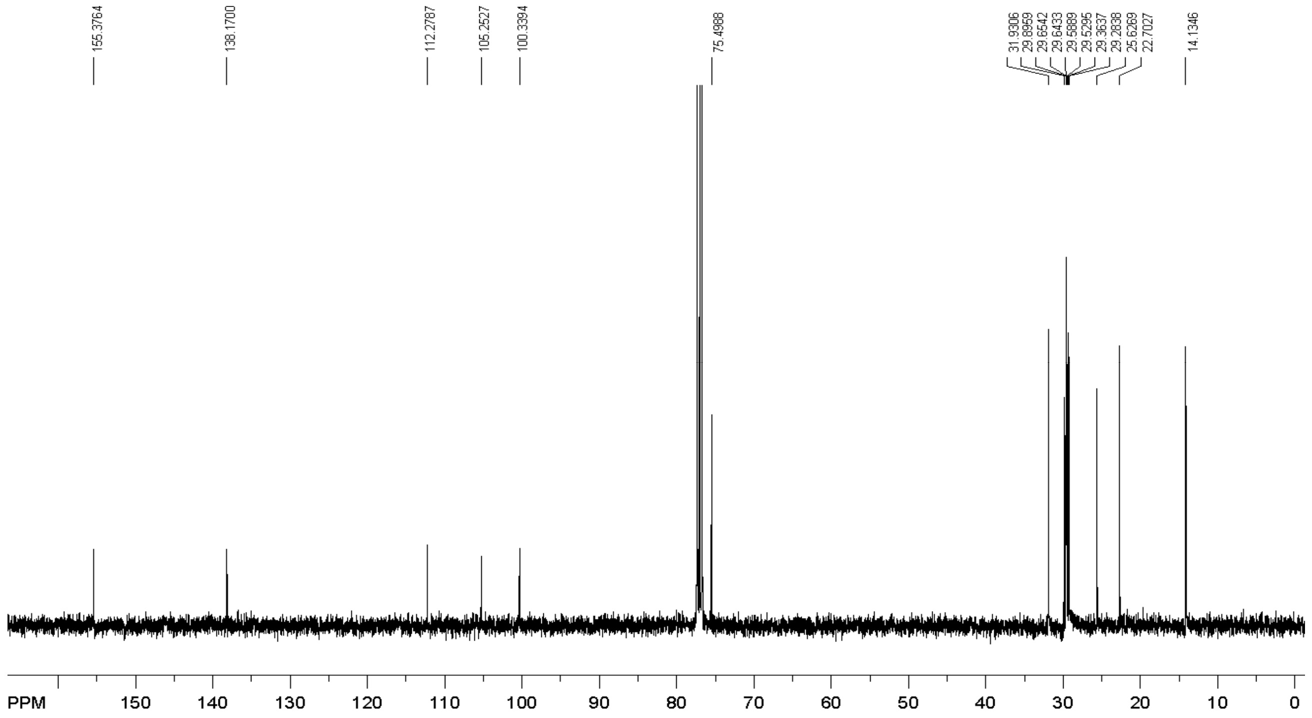

Fig. S2 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 6.

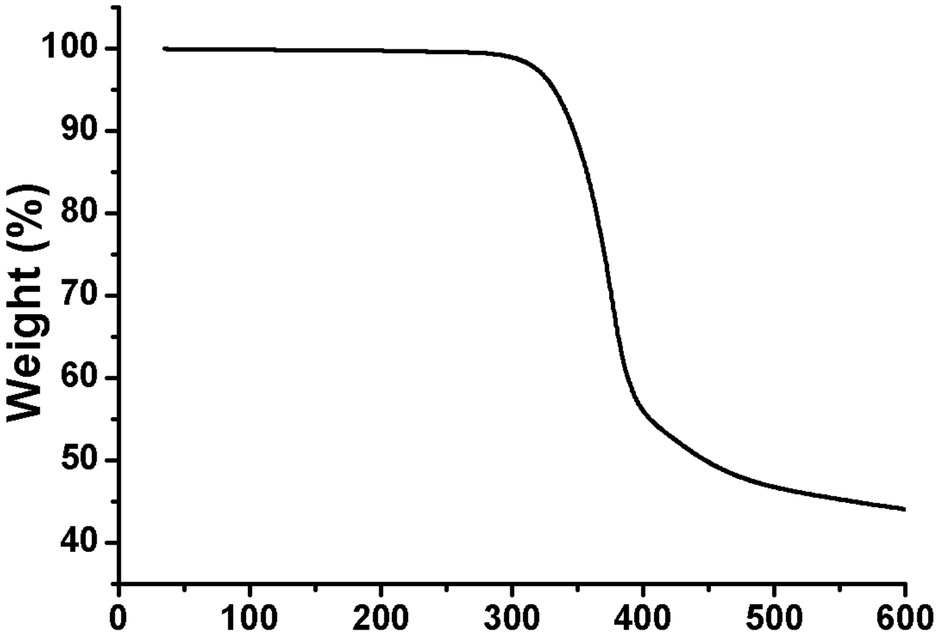

Fig. S3 TGA curve of PBDT-CT with a heating rate of 10 °C min^{-1} under a N_2 atmosphere.

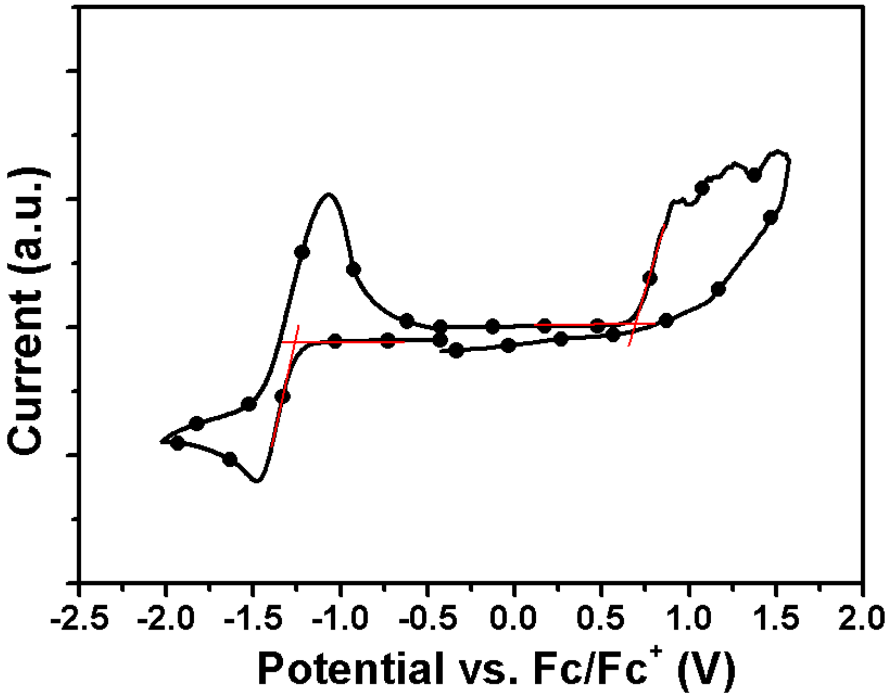

Fig. S4 Cyclic voltammogram of PBDT-CT.

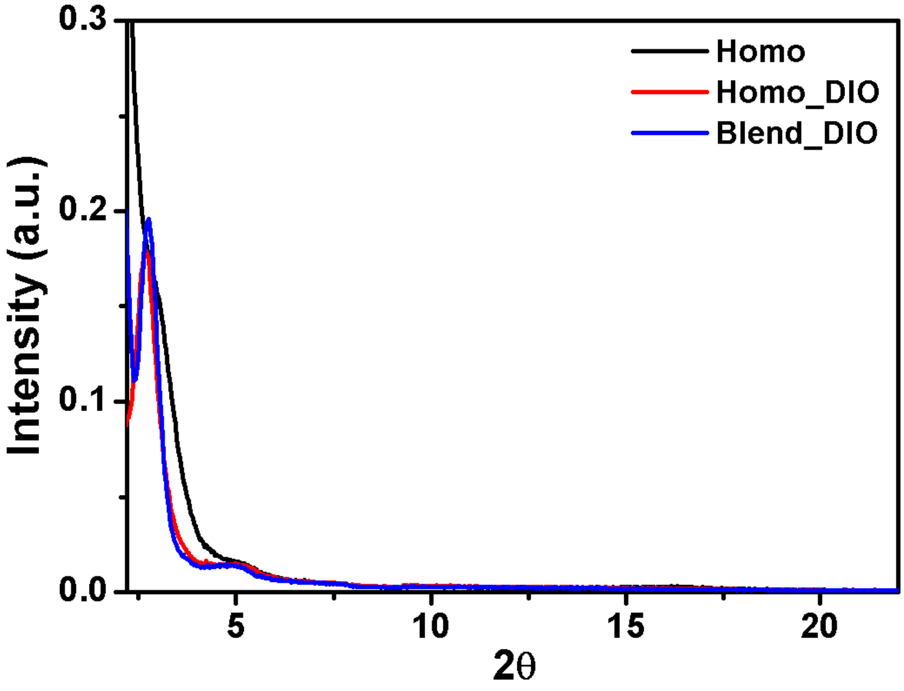

Fig. S5 X-ray scattering spectrum of PBDT-CT.

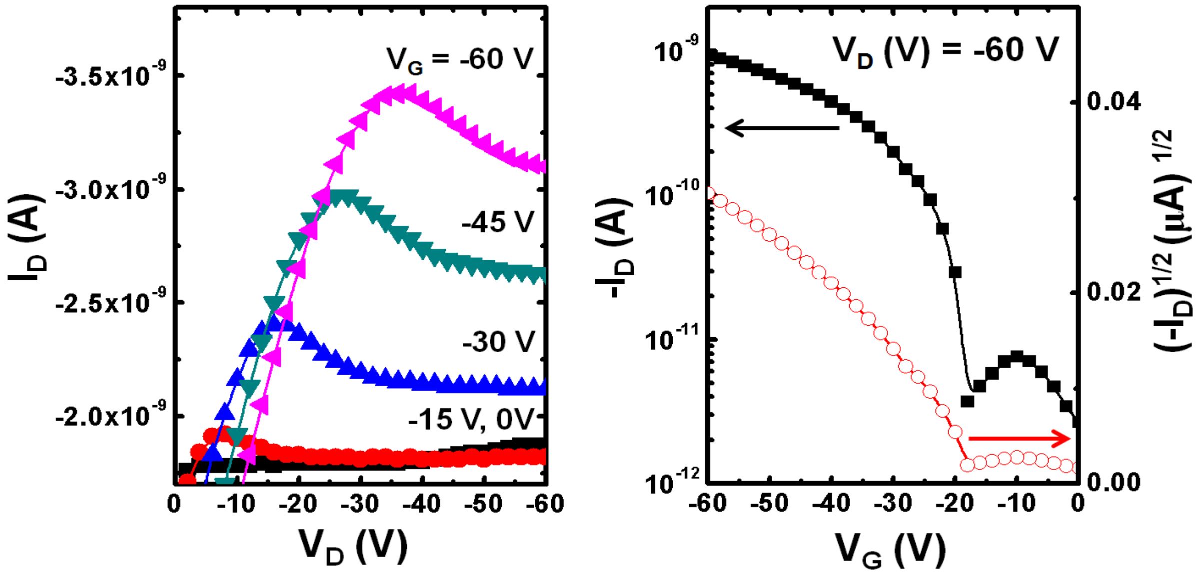

Fig. S6 Field effect transistor (FET) properties of PBDT-CT.

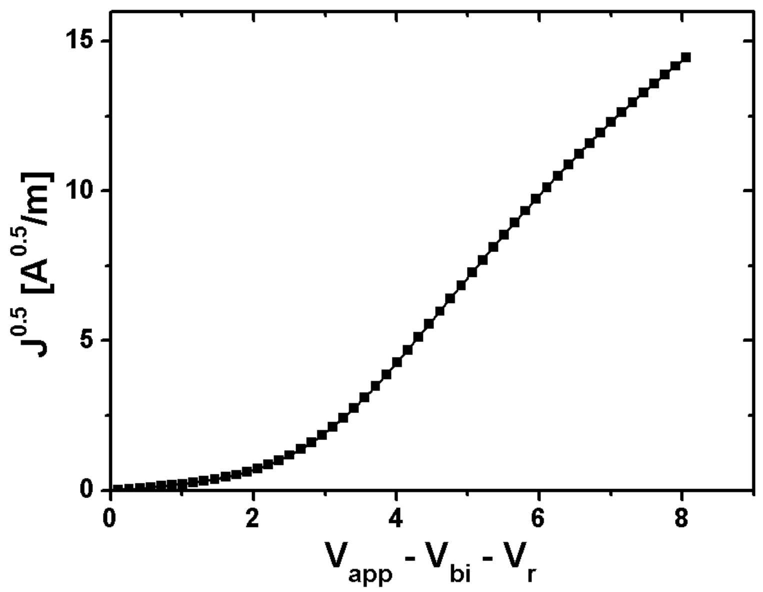

Fig. S7 $J^{0.5}$ vs V plot of the hole-only devices based on PBDT-CT:$PC_{61}BM$.

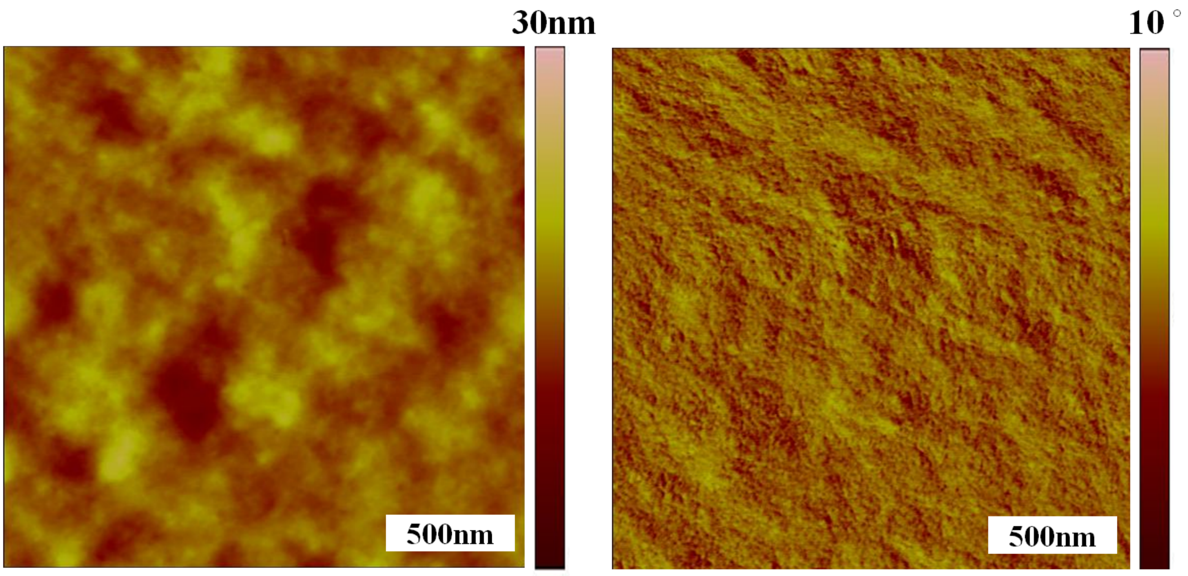

Fig. S8 AFM topography (left) and phase (right) images of the PBDT-CT:$PC_{61}BM$ film with DIO. The vertical scale bars are 30 nm in the height images and 10° in the phase images.

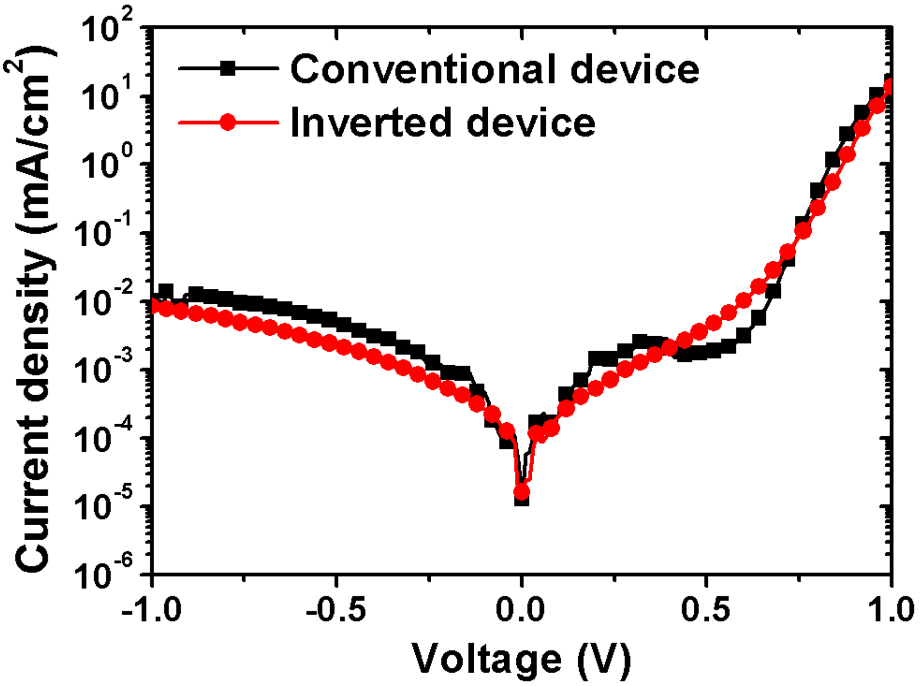

Fig. S9 Dark current density of polymer solar cell based on PBDT-CT:PC$_{61}$BM.

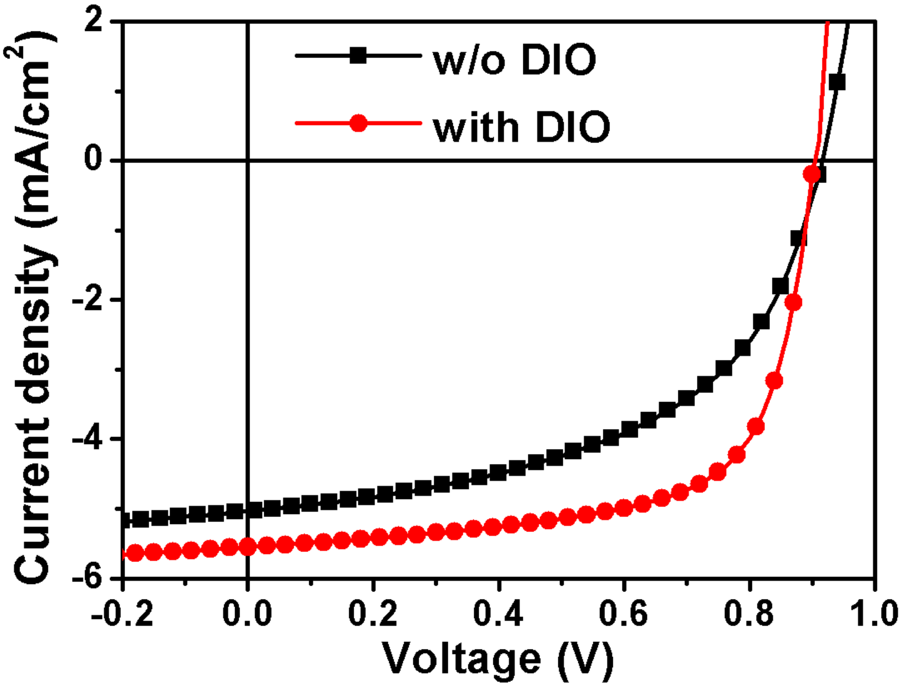

Fig. S10 *J*-*V* curves of polymer solar cell based on PBDT-CT:PC$_{61}$BM without and with DIO.