Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Effects of Conformational Symmetry in Conjugated Side Chains on Intermolecular Packing of Conjugated Polymers and Photovoltaic Properties

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1. Experimental

Characterizations. All monomers were characterized using 1H NMR (400 MHz) and 13C NMR (100 MHz) on a Bruker AVANCE 400 spectrometer in chloroform-d solutions at room temperature. All polymers were characterized using 1H NMR (500 MHz) on a Bruker DRX 500 spectrometer in *o*-dichlorobenzene-d4 at 383K. Number-average (M_n) and weight-average (M_w) molecular weights were determined by gel permeation chromatography (GPC, Shimadzu) in CB at 80 °C.

Electrochemistry. Electrochemical cyclic voltammetry (CV) was conducted on a PowerLab/AD instrument model system (glassy carbon disk as working electrode, Pt wire as counter electrode, Ag/AgCl as reference electrode) in a 0.1 M tetrabutyl ammonium hexafluorophosphate ($n\text{-}Bu_4NPF_6$)-anhydrous acetonitrile solution at a potential scan rate of 50 mV s^{-1} . Polymer film was drop cast onto the glassy carbon working electrode from a 2.0 mg mL^{-1} hot CB solution and dried under nitrogen prior to measurements. The electrochemical onsets were determined at the position at which the current starts to differ from the baseline. The potential of the Ag/AgCl reference electrode was internally calibrated using the ferrocene/ferrocenium redox couple (Fc/Fc+). The energy levels were estimated: HOMO = $-(4.80 + E_{\text{onset, ox}})$, and LUMO = $-(4.80 + E_{\text{onset, red}})$.

Computational Studies. Density functional theory (DFT) calculations were performed using Gaussian 09 software package to obtain an in-depth understanding of the electronic structure of the polymer. Hybrid three-parameter B3LYP functional combined with the 6-31G (d) basis set was used to obtain the optimized structures at the singlet ground state. For simplicity, the 2-butyloctyl- and 2-ethylhexyl chains appended to the conjugated backbone and side aromatic groups were trimmed with methyl chains at the branch positions. HOMO and LUMO energy levels were analyzed using minimized singlet geometries to approximate the ground state.

Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) analysis. Grazing incidence X-ray Wide Angle X-ray Scattering (GIWAXS) measurements were performed using Beamline 3C, 9A at the Pohang Accelerator Laboratory (PAL). The two dimensional GIXS images from the films were analyzed according to the relationship $q = 2\pi/d$ between the scattering vector q and the d spacing. The GIWAXS images shown are normalized with respect to exposure time.

Synthesis of Monomers

4,8-Bis(5-(2-butyloctyloxy)thiophene-2-yl)benzo[1,2-b;4,5-b']dithiophene (5). Under nitrogen atmosphere, 2-(2-butyloctyloxy) thiophene (1) (2.68 g, 10.0 mmol) was dissolved in dry THF (40 mL) and then n-butyllithium solution (11.0 mmol, 6.88 mL, 1.6 M in n-hexane) was added dropwise at -78 °C. After addition, the reaction mixture was maintained at -78 °C for 2 h, followed by the addition of benzo[1,2-b:4,5-b′]dithiophene-4,8-dione (4) (0.55 g, 2.5 mmol) and allowed to warm to 55 °C for 2 h. The solution was cooled down and then SnCl2·2H2O (4.5 g, 20 mmol) in 10% aqueous HCl (12.5 mL) was added. The solution was refluxed for 6 h and then the cooled the mixture was poured into water and extracted with dichloromethane, the organic extraction was washed successively with water and sodium bicarbonate solution twice and the combined organic phase was dried over magnesium sulfate and evaporated to afford the crude product. The crude product was purified on a silica gel column, eluting with pure hexane. Pale yellow viscous oil was obtained. (1.15 g, yield 63%). 1H NMR ($CDCl_3$, 400MHz), δ (ppm): 7.68 (d, 2H), 7.46 (d, 2H), 7.12 (d, 2H), 6.33 (d, 2H), 4.04 (d, 4H), 1.84 (m, 2H), 1.54–1.25 (br, 32H), 0.98–0.87 (m, 12H). 13CNMR (CDCl3, 100 MHz), δ (ppm): 166.86,139.34, 136.79, 127.55, 126.02, 125.74, 123.94, 123.54, 104.65, 38.24, 31.99, 31.36, 31.12,31.03, 29.78, 29.19, 26.95, 23.32, 23.19, 2.83, 14.26.

2,6-Bis(trimethyltin)-4,8-bis(5-(2-butyloctyloxy)thiophene-2-yl)benzo[1,2-b;4,5-b']dithiophene (M1). A solution of compound (5) in dry THF (40 ml) was stirred under nitrogen gas for 30 min, and then 2.5M n-butyllithium solution in hexane (3 ml) was added dropwise at -78 °C. Then the solution was kept at -78 °C for 1 h, and 1.0 M trimethyltin chloride solution in THF (10ml) was added. Then the solution was allowed to warm up to room temperature and stirred overnight. The mixture was poured into water and extracted with ether. The organic phase was evaporated, and the crude product was purified by recrystallization in ethanol to afford pale yellow needles (1.62 g, yield 74%). 1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.70 (s, 2H), 7.12 (d, 2H), 6.34 (d, 2H), 4.04 (d, 4H), 1.84 (m, 2H), 1.5–1.26 (br, 32H), 0.97– 0.86 (m, 12H), 0.40 (s, 18H). 13CNMR (CDCl3, 100 MHz), δ (ppm): 166.65, 143.66, 142.42, 137.64, 131.28, 126.23, 125.82, 122.30, 104.50, 38.29, 32.02, 31.74, 31.58, 31.21, 29.82, 29.13, 28.43, 26.98, 23.20, 22.84, 14.28, -8.16. Elemental analysis: calcd: C48H74O2S4Sn2: C,54.97; H, 7.11; S, 12.23. found: C, 55.30; H, 7.17; S, 12.63.

1-Bromo-4-(2’-butyloctyloxy)benzene (3). Under nitrogen atmosph ere, 4-Bromophenol (8.0 g, 46 mmmol), K_2CO_3 (7.03 g, 51 mmol) were put into three-neck round bottom flask with 100ml DMSO. 1-Bromo-butyloctane (2) (12.7 g, 51 mmol) was added dropwise in room temperature. The mixture was stirred 48h and the mixture was poured into 200ml ice cold water and then extracted with ethylacetate three times. Organic layer was washed with water and dried over magnesium sulfate and evaporated to get crude product. The crude product was purified on a silica gel column with hexane. Clear oil is obtained (14.8 g, 85 %). 1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.36 (d, 2H); 6.78 (d, 2H); 3.80 (d, 2H); 1.77 (m, 1H); 1.54–1.25 (m, 16H); 0.92 (s, 6H)

4,8-Bis(4-butyloctyloxy-1-phenyl)-benzo[1,2-b:4,5-b’]-dithiophene (6). Under nitrogen atmosphere, 1-bromo-4-(2-butyloctyloxy) benzene (3) (7.87 g, 27.6 mmol) was dissolved in dry THF (40 mL) and then n-butyllithium solution (18 mmol, 11.25 mL, 1.6 M in n-hexane) was added dropwise at -78 °C. After addition, the reaction mixture was maintained at -78 °C for 2 h, followed by the addition of benzo[1,2-b:4,5-b′]dithiophene-4,8-dione (4) (1.32 g, 6 mmol) and allowed to warm to 55 °C for 2 h. The solution was cooled down and then SnCl2·2H2O (10.83 g, 48 mmol) in 10% aqueous HCl (12.5 mL) was added. The solution was refluxed for 6 h and then the cooled the mixture was poured into water and extracted with dichloromethane, the organic extraction was washed successively with water and sodium bicarbonate solution twice and the combined organic phase was dried over magnesium sulfate and evaporated to afford the crude product. The crude product was purified on a silica gel column, eluting with pure hexane. White crystals were obtained (2.13 g, 50% yield). 1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.62 (d, 4H), 7.36 (m, 4H), 7.09 (d, 4H), 3.95 (d, 4H), 1.84 (m, 2H), 1.56–1.28 (br, 32H), 0.92 (m, 12H)

2,6-Bis(trimethyltin)-4,8-Bis(4-butyloctyloxy-1-phenyl)-benzo[1,2-b:4,5-b’]-dithiophene (M2). A solution of compound (6) in dry THF (40 ml) was stirred under nitrogen gas for 30 min, and then 2.5M n-butyllithium solution in hexane (3 ml) was added dropwise at -78 °C. Then the solution was kept at -78 °C for 1 h, and 1.0 M trimethyltin chloride solution in THF (10ml) was added. Then the solution was allowed to warm up to room temperature and stirred overnight. The mixture was poured into water and extracted with ether. The organic phase was evaporated, and the crude product was purified by recrystallization in ethanol to afford pale yellow needles (1.62 g, yield 74%). 1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.65 (d, 4H), 7.38 (s, 2H), 7.10 (d, 4H), 3.96 (d, 4H), 1.83 (m, 2H), 1.58-1.28 (br, 32H), 0.93 (m, 12H), 0.35 (t, 18H). 13CNMR (CDCl3, 100 MHz), δ (ppm): 159.06, 141.61, 137.07, 132.05, 130.56, 128.45, 114.65, 70.91, 38.09, 31.90, 29.74, 29.15, 26.91, 23.11, 22.71, 14.14, 8.37. Elemental analysis: calcd : C48H74O2S4Sn2 : C, 60.24 ; H, 7.58 ; S, 6.19 found : C, 60.59 ; H, 7.45 ; S, 6.16

SCLC measurement. The electron-only devices with (ITO/Al/polymers:$PC_{71}BM$/Al) architecture and the hole-only devices with (ITO/MoO_3/PBDT2FBTs:$PC_{71}BM$/MoO_3/Ag) architecture were fabricated. The electrical characteristics were measured with a source/measure unit (Keithley 4200) in a N_2-filled glove box. I-V curves were fitted by using the Mott-Gurney square law.[1] $J = (9/8)\,\varepsilon\mu\,(V^2/L^3)$, where ε is the static dielectric constant of the medium and μ is thecarrier mobility.

2. References

(1) Mott, N. F.; Gurney, R. W. Electronic Processes in Ionic Crystals,1st ed; Oxford University Press: London, **1940**.

3. Supporting Figures

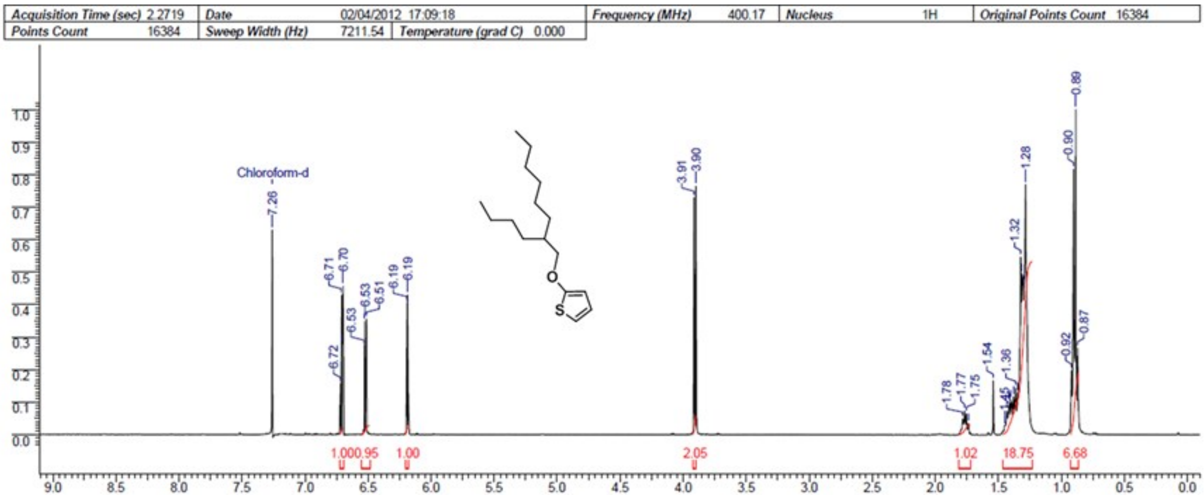


Figure S1. ^{1}H NMR (400 MHz, chlorofrom-d) spectrum of 1 at 298K.

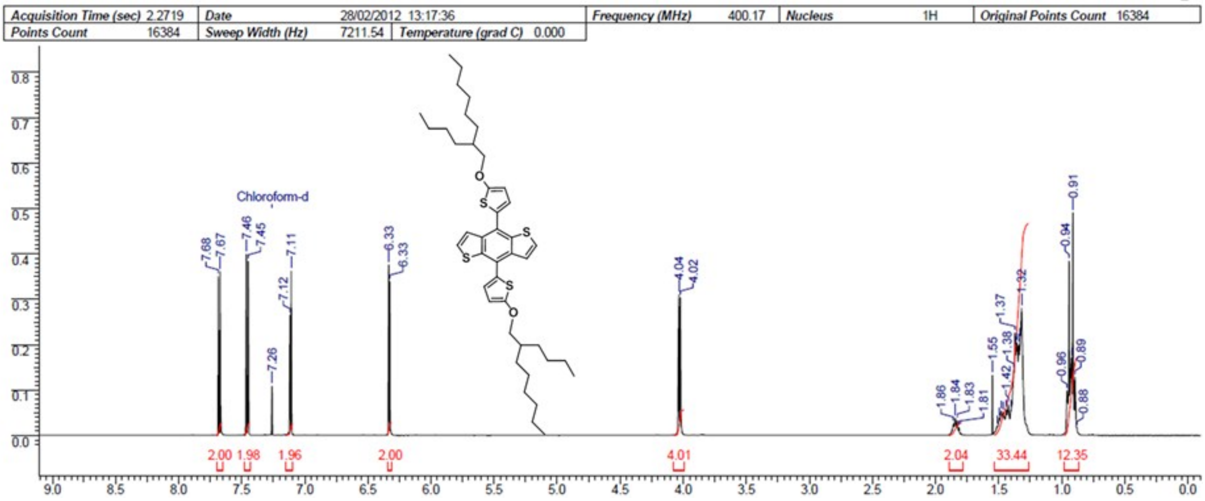
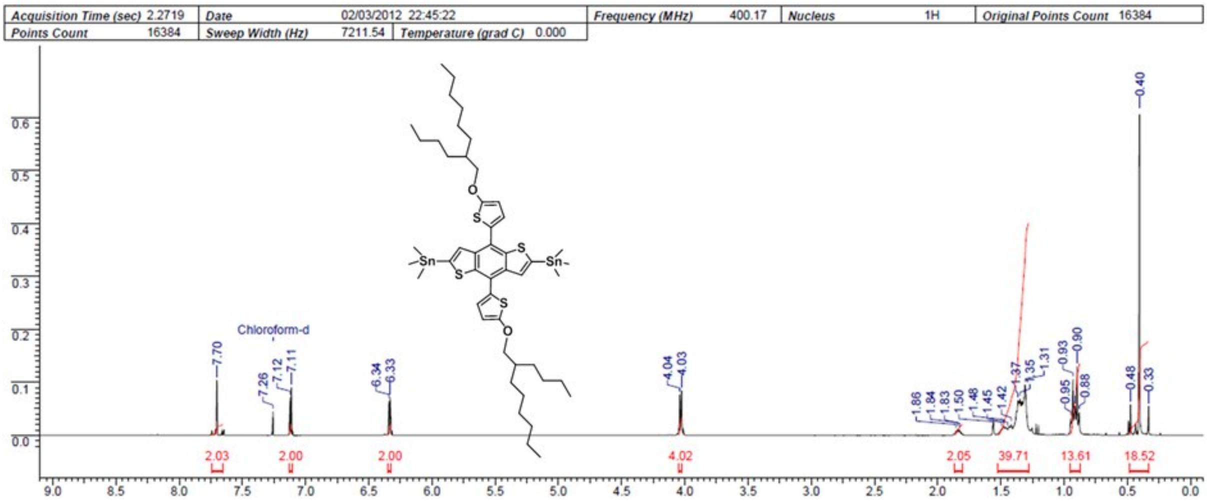


Figure S2. ^{1}H NMR (400 MHz, chlorofrom-d) spectrum of 5 at 298K



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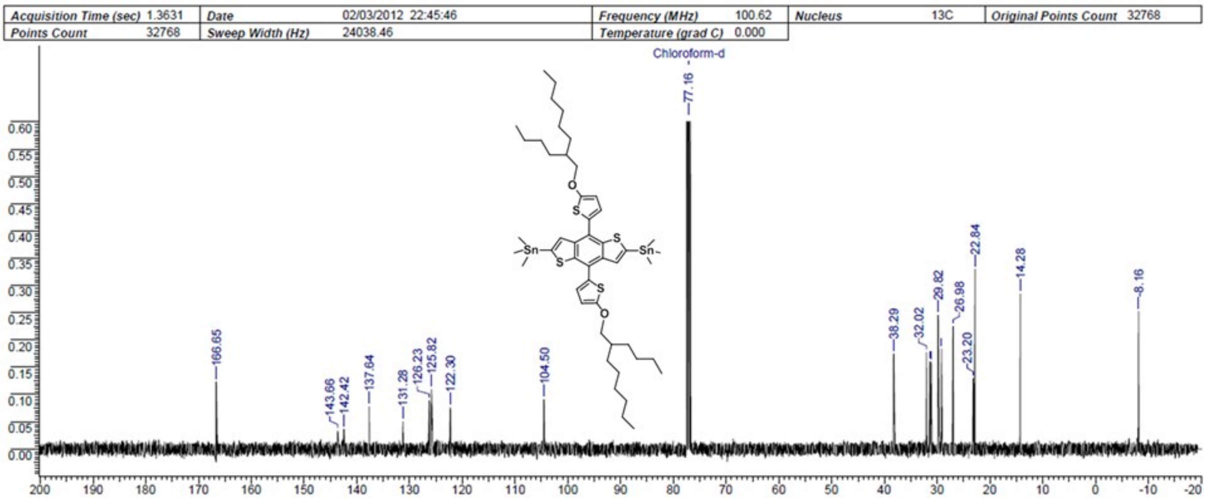

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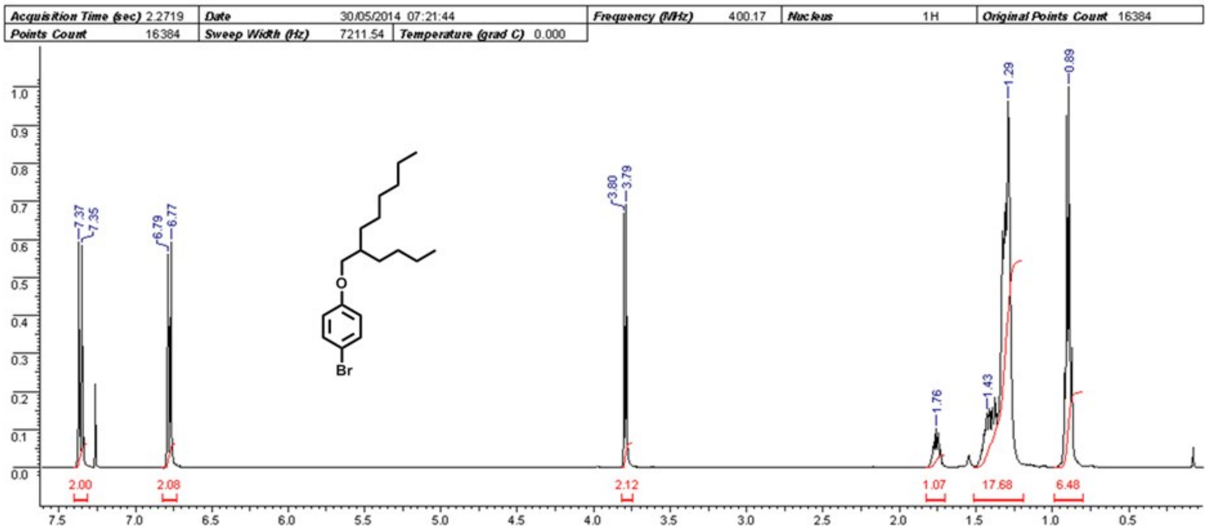

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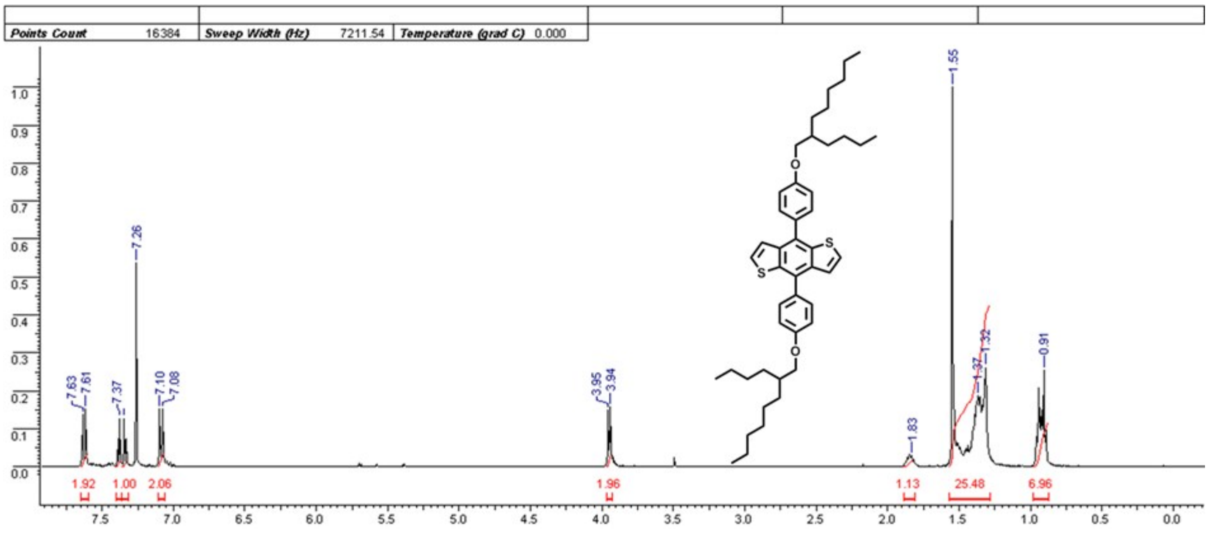

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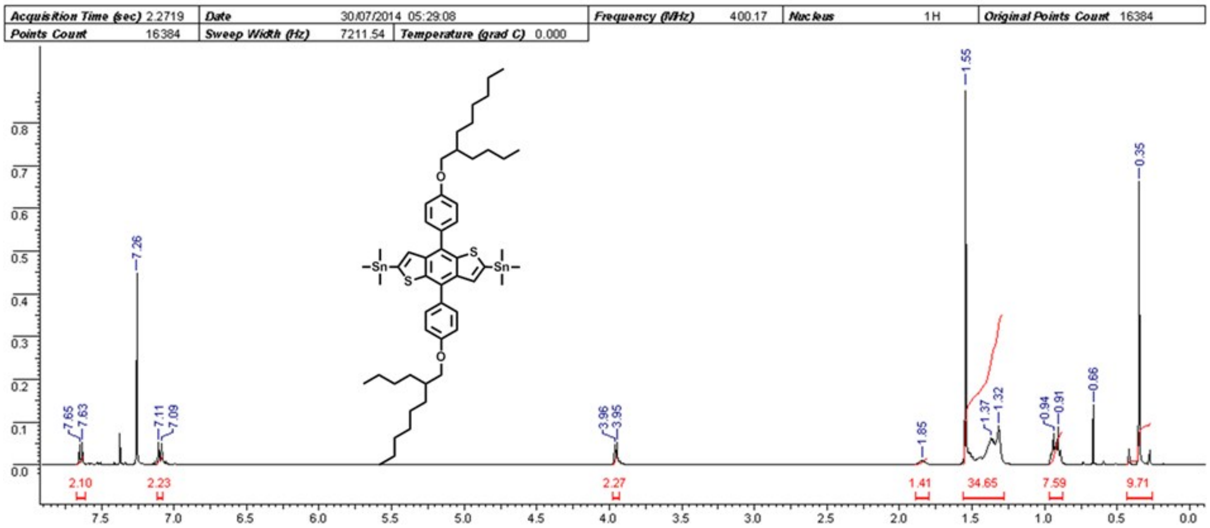


Figure S7. ^{1}H NMR (400 MHz, chlorofrom-d) spectrum of M2 at 298K

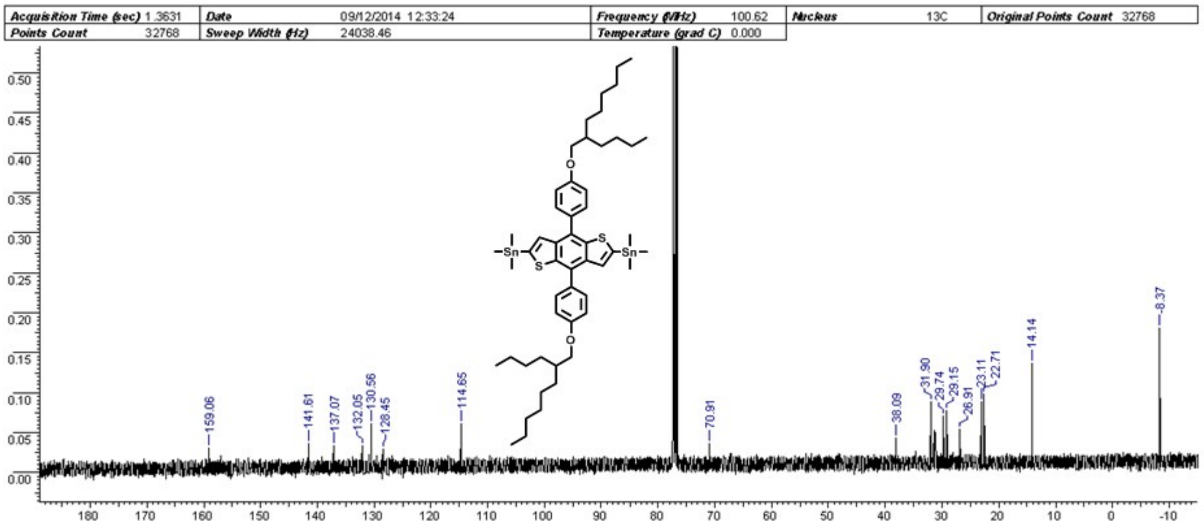


Figure S8. ^{1}H NMR (400 MHz, chlorofrom-d) spectrum of M2 at 298K

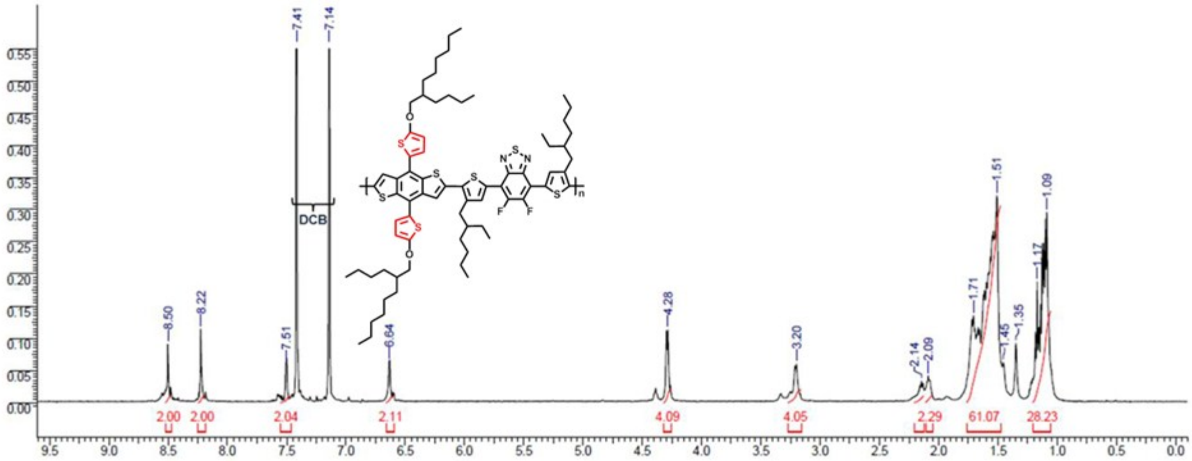


Figure S9. ^{1}H NMR (500 MHz, *o*-dichlorobenzene-d$_5$) spectrum of PBDT2FBT-Th at 383K

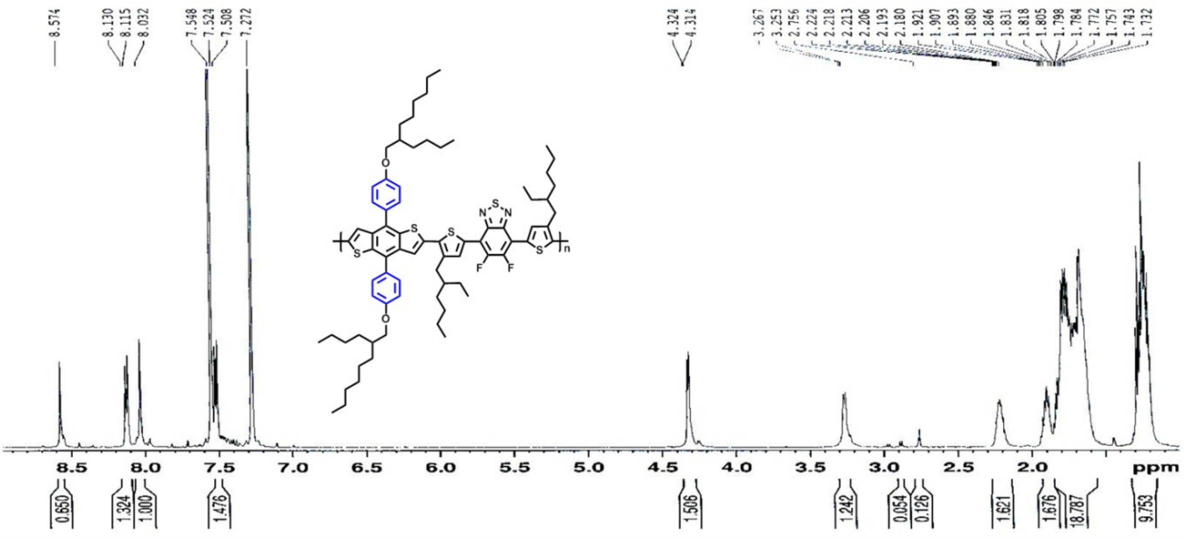


Figure S10. ^{1}H NMR (500 MHz, *o*-dichlorobenzene-d$_5$) spectrum of PBDT2FBT-Ph at 383K

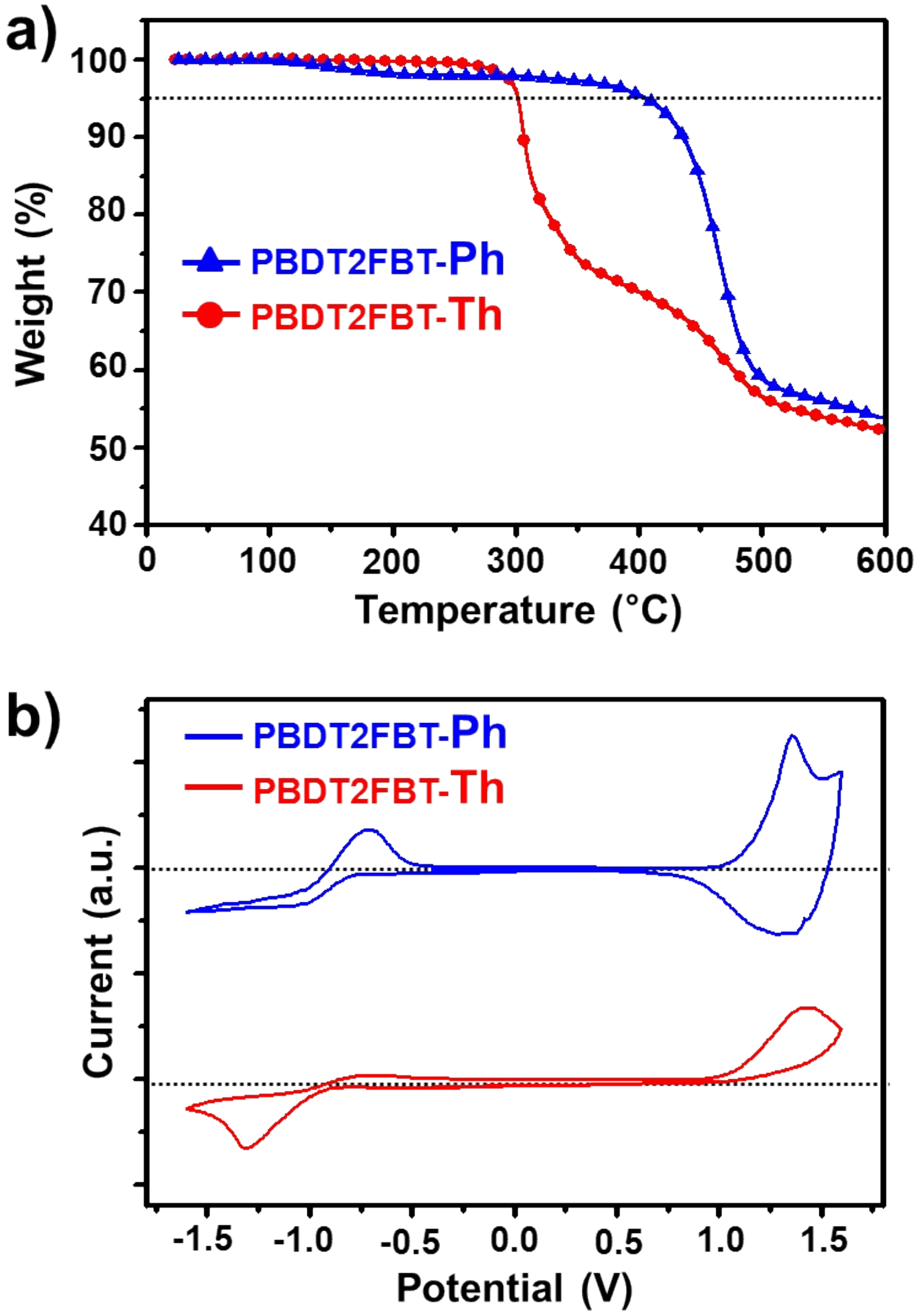


Figure S11. a) TGA plots of PBDT2FBT polymers with a heating rate of 10°C min^{-1}. b) Cyclic voltammograms of the PBDT2FBT in the CH_3CN solutions at a scan rate of 50 mVs^{-1}.

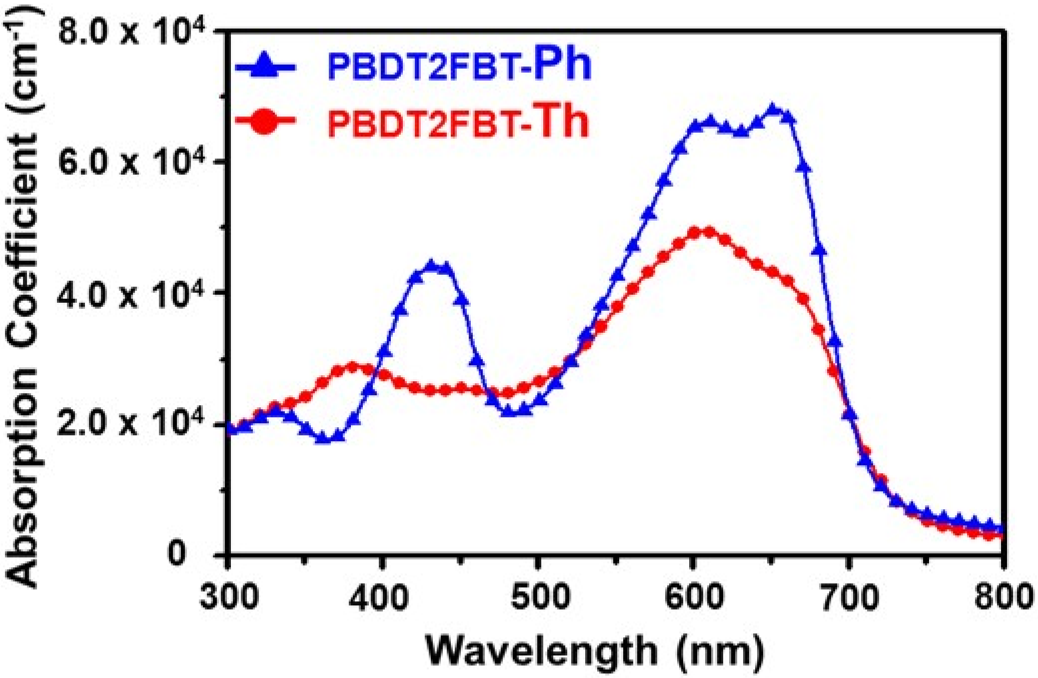


Figure S12. The absorption coefficient of the neat polymer films. The thickness of the polymer films were 30nm for PBDT2FBT-Th, 32 nm for PBDT2FBT-Ph.

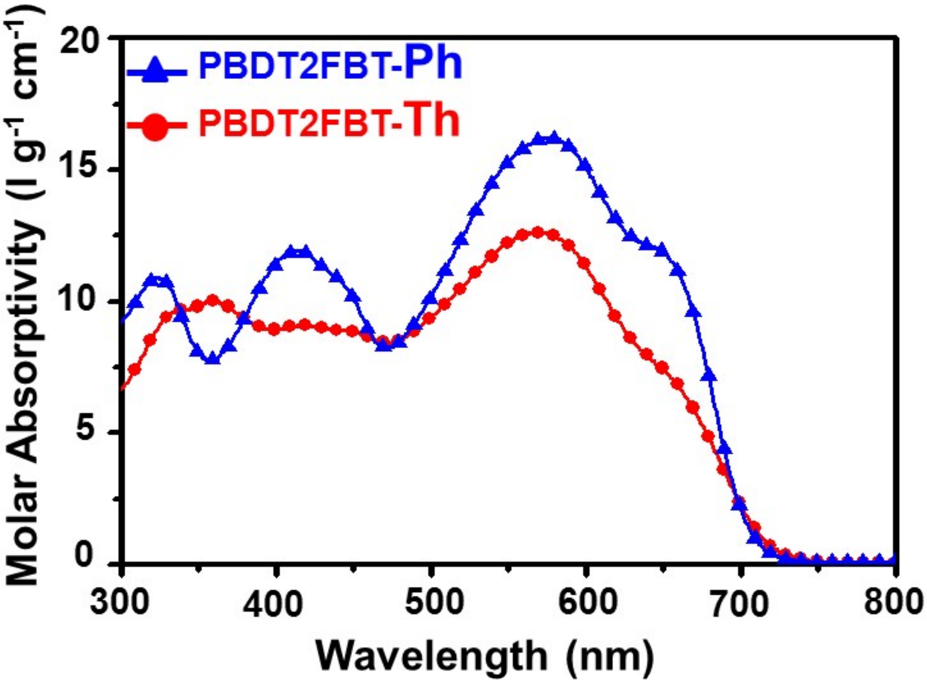


Figure S13. The calculated molar absorptivity of homo polymer in solution.

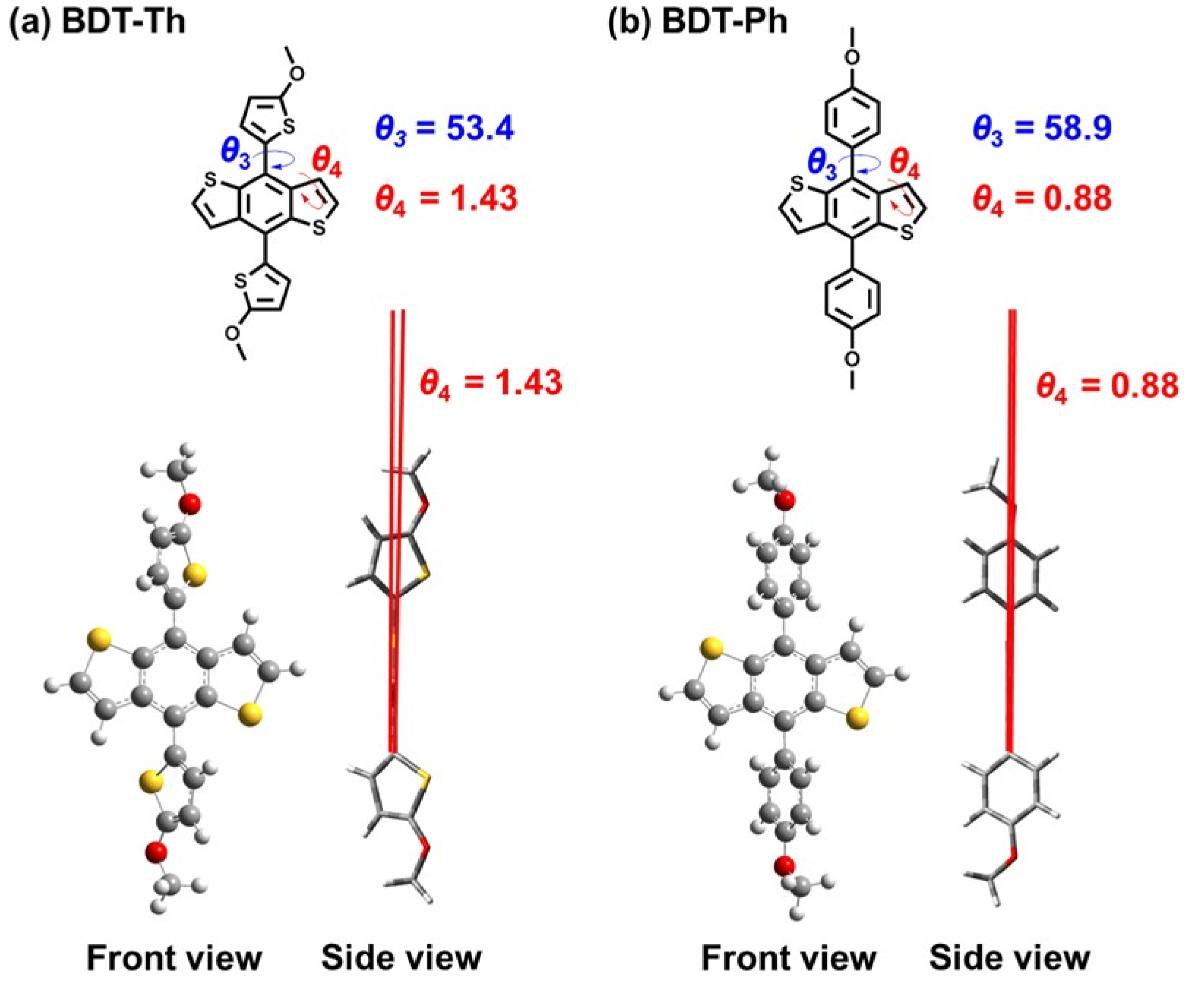
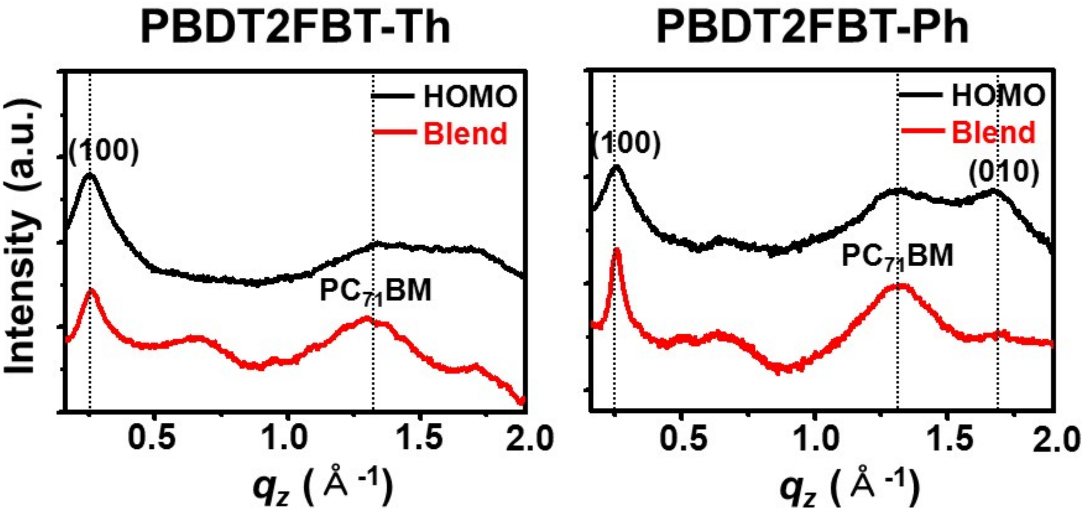


Figure S14. Calculated optimized geometries of donoating unit for (a) PBDT2FBT-Th and (b) PBDT2FBT-Ph.



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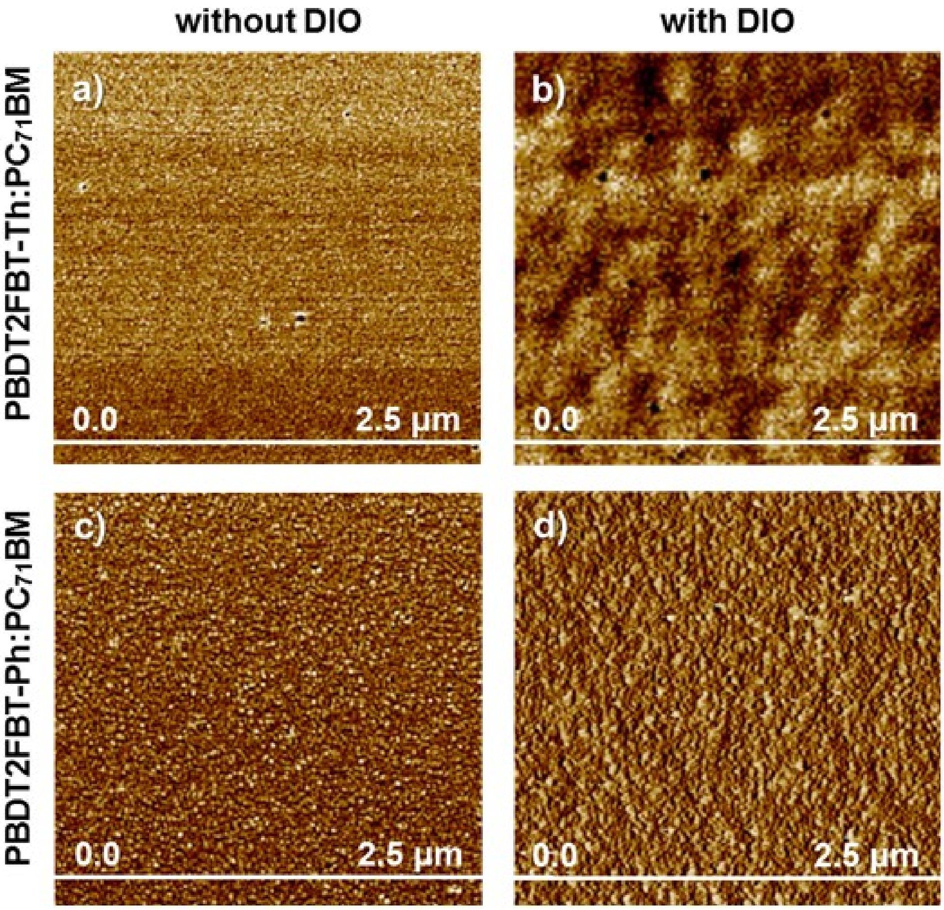

Figure S16. Atomic force microscopy (AFM) phase images (2.5 µm×2.5 µm) of as-cast polymers/PC$_{71}$BM (DIO) blend films prepared by DCB for a-b) PBDT2FBT-Th:PC71BM and PBDT2FBT-Ph:PC71BM. c-d) with DIO for PBDT2FBT-Th:PC71BM and PBDT2FBT-Ph:PC71BM.