

Supporting information

Novel polymer donor based on Dithieno [2,3- d:2',3'-d'']benzo [1,2-b:4,5-b']dithiophene for highly efficient polymer solar cells

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Experiment Section

Materials: 2,2'-((2Z,2'Z)-((4,4,9,9-tetrahexyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(methanylylidene))bis(3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (IDIC), 3,9-bis(2-methylene-((3-(1,1-dicyanomethylene)-6/7-methyl)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene (IT-M) was purchased from Solarmer Materials (Beijing) Inc and were used without any further purification.

Other chemicals were purchased from Sigma-Aldrich, Inc.

Synthesis Procedures of PDBT-F

3-bromo-2-(2-ethylhexyl)thiophene (2): 3-bromothiophene (1) (10 g, 0.061 mol) and anhydrous THF(100 ml) was added in a 250 ml argon purged flask. The system was put into -78 ° C then, LDA(36.8 ml, 0.073 mol) was added into flask dropwise. The mixture was kept at this temperature about 20 min. Then, 3-(bromomethyl) heptane (16.585 g, 0.085 mol) was added into solution. The mixture was stirred at this temperature for 30 min and then the cooling bath was removed. The reactant was continued stirred overnight. After stopping the reaction, the mixture was poured into water then, extracted by dichloromethane twice, and the organic phases were combined.

After removing solvent under vacuum, the residue was purified by chromatography on silica gel with hexane as eluent. The obtained liquid was further purified by reduced pressure distillation. The target product was gained as a colorless oil. ^1H NMR (400MHz, CDCl_3) δ 7.12 (d, 1H), δ 6.90 (d, 1H), 2.75 (d, 2H), δ 1.67 (m, 1H), δ 1.32 (m, 8H), δ 0.92 (d, 6H).

(4-bromo-5-(2-ethylhexyl)thiophen-2-yl)trimethylsilane (3): 3-bromo-2-(2-ethylhexyl)thiophene (2) (10 g, 0.036 mol) and anhydrous THF (100 ml) was added in a 250ml argon purged flask. The system was put into -78°C then, LDA(21.6 ml, 0.043 mol) was added into flask dropwise. The mixture was kept at this temperature about 20 min. Then, chlorotrimethylsilane (5.55 g, 0.051 mol) was added into solution. The mixture was stirred at this temperature for 30 min and then the cooling bath was removed. The reactant was continued stirred overnight. After stopping the reaction, the mixture was poured into water then, extracted by dichloromethane twice, and the organic phases were combined. After removing solvent under vacuum, the residue was purified by chromatography on silica gel with hexane as eluent. The target product was gained as a colorless oil. ^1H NMR (400MHz, CDCl_3) δ 7.00 (s, 1H), 2.75 (d, 2H), δ 1.67 (m, 1H), δ 1.32 (m, 8H), δ 0.92 (d, 6H), δ 0.29 (s, 9H).

(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)trimethylsilane (4): (4-bromo-5-(2-ethylhexyl)thiophen-2-yl)trimethylsilane (3) (10g, 0.029 mol) and anhydrous THF (100ml) was added in a 250 ml argon purged flask. The system was put into -78°C then, n-BuLi(26.98 ml, 0.044 mol) was added into flask dropwise. The mixture was kept at this temperature about 1 h. Then, NFSI (16.34 g, 0.052 mol) was added into solution. The mixture was stirred at this temperature for 30 min and then the cooling bath was removed. The reactant was continued stirred overnight. After stopping the reaction, the mixture was poured into water then, extracted by dichloromethane twice,

and the organic phases were combined. After removing solvent under vacuum, the residue was purified by chromatography on silica gel with hexane as eluent. The target product was gained as a colorless oil. ¹H NMR (400MHz, CDCl₃) δ 6.82 (s, 1H), 2.62 (d, 2H), δ 1.67 (m, 1H), δ 1.32 (m, 8H), δ 0.92 (d, 6H), δ 0.29 (s, 9H).

2-(2-ethylhexyl)-3-fluorothiophene (5): (5-(2-ethylhexyl)-4-fluorothiophen-2-yl)trimethylsilane (4) (5 g, 0.017mol) and TBAF (20.96 ml, 0.020 mol) were solve in THF (50 ml) and stirred overnight. After stopping the reaction, the mixture was poured into water then, extracted by dichloromethane twice, and the organic phases were combined. After removing solvent under vacuum, the residue was purified by chromatography on silica gel with hexane as eluent. The target product was gained as a colorless oil. ¹H NMR (400MHz, CDCl₃) δ 6.96 (d, 1H), δ 6.72 (d, 1H), 2.66 (d, 2H), δ 1.54 (m, 1H),δ 1.28 (m, 8H), δ 0.88 (d, 6H).

5,10-bis(5-ethylhexyl-4-fluorothiophen-2-yl)dithieno[2,3-d:2',3'-d']benzo[1,2-b:4,5-

b']dithiophene (7): In a 50 mL argon purged flask, n-BuLi(2.2 ml, 5.5 mol) was added dropwise to a solution of 2-(2-ethylhexyl)-3-fluorothiophene (5) (0.9 g, 4.2 mmol) in THF (50 mL)at -78 °C. The mixture was then warmed to 50 °C and stirred for about 1.5 h. Subsequently, dithieno[2,3-d:2',3'-d']benzo[1,2-b:4,5-b']dithiophene-5,10-dione(0.47 g, 1.4 mmol) was added to the reaction mixture, which was then stirred for 1 h at 50 °C. After cooling the reaction mixture to ambient temperature, a mixture of SnCl₂·2H₂O (2.7 g, 12 mmol) in 36% HCl (1 mL) was added and the mixture was stirred for additional 1.5 h, after which it was poured into ice water. The mixture was extracted with diethyl ether (3 × 50 mL), and the organic phases were combined. After removing solvent under vacuum, the residue was purified by flash chromatography on silica gel with hexane as eluent to give target objective as light yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, 2H),

7.25 (d, 2H), 7.03 (d, 2H), 2.86 (d,4H), 1.70 (m, 2H), 1.68–1.38 (m, 16H), 1.06–0.88 (t, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 155.71, 153.18, 143.27, 139.25, 133.28, 131.56, 129.78, 123.65, 123.25, 119.93, 118.50, 41.03, 32.49, 29.20, 28.94, 25.81, 23.12, 14.23, 10.94.

5,10-bis(5-ethylhexyl-4-fluorothiophen-2-yl)dithieno[2,3-d:2',3'-d']benzo[1,2-b:4,5-

b']dithiophene -2,7-dibromo (Monomer DTBDT): 5,10-bis(5-ethylhexyl-4-fluorothiophen-2-yl)dithieno[2,3-d:2',3'-d']benzo[1,2-b:4,5-b']dithiophene (7) was added into the mixture of CHCl₃ and HOAc (1:1), then the mixture was stirred overnight. After stopping the reaction, the mixture was poured into water then, extracted by dichloromethane twice, and the organic phases were combined. After removing solvent under vacuum, the residue was purified by chromatography on silica gel with hexane as eluent. The target product was gained as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.26 (d, 2H), 7.00 (d, 2H), 2.86 (d,4H), 1.70 (m, 2H), 1.68–1.38 (m, 16H), 1.06–0.88 (t, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 155.71, 153.17, 142.19, 138.21, 133.33, 131.02, 129.96, 124.20, 122.62, 118.81, 116.67, 41.08, 32.51, 29.33, 28.88, 25.87, 23.10, 14.21, 10.98.

poly{5,10-bis(5-ethylhexyl-4-fluorothiophen-2-yl)dithieno[2,3-d:2',3'-d']benzo[1,2-b:4,5-

b']dithiophene-co-1,3-bis(thiophen-2-yl)-5,7-bis(2-ethylhexyl)-4H,8H-benzo[1,2-c:4,5-c']

dithiophene - 4,8-dione} (PDBT-F): A mixture of 5,10-bis(5-ethylhexyl-4-fluorothiophen-2-yl)dithieno[2,3-d:2',3'-d']benzo[1,2-b:4,5-b']dithiophene -2,7-dibromo (60 mg, 0.067 mmol), BPP (63.34 mg, 0.067 mmol) in CB (4 mL) were purged by argon for 30 min, and then 4 mg of Pd(PPh₃)₄ was added. After being purged for another 20 min, the mixture was allowed to reflux for 12 h. After cooled to room temperature the polymer was precipitated in methanol. The crude product was collected by filtration and then purified by washing extracted on a soxhlet's extractor with methanol, acetone, hexane in succession. The final product was obtained by precipitating the chloroform

solution and then precipitated in methanol as dark blue powder. Weight average molecular weight (M_w) and polydispersity index (PDI) estimated from GPC are 342 kDa and 1.75, respectively

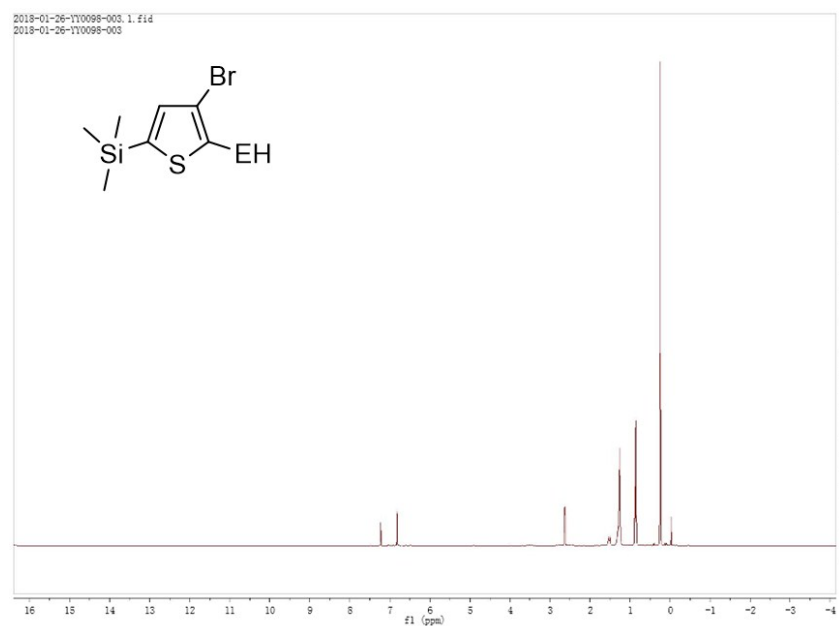
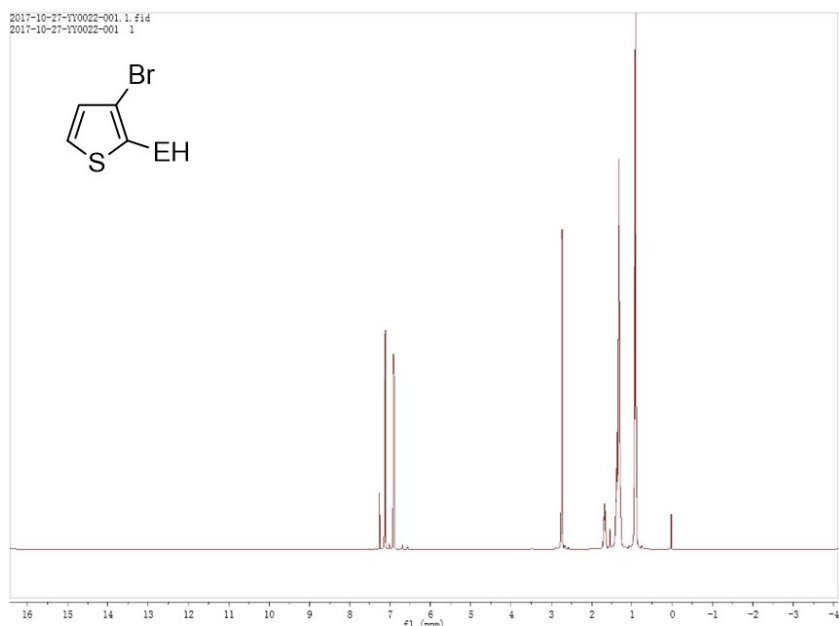
Characterization and Measurement

The chemical structure of compounds mentioned in this work were identified by ¹H NMR, (Avance DPX-300) and MALDI-TOF-MS (Autoflex III) with CDCl₃ as a solvent. The molecular weights of the materials were measured by a Bruker Autoflex III TOF mass spectrometer and SHIMADZULCMS-2010 spectrometer. The energy levels (HOMO and LUMO) of materials were calculated from the onset oxidation and reduction potentials which were detected by cyclic voltammetry (CV) with the film on a glassy carbon working electrode in 0.1 M [n-Bu₄N]⁺ [PF₆]⁻ CH₃CN solution at a potential scan rate of 100 mV s⁻¹, and according to the equation: E_{HOMO/LUMO} = -e(E_{ox/red} + 4.71)(eV), respectively. The UV-vis absorption spectra were measured by a Perkin-Elmer Lambda 950 spectrophotometer. The surface morphology of produced films were investigated by a Veeco Dimension 3100V atomic force microscope. The polymer weights were detected by GPC

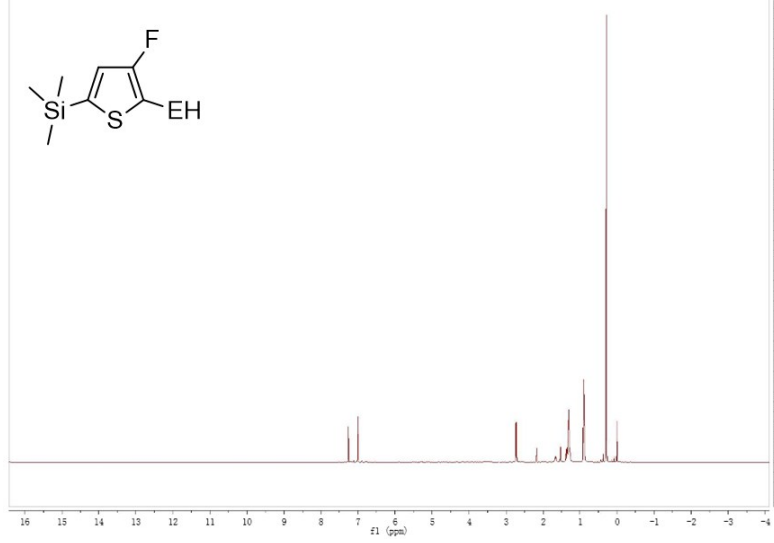
Device Fabrication and Characterization

The PSCs devices structure is followed: ITO glass/PEDOT: PSS/BHJ blend/PFN-Br/Al. The ITO glass as anode was cleaned by distilled water, acetone, isopropanol in ultrasonic cleaner and treated in a ultraviolet ozone chamber. The PEDOT:PSS aqueous solution was filtered through a 0.45 μm filter and spin-coated at 3000 rpm for 1 min onto the treated ITO substrate and annealed at 130 °C for 10 min. The solution of active layer prepared by adding the donor and acceptor with the giving ratio into chloroform. 1,8-diiodooctane (DIO) was used as additive. The active layer was spin-coated onto the PEDOT: PSS at 2400 rpm for 1 min and then thermal annealing at 100 °C for 10 min. The PFN-Br was coated onto the active layer at 3000 rpm for 1 min. Al was deposited about 100 nm

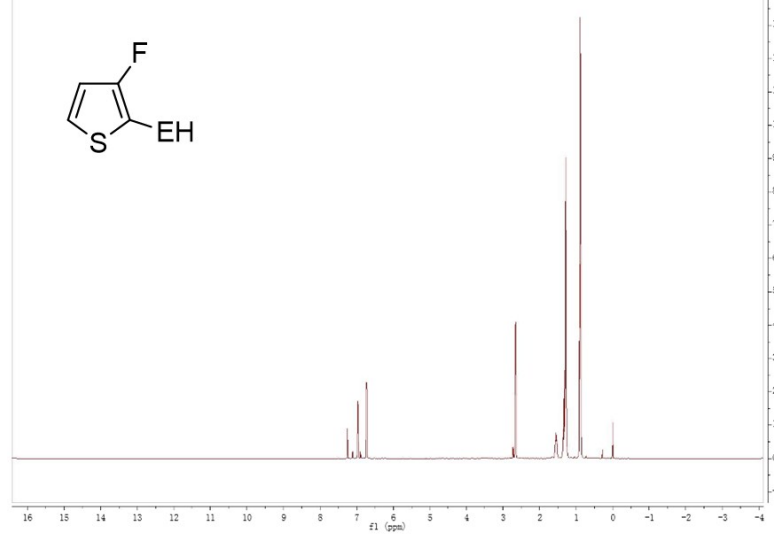
finally. Simulated solar light (100 mW cm² AM 1.5G) provided by a Newport-Oriel® Sol3A 450 W solar simulator was used to measure the photovoltaic characteristics of the devices under simulated solar light (100 mW cm² AM 1.5G). The EQE spectra were determined by a Newport-Oriel® IQE 200™ which was calibrated by a standard Si/Ge solar cell. The thickness of the active layer was investigated using a computer-controlled Dektak 150 Veeco.



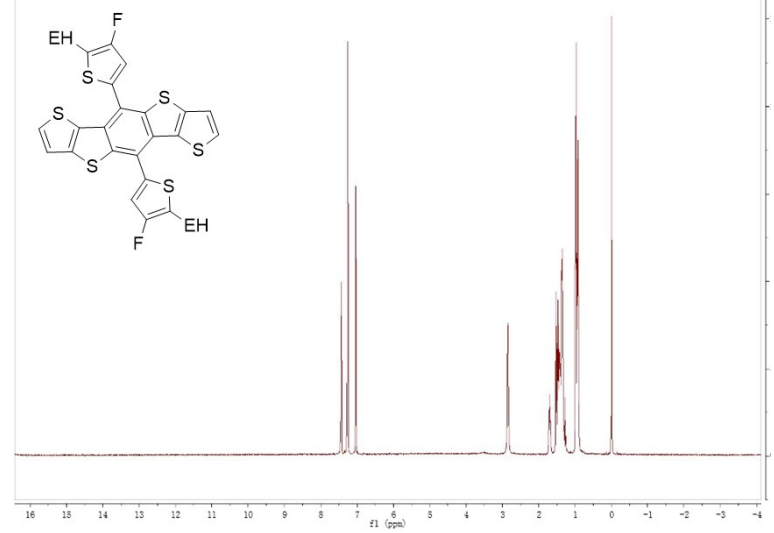
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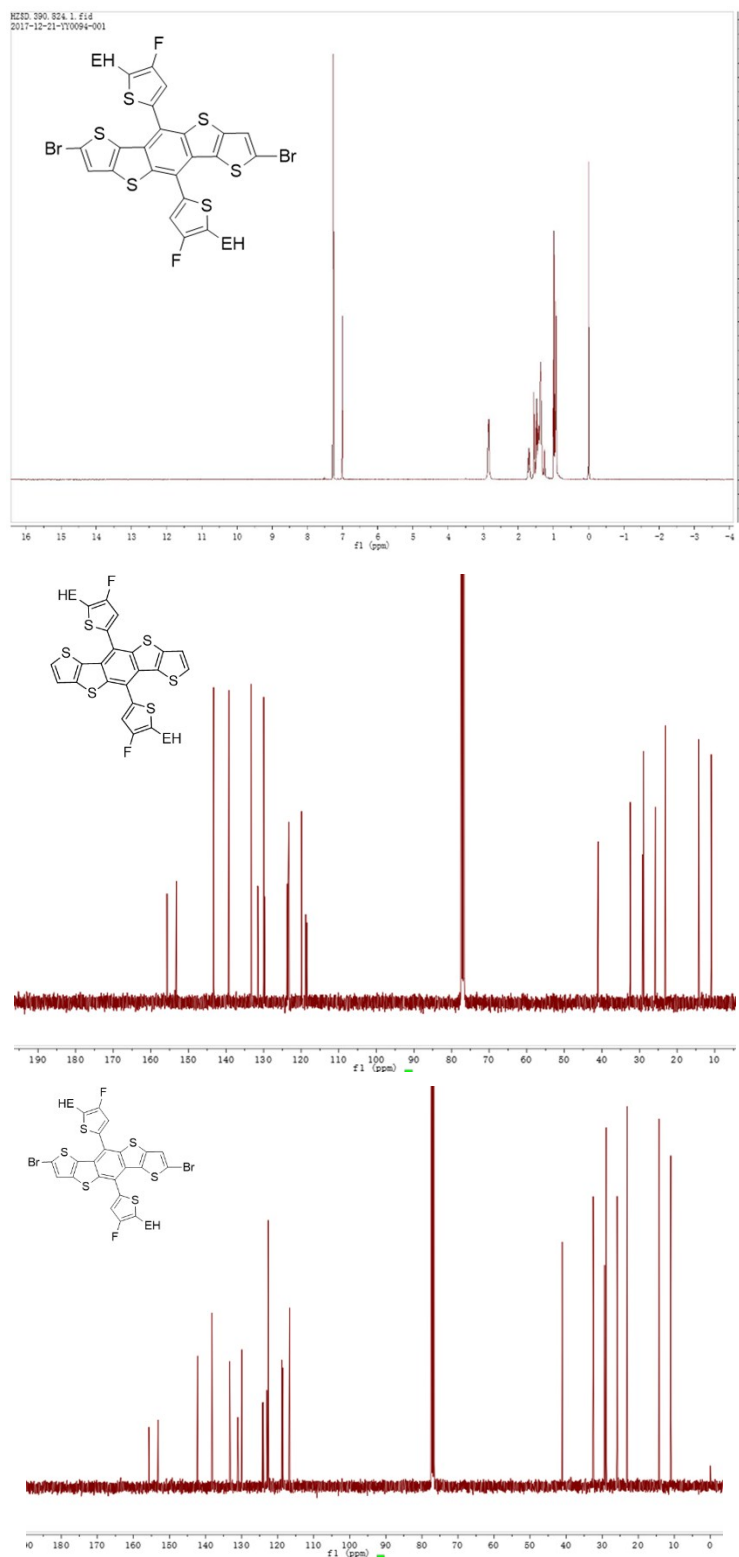


Figure S1 ^1H NMR and ^{13}C NMR spectra of product in synthesis procedure

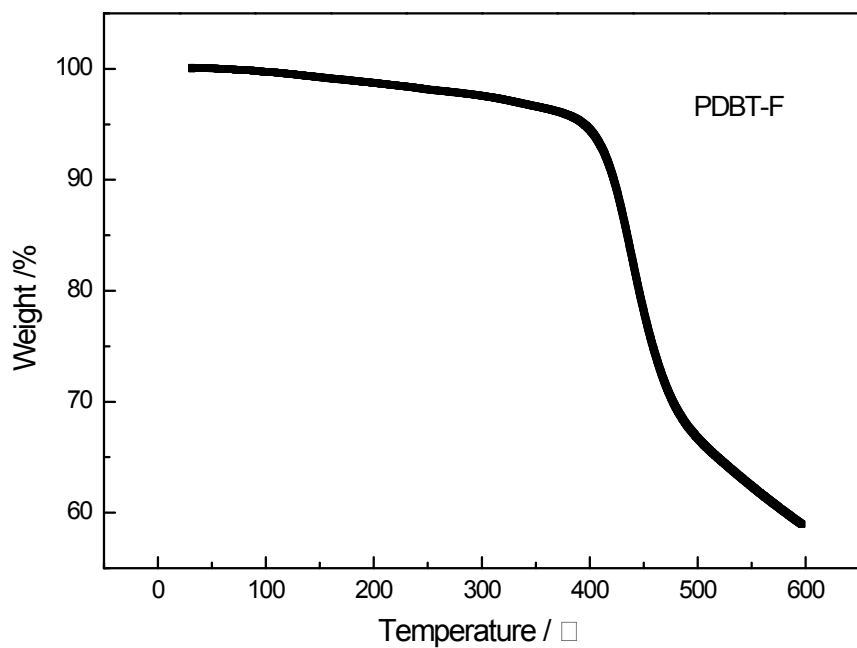


Figure S2 TGA plots of Polymer with a heating rate of 10°C/min under inert atmosphere

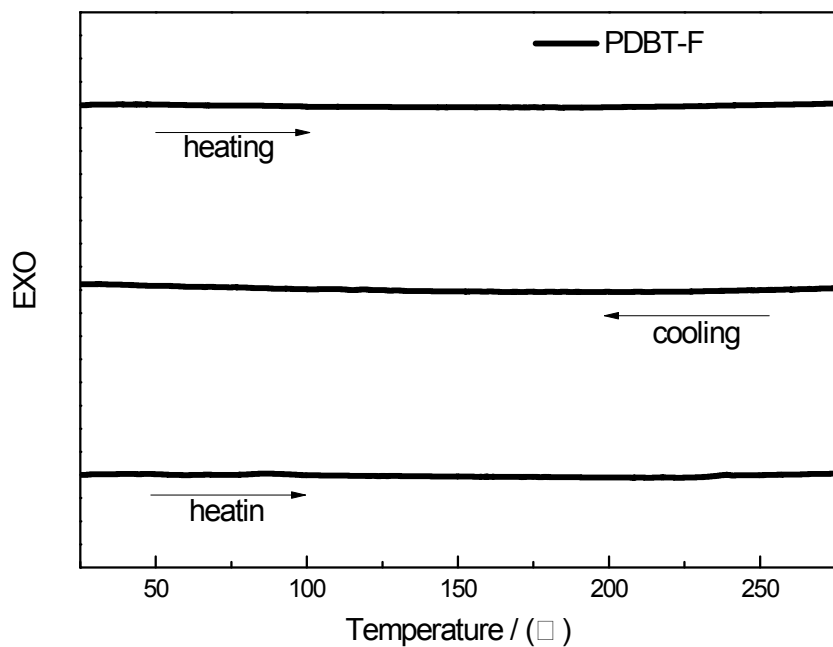


Figure S3 DSC plots of Polymer with a heating rate of 10°C min⁻¹ under the inert

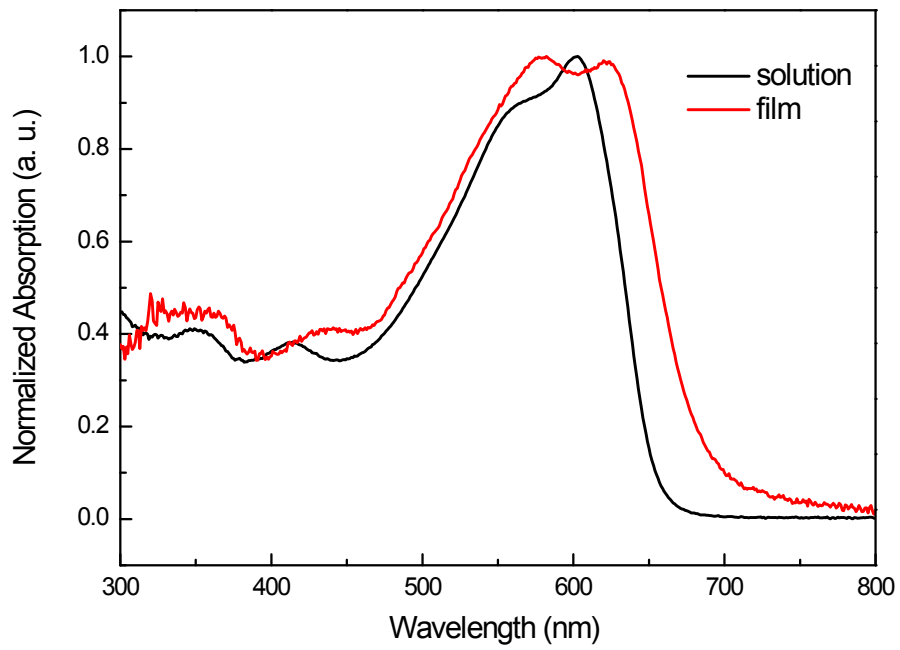


Figure S4 UV-vis absorption spectra of PDBT-F in diluted chloroform and thin film

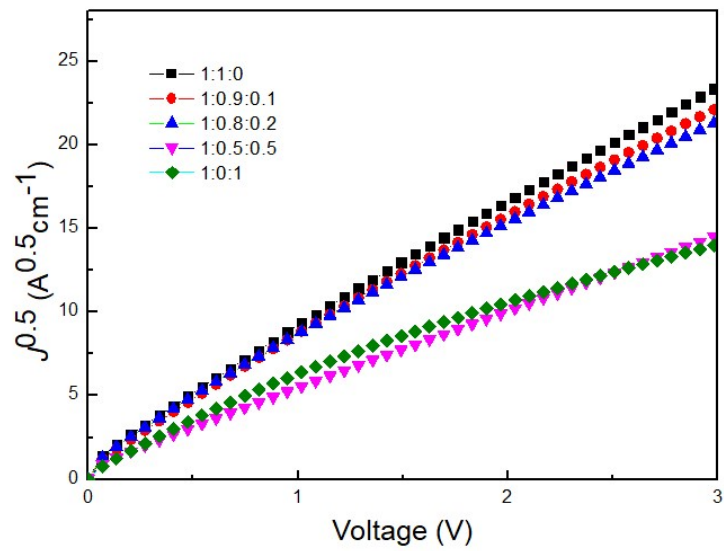


Figure S5 $J^{0.5}$ - V plot for the ternary hole-only devices

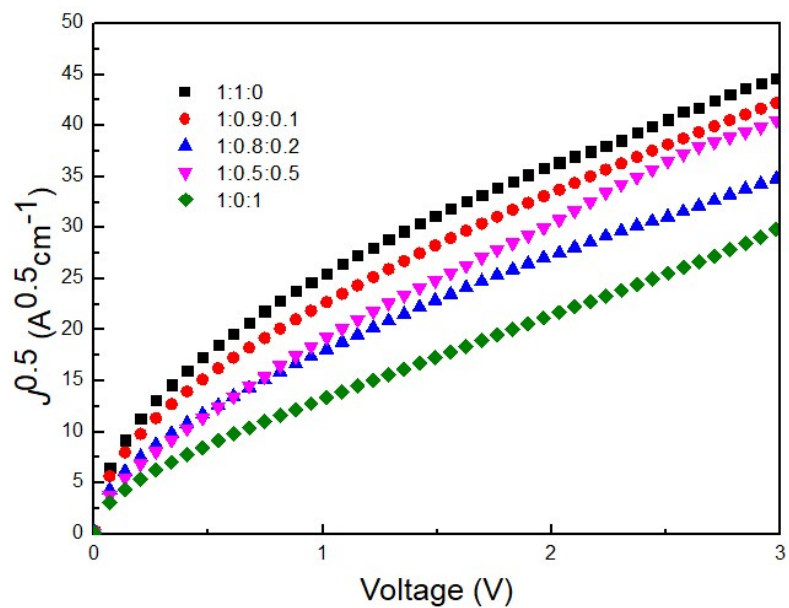


Figure S6 $J^{0.5}$ -V plot for the ternary electron-only devices

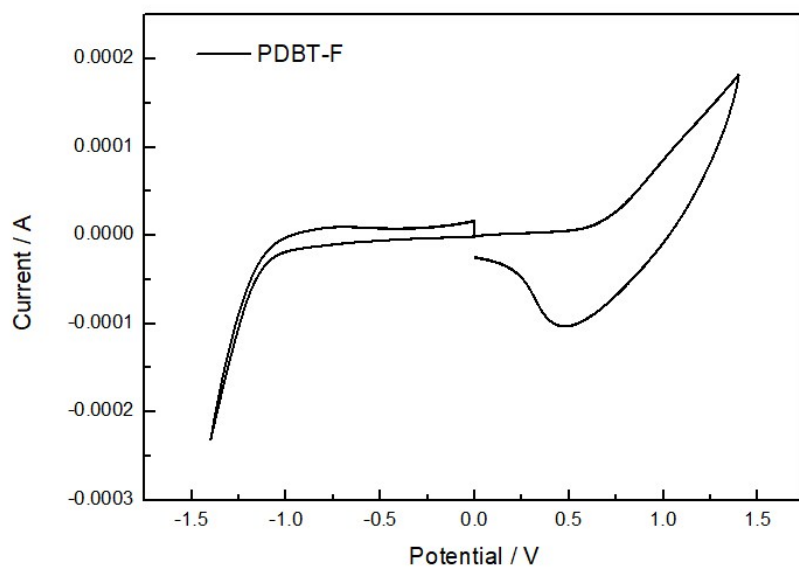


Figure S7 Cyclic voltammograms of the PDBT-F film