Double Acceptor Blocks-based Copolymers for Efficient Organic Solar Cells: Side-chain and π-bridge Engineered High Open-circuit Voltage and Small Driving Force

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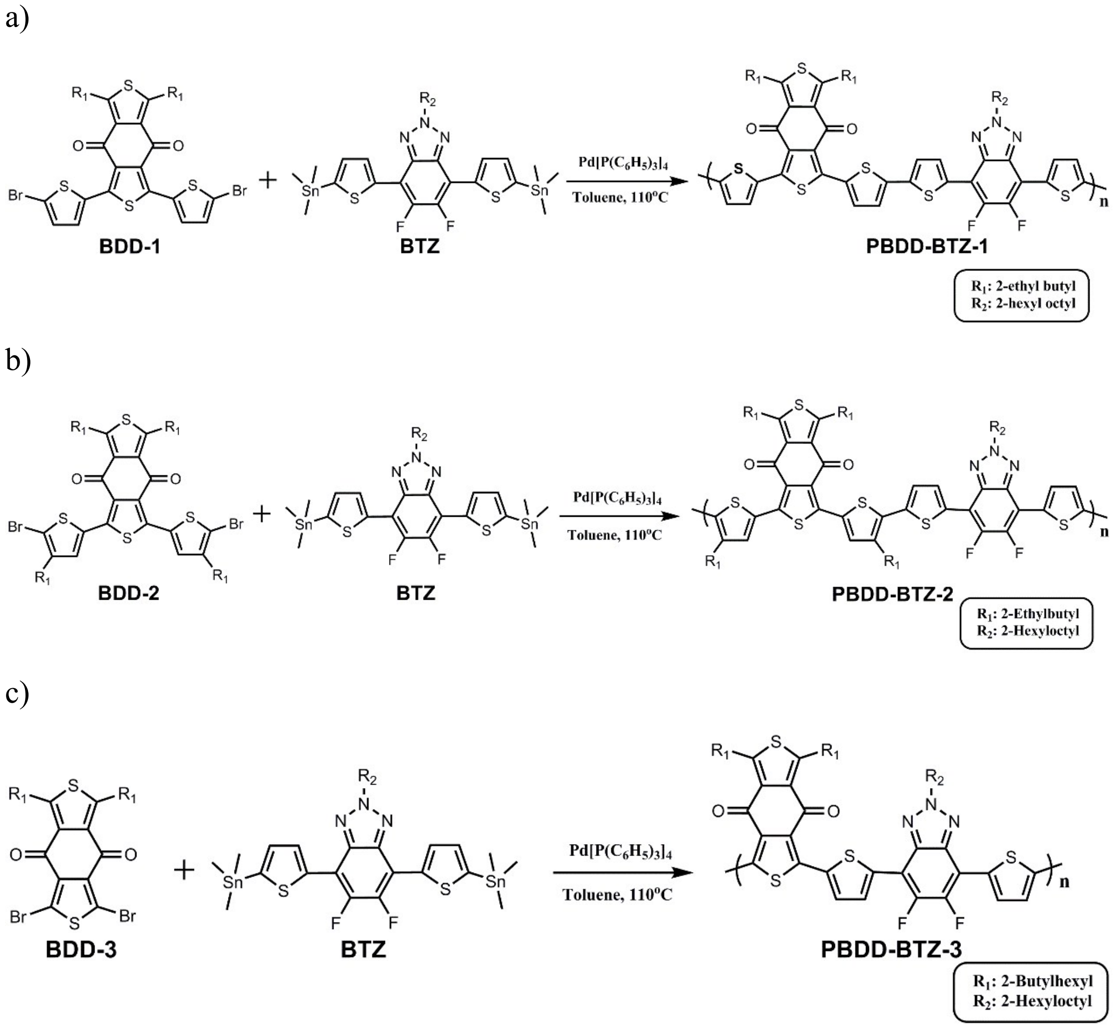
1. Materials

Materials: All reagents and solvents, unless otherwise specified, were purchased from Alfa, Suna Tech, Aldrich and Solarmer Materials Inc. and were used without further purification. BDD derivatives unit were purchased from derthon optoelectronic materials science technology and BTZ unit was purchased from Suna Tech Inc. Indium-tin oxide (ITO) glass was purchased from Delta Technologies Limited, Tetrakis(triphenylphosphine)palladium(0)[Pd(PPh$_3$)$_4$] was obtained from J&K.

1.1 Synthetic of Methods



Scheme S1. The synthetic route of the polymers.

Synthesis of PBDD-BTZ-1:

5,6-difluoro-2-(2-hexyldecyl)-4,7-bis (5-(trimethylstannyl) thiophen-2-yl)-2*H*-benzo[d] [1, 2, 3] triazole (BTZ) (0.174 g, 0.2 mmol) and 1,3-bis(thiophen-2-yl)-5,7-bis(2-ethylhexyl)benzo-[1,2-c:4,5-c′]dithiophene-4,8-dione (BDD-1) monomer (0.153 g, 0.2 mmol) were mixed in 10 ml of toluene. After the solution was flushed with N_2 for 5 min, $Pd(PPh_3)_4$ (18.6 mg, 0.02 mmol) were added, the mixture was further flushed with N_2 for 10 min. The reactant was heated to reflux for 3 hours. Then, the polymer was precipitated by addition of 100 ml methanol, filtered through a Soxhlet thimble, extraction with methanol, hexane, and chloroform. The corresponding polymer was obtained as solid powder from the chloroform fraction by precipitation from methanol. After the polymer was dried under vacuum, obtained purple solid with a yield of ~32 %. ^1H NMR (400 MHz, cdcl$_3$) δ 7.52 (s, 1H), 7.00 (s, 1H), 4.73 (s, 5H), 2.08 – 0.54 (m, 75H).

Synthesis of PBDD-BTZ-2:

5,6-difluoro-2-(2-hexyldecyl)-4,7-bis (5-(trimethylstannyl) thiophen-2-yl)-2*H*-benzo[d] [1, 2, 3] triazole (BTZ) (0.174 g, 0.2 mmol) and 1,3-bis(5-bromo-4-(2-ethylhexyl)thiophen-2-yl)-5,7-bis(2-ethylhexyl)-4*H*,8*H*-benzo[1,2-c:4,5-c'] dithiophene -4,8-dione (BDD-2) monomer (0.198 g, 0.2 mmol) were mixed in 10 ml of toluene. After the solution was flushed with N_2 for 5 min, $Pd(PPh_3)_4$ (18.6 mg, 0.02 mmol) were added, the mixture was further flushed with N_2 for 10 min. The reactant was heated to reflux for 3 hours. Then, the polymer was precipitated by addition of 100 ml methanol, filtered through a Soxhlet thimble, extraction with methanol, hexane, and chloroform. The corresponding polymer was obtained as solid powder from the chloroform fraction by precipitation from methanol. After the polymer was dried under vacuum, obtained purple solid with a yield of ~73 %. ^1H NMR (400 MHz, cdcl$_3$) δ 8.08 (s, 1H), 7.55 (d, J = 24.6 Hz, 1H), 2.40 (s, 1H), 1.83 (s, 2H), 1.64 – 0.75 (m, 39H).

Synthesis of PBDD-BTZ-3:

5,6-difluoro-2-(2-hexyldecyl)-4,7-bis (5-(trimethylstannyl) thiophen-2-yl)-2*H*-benzo[d] [1, 2, 3] triazole (BTZ) (0.174 g, 0.2 mmol) and 1,3-dibromo-5,7-bis(2-

ethylhexyl)-4*H*,8*H*-benzo[1,2-c:4,5-c']dithiophene-4,8-dione (BDD-3) monomer (0.143 g, 0.2 mmol) were mixed in 10 ml of toluene. After the solution was flushed with N_2 for 5 min, $Pd(PPh_3)_4$ (18.6 mg, 0.02 mmol) were added, the mixture was further flushed with N_2 for 10 min. The reactant was heated to reflux for 3 hours. Then, the polymer was precipitated by addition of 100 ml methanol, filtered through a Soxhlet thimble, extraction with methanol, hexane, and chloroform. The corresponding polymer was obtained as solid powder from the chloroform fraction by precipitation from methanol. After the polymer was dried under vacuum, obtained purple solid with a yield of ~58 %. ^1H NMR (400 MHz, $cdcl_3$) δ 7.52 (s, 1H), 7.00 (s, 1H), 3.36 (s, 2H), 2.01 – 0.48 (m, 94H).

2. Instruments

The ^1H NMR spectra were recorded in deuterated solvents on a Bruker ADVANCE 400 NMR Spectrometer. ^1H NMR chemical shifts were reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. Thermogravimetric analysis (TGA) was carried out on a PerkinElmer TGA 7 instrument for thermal analysis at a heating rate of 10 °C/min under nitrogen. Number-average (M_n) and weight-average (M_w) molecular weights were determined with Waters 2410 gel permeation chromatography (GPC) with tetrahydrofuran (THF) used as the eluent. UV-vis absorption spectra were recorded on a Perkin Elmer Lambda 750 spectrophotometer. All film samples were spin-cast on ITO substrates. Solution UV-Vis absorption spectra at elevated temperatures also were collected on a Perkin Elmer Lambda 750 Spectrophotometer. The temperature of the cuvette was controlled with a Perkin Elmer PTP 6+6 Peltier System, which is supplied by a Perkin Elmer PCB 1500 Water Peltier System. Before each measurement, the system was held for at least 10 min at the target temperature to reach thermal equilibrium. A cuvette with a stopper (Sigma Z600628) was used to avoid volatilization during the measurement. Cyclic voltammetry (CV) was performed by a Zahner IM6e electrochemical work station, using Ag/AgCl as the reference electrode, a Pt plate as the counter electrode, and a glassy carbon as the working electrode. Polymers were drop-cast onto the electrode from CB solutions to form thin films. 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile was used as the supporting electrolyte. The scan rate was 0.05 V s^{-1}. The specimen for AFM measurements was prepared using the same procedures those for fabricating devices but without MoO_3/Ag on top of the active layer. Transmission electron microscopy (TEM) images were taken on a JEOL-2100F transmission electron microscope and an internal charge-coupled device (CCD) camera. The specimen for TEM measurement was prepared by spin casting the blend solution on ITO/PEDOT:PSS substrate, then floating the film on a water surface, and transferring to TEM grids.

3. Device fabrication

OSCs devices were fabricated with a conventional device structure of ITO/PEDOT:PSS/polymer: ITIC-Th/PDINO/Al. Specific process is as follows: the etched ITO substrate was ultrasonically cleaned in detergent, water (twice), acetone and isopropanol for 2 hours. After drying, the etched ITO substrate process in UV ozone for 15 minutes and then PEDOT:PSS was spin-casted onto the ITO. Afterwards, the ITO glass was thermally annealed at 150 ℃ for 20 minutes. Next, the active layer was spin-casted on the PEDOT:PSS. Finally, 70 nm Al layer were deposited by evaporation under a pressure of ca. 4×10^{-4} Pa. The PEDOT:PSS was spin-coated at 4000 r.p.m. for 1 min. The concentration of PBDD-BTZ-1: ITIC-Th, PBDD-BTZ-2: ITIC-Th and PBDD-BTZ-3: ITIC-Th of chlorobenzene solution were 20 mg/ml (added 0.5% 1,8-diiodooctane additive). The polymers:ITIC-Th were spin-coated at 1800 r.p.m. for 1 min. Except for the spin coating of the PEDOT:PSS layer onto the ITO substrate, all photovoltaic device fabrication processes were carried out in nitrogen glove box with oxygen and humidity of less than 4 ppm. The test for this work was still measured in nitrogen glove box. The current−voltage (*J*−*V*) characteristics were performed by a Keithley 2400 Source Meter (100 mW/cm2, AM 1.5 G) and all devices area are 4 mm^2. The external quantum efficiency (EQE) tests were based on an Oriel Cornerstone monochromator, which was still performed in the nitrogen glove box.

4. Mobility measurements.

The hole-only devices used a diode configuration of ITO/PEDOT:PSS/active layer/ MoO_3/Ag and the electron-only devices fabricate with ITO/ZnO/active layer/Al by taking current-voltage curve in the range of 0-6 V. The carrier mobilities were measured using the space-charge-limited-current (SCLC) model, which is described by:

$$J = 9\varepsilon_0\varepsilon_r u V^2/8\mathrm{L}^3$$

where J is the current density, L is the film thickness of active layer, ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1}), ε_r is the relative dielectric constant of the transport medium, u is the hole or electron mobility, V is the internal voltage in the device and $V = V_{appl}-V_r-V_{bi}$, where V_{appl} is the applied voltage to the device, V_r is the voltage drop due to contact resistance and series resistance across the electrodes, and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes. The thickness of the BHJ blend for SCLC measurement was about 110 nm. The hole-mobility can be calculated from the slope of the $J^{1/2}$~V curves.

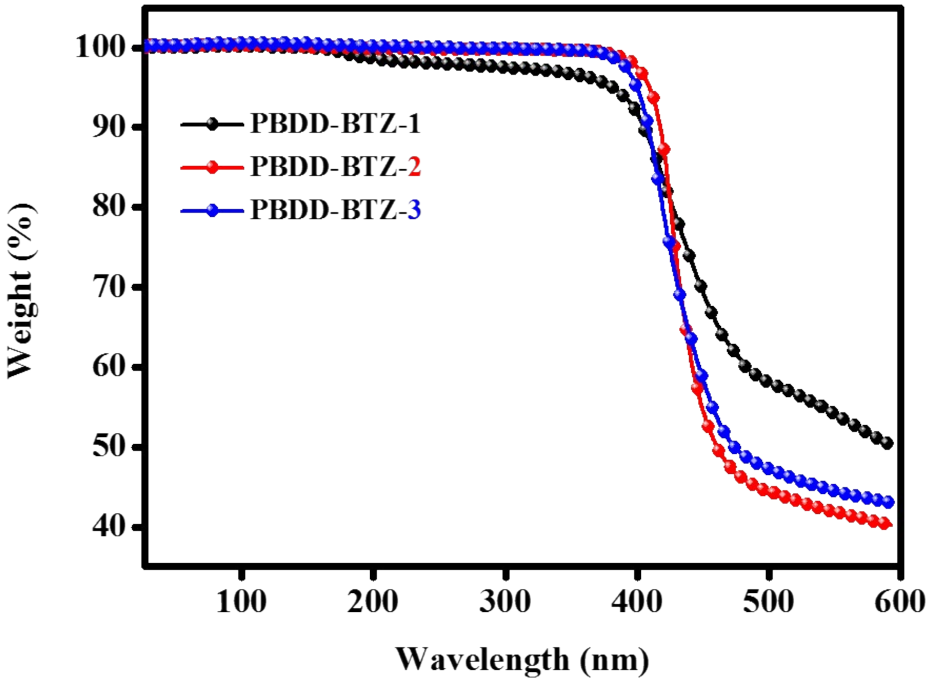


Figure S1. Thermogravimetric analysis (TGA) plot of polymers PBDD-BTZ-1, PBDD-BTZ-2 and PBDD-BTZ-3 with a heating rate of 10 ºC min^{-1} under nitrogen atmosphere.

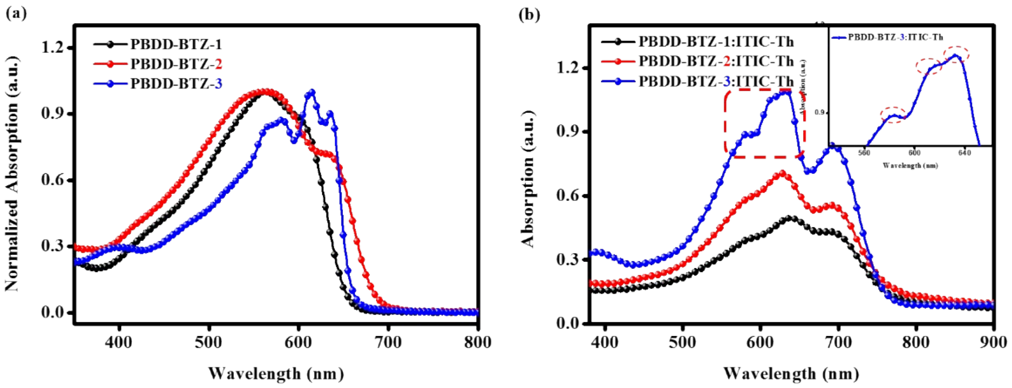


Figure S2. (a) Normalized absorption of solution UV-vis absorption of PBDD-BTZ-1, PBDD-BTZ-2 and PBDD-BTZ-3; (b) The corresponding UV spectra of the blend films.

7. SCLC Mobility Measurements

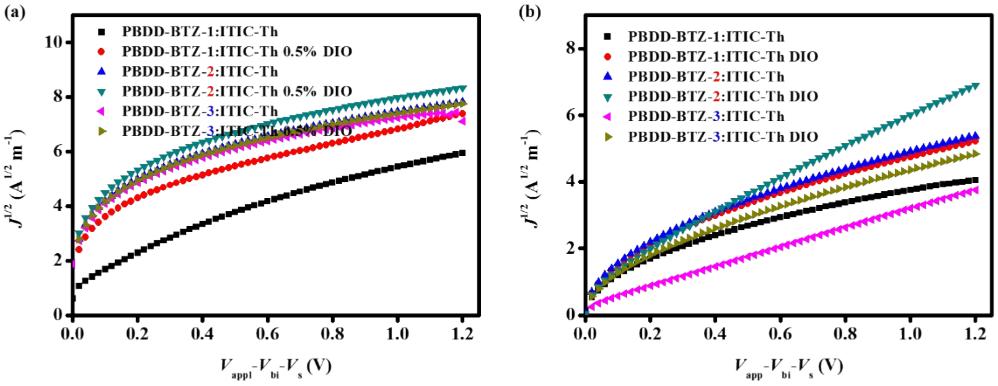


Figure S3. (a) The only-hole mobilities of the blends; (b) the only-electron mobilities of the corresponding blends.

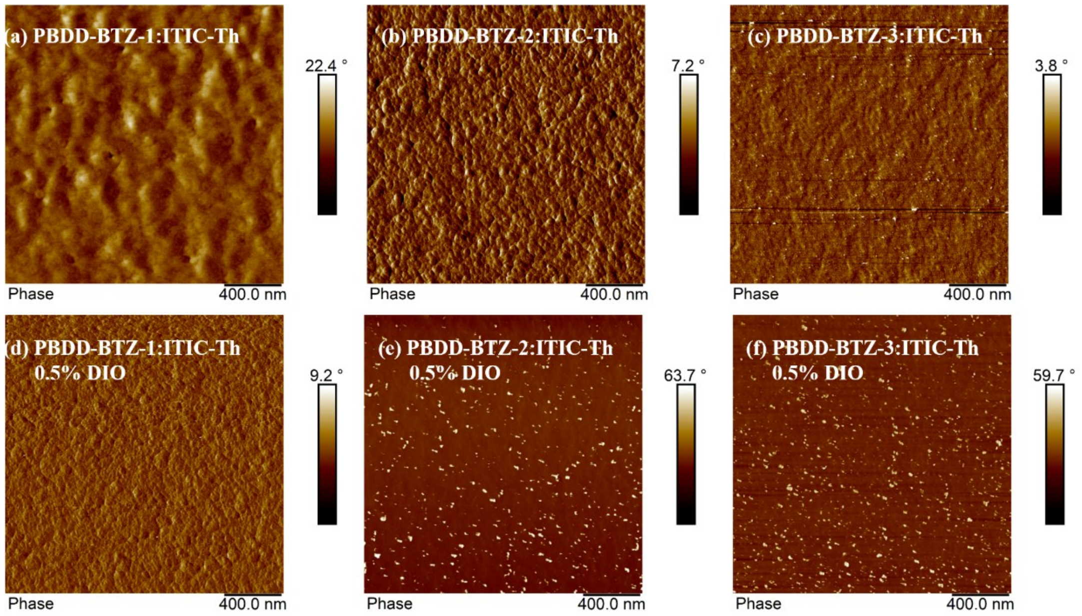


Figure S4. AFM phase images of a,d) PBDD-BTZ-1:ITIC-Th blends; b,e) PBDD-BTZ-2:ITIC-Th blends and c,f) PBDD-BTZ-3:ITIC-Th blends.

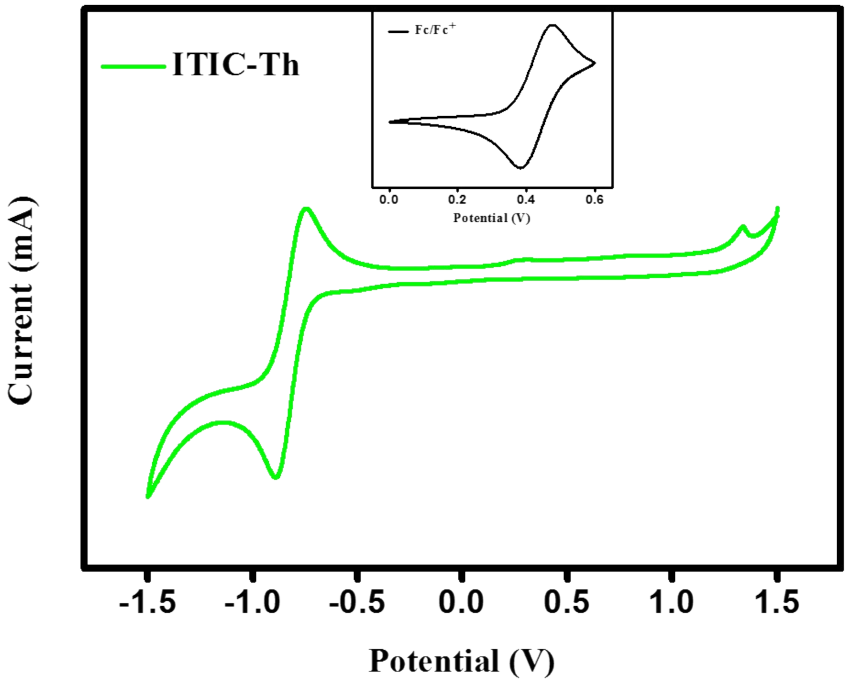


Figure S5. Cyclic voltammogram of the acceptor ITIC-Th film in CH_2CH3CN/0.1 mol/L Bu_4NPF_6 solutions at a scan rate 20 mV/s.

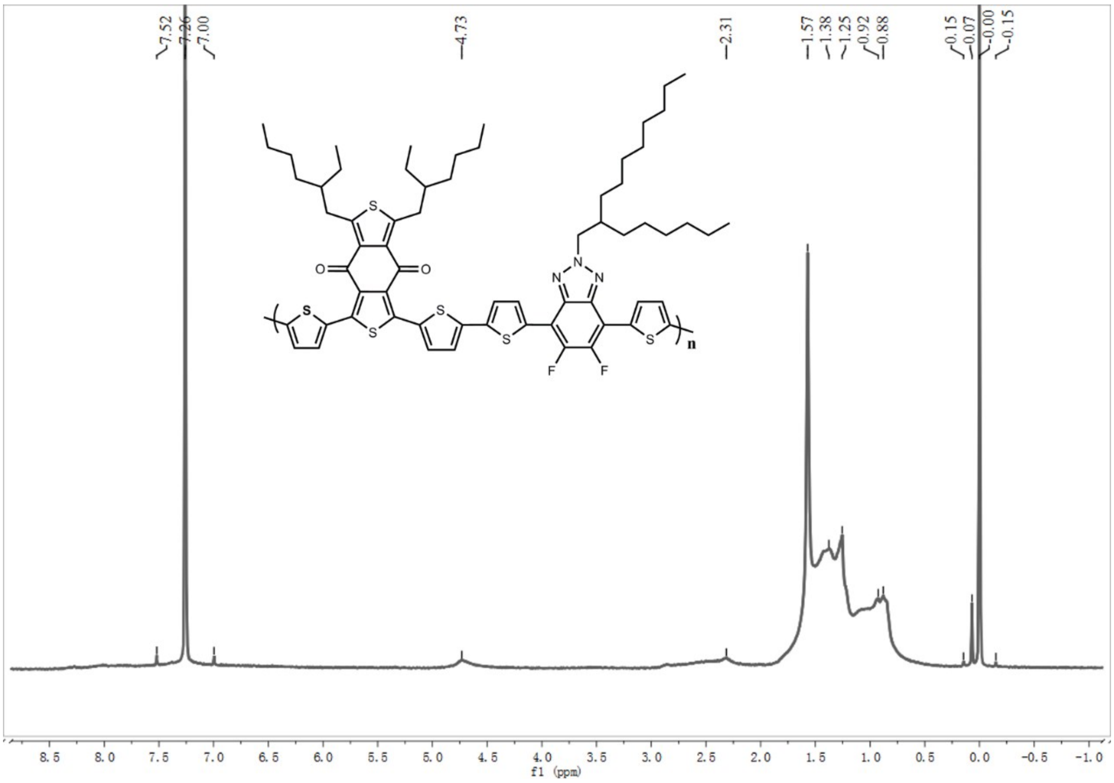


Figure S6. ^{1}H NMR of PBDD-BTZ-1.

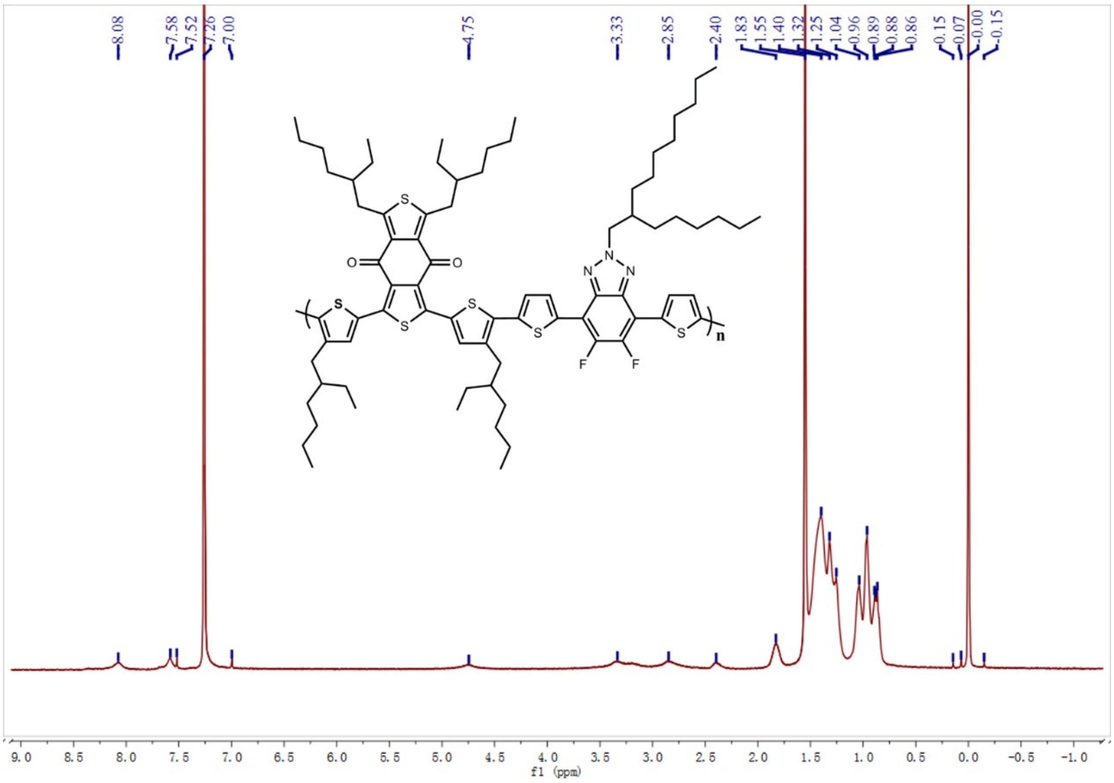


Figure S7. ^{1}H NMR of PBDD-BTZ-2.

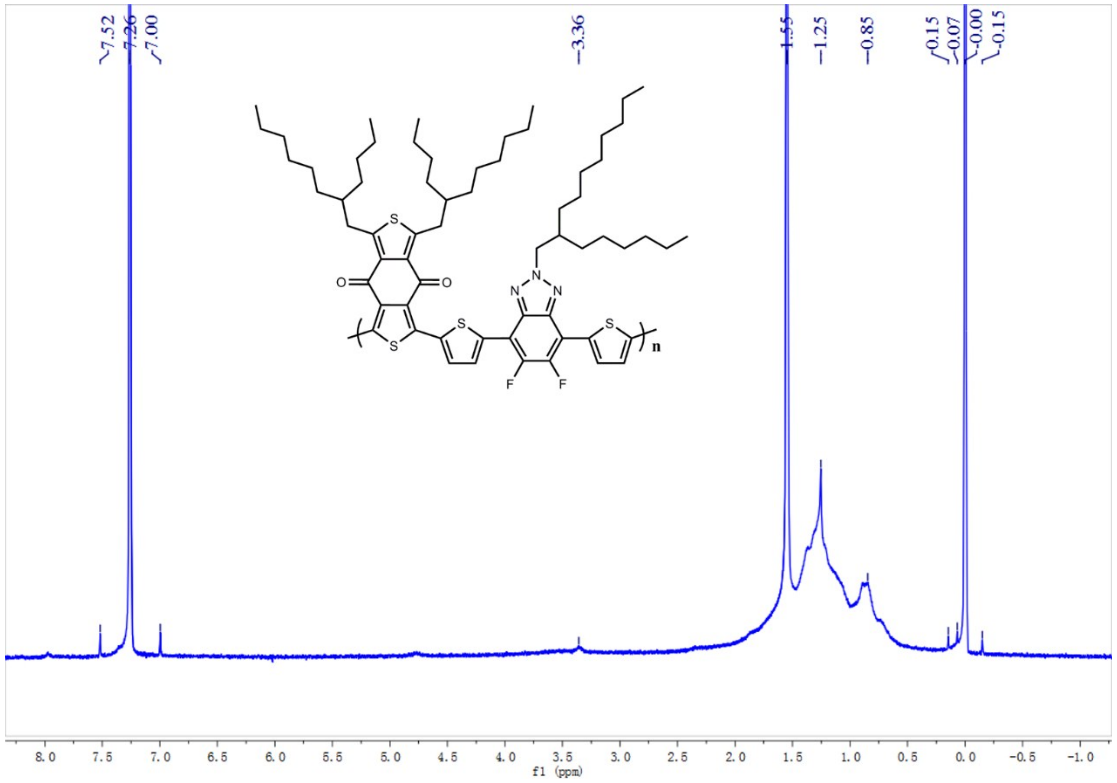


Figure S8. ^{1}H NMR of PBDD-BTZ-3.