

Supplementary Information

Unsubstituted benzo[1,2-*b*:4,5-*b'*]dithiophene-based low band-gap polymer for high performance organic photovoltaics

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1. Characterization

^1H NMR spectra were obtained from a Bruker Avance DPX 300 or Bruker Avance 500 NMR spectrometer using deuterated chloroform as a solvent. Size exclusion chromatography was performed on Agilent 1200 GPC System (eluted with CHCl_3) where the working temperature was room temperature and the concentration of the samples was 1.0 mg mL^{-1} . Prior to the analysis, the solution was stirred at 50°C for 24 h, and then at room temperature for 2 h and filtered with PTFE $0.45 \mu\text{m}$ syringe filter. The molecular weights were calculated according to relative calibration with polystyrene standards and toluene as a flow marker. TGA analysis was undertaken using a TA Instrument Q500 at a heating rate of $20^\circ\text{C}/\text{min}$. UV-Vis absorption spectra were obtained from a Lambda 25 (Perkin Elmer) spectrometer. Cyclic voltammetry experiments were carried out on a potentiostat/galvanostat (VMP 3, Biologic) in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. Platinum wire and gold electrode were used as a counter and a working electrode, respectively, and silver/silver ion (Ag in 0.1 M AgNO_3 solution) was used as a reference electrode. The configuration of the solar cell device is ITO/PEDOT:PSS/active layer/LiF/Al. The active layer solution was spin coated onto the PEDOT:PSS (Clevious AI 4083, 40 nm of thickness) coated ITO glass. After drying of the active layer completely, LiF (1 nm) and Al (100 nm) were thermally deposited as a cathode under 5×10^{-6} Torr. The photovoltaic performance was measured under nitrogen atmosphere inside a glove box. The current density–voltage (J – V) characteristics were measured with a Keithley 2400 source-meter under AM 1.5 G ($100 \text{ mW} \cdot \text{cm}^{-2}$) simulated by a Newport-Oriel solar simulator. The light intensity was calibrated using a NREL–certified photodiode and light source meter prior to each measurement. The active area was 0.06 cm^2 . The incident photon–to–current efficiency (IPCE) was measured using a lock-in amplifier with a current preamplifier under short circuit current state with illumination of monochromatic light. The thin film morphology was characterized by transmission electron microscopy (TEM) with a JEOL 2000 FX MARK II operating at 200 kV of acceleration voltage. Space charge limited current (SCLC) devices were fabricated through the same procedure of the solar cell device except for Au cathode (50 nm) instead of the LiF/Al cathode. For TEM observation, the solar cell device was immersed in deionized water and then the active layer was floated onto the Cu grid. Grazing incidence wide angle x-ray scattering spectra were obtained at the Advanced Light Source at the Lawrence Berkeley National Laboratory. The experimental set-up and sample cell were designed for the surface studies on thin films. The PBDTDPP solution in CF was spin coated on UV– O_3 treated Si wafer. An X-ray beam impinged onto the sample at a grazing angle above and below the critical angle of the polymer film ($\alpha_c=0.16$), but below the critical angle of the silicon substrate ($\alpha_c=0.22$). The wavelength of X-rays used was 1.240 \AA , and the scattered intensity was detected by using two-dimensional charge-coupled device camera.

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2. Materials

2,6-Bis(trimethylstannyl)[1,2-*b*:4.5-*b'*]dithiophene (BDT)¹, 2,6-bis(trimethylstannyl)-4,8-di(2-ethylhexyloxy)benzo[1,2-*b*:4.5-*b'*]dithiophene² and 3,6-bis-(5-bromo-thiophen-2-yl)-*N,N'*-bis(2-octyl-1-dodecyl)-1,4-dioxo-pyrrolo[3,4-*c*]pyrrole (DPP)³ were prepared according to the literatures.

Synthesis of PBDTDPP

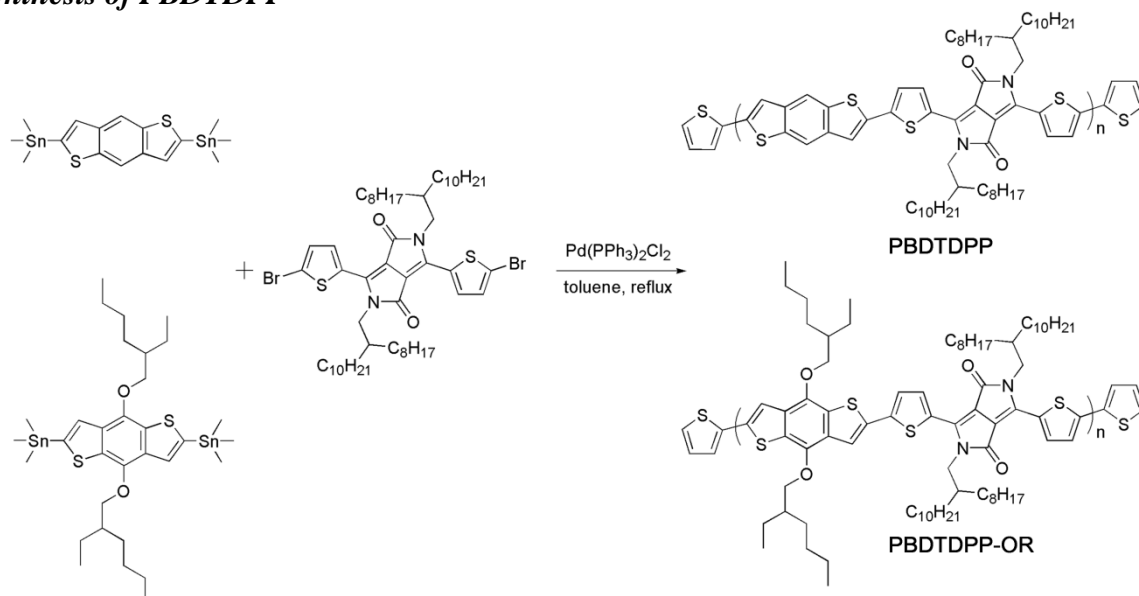
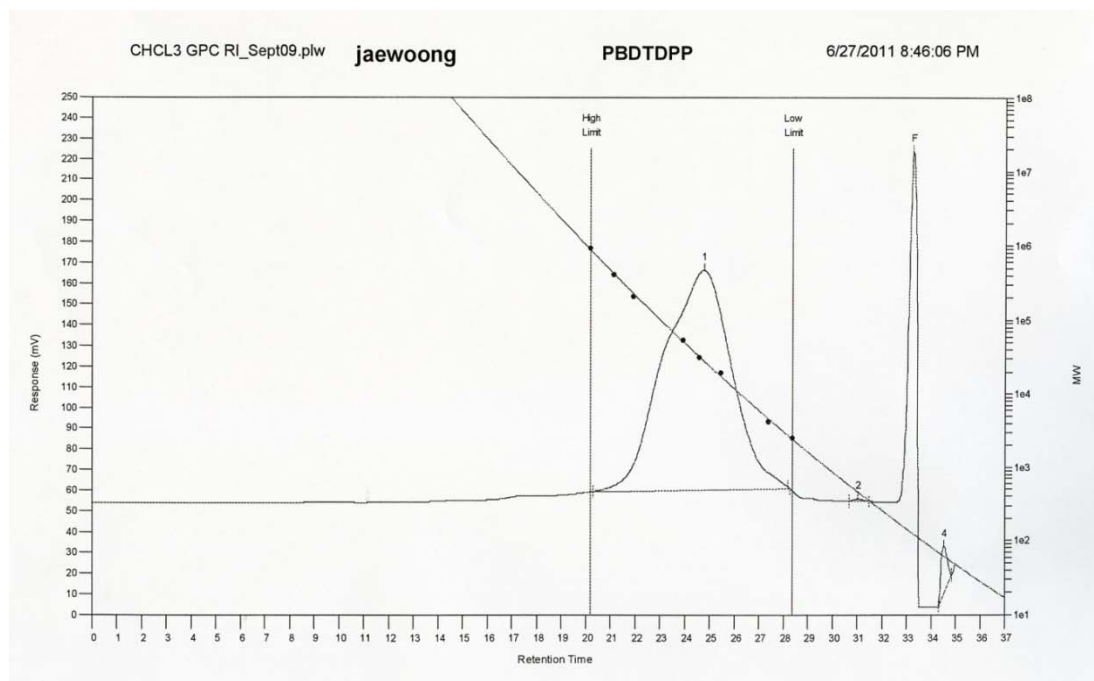


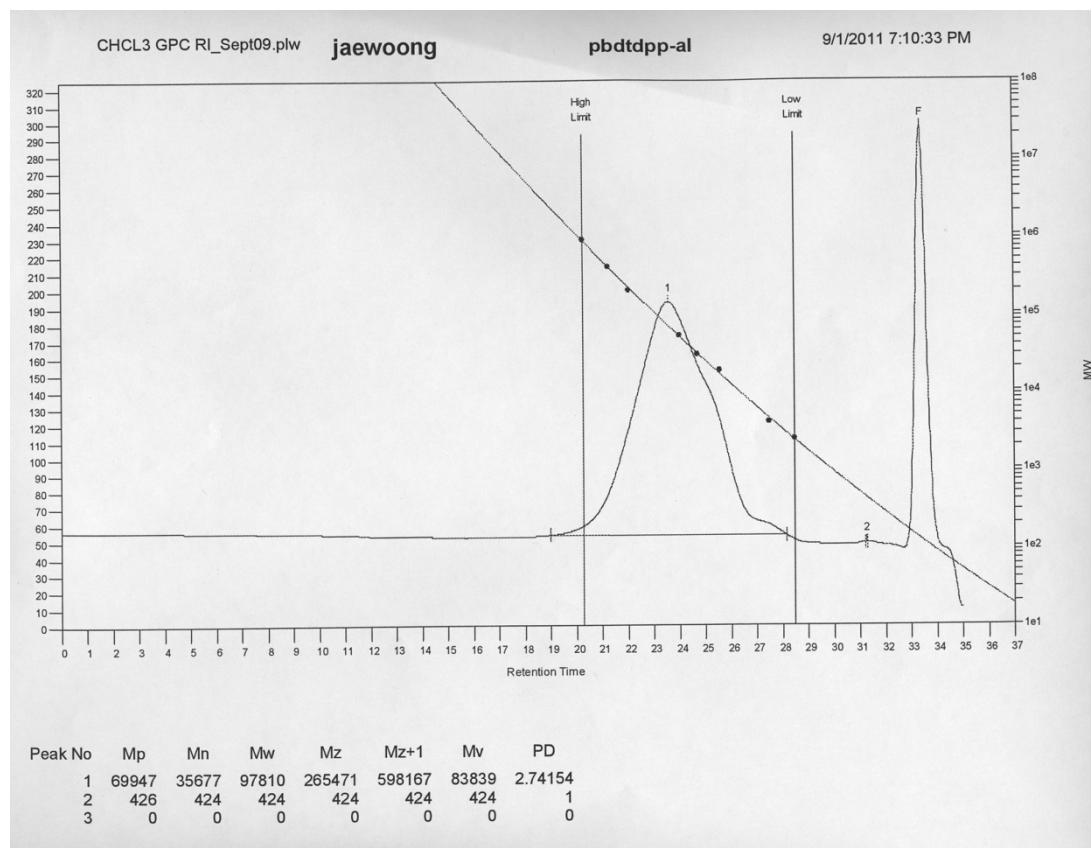
Figure S1. Synthesis scheme of PBDTDPP and PBDTDPP-OR.

After 87.7 mg of 2,6-bis(trimethylstannyl)[1,2-*b*:4.5-*b'*]dithiophene (0.17 mmol) and 173.3 mg of DPP (0.17 mmol) was dissolved in 3.5 ml of anhydrous toluene in a 25 ml round-bottom flask under nitrogen, the solution was degassed for 30 min, and then 3.5 mg of bis(triphenylphosphine)palladium(II)dichloride (5.3 μ mol) was added to the solution. The solution was refluxed for 24 h followed by end-capping using 2-bromothiophene and 2-tributyltinthiophene successively. After cooling down to room temperature, the solution was precipitated in methanol, filtered, and then purified by Soxhlet extraction by methanol, acetone, hexane, and then chloroform. Finally the chloroform fraction was concentrated, and then precipitated again in methanol. The PBDTDPP was obtained as a dark purple solid which was obtained after filtering by PTFE filter and dried overnight. (135 mg, Yield: 90%, M_n : 22.6 kDa, M_w : 49.8 kDa)



Synthesis of PBDTDPP-OR

PBDTDPP-OR was prepared through the same procedure of preparation of PBDTDPP, except the use of 2,6-bis(trimethylstannyl)-4,8-di(2-ethylhexyloxy)benzo[1,2-*b*:4.5-*b'*]dithiophene instead of 2,6-bis(trimethylstannyl)[1,2-*b*:4.5-*b'*]dithiophene in the polymerization step. (148 mg, Yield: 92%, M_n : 35.7 kDa, M_w : 97.8 kDa)



3. UV-Vis absorption spectra of PBDTDPP and PBDTDPP-OR

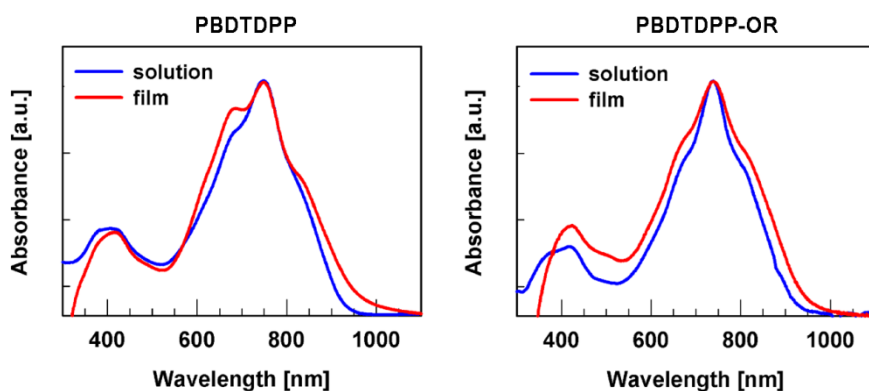


Figure S2. UV-Vis absorption spectra of PBDTDPP and PBDTDPP-OR.

4. Electrochemical measurements of PBDTDPP and PBDTDPP-OR

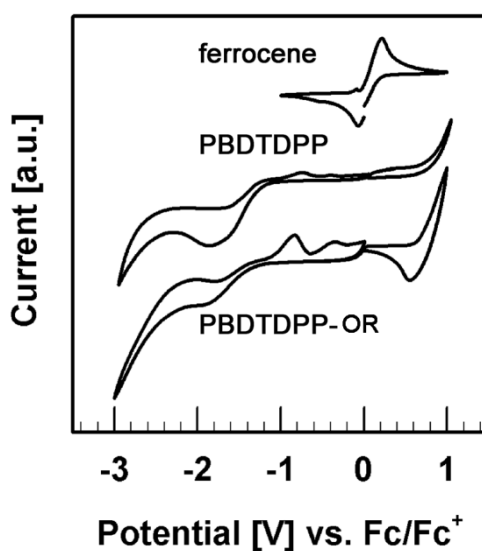


Figure S3. Cyclic voltammetry measurements of PBDTDPP and PBDTDPP-OR.

5. SCLC charge transport of PBDTDPP and PBDTDPP-OR

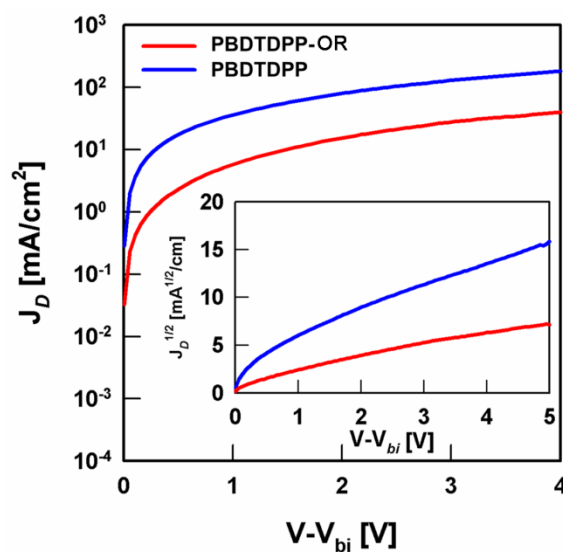


Figure S4. SCLC hole mobilities of PBDTDPP and PBDTDPP-OR.

6. Photovoltaic properties of PBDTDPP-OR

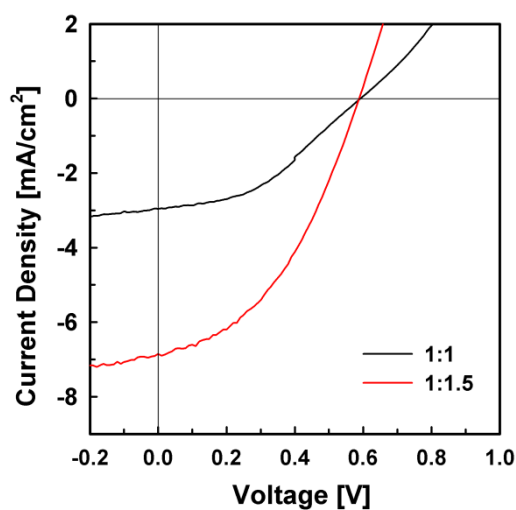


Figure S5. J–V curves based on PBDTDPP-OR.

Table S1 Photovoltaic properties of PBDTDPP-OR.

PBDTDPP-OR: PC ₇₁ BM (w/w)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
1:1	0.59	2.90	38.5	0.66
1:1.5	0.59	6.70	40.1	1.56

7. References

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3. P. Sonar, S. P. Singh, Y. Li, Z. Ooi, T. Ha, I. Wong, M. S. Soh and A. Dodabalapur, *Energy Environ. Sci.*, 2011, **4**, 2288.