

Electronic supplementary information for:

Enhanced power-conversion efficiency in bulk heterojunction solar cells based on conjugated polymer with isoindigo side chain using an inverted device structure

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S1. Materials and Characterization

Tetrakis(triphenylphosphine)palladium(0) ($\text{Pd}(\text{PPh}_3)_4$) (98%) were obtained from Puyang Huicheng Chemical Co, Ltd and used without further purification. All other starting materials were purchased from Pacific ChemSource or Alfa Aesar in analytical grade. Tetrahydrofuran (THF) and toluene were dried and distilled from sodium/benzophenone prior to use. DMF was dried and distilled under reduced pressure. All chromatographic separations were carried out on silica gel (200-300 mesh). All other solvents and chemicals used in this work were analytical grade and used without further purification.

The ^1H NMR and ^{13}C NMR spectra were measured with Bruker AVANCE 400 spectrometer. UV-visible absorption spectra of the polymers were measured on a

Perkin-Elmer Lamada 25 UV/vis/NIR spectrometer. The photoluminescence emission spectra (PL) were recorded with Perkin-Elmer LS-55 luminescence spectrometer. The elemental analysis of the monomers was performed with an Elementar Vario EL III element analyzer for C, H, N and S determination. The average molecular weight and polydispersity index (PDI) of the polymers were determined using Waters 1515 gel permeation chromatography (GPC) analysis with THF as eluent and polystyrene as standard. Thermogravimetric analysis (TGA) measurement was conducted with a Netzsch TG 209 analyzer under nitrogen at a heating rate of 20 °C/min. All the polymers were heated up to 150 °C first and held for 3 min to remove thermal history, followed by cooling at the rate of 20 °C/min to 50 °C and then by heating at the rate of 20 °C/min to 700 °C. Differential scanning calorimetry (DSC) analysis was made on a TA DSC Q10 instrument at a scan rate of 20 °C/min. Electrochemical redox potentials were obtained by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) using a three-electrode configuration and an electrochemistry workstation (ZAHNER ZENNIUM). CV was conducted on an electrochemistry workstation with the thin film on a Pt plate as the working electrode, Pt slice as the counter electrode, saturated calomel electrode (SCE) as the reference electrode and with 0.1 M tetra-n-butylammonium hexafluorophosphate (Bu₄NPF₆) (as a supporting electrolyte) in anhydrous acetonitrile solution at a scan rate of 50 mV s⁻¹. MALDI-TOF mass spectrometric measurements were performed on Bruker Autoflex III. All AFM measurements were performed using a Digital Instruments EnviroScope in tapping mode.

S2. Synthesis Procedures

6,-Bromo-di(2-ethylhexyl)isoindigo,¹ (2,5-dibromothiophen-3-ylmethyl)phosphonic acid diethyl ester² and (5-(1,3-dioxolan-2-yl)thiophen-2-yl)tributylstannane³ were synthesized according to the procedure reported in the literatures. 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene were purchased without further purification.

Synthesis of compound 1

6,-Bromo-di(2-ethylhexyl)isoindigo (1.50 g, 2.65 mmol),

(5-(1,3-dioxolan-2-yl)thiophen-2-yl)tributylstannane (1.54 g, 3.45 mmol) and Pd(PPh₃)₄ (0.1 g, 0.08 mmol) were dissolved in degassed toluene (50 mL) and the solution was stirred at 100 °C for 72 h under nitrogen atmosphere. Then the mixture was cooled to room temperature and poured into dilute aqueous HCl (10 mL) solution. This solution was stirred for 30 min and then extracted with dichloromethane. The organic phase was washed with water, dried over anhydrous MgSO₄, filtered, and finally removed solvent by rotary evaporation. The crude product was purified on column chromatography using silica gel using petroleum ether/dichloromethane (1:1, v:v) as eluent to give 0.90 g **1** as a red solid (Yield: 58.8%). FT-IR (KBr, cm⁻¹): 1661 (ν_{C=O}). ¹H NMR (400 MHz, CDCl₃, δ/ppm): 9.92 (s, 1H), 9.25-9.23 (d, *J* = 8.4 Hz, 1H), 9.17-9.15 (d, *J* = 8.0 Hz, 1H), 7.78-7.77 (d, *J* = 3.6 Hz, 1H), 7.49-7.48 (d, *J* = 4.0 Hz, 1H), 7.38-7.34 (t, *J* = 8.0 Hz, 2H), 7.07-7.03 (t, *J* = 7.4 Hz, 2H), 6.79-6.77 (d, *J* = 7.6 Hz, 1H), 3.73-3.68 (m, 4H), 1.87 (s, 2H), 1.39-1.32 (m, 16H), 0.99-0.89 (m, 12H). MALDI-TOF MS (C₃₇H₄₄N₂O₃S) *m/z*: calcd for 596.822; found 597.248.

Synthesis of compound 2

Compound 1 (0.80 g, 1.34 mmol) and (2,5-dibromothiophen-3-ylmethyl)phosphonic acid diethyl ester (0.79 g, 2.0 mmol) were dissolved in THF (25 mL) and the solution was stirred at room temperature for 30 min under nitrogen atmosphere. Then potassium tertbutoxide (0.224 g, 2.0 mmol) was dissolved in THF (30 mL) and added dropwise to the solution. The reaction mixture was stirred for 4 h at room temperature, and then heated to 50 °C reflux for 20 h. After cooling to room temperature, the reaction mixture was poured into dilute aqueous HCl (20 mL) solution and extracted with dichloromethane. The organic phase was washed with water and dried over anhydrous MgSO₄, and then the solvent was removed by rotary evaporation. The crude product was purified on silica gel column chromatography using petroleum ether/dichloromethane (2:1, v:v) as eluent to give 0.42 g **2** as a dark red solid (Yield: 37.5%). FT-IR (KBr, cm⁻¹): 938 (trans-vinylene). ¹H NMR (400 MHz, CDCl₃, δ/ppm): 9.19-9.14 (m, 2H), 7.36-7.33 (m, 3H), 7.18 (s, 1H), 7.09-7.05 (m, 3H), 7.00-6.98 (d, *J* = 5.2 Hz, 1H), 6.79-6.77 (d, *J* = 7.6 Hz, 2H), 3.74-3.68 (m, 4H), 1.87 (s, 2H), 1.37-1.25 (m, 16H), 0.99-0.89 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz, δ/ppm): 168.51, 168.30, 145.74, 145.08, 143.55, 142.59, 138.70, 137.25, 132.65,

132.53, 132.08, 130.38, 129.78, 128.33, 127.21, 124.85, 124.11, 122.076, 121.88, 121.24, 120.00, 118.93, 112.09, 110.30, 108.08, 104.58, 44.22, 44.12, 37.83, 37.65, 30.91, 30.82, 29.72, 28.99, 28.80, 24.39, 24.17, 23.11, 14.21, 14.07, 10.86, 10.75. Anal. Calcd for $C_{42}H_{56}Br_2N_2O_2S_2$: C, 60.43; H, 5.55; N, 3.36; S, 7.68. Found: C, 61.08; H, 6.18; N, 3.49; S, 7.39. MALDI-TOF MS ($C_{42}H_{46}Br_2N_2O_2S_2$) m/z : calcd for 834.765; found 835.077.

Synthesis of PBDT-TID

In a 50 mL three-neck round bottom flask, compound **2** (0.17 g, 0.21 mmol) and 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene (0.16 g, 0.21 mmol) were dissolved in degassed toluene (25 mL). The reaction mixture was deoxygenated with nitrogen for 30 min. Then, $Pd(PPh_3)_4$ (50 mg, 33.75 μ mol) was added under nitrogen and then the mixture was heated to 100 °C for 72 h. After cooled to room temperature, the mixture was poured into methanol (200 mL). A red precipitate was collected by filtration. The product was purified by washing with methanol and hexane in a Soxhlet extractor for 24 h each. It was extracted with hot chloroform in an extractor for 24 h. After removing solvent by rotary evaporation, a red solid was collected (0.2 g, 85.1%). 1H NMR (400 MHz, $CDCl_3$, δ /ppm): 9.14-9.05 (br, 4H), 7.00-6.73 (br, 10H), 4.19-3.63 (br, 8H), 1.83-0.91 (br, 60H). $M_n = 52.0$ kg mol $^{-1}$, PDI = 2.24.

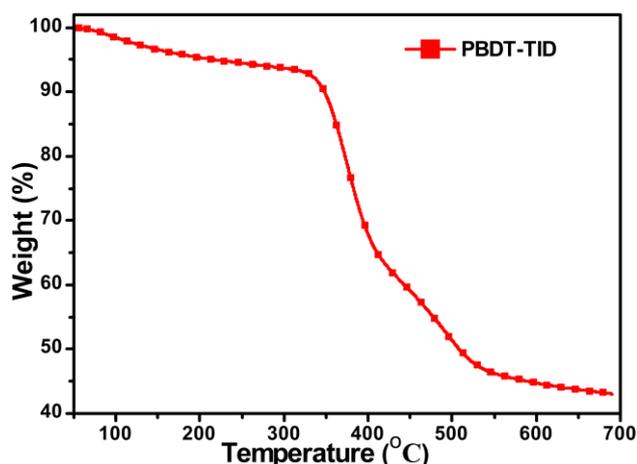


Fig. S1 TGA plot of **PBDT-TID** collected under N_2 at a heating rate of 20 °C/min.

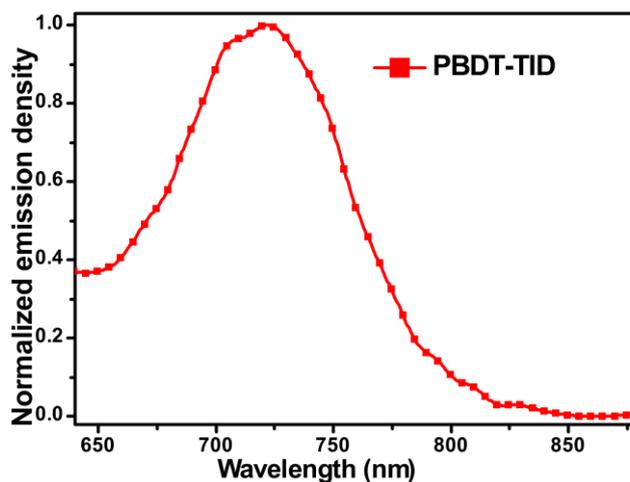


Fig. S2 Photoluminescence spectra of **PBDT-TID** in the CHCl_3 solution.

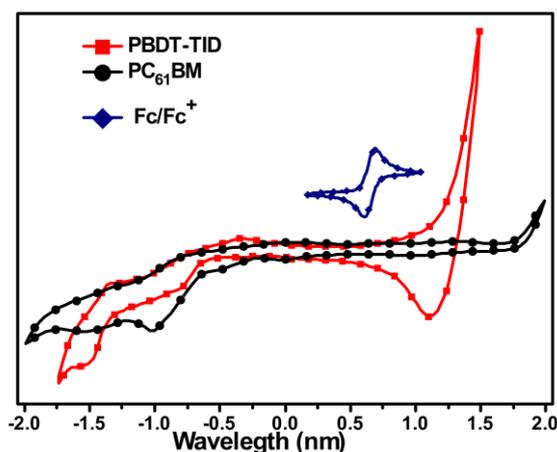


Fig. S3 Thin film cyclic voltammograms of **PBDT-TID** and PC_{61}BM on a Pt disk in 0.1 mol/L Bu_4NPF_6 acetonitrile solution.

S3. PSC Device Fabrication and Characterization

The photovoltaic cells were constructed in the traditional sandwich structure through several steps. The BHJ solar cells were prepared on pre-patterned commercial indium tin oxide (ITO) glass substrates. The thickness and sheet resistance of the ITO are 120 nm and 12 Ω /square, respectively. The active area of each solar cell device is 0.5 cm^2 . The ITO coated glass substrates were cleaned by successive ultrasonic treatment in acetone and isopropyl alcohol, then treated with a nitrogen-oxygen plasma oven for 5 min. The photovoltaic cells were constructed in the conventional device configuration with traditional sandwich structure through the following several

steps. First, a poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT-PSS, from Bayer AG) thin film was spin-coated from an aqueous solution on a cleaned ITO glass substrate giving a thickness of about 30 nm as measured by Ambios Technology XP-2 surface profilometer, and then baked at 100 °C for 15 min. Secondly, an active layer (or 100 nm) was spin-coated on top of the PEDOT-PSS from the a solution of chlorobenzene (20 mg/mL in CB) of the polymer:PC₆₁BM blends (1:2 - 1:4 weight ratio), and then annealed at 100°C for 15 min in a nitrogen-filled glove box. Finally, 0.5 nm of LiF and 100 nm of aluminum (Al) cathodes were deposited on the top of the active layer in a vacuum of $2-8 \times 10^{-7}$ Torr to complete the photovoltaic device fabrication. For inverted device, the similar procedure was used, and titanium (diisopropoxide) bis(2,4-pentanedionate) (TIPD) was used as buffer layer material.⁴

Current density-voltage (*J-V*) characteristics were measured by a Keithley 2602 Source Meter under 100 mW cm⁻² irradiation using a 500W Xe lamp equipped with a global AM 1.5 filter for solar spectrum simulation, and the incident light intensity was calibrated using a standard Si solar cell. The measurement of monochromatic incident photon-to-current conversion efficiency (IPCE) was performed using a Zolix DCS300PA Data acquisition system. The performance parameters of detailed conventional and inverted device structures were summarized in the **Table S1**.

Table S1 Photovoltaic properties and hole mobility of the polymer **PBDT-TID**.

Devices	Polymer /PC ₆₁ BM	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE _{max} (PCE _{ave}) (%)	μ_h (Average) (cm ² V ⁻¹ s ⁻¹)
Conventional	1:2	10.63	0.78	0.34	2.81(2.45)	-
	1:3	12.65	0.80	0.52	5.25(5.10)	2.5×10^{-3}
	1:4	8.47	0.76	0.31	2.02(1.10)	-
Inverted	1:3	15.07	0.82	0.53	6.51(6.07)	-

Conventional Device Structure:

ITO/PEDOT:PSS(30nm) / Polymer:PC₆₁BM (~100nm)/LiF(0.5nm) /Al (100nm)

Inverted Device Structure:

ITO/ TIPD (12 nm) / **PBDT-TID**:PC₆₁BM (~100 nm)/ MoO₃(24 nm) /Al (100 nm)

S4. Hole Mobility for FET Device Fabrication and Characterization

To understand the influence of charge carrier mobility of the polymer film on the photovoltaic properties. **PBDT-TID**-based FETs with a bottom-gate bottom-contact (BGBC) configuration were fabricated on highly-doped silicon wafer with 300 nm SiO₂ insulator, which was used as gate electrode. The source-drain gold electrodes (30 nm) were prepared by photolithography. The substrates were then subjected to series of cleaning. Next, octadecyltrichlorosilane (OTS) modification was performed on the surface of SiO₂ gate dielectrics. Then, a layer of polymer semiconductor film (~40 nm) was deposited on the OTS-treated substrates by spin-coating from a polymer solution in *o*-dichlorobenzene (10 mg/mL) at a speed of 1200 rpm for 40 s. For annealing FETs, the samples were further placed on a hotplate at 120 °C for 5 minutes. FETs were then measured by using a Keithley 4200 SCS semiconductor parameter analyzer. Different channel lengths (L) of the FET devices ($L = 30$ or $40 \mu\text{m}$) and the same channel widths (W) of $1400 \mu\text{m}$ were used to optimize device performance. The field-effect mobility in saturation (μ) is calculated from equation:

$$I_{\text{DS}} = (W/2L) C_i \mu (V_{\text{GS}} - V_{\text{th}})^2$$

where W/L is the channel width/length, C_i is the gate dielectric layer capacitance per unit area, and V_{GS} and V_{th} are the gate voltage and threshold voltage, respectively. The hole mobility of the pure polymer was measured and confirmed a hole mobility of $2.5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively.

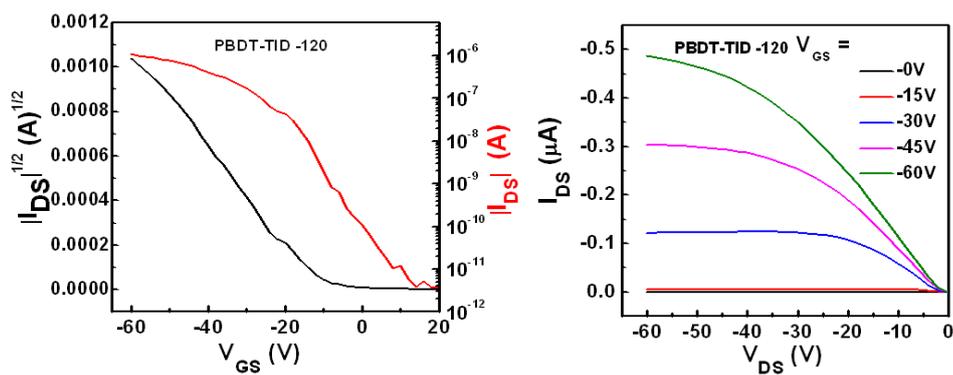


Fig. S4 Output characteristics (right) at various gate biases V_g and square-root of the drain current of the transfer characteristics (left) for **PBDT-TID** FET.

S5. References

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