Supporting Information

Isoindigo fluorination to enhance photovoltaic performance of donor-accepter conjugated copolymers

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1. Synthetic details

Materials and methods

All reagents were purchased from Aladdin Co., Alfa Aesar Co. and Aldrich Chemical Co. without further purification, unless stated otherwise. 6,6'-Dibromo-N,N'-(2-ethylhexyl)isoindigo (**1**), 6,6'-bibromo-7,7'-difluoro-N,N'-(2-ethylhexyl)isoindigo (**2**) and 2,6-bis(trimethyltin)-4,8-di(2,3-dioctylthiophen-5-yl)-benzo[1,2-b:4,5-b']dithiophene (**9**) were synthesized according to the previous literature method.[1,2] ^{1}H NMR spectra were recorded on a Bruker Avance-400 spectrometer with *d*-chloroform as solvent and tetramethylsilane as internal standard. Elemental analysis was performed by a Carlo Erba 116 Elemental Analyzer. Molecular weights of the copolymers were determined using Waters 1515 GPC analysis with THF as eluent and polystyrene as standard. UV-vis spectra were obtained on a Carry 300 spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements were conducted on a TA Instrument Model SDT Q600 simultaneous TGA/DSC analyzer at a heating rate of 10 ^{o}C min^{-1} and under a N_2 flow rate of 90 mL min^{-1}. Atomic force microscopy (AFM) measurements were performed under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA operating in the tapping mode.

Synthesis of monomers

6,6’-Bis(thiophen-2-yl)-N,N’-(2-ethylhexyl)isoindigo (**3**)

6,6’-Dibromo-N,N’-(2-ethylhexyl)isoindigo (**1**) (3.98 g, 6.20 mmol), 2-tributylstannylthiophene (5.80 g, 15.5 mmol), $Pd_2(dba)_3$ (0.017 g, 0.03 mmol), and $P(o\text{-tol})_3$ (0.036 mg, 0.12 mmol) were dissolved in 60 mL anhydrous THF. The reaction mixture was heated to 80 ^{o}C for 12 h under an argon atmosphere. After cooling to room temperature, the organic layer was extracted with dichloromethane (100 mL), washed successively with water and then dried over anhydrous $MgSO_4$. After the removal of the solvent under reduced pressure, the residue was purified by column chromatography with 1:2 (v/v) dichloromethane/hexane as the eluent to give the pure compound **3** as a purple solid (6.29 g, 78%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.20 (d, 2H), 7.45 (d, 2H), 7.38 (d, 2H), 7.34 (d, 2H), 7.18-7.10 (m, 2H), 6.98 (s, 2H), 3.70 (d, 4H), 1.92 (m, 2H), 1.46-1.18 (m, 16H), 0.92-0.85 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 168.56, 145.64, 144.51, 137.75, 131.96, 130.18, 128.32, 125.98, 124.02, 120.96, 119.28, 104.90, 44.46, 36.42, 30.04, 28.59, 24.42, 23.38, 14.10, 10.82. Anal. calcd for $C_{40}H_{46}N_2O_2S_2$: C, 73.81; H, 7.12; N, 4.30; found: C, 73.77; H, 7.11; N, 4.33.

6,6’- Bis(thiophen-2-yl)-7,7’-difluoro-N,N’-(2-ethylhexyl)isoindigo (**4**)

Compound **4** was synthesized as a purple solid with a yield of 75% according to the method for compound **3** described above. ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.05 (d, 2H), 7.48 (d, 2H), 7.40 (d, 2H), 7.36 (d, 2H), 7.21-7.12 (m, 2H), 3.92 (d, 4H), 1.88 (m, 2H), 1.43-1.20 (m, 16H), 0.93-0.86 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 167.46, 145.11, 144.24, 138.25, 132.13, 131.21, 128.85, 126.43, 124.88, 121.05, 120.62, 108.45, 44.84, 36.66, 30.52, 29.24, 26.36, 23..5, 14.12, 10.96. Anal. calcd for $C_{40}H_{44}F_2N_2O_2S_2$: C, 69.94; H, 6.46; N, 4.08; found: C, 69.90; H, 6.48; N, 4.05.

6,6’- Bis(5-bromothiophen-2-yl)-N,N’-(2-ethylhexyl)isoindigo (**5**)

To a solution of compound **3** (1.63 g, 2.5 mmol) in 50 mL anhydrous THF, N-bromosuccinimide (NBS) (0.89 g, 5.02 mmol) was added in several portions over 30 min in the dark. The reaction mixture was subsequently stirred at room temperature for 2 h. After that, the mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water, and dried over anhydrous $MgSO_4$. After the removal of the solvent under reduced pressure, the residue was purified by column chromatography with 1:2 (v/v) dichloromethane/hexane as the eluent to give the pure compound **5** as a purple solid (0.85 g, 42%). ^1H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.18 (d, 2H), 7.21 (d, 2H), 7.18 (d, 2H), 7.08 (d, 2H), 6.86 (s, 2H), 3.71 (d, 4H), 1.90 (m, 2H), 1.45-1.16 (m, 16H), 0.90-0.83 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 168.48, 145.70, 145.03, 137.12, 131.93, 131.25, 130.64, 124.33, 121.16, 118.88, 112.32, 104.60, 44.48, 36.36, 30.02, 28.75, 24.46, 23.42, 14.10, 10.86. Anal. calcd for $C_{40}H_{44}Br_2N_2O_2S_2$: C, 59.41; H, 5.48; N, 3.46; found: C, 59.37; H, 5.50; N, 3.42.

6,6’- Bis(5-bromothiophen-2-yl)-7,7’-difluoro-N,N’-(2-ethylhexyl)isoindigo (**6**)

Compound **6** was synthesized as a purple solid with a yield of 40% according to the method for compound **5** described above. ^1H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.15 (d, 2H), 7.23 (d, 2H), 7.20 (d, 2H), 7.11 (d, 2H), 3.95 (d, 4H), 1.86 (m, 2H), 1.44-1.18 (m, 16H), 0.92-0.86 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 167.65, 145.46, 144.84, 137.43, 132.37, 132.20, 130.48, 124.53, 121.35, 118.92, 112.41, 104.65, 44.52, 36.71, 30.58, 28.96, 25.36, 23.44, 14.10, 10.94. Anal. calcd for $C_{40}H_{42}Br_2F_2N_2O_2S_2$: C, 56.88; H, 5.01; N, 3.32; found: C, 56.85; H, 5.00; N, 3.35.

Synthesis of copolymers

PBDTT-ID

Monomer **5** (0.242 g, 0.3 mmol) and monomer **9** (0.339 g, 0.3 mmol) and were dissolved in 15 mL toluene. The solution was flushed with argon for 10 min, and then Pd_2dba_3 (5.5 mg, 2 mol%) and P(*o*-tolyl)$_3$ (7.3 mg, 8%) were added into the flask. The flask was purged three times with successive vacuum and argon filling cycles.

The polymerization reaction was heated to 110 °C and the mixture was stirred for 48 h under an argon atmosphere. 2-Tributylstannyl thiophene (23.7 mL) was added to the reaction, and then after two hours 2-bromothiophene (7.5 mL) was added. The mixture was stirred overnight to complete the end-capping reaction. The mixture was cooled to room temperature and poured slowly into 350 mL methanol. The precipitate was filtered and washed with methanol and hexane in a Soxhlet extraction apparatus to remove the oligomers and catalyst residues. Finally, the polymer was extracted with chloroform. The solution was condensed by evaporation and precipitated into methanol. The polymer **PBDTT-ID** was collected as a dark purple solid with a yield of 76%. ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.10 (br, 2H), 8.06-6.45 (m, 12H), 3.82 (br, 4H), 3.26-2.48 (m, 8H), 2.10-1.12 (m, 66H), 1.10-0.70 (m, 24H). Anal. Calcd for $(C_{90}H_{116}N_2O_2S_6)_n$: C, 74.53; H, 8.06; N, 1.93. Found: C, 73.86; H, 7.55; N, 1.98.

PBDTT-FID

Polymer **PBDTT-FID** was synthesized as dark purple solid with the yield of 82% according to the method of polymer **PBDTT-ID** described above using monomer **6** instead of compound **9**. ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.22 (br, 2H), 8.05-6.40 (m, 10H), 3.80 (br, 4H), 3.22-2.40 (m, 8H), 2.08-1.13 (m, 66H), 1.10-0.65 (m, 24H). Anal. Calcd for $(C_{90}H_{116}F_2N_2O_2S_6)_n$: C, 72.73; H, 7.73; N, 1.88. Found: C, 72.01; H, 7.23; N, 1.92.

2. Cyclic voltammetry (CV) measurements and Fig. S1

Cyclic voltammetry (CV) measurements were carried out on the CHI660 potentiostat/galvanostat electrochemical workstation at a scan rate of 50 mV s^{-1}, with a platinum wire counter electrode and an Ag/AgCl reference electrode in anhydrous nitrogen-saturated 0.1 mol L^{-1} acetonitrile (CH_3CN) solution of tetrabutylammonium perchlorate (Bu_4NClO_4). A Pt plate coated with thin film of the studied copolymer, a Pt wire and and an Ag/AgCl (0.1 M) were used as the work electrode, counter electrode and reference electrode, respectively. The energy level of the Ag/AgCl reference electrode was calibrated against the Fc/Fc$^+$ system to be 4.40 eV according to the previous methods.[3]

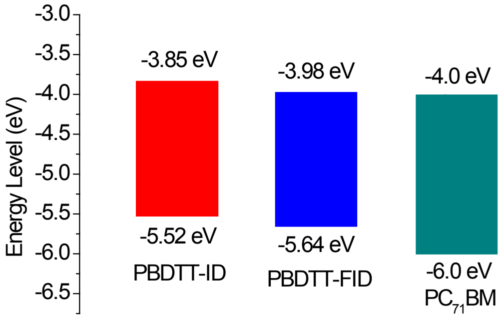

Fig. S1. HOMO and LUMO energy levels of **PBDTT-ID**, **PBDTT-FID** and PC$_{71}$BM.

3. Theoretical calculations and Fig. S2

The electronic properties of **BDTT-ID** and **BDTT-FID** trimers were simulated by density functional theory (DFT) calculations at the B3LYP/6-31G(d) level using the Gaussian 03 program suite.[4] The alkyl chains were replaced by methyl groups to save calculation time and simplify calculations process, which did not significantly affect the equilibrium geometries and the electronic properties.

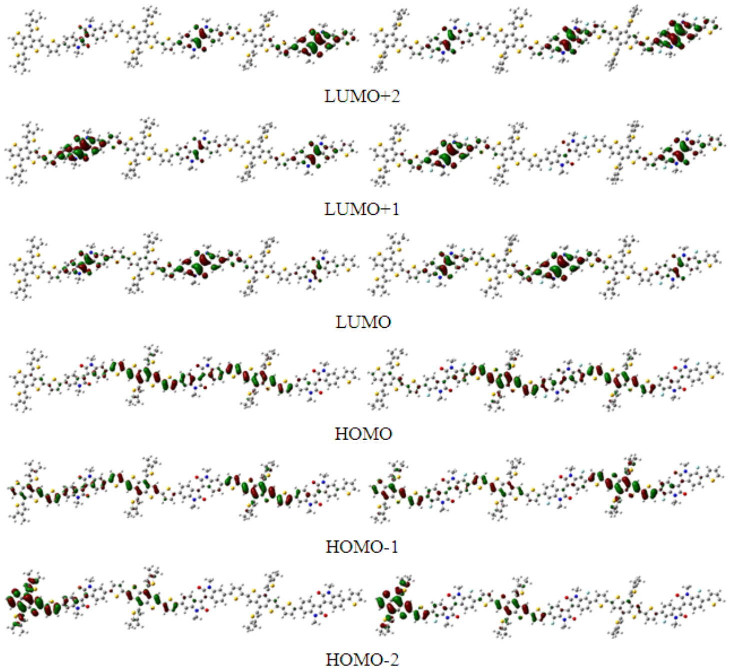

Fig. S2. Calculated HOMO and LUMO orbital diagrams for BDTT-ID (left) and BDTT-FID (right).

4. Hole mobility measurements (SCLC) and Fig. S3

Hole-only devices, with a structure of ITO/PEDOT/polymer/MoO_3/Au, were fabricated to determine the hole mobilities using the space charge limited current (SCLC) method reported previously.[5] The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by the following equation:

$$\mathrm{J} = \frac{9}{8}\varepsilon_0 \varepsilon_r \mu_h \frac{V^2}{d^3}$$

where J is the current, μ_h is the zero-field mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, d is the thickness of the active layer, and V is the effective voltage. The effective voltage can be obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the substrate's series resistance from the applied voltage (V_{appl}), $V = V_{appl} - V_{bi} - V_s$. The hole mobility can be calculated from the slope of the $J^{1/2} \sim V$ curves.

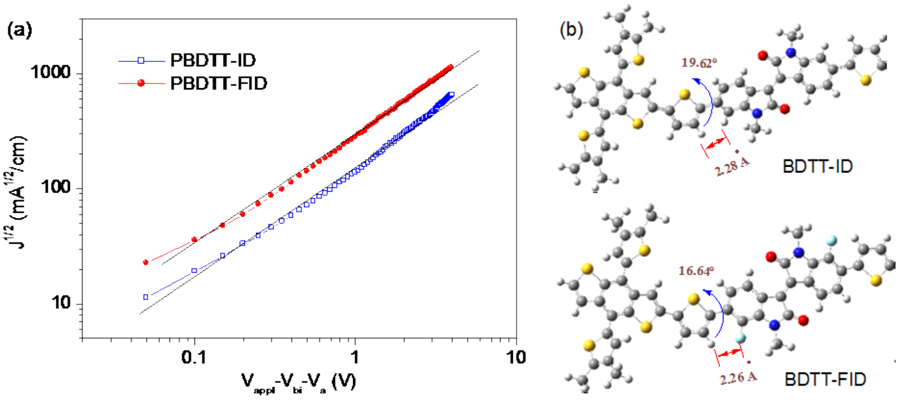

Fig. S3 (a) $J^{1/2}$-V characteristics of PBDTT-ID and PBDTT-FID hole-only devices measured at ambient temperature. (b) Optimized molecular structures of BDTT-ID and BDTT-FID models of PBDTT-ID and PBDTT-FID.

5. Atomic Force Microscopy (AFM) and Fig. S4

The surface morphology of blended films of copolymer:$PC_{71}BM$ was studied by atom force microscopy (AFM) performed on a Nanoscope IIIa (Digital Instruments, CA) multimode AFM in the tapping mode.

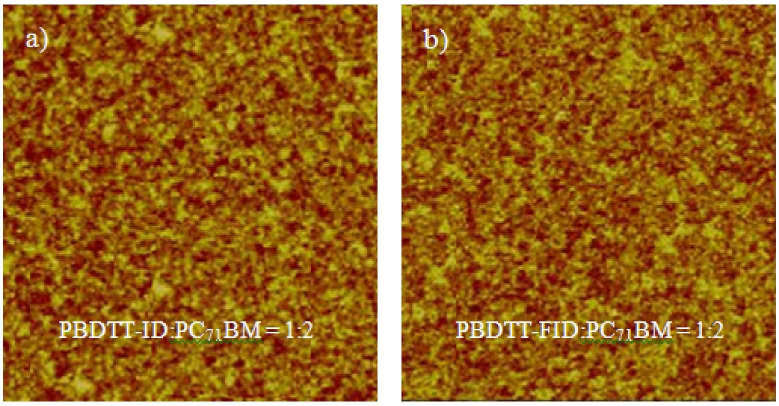

Fig. S4 AFM topographic images of the active blend films (copolymer:$PC_{71}BM$=1:2, w/w) with 3% DIO. (a) PBDTT-ID, (b) PBDTT-FID. Image size: 2×2 μm^2.

6. Device fabrication

Conventional polymer solar cells were fabricated with ITO glass as an anode, Ca/Al as a cathode, and blend film of the copolymer and $PC_{71}BM$ as a photosensitive layer. After spin-coating a 30 nm layer of PEDOT:PSS onto the pre-cleaned ITO substrate, the photosensitive layer (thickness for **PBDTT-ID**: 90 nm; for **PBDTT-FID**: 85 nm) was subsequently prepared by spin-coating a blend solution of the copolymer and $PC_{71}BM$ (w/w) in *o*-dichlorobenzene on the ITO/PEDOT:PSS electrode with a typical concentration of 10 mg mL^{-1}. For the inverted devices, an about 40 nm ZnO thin film was deposited on the surface of ITO glass. The ZnO layer was pretreated with UV-ozone for 10 minutes and the conjugated polyelectrolyte of poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)] dibromide (PNFBr) (5 nm) was spin-coated on the top of ZnO layer. The photoactive layer of PBDTT-FID:$PC_{71}BM$ composite (1:2; 95 nm) was then spin-coated on the top of above layer from 1,2-dichlorobenzene solution. The photoactive layer was then thermally annealed at 110 °C for 10 minutes. Subsequently, about 10 nm MoO_3 and 100 nm Ag were deposited in turn through shadow masks by thermal evaporation. The device area was 0.09 cm^2. The current-voltage (*I*-*V*) characterization of the devices was carried out on a computer-controlled Keithley 236 Source Measurement system. The EQE was measured at a chopping frequency of 280 Hz with a lock-in amplifier (Stanford, SR830 DSP) during illumination with the monochromatic light from a xenon lamp. A solar simulator was used as the light source, and the light intensity was monitored by a standard Si solar cell. The thickness of films was measured using a Dektak 6 M surface profilometer.

Table S1. Photovoltaic properties of **PBDTT-ID** and **PBDTT-FID** based solar cell devices with copolymer/ $PC_{71}BM$ (1:2, w/w) blends.

Polymer	Device	Thickness [nm]	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF	PCE_{max} [%]	J_{sc} (calc.) [mA cm^{-2}]
PBDTT-ID	Conventional	90	8.95	0.88	0.60	4.76	8.90
PBDTT-FID	Conventional	85	9.62	0.94	0.61	5.52	9.54
PBDTT-FID	Inverted[a]	100	10.16	0.90	0.62	5.70	10.20
PBDTT-FID	Inverted[b]	95	11.30	0.92	0.68	7.04	11.22

[a] without PNFBr interfacial layer. [b] with PNFBr interfacial layer.

6. References

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