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Electronic Supplementary Information

Modulation of Bulk Heterojunction Morphology through Small π-Bridge Change for Polymer Solar Cells with Enhanced Performance

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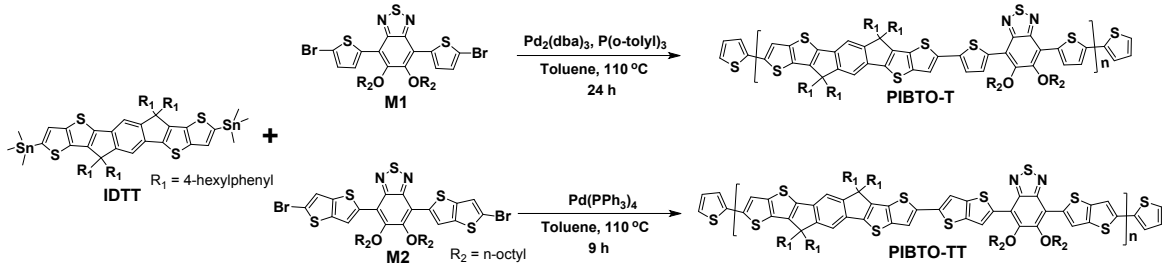
Experimental section



Scheme S1. Synthesis of **PIBTO-T** and **PIBTO-TT**.

Materials: Bis-stannylated indacenodithieno[3,2-b]thiophene (**IDTT**) was purchased from Derthon Optoelectronic Materials Science & Technology Co., Ltd. Monomers **M1** and **M2** were prepared according to the literature procedures.[1-2] All other reagents were purchased from Aldrich Inc., Aladdin-Reagent Inc., and Adamas-beta Ltd., and used as received.

Synthesis of PIBTO-T: **IDTT** (0.30 g, 0.22 mmol) and **M1** (0.16 g, 0.22 mmol) were dissolved in toluene (20 mL). The mixture was purged with nitrogen for 1 h at room temperature. After the addition of $Pd_2(dba)_3$ (4 mg) and P(*o*-tolyl)$_3$ (10 mg), the mixture was heated to reflux for 24 h under nitrogen atmosphere. Then, a drop of 2-tributylstannylthiophene was added to the mixture and reacted for 3 h. Finally, two drops of 2-bromothiophene was added to the mixture and reacted overnight to complete the end-capping reaction. The reaction mixture was precipitated into methanol and filtered. The collected precipitate was subjected to Soxhlet extraction with methanol, acetone, hexane, and chloroform for 24 h each. The chloroform extract was concentrated, and then precipitated into methanol. The target polymer was collected by filtration and dried in *vacuo* at 50 °C overnight to give a black solid (0.32 g, 87%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 8.68 (br, 2H), 7.64 (br, 2H), 7.32 (br, 4H), 7.26 (br, 8H), 7.16 (br, 8H), 4.15 (br, 4H), 2.58 (br, 8H), 1.95 (br, 4H), 1.62 (m, 8H), 1.49 (m, 4H), 1.33 (m, 40H), 0.91 (m, 18H). GPC: M_n =43.1 kDa, PDI = 1.9.

Synthesis of PIBTO-TT: **IDTT** (0.30 g, 0.22 mmol) and **M2** (0.18 g, 0.22 mmol) were dissolved in toluene (20 mL). The mixture was purged with nitrogen for 1 h at room temperature. After the addition of 14.5 mg of $Pd(PPh_3)_4$, the mixture was heated to reflux for 9 h under nitrogen atmosphere. Then, a drop of 2-tributylstannylthiophene was added to the mixture and reacted for 3 h. Finally, two drops of 2-bromothiophene was added to the mixture and reacted overnight to complete the end-capping reaction. The reaction mixture was precipitated into methanol and filtered. The collected precipitate was subjected to Soxhlet extraction with methanol, acetone, hexane, dichloromethane and chloroform for 24 h each. The chloroform extract was concentrated and then precipitated into methanol. The target polymer was collected by filtration and dried in *vacuo* at 50 °C overnight to give a black solid (0.26 g, 69%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 8.94 (br, 2H), 7.61 (br, 2H), 7.43 (br, 4H), 7.23-7.10 (m, 16H), 4.13 (br, 4H), 2.59 (br, 8H), 2.05 (br, 4H), 1.61 (m, 8H), 1.53(m, 4H), 1.31 (m, 4H), 0.90 (m, 18H). GPC: M_n = 42.8 kDa, PDI = 1.6.

General characterization. A Lambda 35 UV/vis spectrophotometer was used for ultraviolet-visible absorption measurements. ^{1}H NMR (400 MHz) spectra were collected on a Bruker AVANCE 400 spectrometer, using tetramethylsilane (TMS) as a proton reference and $CDCl_3$ as a solvent. Gel Permeation Chromatography (GPC) measurements were performed on a Waters 1515 system using 1,2,4-trichlorobenzene as the eluent at 150 °C. Cyclic voltammetry measurements were carried out by using an electrochemical workstation (CHI 604E) in acetonitrile solution with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Pt plate, Pt wire and $Ag/AgNO_3$ were applied as the working electrode, counter electrode and reference electrode, respectively. HOMO/LUMO energy levels were calculated by using the equation of $E_{HOMO/LUMO} = -(4.82 + \varphi_{ox}/\varphi_{red})$ eV. Surface morphology of the active layers was characterized by AFM (Dimension Icon) in tapping mode. A Bruker Dektak XT surface profilometer was used to determine the thicknesses of polymer blend films.

Fabrication and Characterization of Polymer Solar Cells. The devices were fabricated with a configuration of indium tin oxide (ITO)/PEDOT:PSS/polymer:$PC_{71}BM$/PDIN/Al, where PEDOT:PSS and PDIN are poly(3,4-ethylenedioxythiophene):polystyrenesulfonate and 2,9-bis(3-(dimethylamino)propyl) anthrax[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone, respectively. PEDOT:PSS was spin-coated with a thickness of ~40 nm on the ITO-coated glass and annealed at 140 °C for 15 min in air. The active layers (thickness of ~100 nm) were prepared by spin-coating the polymer:$PC_{71}BM$ blend solutions at 1000 rpm for 1 min in a glove-box. A solution (0.2% acetic acid) of PDIN in methanol with a concentration of 1.5 mg/mL was spin-coated on the active layer at 3000 rpm for 30 s, giving a PDIN layer (~14 nm). Ultimately, aluminum (100 nm) was thermally evaporated on the top of the PDIN layer to form the negative

electrode. The effective active area of the cell was 6 mm^2. After a simple encapsulation by epoxy kits (general purpose, Sigma Aldrich) in glove-box, the PSCs were tested in ambient atmosphere at room temperature.

J-V characteristics were measured under AM 1.5 G irradiation (100 mW/cm^2) on an Oriel sol3A simulator (Newport) using a Keithley 2400 source meter. The light intensity for the *J-V* measurements was calibrated with a NREL-certified silicon reference cell. The EQE spectra were measured using the QE/IPCE measurement kit (QE-PV-SI) from Newport.

Hole- and Electron-Only Device Fabrication and Characterization. Hole-only and electron-only diodes with device structures of ITO/PEDOT:PSS/polymer:$PC_{71}BM$/MoO_3/Au and ITO/ZnO/polymer:$PC_{71}BM$/ Ca/Al, respectively, were fabricated to measure the hole and electron mobilities using the SCLC method.[3] The active layer and electrodes were prepared using the same method as that used in the solar cell fabrication. The current was measured by using a Keithley 2440 source measurement unit. The SCLC mobilities were calculated by fitting the dark current to the model of a single carrier SCLC, which is described as:[3]

$$J = \frac{9}{8}\varepsilon_r \varepsilon_0 \mu \frac{V^2}{L^3}$$

where *J* is the current density (A m^{-2}), ε_r is the dielectric constant of the polymer (assumed to be 3), ε_0 is the permittivity of empty space (8.85×10^{-12} F m^{-1}), μ is the carrier mobility, *V* is the voltage drop across the device ($V=V_{appl} - V_{bi}$, where V_{appl} is the applied voltage to the device, and V_{bi} is the built-in voltage due to the difference in work function of the two electrodes), and *L* is the film thickness of the active layer. The hole or electron mobility can be calculated from the slope of the $J^{1/2}$-*V* curves.

GIWAXS Characterization. GIWAXS characterization of the thin films was performed on beam line 7.3.3[4] at the Advanced Light Source. Samples were prepared on Si substrates. The 10 keV X-ray beam was incident at a grazing angle of 0.11-0.15° for an optimized signal-to-background ratio. The scattered X-rays were detected using a Dectris Pilatus 2M photon counting detector.

***Small Angle Neutron Scattering*.** The small angle neutron scattering (SANS) experiments on the polymer:$PC_{71}BM$ blends were completed on the General Purpose SANS instrument at the High Flux Isotope Reactor at Oak Ridge National Laboratory. The raw data were corrected for scattering from the empty cell, detector dark current, and detector sensitivity. The corrected data were then normalized to an absolute scale using a Porasil-A standard.

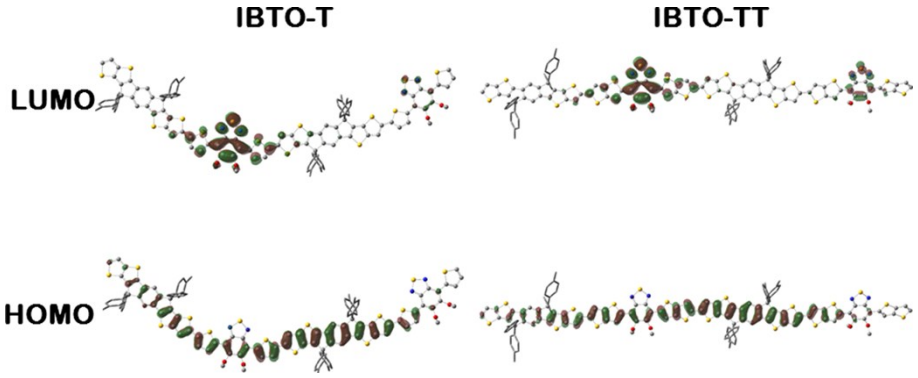


Fig. S1 DFT-calculated LUMO and HOMO of the geometry optimized structures of analogous dimers of **PIBTO-T** (left), and **PIBTO-TT** (right).

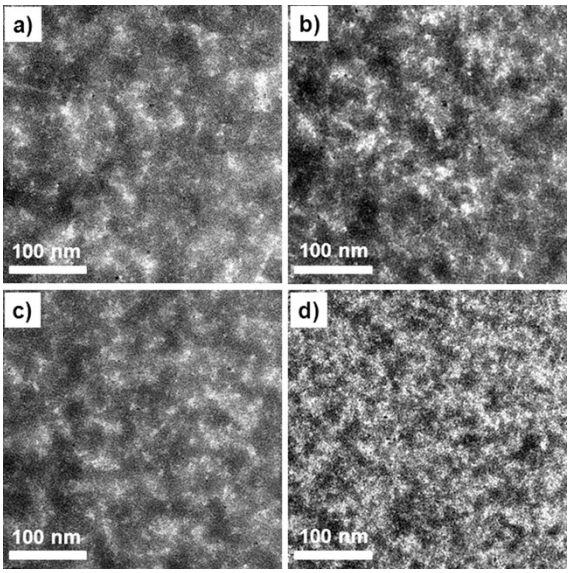


Fig. S2 TEM images of PIBTO-T:$PC_{71}BM$ (a, c) and PIBTO-TT:$PC_{71}BM$ (b, d) blend films without (top row) and with DIO (bottom row).

Table S1. Hole and electron mobilities of the **PIBTO-T**:$PC_{71}BM$ and **PIBTO-TT**:$PC_{71}BM$ blends with and without DIO measured by the SCLC method.

Copolymers	DIO (%, v/v)	μ_h ($cm^2\ v^{-1}\ s^{-1}$)	μ_e ($cm^2\ v^{-1}\ s^{-1}$)	μ_e/μ_h
PIBTO-T:$PC_{71}BM$	0	2.20×10^{-6}	3.36×10^{-5}	15.27
PIBTO-T:$PC_{71}BM$	0.5	8.11×10^{-6}	2.04×10^{-5}	2.52
PIBTO-TT:$PC_{71}BM$	0	1.95×10^{-5}	5.56×10^{-5}	2.85
PIBTO-TT:$PC_{71}BM$	0.5	2.63×10^{-5}	5.01×10^{-5}	1.90

References

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