Supplementary Information

Structure-Property Relationships of Oligothiophene-Isoindigo Polymers for Efficient Bulk-Heterojunction Solar Cells

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Experimental Section:

NMR Spectroscopy: ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were acquired from a Varian Inova 400 MHz NMR spectrometer. Tetramethylsilane was used as an internal reference with deuterated chloroform as solvent.

Size exclusion chromatography (SEC): SEC was performed on Waters Alliance GPCV2000 with a refractive index detector. Columns: Waters Styvagel HT GE×1, Waters Styvagel HMW GE×2. The eluent was 1,2,4-trichlorobenzene. The working temperature was 135 °C, and the resolution time was 2 h. The concentration of the samples was 0.5 mg mL^{-1}, and all solution were filtered (filter: 0.45 μm) prior to the analysis. The molecular weights were calculated according to relative calibration with polystyrene standards.

UV-Vis measurement: UV-Vis absorption spectra were measured with a Perkin Elmer Lambda 900 UV-Vis-NIR absorption spectrometer. The electroluminescence and the photoluminescence spectra were obtained by an Andor spectrometer (Shamrock sr-303i-B, coupled to a Newton EMCCD detector).

Electrochemical studies: Cyclic voltammetry (CV) measurements were carried out on a CH-Instruments 650A Electrochemical Workstation. A three-electrode setup was used with platinum wires both as working electrode and counter electrode, and Ag/Ag$^+$ was used as reference electrode calibrated with ferrocene/ferrocenyl couple (Fc/Fc$^+$). A 0.1 M solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in anhydrous acetonitrile was used as supporting electrolyte. The polymer was deposited onto the working electrode from chloroform solution. In order to remove oxygen from the electrolyte, the system was bubbled with nitrogen prior to each experiment. The nitrogen inlet was then moved to above the liquid surface and left there during the scans. The scan rate is 100 mV/s.

Variable angle spectroscopic ellipsometry (VASE): The samples for VASE measurements were prepared from *o*-DCB solution for P*n*TI and *o*-DCB:DIO (2.5% by Volume) solutions for P*n*TI blends in a D:A weight ratio of 2:3. Samples were spin-coated on cleaned silicon substrates with a 1 nm oxide layer. A RC2 instrument (J.A. Woolam Co., Inc) was used to perform VASE measurements with the incident angles being varied from 45 to 75° in steps of 10° on the prepared thin films. The modeling of the VASE measurements was performed by using the software Complete Ease (J.A. Woolam Co., Inc). The optical constants *n* and *k* were obtained by Tauc-Lorentz oscillators for P*1*TI and P*3*TI while B-splines[1] were used for P*5*TI and P*6*TI.

PV device fabrication and characterization: The BHJ photovoltaic devices were fabricated with a device geometry of glass/ITO/PEDOT:PSS(40 nm)/active layer/LiF(0.6 nm)/Al(100 nm). The ITO coated glass substrates were cleaned by using acetone and detergent. The substrates were then treated by TL-1, which is the mixture of water, ammonia (25%), and hydrogen peroxide (28%) (5:1:1 by volume). PEDOT:PSS 4083 (Heraeus Precious Metals GmbH & Co. KG) was spin-coated atop the cleaned substrates and heated for 10 minutes at 130 °C to remove the remaining water. Then, the substrates coated with PEDOT:PSS 4083 were moved into a glove box filled with N_2. The active layers were spin-coated from *o*-DCB:DIO (2.5% by volume) solutions onto the substrates. Then, the substrates were transferred into a vacuum chamber mounted in the glove box, where 0.6 nm LiF and 100 nm Al were thermally evaporated through a shadow mask under a pressure less than 4×10^{-6} mbar. The active area for the PV device defined by the overlap area between ITO anode and metal cathode is about 0.04 cm^2, which is calibrated by optical microscopy. The *J-V* curves were collected by using a Keithley 2400 Source Meter under AM1.5 illumination provided by a solar simulator (Model SS-50A, Photo Emission Tech., Inc.) with an intensity of 1000 W m^{-2}. EQE spectra were measured using a Newport Merlin lock-in. The chopped monochromatic light was illuminated on the solar cells through the ITO side. The thickness of the active layers was obtained by a Dektak surface profiler.

IQE and $J_{\text{sc-max}}$: IQE spectra were determined by the Transfer Matrix Model (TMM). The optical constants n and k for the active layer were collected by VASE, and the reflectance of the PV devices was measured by a UV/VIS spectrometer (Lambda 950) with an integrating sphere. The same optical constants n and k were also used to model the $J_{\text{sc-max}}$ by TMM with 100% IQE.

TEM: The samples for TEM were prepared as described above for the solar cells but without LiF/Al electrode deposition. The active layers were then placed onto a copper grid by the water dispersion of PEDOT:PSS, which is used as the sacrificial layer to lift-off the active layers. TEM was performed on the prepared samples with a Philips CM20/ST transmission electron microscope operated at 200 kV.

EQE_{EL} measurement: The EQE_{EL} was recorded from a home built system with a Hamamatsu silicon photodiode 1010B. A Keithley 2400 is used for supplying voltages and recording injected current, and a Keithley 485 for measuring the emitted light intensity.

PL and EL measurements: EL, PL and field-dependent PL spectra were recorded by using an Andor spectrometer (Shamrock sr-303i-B, coupled to a Newton EMCCD detector). An external current/voltage source meter was connected to prepared PV devices comprising pure or blend films to support an external electric field for EL and field-dependent PL measurements. The pumping light source used to measure PL and field-dependent PL is a red laser (CW He-Ne 632 nm) with an intensity of 2 mW cm^{-2}.

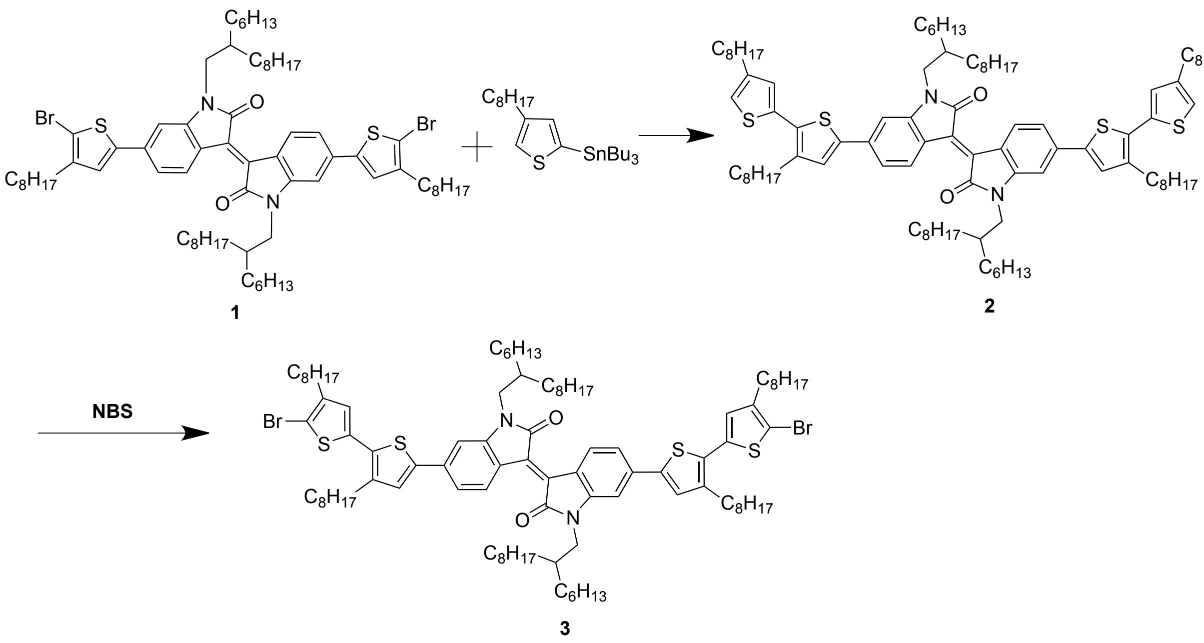
OFET device fabrication: Silicon substrates with a 200 nm layer of thermally grown oxide and thermally evaporated gold source and drain contacts were treated with an octadecyltrichlorosilane (OTS) self-assembled monolayer. Isotropic films were spun cast from solution (5 mg mL^{-1}) from chloroform at 1000 rpm. Annealed films were heated on a hot plate at 170 °C for 1 hr in a N_2 glove box (<1 ppm O_2). Mobility was evaluated in the linear regime for 4-5 devices per thickness.

DSC measurement: DSC measurements were performed under nitrogen at a scan rate of 10 °C min^{-1} with a Perkin Elmer Pyris 1 equipped with a Perkin Elmer Intra cooler 1P. P*1*TI was heated from 0 to 340 °C, the other three polymers from 0 to 300 °C. Peak melting temperatures and enthalpies of fusion were extracted from first heating thermograms of material that had been solidified from chloroform. Peak crystallisation temperatures from the first cooling scan are quoted. P*1*TI did not display a crystallisation exotherm; likely due to thermal degradation.

GIWAXS measurement: Films used for XRD were spun on silicon with native oxide. Substrates for P*n*TI were treated with OTS and prepared as described in the OFET section above. Blend films were spin-coated from *o*-DCB:DIO (2.5% by volume) solutions onto untreated substrates in a D:A weight ratio of 2:3. X-ray scattering was performed at the Stanford Synchrotron Radiation Lightsource (SSRL) on beam line 11-3 (2D scattering with an area detector, MAR345 image plate, at grazing incidence) with an incident energy of 12.7 keV. The incidence angle was slightly larger than the critical angle, ensuring that we sampled the full film depth.

Synthetic Procedures:

All reagents and starting materials were purchased from Aldrich and used without further purification, unless otherwise noted. 2,5-Bis(trimethylstannyl)thiophene and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene were purchased from Solarmer Materials Inc. Compound **1** and tributyl(4-octylthiophen-2-yl)stannane were prepared according to the literature methods.[2,3]



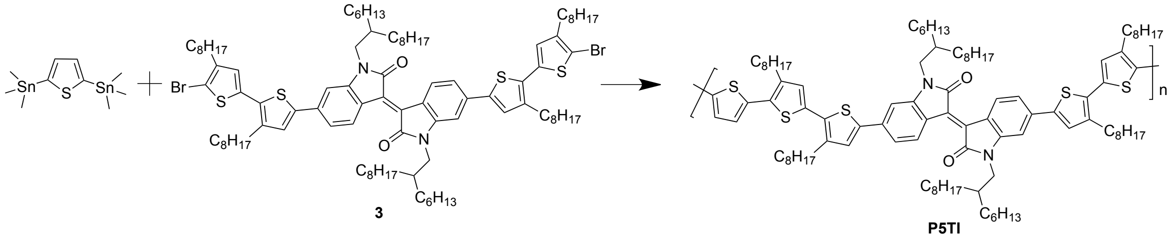
Synthesis of (*E*)-6,6'-bis(3,4'-dioctyl-[2,2'-bithiophen]-5-yl)-1,1'-bis(2-hexyldecyl)-[3,3'-biindolinylidene]-2,2'-dione (2)

To the solution of compound **1** (2.26 g, 1.80 mmol) and tributyl(4-octylthiophen-2-yl)stannane (2.18 g, 4.49 mmol) in anhydrous tetrahydrofuran (THF, 50 mL) bubbled with nitrogen, tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) (15 mg) and tri(*o*-tolyl)phosphine (P(*o*-tol)$_3$) (30 mg) were added in one portion. The solution was bubbled with nitrogen for another 20 min. The mixture was stirred overnight at 80 °C under nitrogen. Then the mixture was cooled to room temperature and poured into water. The organic phase was extracted by diethyl ether, and then washed with water, dried over $MgSO_4$. After the removal of the solvent under reduced pressure, the solids were purified by silica chromatography with dichloromethane:hexane = 1:3 as the eluent to afford the compound **2** (1.85 g, 69.1%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.15 (d, J = 8.4 Hz, 2H), 7.27 (dd, J = 1.6 Hz, 2H), 7.23 (s, 2H), 7.01 (d, J = 1.4 Hz, 2H), 6.94 (d, J = 1.6 Hz, 2H), 6.92 (d, J = 1.1 Hz, 2H), 3.71 (d, J = 7.1 Hz, 4H), 2.78 (m, 4H), 2.62 (m, 4H), 1.94 (b, 2H), 1.73 – 1.57 (m, 8H), 1.52 – 1.12 (m, 88H), 0.96 – 0.80 (m, 24H).

(*E*)-6,6'-bis(5'-bromo-3,4'-dioctyl-[2,2'-bithiophen]-5-yl)-1,1'-bis(2-hexyldecyl)-[3,3'-biindolinylidene]-2,2'-dione (3)

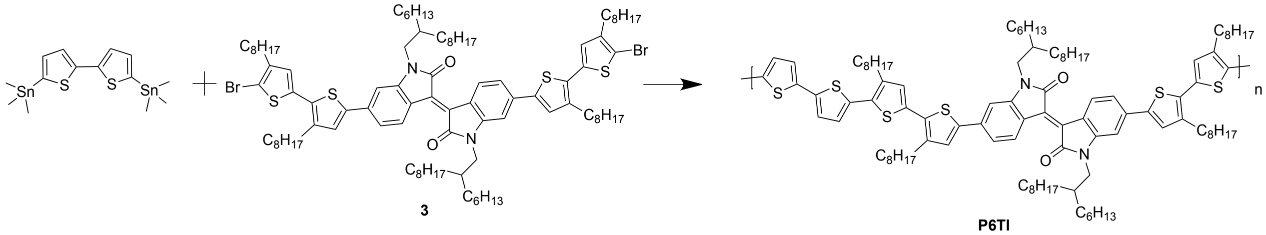
To the solution of the compound **2** (1.28 g, 0.86 mmol) in fresh distilled THF (30 mL), *N*-bromosuccinimide (NBS) (0.32 g, 1.81 mmol) was added in several portions in 0.5 h at room temperature. After the addition of NBS, the mixture was stirred for another 2 h, and then poured into water. The organic phase was extracted by diethyl ether, washed by water, dried over $MgSO_4$. After the purification by silica chromatography with hexane:dichloromethane = 3:1 as the eluent, compound **3** was obtained (1.15 g, 81.1%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.15 (d, J = 8.4 Hz, 2H), 7.24 (m, 4H), 7.22 (s, 2H), 6.93 (d, J = 1.7 Hz, 2H), 6.86 (s, 2H), 3.70 (d, J = 7.3 Hz, 4H), 2.73 (m, 4H), 2.57 (m, 4H), 1.93 (b, 3H), 1.72 – 1.57 (m, 8H), 1.49 – 1.15 (m, 88 H), 0.86 (m, 24H).

Synthesis of P5TI



In a 25 mL dry flask, 2,5-bis(trimethylstannyl)thiophene (82 mg, 0.2 mmol), **3** (329 mg, 0.2 mmol), tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) (6 mg) and tri(*o*-tolyl)phosphine (P(*o*-Tol)$_3$) (10 mg) were dissolved in degassed toluene (7 mL). The mixture was vigorously stirred at 100 °C for 1 h under nitrogen. After cooling to r. t., the solution was poured into acetone. The polymer was collected by filtration through a 0.45 μm Teflon filter. The polymer was then washed in a Soxhlet extractor with acetone and diethyl ether for 24 h each. Next, the polymer was Soxhlet-extracted with chloroform, and this chloroform fraction was purified by passing it though a short silica gel column and then precipitated from acetone. Finally, the polymer was collected by filtration through a 0.45 μm Teflon filter and dried under vacuum at 40 °C overnight (272 mg, 85%).

Synthesis of P*6*TI



P*6*TI was synthesized from the monomers 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (98 mg, 0.2 mmol) and **3** (329 mg, 0.2 mmol) by following the same procedure as for P*5*TI (290 mg, 86%).

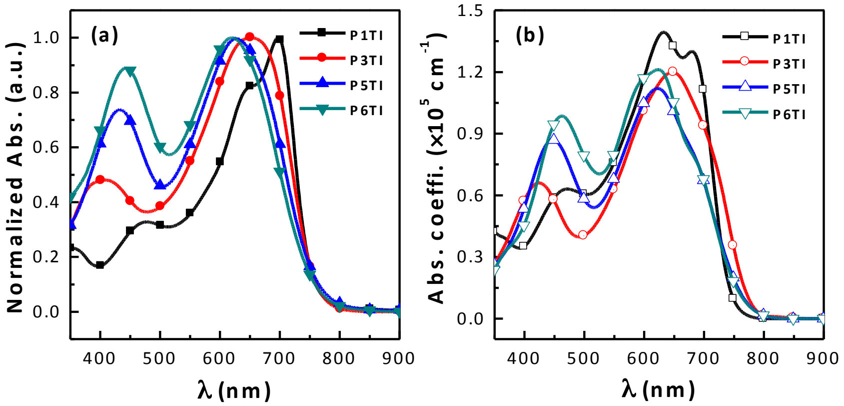


Figure S1. (a) Absorption spectra collected from P*n*TI chloroform solutions and (b) absorption coefficient (α) spectra of P*n*TI films prepared from *o*-DCB solutions determined by variable angle spectroscopic ellipsometry (VASE).

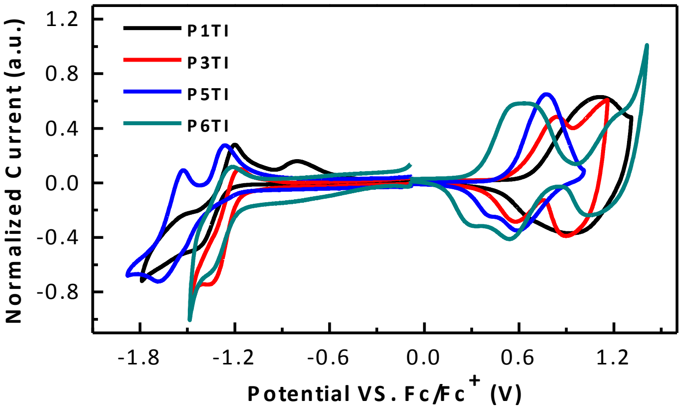


Figure S2. Cyclic voltammetry curves measured from P*n*TI films obtained from chloroform solutions.

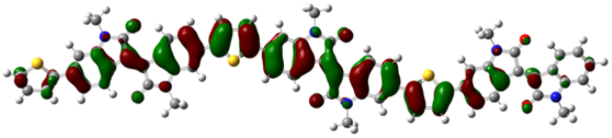
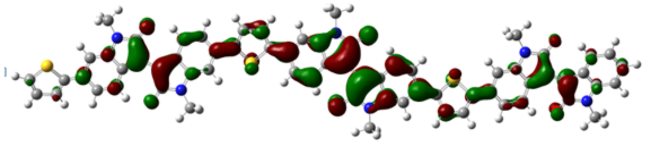
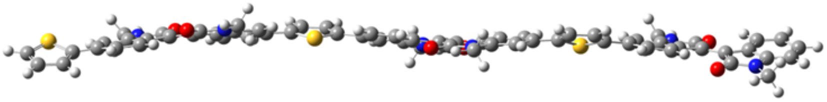
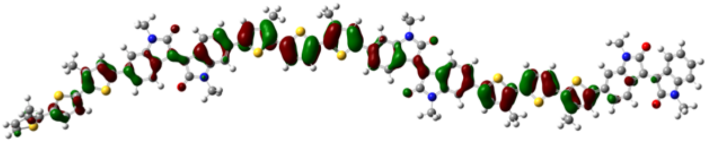
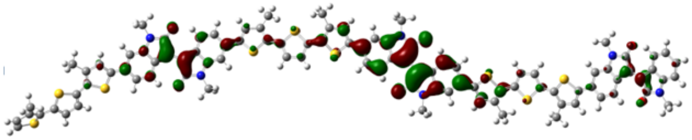
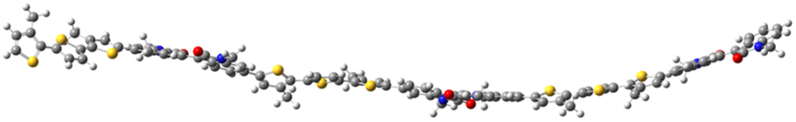
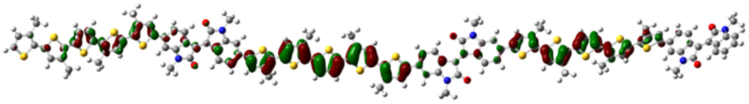
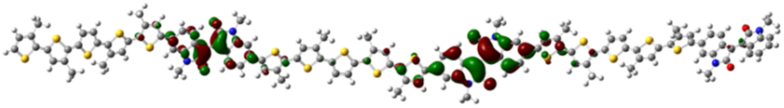
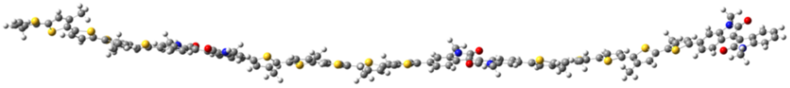
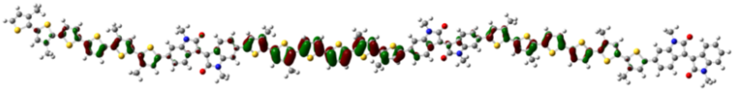
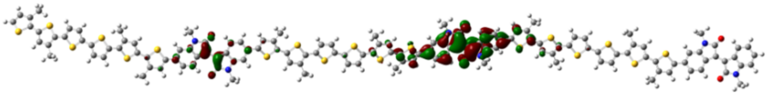
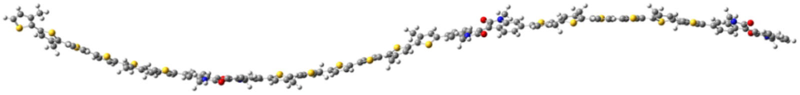
P*1*TI	HOMO	
	LUMO	
	Side view	
P*3*TI	HOMO	
	LUMO	
	Side view	
P*5*TI	HOMO	
	LUMO	
	Side view	
P*6*TI	HOMO	
	LUMO	
	Side view	

Figure S3. The HOMO and LUMO orbital distributions of P*n*TI models.

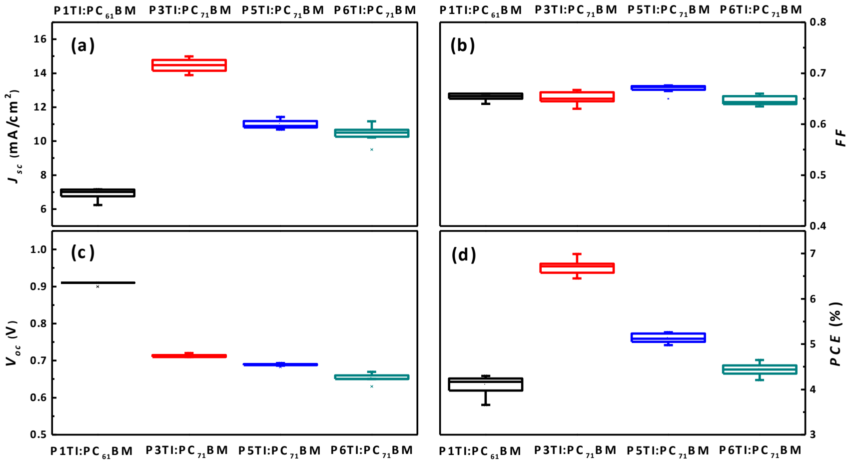


Figure S4. Statistical box graphs for (a) J_{sc}, (b) FF, (c) V_{oc} and (d) PCE of the P*n*TI:PCBM PSCs obtained from eight PV devices.

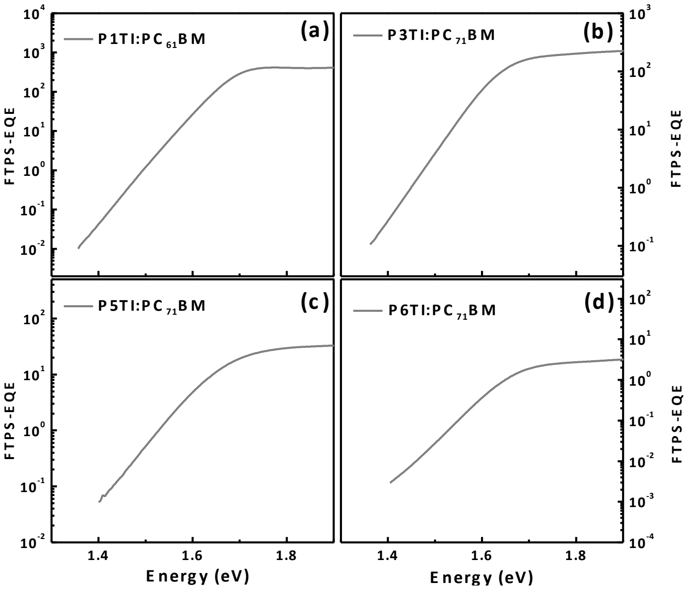


Figure S5. FTPS-EQE spectra for P*n*TI:PCBM based solar cells.

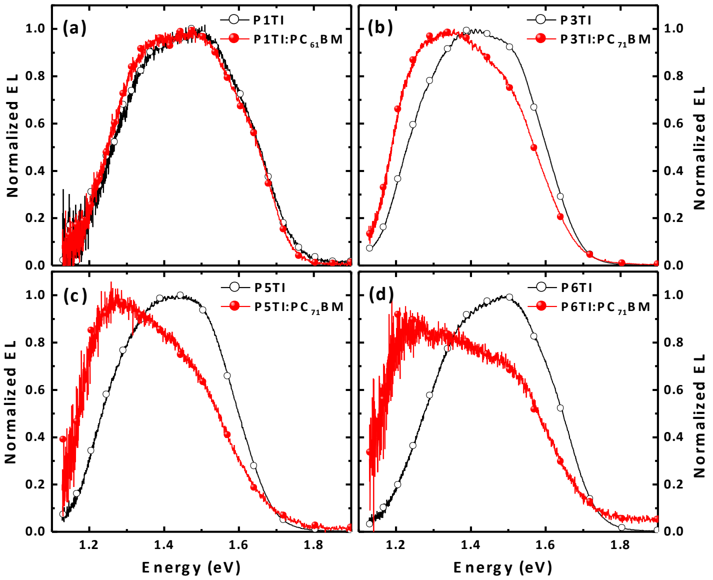


Figure S6. The EL spectra obtained under a forward bias for pure (open circles) and blend films (solid circles) for a) P*1*TI, b) P*3*TI, c) P*5*TI and d) P*6*TI systems

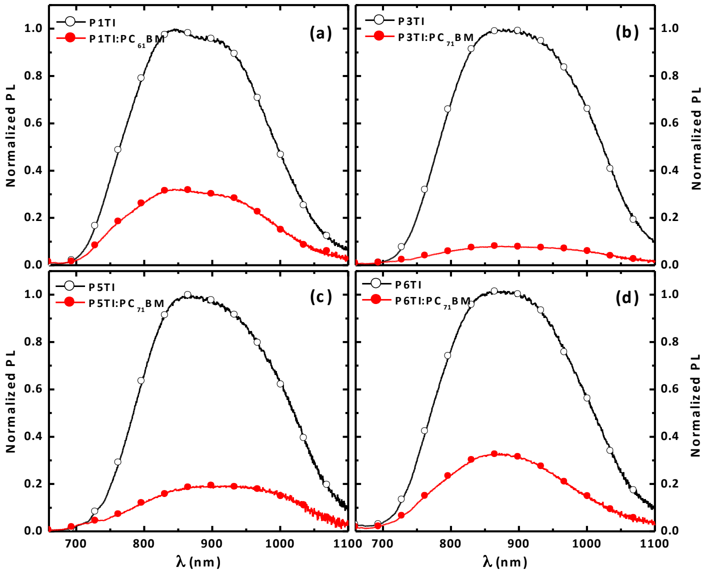


Figure S7. Normalized PL spectra of pure polymer films prepared from *o*-DCB solutions (open circles) and blend films spin-coated from *o*-DCB:DIO (2.5%, by volume) solutions (solid circles) for a) P*1*TI, b) P*3*TI c) P*5*TI and d) P*6*TI system.

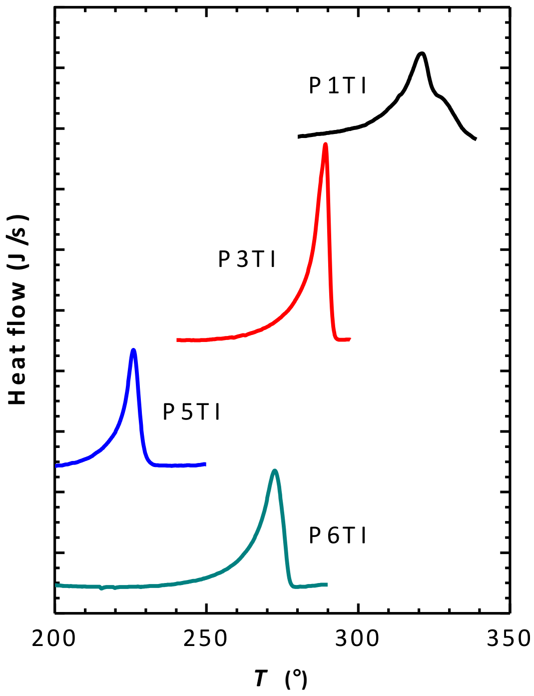
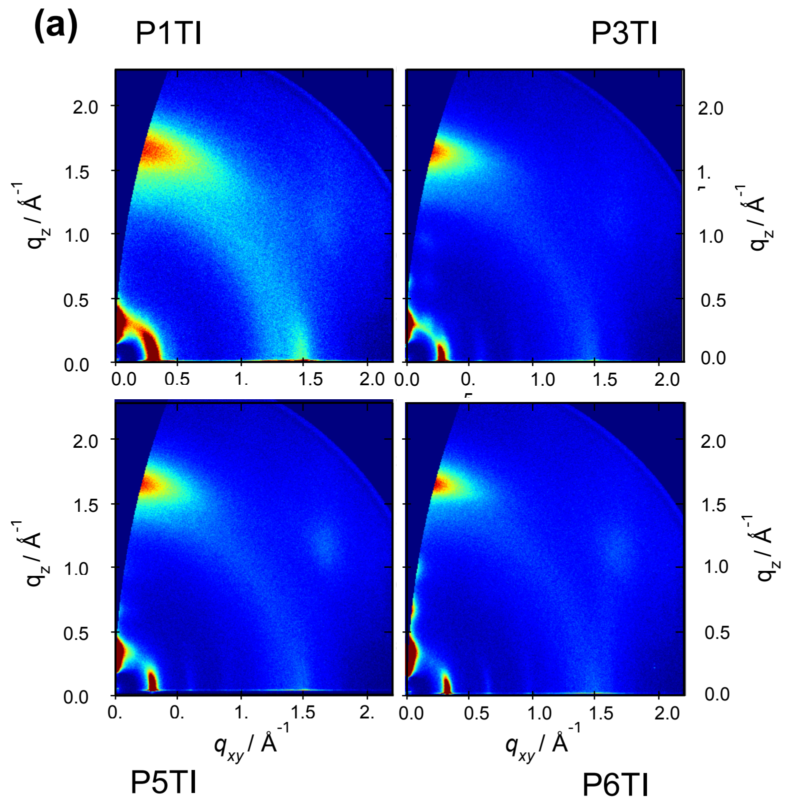


Figure S8. Melting endotherms of P*n*TI polymers from DSC first heating thermograms.


(a)
P1TI
P3TI
P5TI
P6TI
q_z / Å^{-1}
q_{xy} / Å^{-1}
0.0
0.5
1.0
1.5
2.0

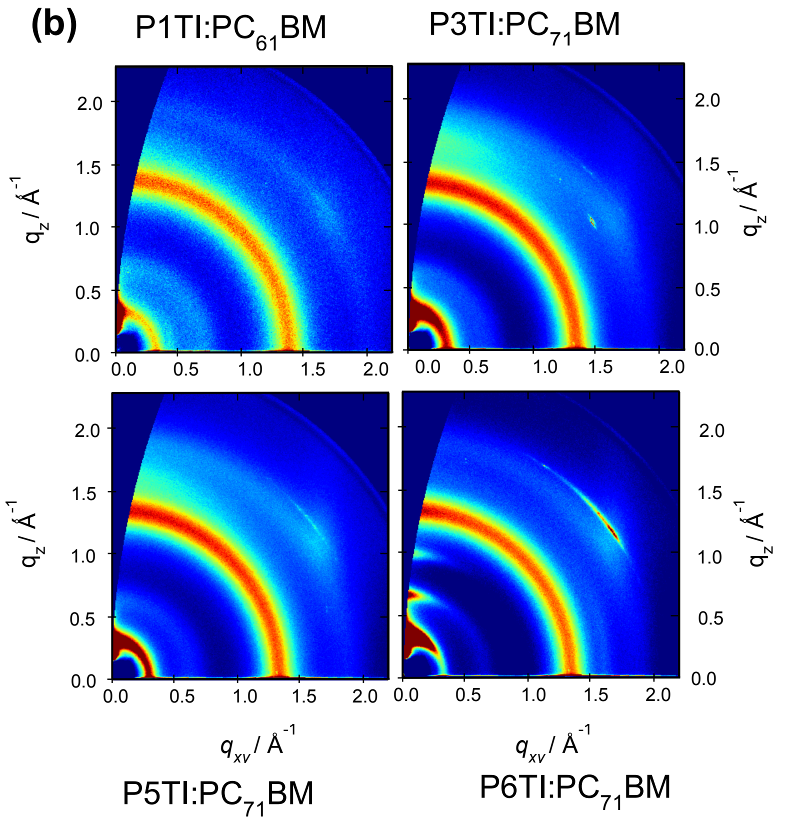

(b)
P1TI:PC$_{61}$BM
P3TI:PC$_{71}$BM
P5TI:PC$_{71}$BM
P6TI:PC$_{71}$BM
q_z / Å^{-1}
q_{xy} / Å^{-1}
0.0
0.5
1.0
1.5
2.0

Figure S9. GIWAXS patterns of (a) P*n*TI films spin-coated from CF solutions and annealed at 170°C and (b) P*n*TI:PCBM blend films prepared from *o*-DCB:DIO (2.5%, by volume) solution.

References

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2. E. Wang, Z. Ma, Z. Zhang, K. Vandewal, P. Henriksson, O. Inganäs, F. Zhang, and M. R. Andersson, *J. Am. Chem. Soc.*, 2011, **133**, 14244–14247.
3. T. Cai, Y. Zhou, E. Wang, S. Hellström, F. Zhang, S. Xu, O. Inganäs, and M. R. Andersson, *Sol. Energy Mater. Sol. Cells*, 2010, **94**, 1275–1281.