

Supplementary Material (ESI) for Polymer Chemistry  
This journal is (c) The Royal Society of Chemistry 2011

## Supporting Information

### An Isoindigo and Dithieno[3,2-b:2',3'-d]silole Copolymer for Polymer Solar Cells

Romain Stalder,<sup>a</sup> Caroline Grand,<sup>a</sup> Jegadesan Subbiah,<sup>b</sup> Franky So<sup>b</sup> and John R. Reynolds<sup>\*\*a</sup>

*The George and Josephine Butler Polymer Research Laboratory,  
Department of Chemistry  
Center for Macromolecular Science and Engineering  
University of Florida  
Gainesville, FL, 32611 (USA)  
E-mail: reynolds@chem.ufl.edu*

#### Experimental Details

Toluene was degassed via the freeze-pump-thaw method 5 times prior to reaction. 6,6'-dibromo-N,N'-(2-ethylhexyl)-isoindigo<sup>1</sup> and 2,2'-bistrimethylstannyl-4,4'-bis-(2-ethylhexyl)-dithieno[3,2-b:2',3'-d]silole<sup>2,3</sup> were synthesized following previously reported procedures. All other reagents and starting materials were purchased from commercial sources and used without further purification, unless otherwise noted. <sup>1</sup>H-NMR spectra were collected on a Varian Inova 2 500 MHz instrument using CDCl<sub>3</sub> as a solvent and the residual CHCl<sub>3</sub> peak as references (<sup>1</sup>H: δ = 7.26 ppm). Elemental analyses were carried out by the CHN elemental analysis service in the Chemistry Department of the University of Florida. Analytical HPLC was done on a Hitachi EZ chrome system, using a Lachrom ultra 4.6 mm X 150 mm C18 (TMS endcapped, 5 μm particle size) column, using 25% acetonitrile 75% acetone at 2 mL/min as eluent and detected at 340 nm. Preparative HPLC was done using the Lachrom ultra 21.2 mm X 250 mm C18 (TMS endcapped, 10 μm particle size) column at using 25% acetonitrile 75% acetone at 8 mL/min as eluent and detected at 340 nm. Gel permeation chromatography (GPC) was performed using a Waters Associates GPCV2000 liquid chromatography system with its internal differential refractive index detector (DRI) at 40°C, using two Waters Styragel HR-5E columns (10 μm PD, 7.8 mm i.d., 300 mm length) with HPLC grade THF as the mobile phase at a flow rate of 1.0 mL / min. Injections were made at 0.05 - 0.07 % w/v sample concentration using a 220.5 μL injection volume. Retention times were calibrated against narrow molecular weight polystyrene standards (Polymer Laboratories; Amherst, MA). Absorption spectra measurements were performed using a Varian Cary 500 UV-vis / NIR spectrophotometer. Thin films were sprayed onto glass slides from toluene solution for the solid state absorption experiments. Electrochemical measurements were carried out using an EG&G Princeton Applied Research model 273A potentiostat / galvanostat used under the control of Corrware II in a 3-electrode cell configuration, using Pt button working electrodes, Ag/Ag<sup>+</sup> (used for non-aqueous solutions) reference electrodes, and Pt flag counter electrodes. Thermogravimetric analysis (TGA) was performed on TA Instruments TGA Q1000 Series using dynamic scans under nitrogen.

## Synthetic details

### **Poly 5,5'-(4,4'-bis-(2-ethylhexyl)-dithieno[3,2-b:2',3'-d]silole)-*alt*-6,6'-N,N'-(2-ethylhexyl)-isoindigo, P(ii-DTS).**

The faint yellow oil 2,2'-bistrimethylstannyl-4,4'-bis-(2-ethylhexyl)-dithieno[3,2-b:2',3'-d]silole (monomer **2**)<sup>2,3</sup> was added in a tared clean glass vial, which was kept under vacuum. The oil, weighing 381.6 mg (0.510 mmol) once dry, was then diluted in 1 mL of hexanes and transferred to a dry Schlenk flask equipped with a stir bar. The dilution/transfer of **2** was repeated four times so that the compound was completely transferred to the reaction Schlenk flask, as a total of 5 mL of hexanes solution. The hexanes were then evaporated carefully under vacuum for 2 hours at room temperature. After refilling the reaction flask with argon, 6,6'-dibromo-N,N'-(2-ethylhexyl)-isoindigo<sup>1</sup> (monomer **1**, 330.4 mg, 0.510 mmol), Pd<sub>2</sub>dba<sub>3</sub> (chloroform adduct, 15 mg, 0.015 mmol) and P(*o*-tyl)<sub>3</sub> (10 mg, 0.03 mmol) were added to the flask and purged with 3 vacuum/argon refill cycles. Degassed toluene (5 mL, 5 freeze-pump-thaw cycles prior to addition) was then added to the flask and the reaction medium was stirred and heated to 85°C under argon. The reaction medium viscosity had notably increased after 12 hours at 85°C, and was left to stir for an additional 2 days at 85°C after which the temperature was increased to 100°C for 2 hours. After the reaction medium was cooled back to 85°C, a solution of 2-bromothiophene (0.2 mmol) in degassed toluene (2 mL) was added to the flask along with a small amount of the catalytic system and allowed to react for 6 hours. A solution of 2-(tributylstannyl)-thiophene (0.2 mmol) in degassed toluene (2 mL) was subsequently added to the flask and allowed to react for 12 hours. At this point, the reaction medium was then cooled to 60°C and a spatula tip of diethylammonium diethyldithiocarbamate was added to the flask. After 2 hours of stirring at 60°C, the reaction medium was precipitated into methanol (200 mL). The precipitates were filtered and collected into a cellulose thimble, then purified in a Soxhlet apparatus using methanol (1 day), hexanes (12 hours) and chloroform (2 hours). The methanol and hexanes fractions were discarded, while the chloroform fraction was precipitated into methanol (200 mL). The precipitates were collected and dried to afford 445 mg of dark purple solids (0.494, 97%). GPC: Mn = 36,000 kDa; Mw = 99,600; PDI = 2.77. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 9.4-8.8 ppm (br, 2H), 7.8-7.0 (br, 4H), 6.8-6.2 (br, 2H), 4.0-3.6 (br, 4H), 2.0-1.0 (br, 40H), 1.0-0.6 (br, 24H). Elemental Analysis Calc. for C<sub>56</sub>H<sub>76</sub>O<sub>2</sub>S<sub>2</sub>Si: C, 74.61; H, 8.50; N, 3.11. Found: C, 74.22; H, 8.61; N, 3.02.

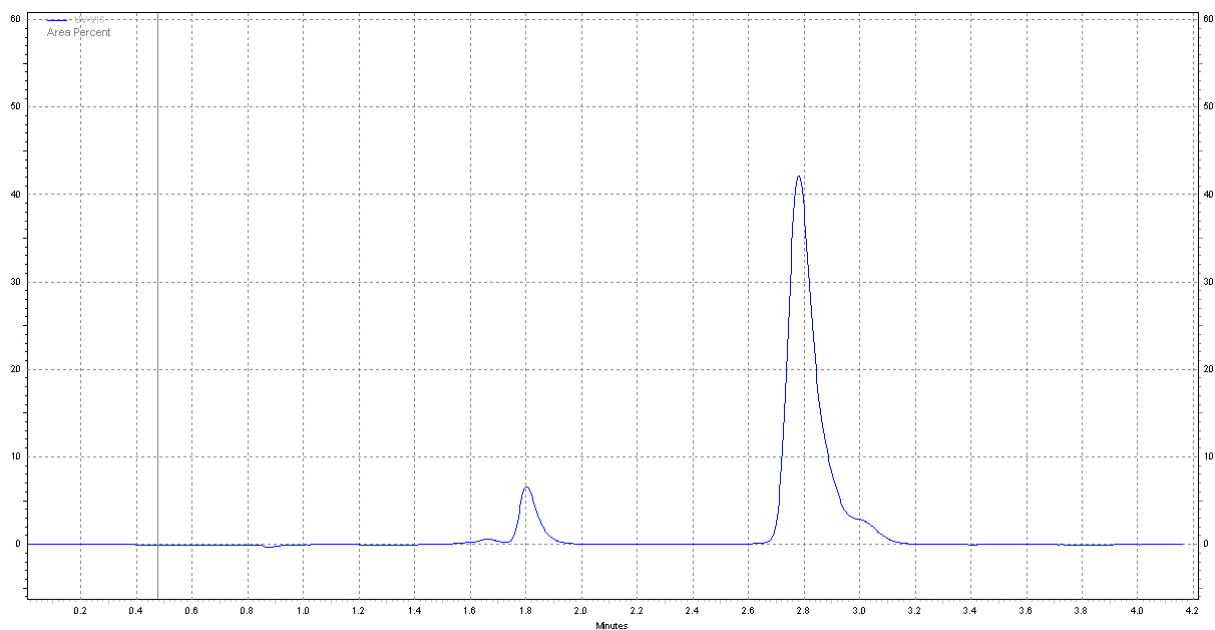


Figure S1. Analytical HPLC trace of ditin-DTS monomer **2** prior to preparative HPLC purification.

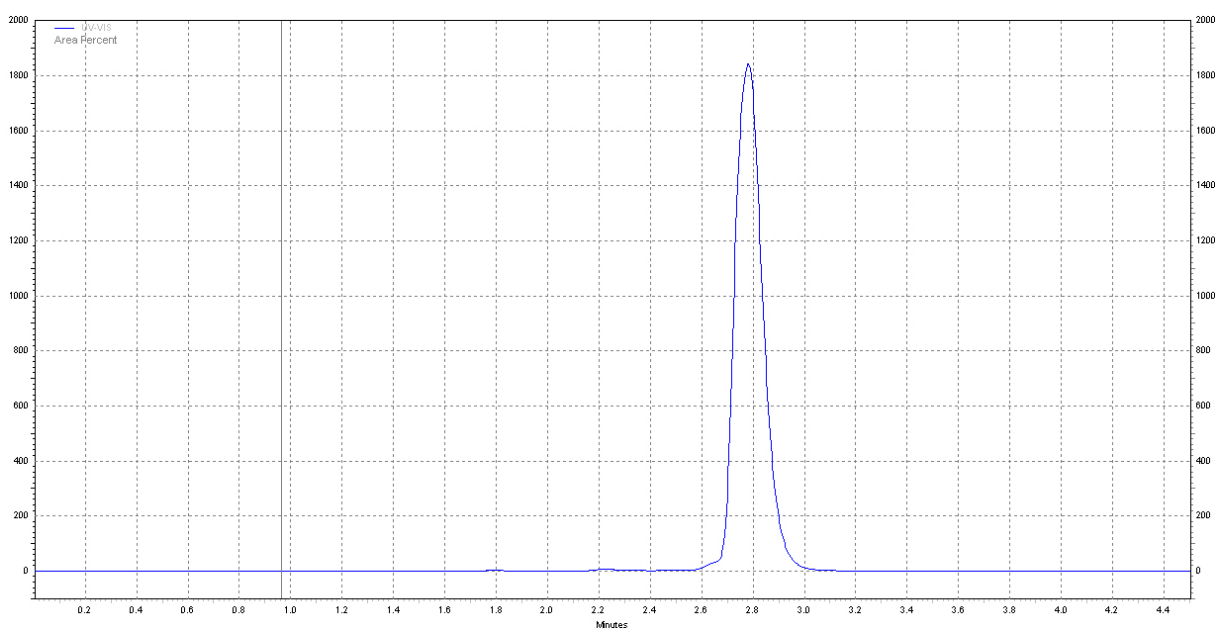


Figure S2. Analytical HPLC trace of ditin-DTS monomer **2** after preparative HPLC purification.

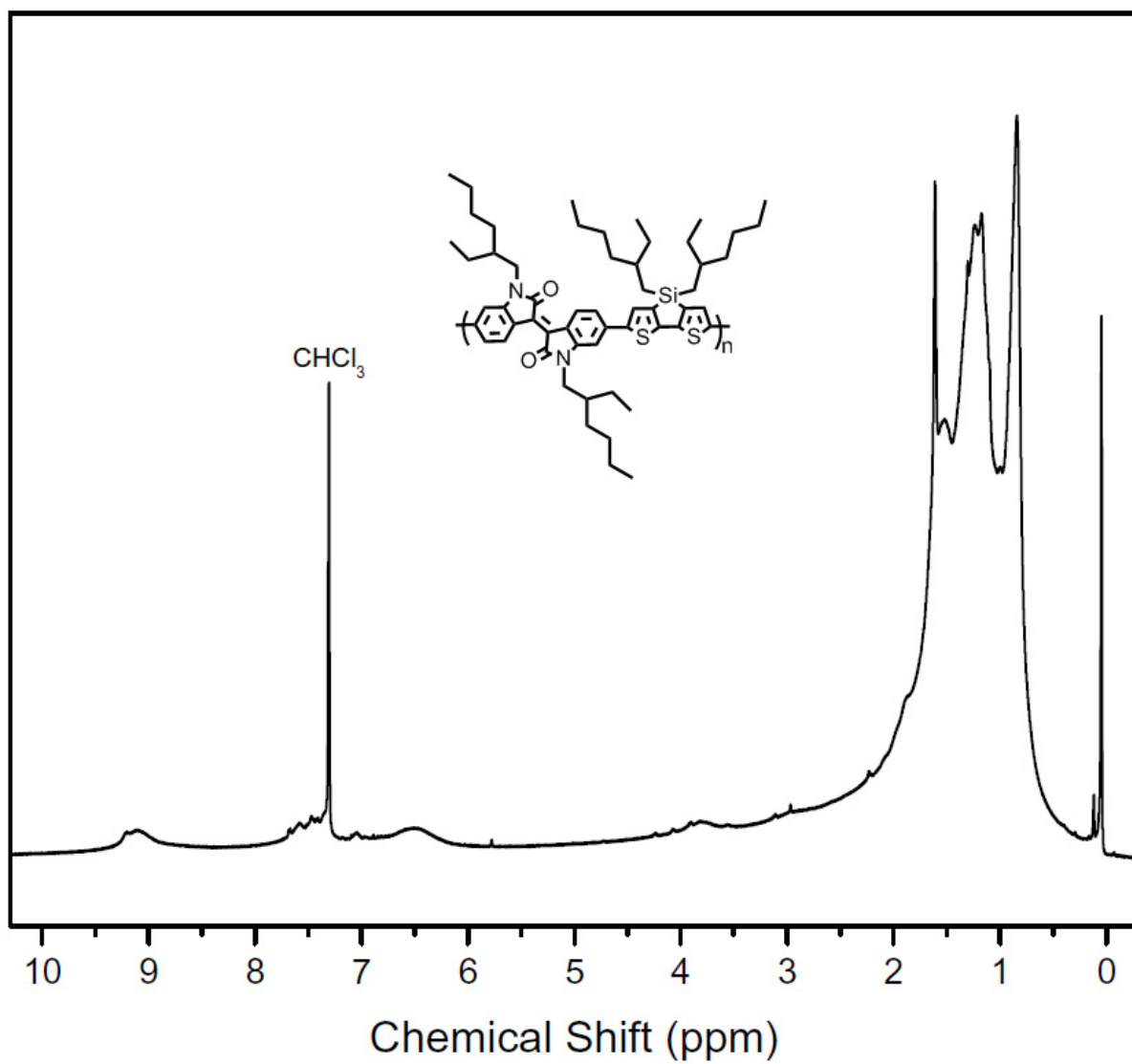


Figure S3.  $^1\text{H}$  NMR spectrum of **P(ii-DTS)** in  $\text{CDCl}_3$ .

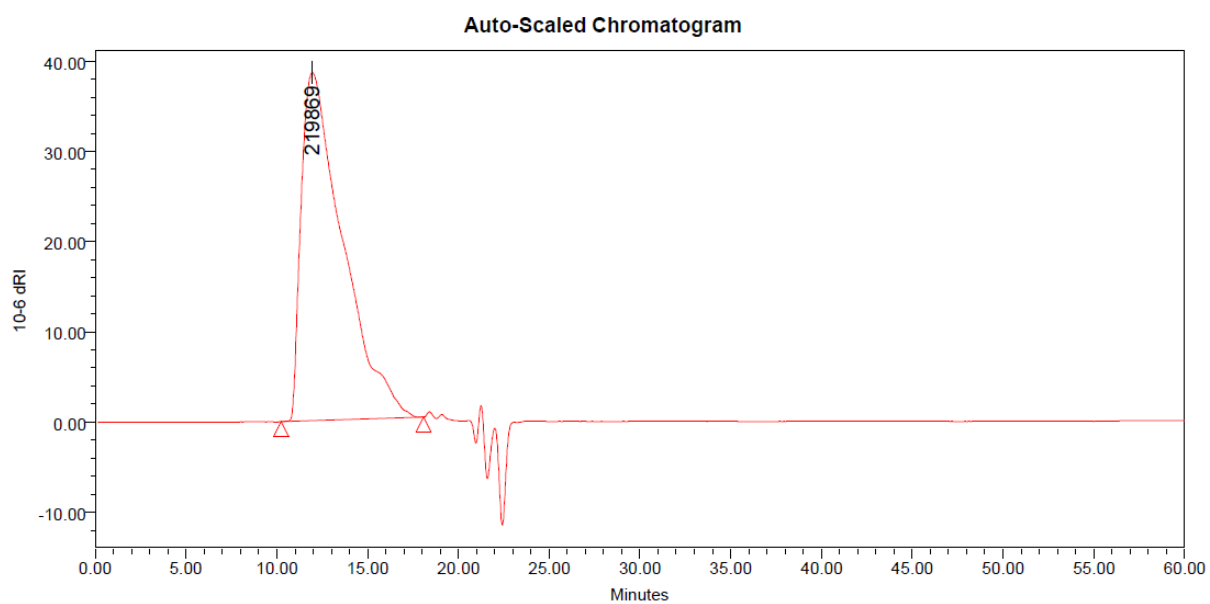


Figure S4. GPC trace of **P(iI-DTS)** in THF eluent.

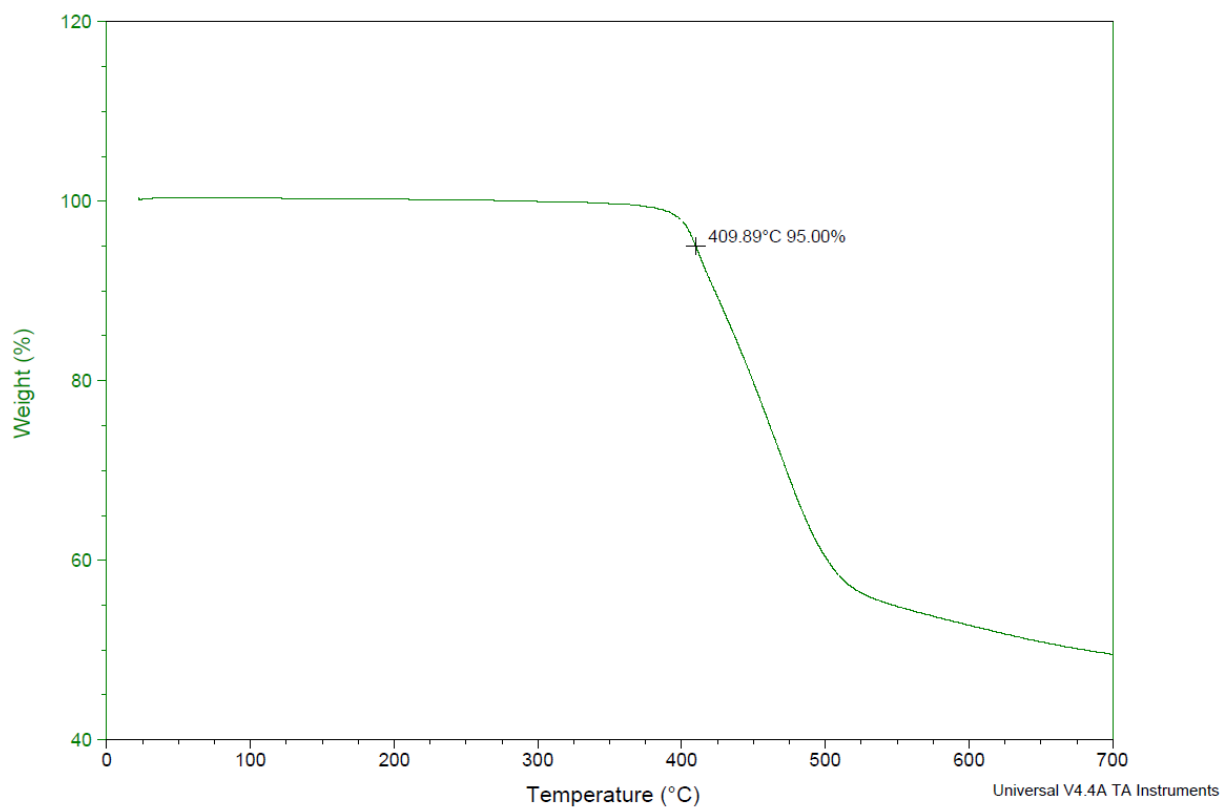


Figure S5. TGA thermogram of **P(iI-DTS)** under N<sub>2</sub> flow.

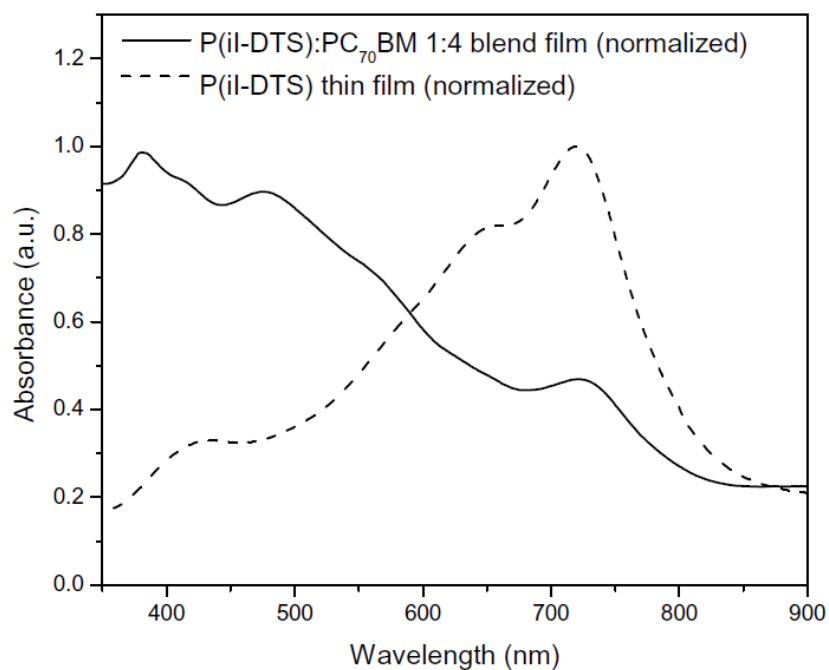


Figure S6. UV-vis absorption spectra of **P(iI-DTS)** thin film and of **P(iI-DTS):PC<sub>70</sub>BM 1:4** blend film.

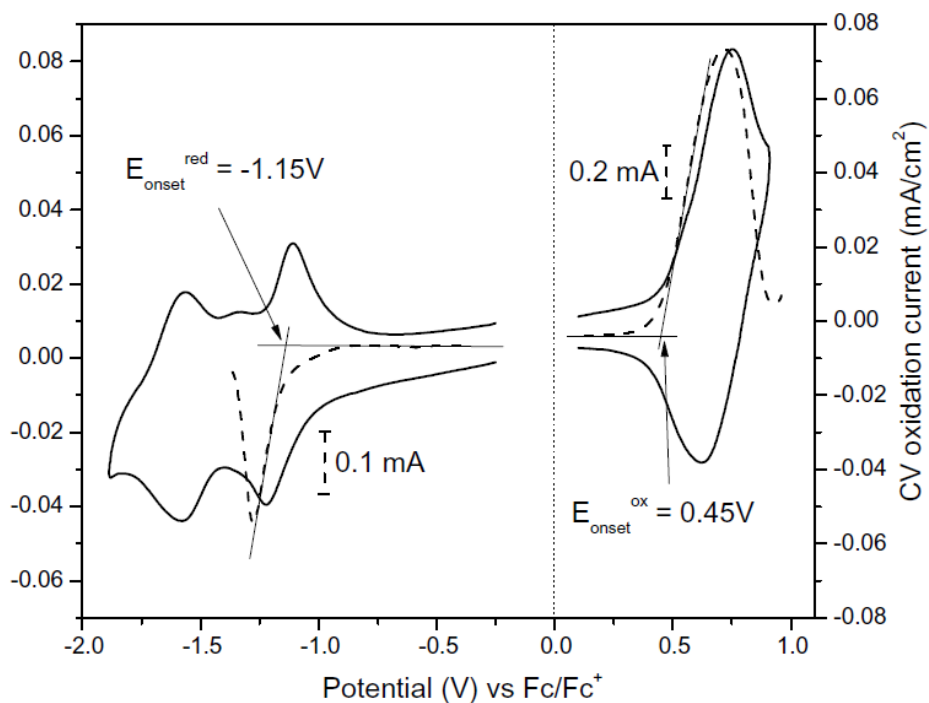


Figure S7: CV and DPV of **P(iI-DTS)** thin films on Pt-buttons in 0.1M TBAPF<sub>6</sub> in ACN at 50mV/s.

## Device Fabrication Procedure

Bulk-heterojunction (BHJ) solar cells were fabricated by the spin coating of 30-nm-thick layers of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS; Baytron AI 4083 from HC Starck) on a ultrasonically cleaned, indium tin oxide (ITO) coated, patterned glass substrates, followed by backing on a hot plate at 180 °C for 10 min. An active layer of the device consisting of the blend of polymer P(iI-DTS) and PC<sub>70</sub>BM (99% pure, Solenne BV) with a ratio of 1:4 (with and without 4% DIO) was then spin coated from chlorobenzene solvent with a thickness of 105 nm. The device was subsequently heated on a hotplate at 150 °C for 10 min. LiF (1 nm) and aluminum (100 nm) were thermally evaporated at a vacuum of  $\sim 10^{-7}$  mbar on top of active layer as a cathode.

For the inverted geometry, a thin layer of sol-gel ZnO (35nm) was spin coated onto ITO-coated glass. The ZnO sol-gel films were then annealed in air for 30min at 200°C. The same process for the active layer in the conventional architecture was used for the inverted devices. After annealing the active layer, a thin layer of MoO<sub>3</sub> (10 nm) was thermally evaporated and then Ag electrode was deposited to complete the inverted device structure. The area of the devices was 0.04 cm<sup>2</sup>. The current density-voltage measurements of the devices were carried out using a 150 W Newport ozone free xenon arc lamp as the light source in conjunction with a Keithley 4200 semiconductor parameter analyzer system. Solar measurements were carried out under 1000 W/m<sup>2</sup> AM 1.5G illumination conditions. Device fabrication was done under nitrogen atmosphere and characterizations were performed in an ambient environment without any encapsulation.

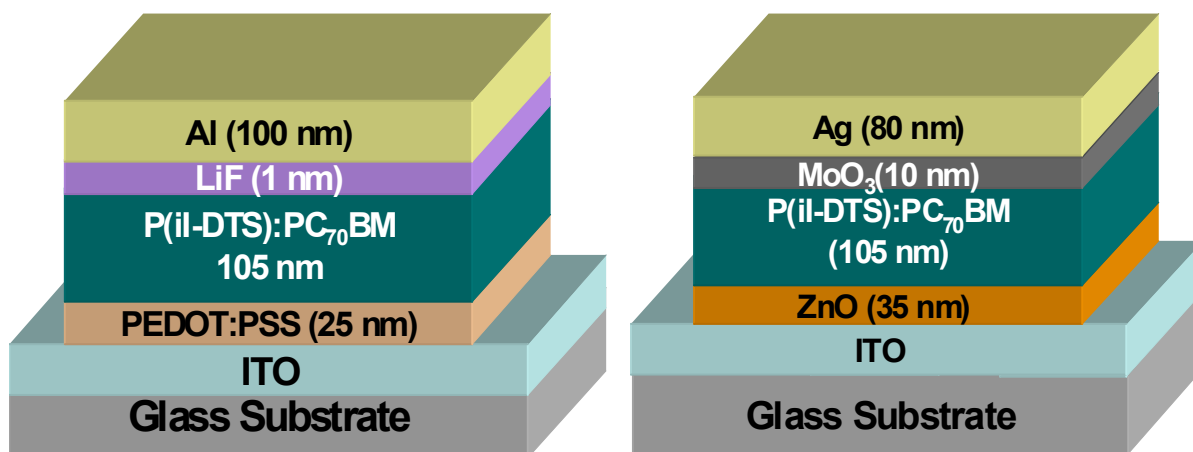


Figure S8. (a) Schematic diagram of the P(iI-DTS) polymer solar cell with conventional and (b) inverted geometry.

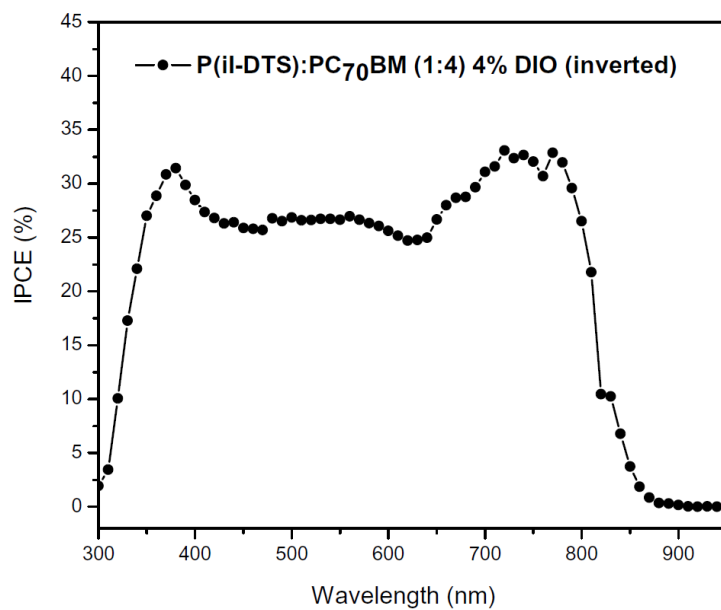


Figure S9. IPCE of the  $P(iI-DTS):PC_{70}BM$  in inverted cells.

### References:

- (1) Mei, J.; Graham, K. R.; Stalder, R.; Reynolds, J. R. *Org. Lett.* **2010**, *12*, 660-663.
- (2) Amb, C. M.; Chen, S.; Graham, K. R.; Subbiah, J.; Small, C. E.; So, F.; Reynolds, J. R. *J. Am. Chem. Soc.* **2011**, *133*, 10062-10065.
- (3) Hou, J.; Chen, H.-Y.; Zhang, S.; Li, G.; Yang, Y. *J. Am. Chem. Soc.* **2008**, *130*, 16144-16145.