

## **(Poly(benzo[2,1-b:3,4-b']dithiophene-alt-isoindigo): a low bandgap polymer showing high open circuit voltage in polymer solar cells)**

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### ***Instruments.***

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker arx-400 spectrometer. Absorption spectra were taken on a Hitachi U-3010 UV-Vis spectrophotometer. The molecular weight of polymers was measured by GPC method, and polystyrene was used as a standard by using chloroform as eluent. TGA measurement was performed on a TA Instruments, Inc., TGA-2050. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e Electrochemical Workstation with Pt disk, Pt plate, and Ag/Ag<sup>+</sup> electrode as working electrode, counter electrode and reference electrode respectively, in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) acetonitrile solution.

### ***Fabrication of polymer solar cells.***

Polymer solar cell devices with the structure of ITO/PEDOT-PSS/Polymer:PC<sub>70</sub>BM/Ca(10 nm)/Al(80 nm) were fabricated under conditions as follows: patterned indium tin oxide (ITO)-coated glass with a sheet resistance of 10-15 ohm/square was cleaned by a surfactant scrub and then underwent a wet-cleaning process inside an ultrasonic bath, beginning with deionized water followed by acetone and isopropanol. After oxygen plasma cleaning for 10 min, a 40 nm thick poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Bayer Baytron 4083) anode buffer layer was spin-cast onto the ITO substrate and then dried by baking in an oven at 150 °C for 15 min. The active layer, with a thickness in the range of 90-100 nm, was then deposited on top of the PEDOT: PSS layer by casting from a 10 mg/ml *o*-DCB solution. Finally, 10 nm Ca and 80 nm Al layer were successively deposited in vacuum onto the active layer at a pressure of ca.  $4 \times 10^{-4}$  Pa. The overlapping area between the cathode and anode defined a pixel size of 4 mm<sup>2</sup>. The whole thicknesses of the PSCswere measured by an Ambios Technology XP-2 surface profilermeter. Current density–voltage( J–V) characteristics were measured by a computer controlled Keithley 2602 source measurement moiety in the dark and under AM 1.5 illumination conditions, 100 mW cm<sup>-2</sup>. The measurement of External Quantum Efficiency (EQE) was performed using a Zolix DCS300PA Data acquisition system. Except for the deposition of the PEDOT:PSS layers, all the fabrication processes were carried out inside a controlled atmosphere of nitrogen dry box containing less than 10 ppm oxygen and moisture.

## ***Synthesis.***

### **Materials**

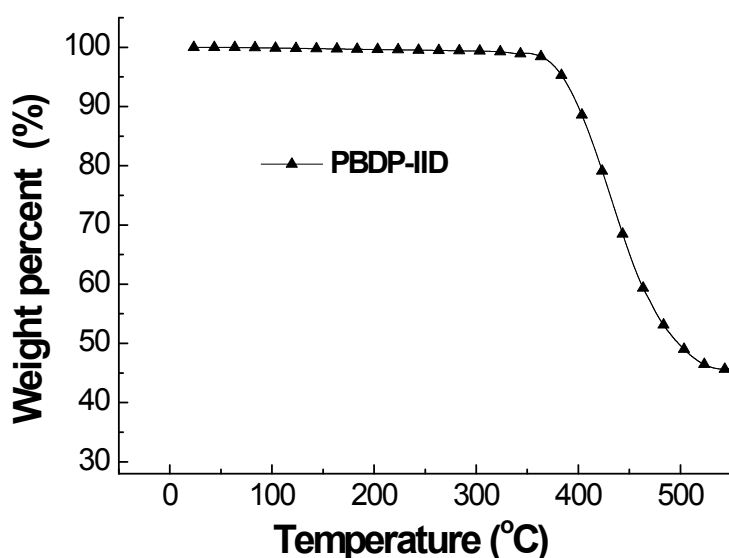
2,6-Bis(trimethyltin)-4,8-diethylhexyloxybenzo[1,2-b;3,4-b]dithiophene (M1) was prepared according to Reference 1. The isoindigo was synthesized according to similar reference 2.

### **6,6'-Dibromo-N,N'-(2-octyldodecanyl)-isoindigo (IID)**

Compound (3) (0.84 g, 2 mmol) and anhydrous potassium carbonate (1.66 g, 12 mmol) were dissolved in N,N-dimethylformamide (30 ml) in a two-neck flask and heated to 100 °C under argon protection. 7-(bromomethyl)pentadecane (1.83 g, 6 mmol) was injected one time by syringe. When the reaction was kept at 100 °C for 12 h, the solution was cooled to room temperature and poured into 400 mL ice-water and extracted with chloroform. Subsequently, the organic layer was concentrated by rotary evaporating the solvent and the residue was purified by silica gel chromatography using hexane: dichloromethane (2:1) as eluent to obtain a red solid powder (0.76 g, yield 44%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (ppm): 9.01 (d, 2H), 7.14 (d, 2H), 6.86 (s, 2H), 3.59 (m, 4H), 1.78 (m, 2H), 1.45-1.24 (m, 48H), 0.89 (m, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz), δ (ppm): 168.01, 146.11, 132.77, 130.97, 126.61, 125.41, 120.34, 111.43, 44.31, 36.67, 32.03, 31.89, 31.77, 30.05, 29.71, 29.60, 29.55, 29.48, 29.33, 29.25, 26.36, 22.68, 14.11, 14.08.

**PBDP-IID** 0.5 mmol of 1,1'-Bis(2-octyldodecanyl)-6,6'-dibromoisindigo (IID) and 0.5 mmol of BDP monomer were put into a three-neck flask. Then 15 mL of degassed

toluene was added under the protection of argon. The solution was flushed with argon for 10 min, and then 30 mg of Pd(PPh<sub>3</sub>)<sub>4</sub> was added. After another flushing with argon for 20 min, the reactant was heated to reflux for 20 h. Then the reactant was cooled to room temperature, and the polymer was precipitated by adding 50 mL methanol, and filtered through a Soxhlet thimble, then subjected to Soxhlet extraction with methanol, hexane, and chloroform. The polymer was recovered as solid from the chloroform fraction by rotary evaporation. The solid was dried under vacuum for 1 day to get deep dark green solid powder, Yield: 64%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz),  $\delta$  (ppm): 9.01 (br, 2H), 7.66-6.74 (br, 6H), 3.71 (br, 4H), 3.01 (br, 4H), 1.98- 0.83 (m, 92H). Anal. Calcd. for C<sub>86</sub>H<sub>131</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 80.13; H, 10.24; N, 2.17; Found: C 79.81, H 10.11, N, 2.16.  $M_w$  =37.6K; polydispersity = 2.3.



**Figure 1.** TGA plots of the PIID-IIID with a heating rate of 10 °C /min in the air.

1. L. J. Huo, X. Guo, Y. F. Li and J. H. Hou , *Chem. Commun.*, 2011, 47, 8850-8852.
2. Mei, J. G.; Graham, K. R.; Stalder R.; Reynolds J. R. *Org. Lett.*, **2010**, *12*, 660-663