

**Crystalline Low Band-gap Alternating Indolocarbazole and Benzothiadiazole-cored  
Oligothiophene Copolymer for Organic Solar Cell Applications**

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Experimental:

**4,7-Bis(3,4'-dioctyl-2,2'-bithiophen-5-yl)-2,1,3-benzothiadiazole (5):** Pd(PPh<sub>3</sub>)<sub>4</sub> (116 mg, 0.1 mmol) was added to a solution of **4** (3.41 g, 5.0 mmol) and trimethyl-(4-octyl-2-thienyl)stannane (**2**, 5.39 g, 15.0 mmol) in anhydrous DMF (30 mL). The mixture was stirred under argon for 24 h at 100 °C and then allowed to cool to room temperature. Saturated NaHCO<sub>3</sub> aqueous solution (20 mL) and hexanes (50 mL) were added. The aqueous layer was removed, and the organic layer was washed three times with distilled water, and then was dried over magnesium sulfate. The solvent was removed under a reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexanes) to give compound **5** (4.02 g, 88%). <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>, δ, ppm) 8.13 (s, 2H), 8.07 (s, 2H), 7.20 (s, 2H), 7.18 (s, 2H), 2.88 (t, 4H), 2.68 (t, 4H), 1.82-1.66 (m, 8H), 1.48-1.24 (m, 40H), 0.88 (t, 12H).

**4,7-Bis(5'-bromo-3,4'-dioctyl-2,2'-bithiophen-5-yl)-2,1,3-benzothiadiazole (6):** A mixture of **5** (2.19 g, 2.40 mmol), *N*-bromosuccinimide (NBS) (0.854 g, 4.8 mmol), silica gel (0.2 g) in dichloromethane (10 mL) was stirred at -10 °C for 4 h. The reaction was quenched with water (100 mL) and then extracted with dichloromethane for 2 times. The combined CH<sub>2</sub>Cl<sub>2</sub> solution was washed with water and dried over magnesium sulfate. The concentrated solution was then purified by a silica gel column using hexanes as the eluent to give the desired product **6** as a dark purple solid (2.08 g, 81%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, δ, ppm) 8.10 (s, 2H), 8.05 (s, 2H), 7.12 (s, 2H), 2.84 (t, 4H), 2.63 (t, 4H), 1.70 (m, 8H), 1.48-1.20 (m, 40H), 0.86 (t, 12H). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, δ, ppm) 153.2, 143.4, 141.5, 138.2, 136.7, 132.6, 131.5, 127.6, 126.1, 125.6, 109.9, 32.7, 31.4, 30.44, 30.37, 30.33, 30.27, 30.23, 30.16, 30.10, 30.04, 30.01, 23.48, 23.47, 14.8.

**3,9-dibromo-5,11-di(2-hexyldecyl)indolo[3,2-b]carbazole (8).** To a 100 mL flask were added 3,9-dibromoindolo[3,2-b]carbazole, **7** (400 mg), benzyltriethylammonium chloride (22 mg), 1-(2-hexyl decyl) bromide (890 mg), DMSO (10 mL), and THF (5 mL). Then NaOH aqueous solution (50 wt%, 0.5 mL) was dropwise added with stirring. The resulting red solution was further stirred at room temperature overnight. The reaction was quenched by 50 mL of water containing 2 mL of CH<sub>3</sub>COOH. The resulting milky solution was extracted with hexanes (3 x 25 mL). The organic layers were combined, dried over MgSO<sub>4</sub>, concentrated under reduced pressure. Purification by column chromatography on silica gel afforded 0.744 g of yellow powder in 89.3 % yield. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, δ, ppm) 7.97 (s, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 1.6 Hz, 2H), 7.40 (dd, *J*<sub>1</sub> = 8.4 Hz, *J*<sub>2</sub> = 1.6 Hz, 2H), 3.86 (d, *J* = 7.6 Hz, 4H), 2.15 (m, 2H), 1.40-1.10 (m, 48 H), 0.90 (t, *J* = 6.8 Hz, 6H), 0.86 (t, *J* = 6.8 Hz, 6H). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, δ) 143.50, 137.27, 123.07, 122.28, 121.77, 121.71, 120.13, 112.37, 99.69, 47.84, 37.63, 32.27, 32.16, 32.04, 30.30, 29.95, 29.73, 26.72, 26.68, 23.07, 23.03, 14.35, 14.32.

**3,9-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,11-di(2-hexyldecyl)indolo[3,2-b]carbazole (9).** In a 50 mL oven-dried flask, dibromoindolocarbazole, **10** (500 mg, 0.58 mmol) and anhydrous THF (12 mL) were added under Ar using a standard Schlenk technique. Then n-butyl lithium (2.5M, 0.53 mL) was added at -78 °C via a syringe with stirring. After stirring at -78 °C for 3 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.35 mL, 1.74 mmol) was added. The reaction solution was allowed to warm to room temperature overnight. The mixture was poured into water and then extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over MgSO<sub>4</sub>. The solution was

concentrated and purified by column chromatography on silica gel to afford 0.368 g of yellow powder in 66.4 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm) 8.42 (s, 2H), 8.34 (d,  $J = 7.6$  Hz, 2H), 8.27 (d,  $J = 7.6$  Hz, 2H), 8.16 (s, 2H), 4.09 (d,  $J = 7.6$  Hz, 4H), 2.32 (m, 2H), 1.40-1.10 (m, 72H), 0.90 (t,  $J = 6.8$  Hz, 6H), 0.86 (t,  $J = 6.8$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ,  $\delta$ , ppm) 142.56, 137.66, 127.37, 126.10, 125.18, 123.95, 120.14, 116.03, 100.05, 83.74, 47.88, 37.71, 32.29, 32.19, 32.10, 30.33, 29.97, 29.74, 26.77, 26.71, 25.09, 23.08, 23.03, 14.35.

**The preparation of the alternating copolymer, P(InCzTh<sub>2</sub>BTD).** To a 50 mL one-necked flask were added oligothiophene dibromide **6** (1.025 eq) and indolo[3,2-b]carbazole diboronate **9** (1 eq). The flask equipped with a condenser was then evacuated and filled with argon 3 times to remove traces of air.  $\text{Pd}(\text{PPh}_4)_3$  (0.5% eq) was then added under an argon atmosphere. In another 50 mL flask, tricapyrylmethylammonium chloride (Aliquat<sup>®</sup> 336) (3 drops), 2 M  $\text{K}_2\text{CO}_3$  aqueous solution (3.3 eq), and toluene were added. The resulting mixture was degassed and then transferred to the reaction flask via a syringe. The reaction flask was again evacuated and filled with argon once more. The mixture was then heated to reflux with stirring and maintained for 48 hours under argon. Phenyl boronic acid (0.15 eq) solution in degassed toluene was then added. The solution was further refluxed for another 8 h. The polymerization mixture was cooled to room temperature and precipitated into methanol. The resultant polymer was collected, dried, and further purified by re-dissolving in warm chlorobenzene, followed by filtering, and precipitating into methanol again. The fibrous polymer was collected and washed with hexanes on Soxhlet extraction apparatus to yield 0.312 g polymer (89.9 % yield).

Mn: 19,500, PDI: 2.08. (relative to polystyrene standards). Anal. calcd for C<sub>104</sub>H<sub>148</sub>N<sub>4</sub>S<sub>5</sub>: C 77.37, H 9.24, N 3.47; found: C 77.21, H 9.17, N 3.44.

**Characterization:** <sup>1</sup>H NMR spectra were recorded on a 400 MHz Varian Unity Inova spectrometer. UV-vis absorption spectra were recorded on a Hewlett-Packard 8453 spectrometer. Excitation and emission spectra were obtained with a Spex Fluorolog 3 spectrometer. The molecular weight of the polymer was determined by size exclusion chromatography (SEC) using a Viscotek SEC system, which consists of a Viscotek VE1122 HPLC pump coupled with a Viscotek TDA Triple detector and a Viscotek 2501 UV detector operated at 260 nm. A set of ViscoGEL columns (G4000H, G5000H and G6000H) was used and calibrated using a set of polystyrene standards in THF. For SEC test, the polymer was first dissolved in dichlorobenzene, and then mixed with THF. The differential scanning calorimetry (DSC) analysis and the thermogravimetric analysis (TGA) were performed under a nitrogen atmosphere (50 mL/ min) on a TA Instruments DSC 2920 and a TGA 2950 thermogravimetric analyzer, respectively, at a heating rate of 10 °C/min. Cyclic voltammetry (CV) measurements were carried out under argon in a three-electrode cell using 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in anhydrous CH<sub>3</sub>CN as the supporting electrolyte. The polymers were coated on the platinum-working electrode. The CV curves were recorded referenced to an Ag quasi-reference electrode, which was calibrated using a ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple (4.8 eV below the vacuum level) as an external standard. The  $E_{1/2}$  of the Fc/Fc<sup>+</sup> redox couple was found to be 0.40 V vs the Ag quasi-reference electrode. Therefore, the HOMO and LUMO energy levels of the copolymers can be estimated using the empirical equation  $E_{\text{HOMO}} = -(E_{\text{on}}^{\text{ox}} + 4.40)$  eV and

$E_{\text{LUMO}} = -(E_{\text{on}}^{\text{red}} + 4.40) \text{ eV}$ , respectively, where  $E_{\text{on}}^{\text{ox}}$  and  $E_{\text{on}}^{\text{red}}$  stand for the onset potentials for oxidation and reduction relative to the Ag quasi-reference electrode, respectively.

**PV Device Fabrication and Testing.** ITO-coated glass substrates ( $15 \text{ } \Omega/\square$ ) were patterned by conventional wet-etching process using a mixture of HCl (6 N) and HNO<sub>3</sub> (0.6 N) as the etchant. The active area of each solar cell device was  $5 \times 7 \text{ mm}^2$ . After patterning, the substrates were rinsed in deionized water, and then ultrasonicated sequentially in acetone (20 °C) and 2-propanol (65 °C). Immediately prior to device fabrication, the ITO substrate was treated in a UV-ozone oven for 15 min. A poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT-PSS) thin film (50 nm) was spin-coated at 5000 rpm from its aqueous solution onto the treated substrate, and then baked at 120 °C under vacuum for 2 h. The active layer composed of the **P(InCzTh<sub>2</sub>BTD)/PC<sub>61</sub>BM** blend at a weight ratio of 1:2 was then spin-coated on top of PEDOT-PSS from 1,2-dichlorobenzene solutions at 600 rpm for 60 s. The film was kept in a Petri dish overnight. The thickness of the resulting film was found to be about 110 nm, as measured with a Dektak III surface profilometer. The device fabrication was completed by the vacuum deposition of LiF (1 nm) and Al cathode (100 nm). The solar cells with no protective encapsulation were subsequently tested in air under air mass (AM) 1.5 simulated solar illumination ( $100 \text{ mW/cm}^2$ , Sciencetech Inc., Model SF150). Current–voltage (*I-V*) characteristics were recorded using a computer-controlled Keithley 2400 source meter.

Figure SI-1,  $^1\text{H}$  NMR Spectrum of 4,7-Bis(3,4'-dioctyl-2,2'-bithiophen-5-yl)-2,1,3-benzothiadiazole (5) in  $\text{C}_6\text{D}_6$ .

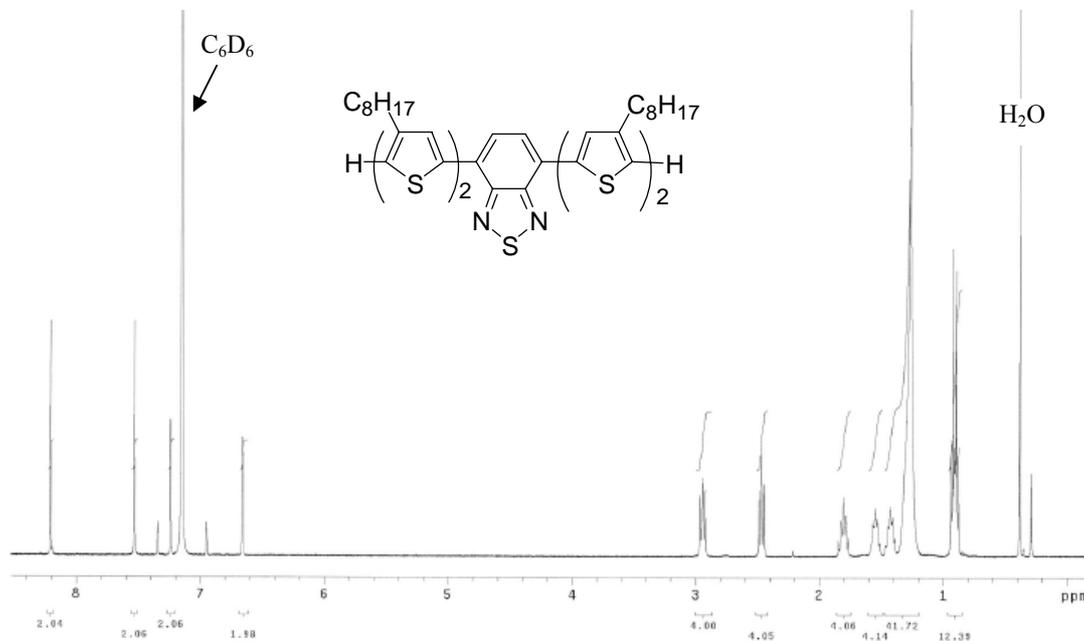


Figure SI-2,  $^1\text{H}$  NMR Spectrum of 4,7-Bis(5'-bromo-3,4'-dioctyl-2,2'-bithiophen-5-yl)-2,1,3-benzothiadiazole (6) in  $\text{C}_6\text{D}_6$ .

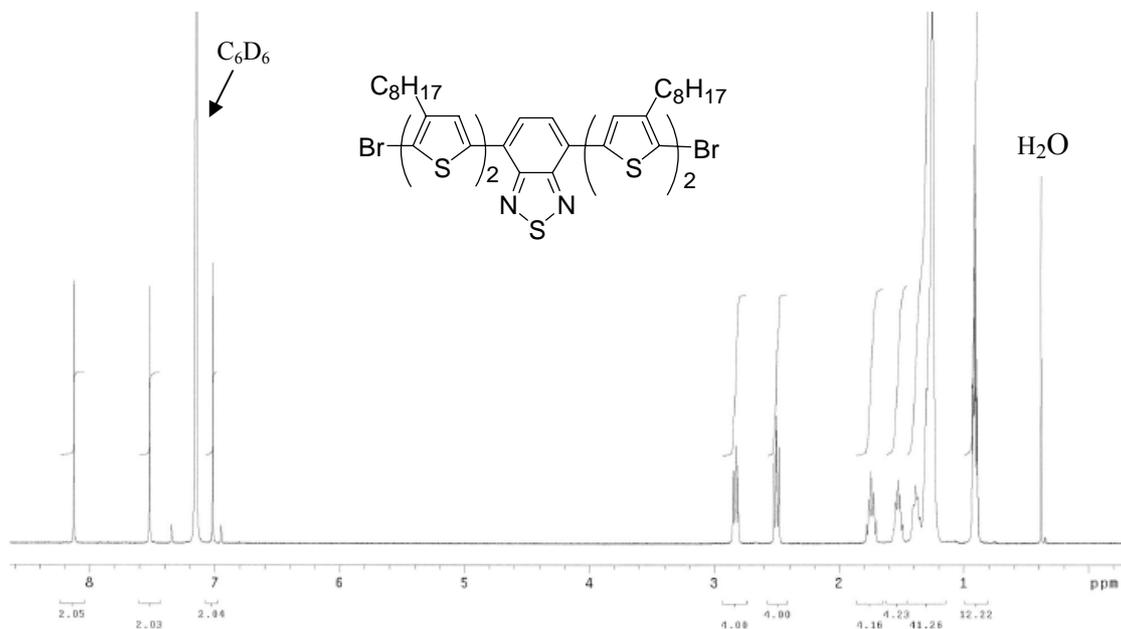


Figure SI-3,  $^1\text{H}$  NMR Spectrum of 3,9-dibromo-5,11-di(2-hexyldecyl)indolo[3,2-b]carbazole (8) in  $\text{C}_6\text{D}_6$ .

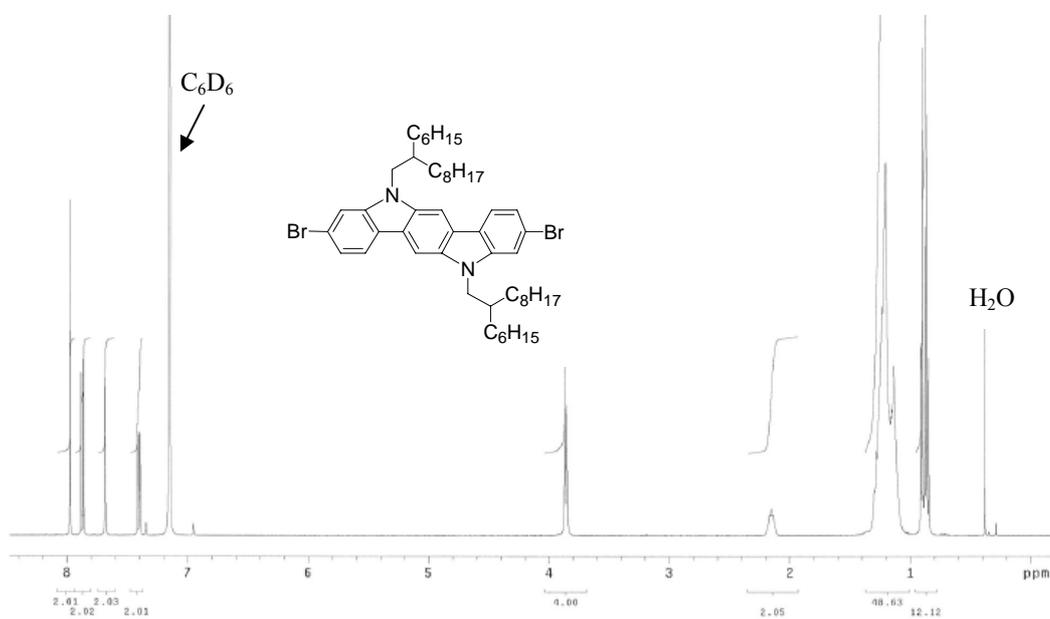


Figure SI-4,  $^1\text{H}$  NMR Spectrum of 3,9-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,11-di(2-hexyldecyl)indolo [3,2-b]carbazole (9) in  $\text{C}_6\text{D}_6$ .

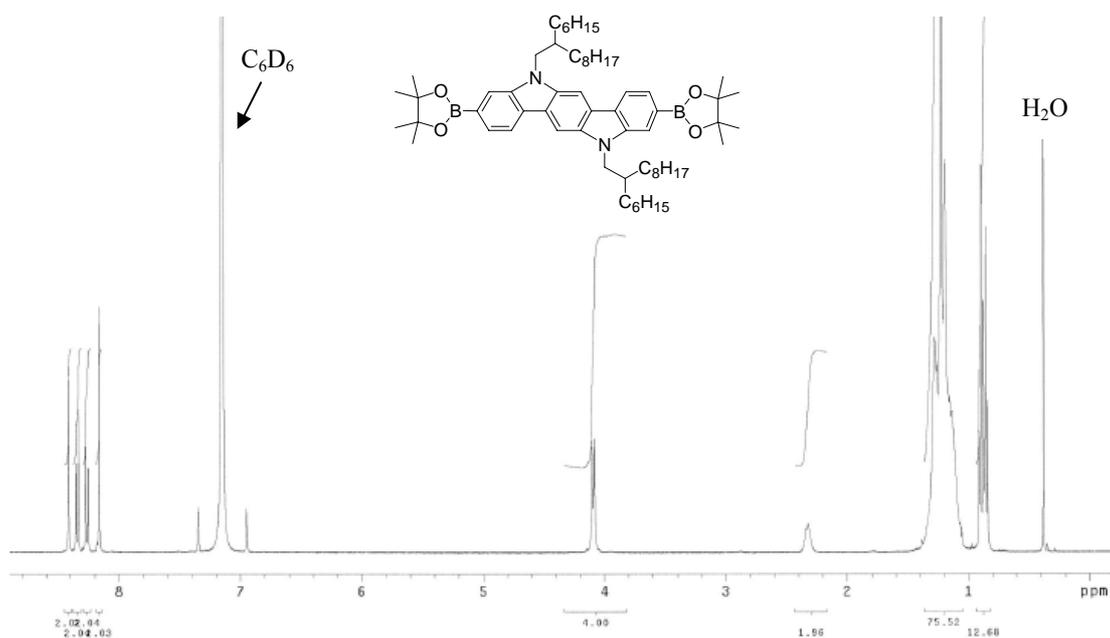


Figure SI-5, SEC curve of P(InCzTh<sub>2</sub>BTD) using THF as eluent.

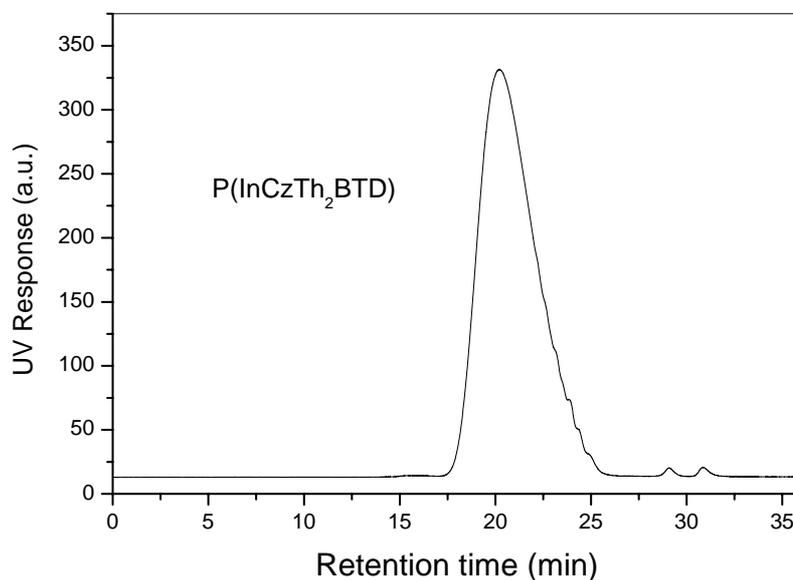


Figure SI-6, CV curves of P(InCzTh<sub>2</sub>BTD) collected from a three-electrode cell using 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in anhydrous CH<sub>3</sub>CN as the supporting electrolyte under the protection of argon. The polymer was coated on the Pt-working electrode, a Pt wire as counter electrode and an Ag quasi-reference electrode were used.

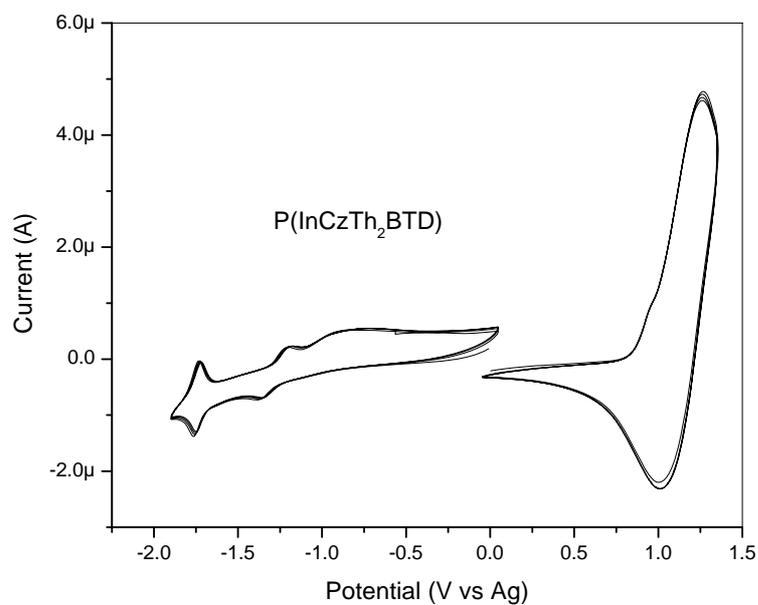


Figure SI-7. UV spectrum of the **P(InCzTh<sub>2</sub>BTD)/PC<sub>61</sub>BM** (1:2 by weight) blend film spin coated from the 1,2-dichlorobenzene solution with slow solvent evaporation.

