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# Supporting Information

# Isoindigo-Based Copolymers for Polymer Solar Cells with Efficiency Over 7%

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## Materials and Methods.

All chemical reagents were received from Acros and Aldrich and used without purification, unless otherwise mentioned. 6-Bromoisatin and 6-bromoxindole were purchased from Matrix Scientific. 1-bromo-2-hexyldecane, 6,6'-Dibromoisoindigo, and (E)-6,6'-Bis(5-bromo-4-octylthiophen-2-yl)-1,1'-bis(2-hexyldecyl)-[3,3'-biindolinylidene]-2,2'-dione (**1**) were synthesized according to the literature procedures.[1, 2] Tetrahydrofuran (THF) for reaction was dried with Na/benzophenone before used. $^1$H NMR spectra were recorded on a Bruker DPX400 400 MHz spectrometer and $CDCl_3$ were used as solvent. The molecular weight and molecular weight distribution of synthesized polymers were measured either using a Viscotek

GPCmax and THF used as an eluent at 35°C or a Viscotek HT-GPC and 1,2,4-trichlorobenzene used as an eluent at 135 °C. For both GPC, polystyrene is worked as standard. The optical absorption spectra of all synthesized polymers were measured using a Perkin Elmer Lambda 35 UV/VIS spectrometer. The electrochemical properties measurements were determined using a CHI 4052 cyclic voltammetry in a dry acetonitrile solution of 0.1M tetrabutylammonium perchlorate (TBAP). The samples were spin-coated onto ITO glass from 10 mg/mL polymer solutions and used as working electrode. Pt wire is used as auxiliary electrode and $Ag/Ag^+$ as reference electrode. The scan rate was kept at 100 mV/s and the electrolyte solution was bubbled by nitrogen for five minutes before each scan. The HOMO and LUMO energy levels of the copolymers were calculated according to the following equation using ferrocene (Fc) as the internal standard,

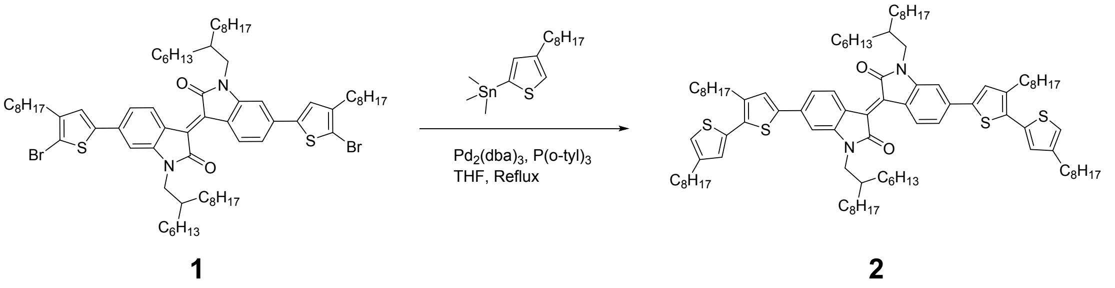
$$E_{HOMO}(e.V.) = -\left(E_{onset,ox.vs.Fc^+/Fc} + 5.13\right)$$

For surface morphology, the topographic observation of the film sample film was analyzed by AFM (Digital Instruments, Nanoscopes III) using tapping mode. The measurement was performed in ambient condition with a vibration isolation system. Imaging was done by using a commercially available silicon cantilevers with thickness 5.0±1 μm, length of 225±10 μm, and width of 33±7.5μm, resonance frequency of 96-175 kHz and force constant of 5-37 N/m.

**Synthetic procedure.**

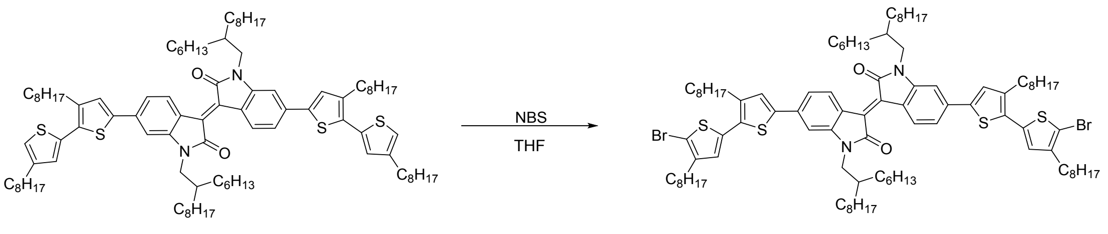
**Trimethyl(4-octylthiophen-2-yl)stannane** 2.5 M *n*-butyllithium in hexane (100 mmol, 40.00 ml) was added into a solution of 3-octylthiophene (100 mmol, 19.64 g) and 100 ml THF at -78°C under nitrogen atmosphere. The reaction was allowed to proceed for one hour and then warmed up at RT for another one hour. The reaction solution was again cooled to -78°C and followed by introducing 1M trimethyltin chloride in THF (100 mmol, 100 ml). After the trimethyltin chloride was completely added, the reaction solution was raised back to RT and the reaction was proceed for overnight. The reaction solution was diluted with hexanes and washed with brine and finally dried over anhydrous $MgSO_4$ to remove extra water. After concentration by rotary evaporation, the residue was purified by column chromatography (Celite, hexanes) to yield pale yellow liquid (29.45 g, 82 %). $^1$H NMR (400MHz, CDCl3): δ 7.20(s, 1H), 7.01(s, 1H), 2.65(t, *J*=7.6Hz, 2H), 1.64(qui, *J*=7.6Hz, 2H), 1.45-1.17(m, 10H), 0.89(t, *J*=6.7Hz, 3H), 0.36(s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$, δ): 144.97,137.00, 125.99, 33.25, 31.11, 30.34, 30.06, 29.86, 29.90, 29.62, 23.03, 14.46, -7.94. Element analysis: Theory: C(%): 50.16 S(%): 8.93 H(%): 7.86 Found: C(%): 54.84 S(%): 8.61 H(%): 8.92.

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



Trimethyl(4-octylthiophen-2-yl)stannane (4.28 g, 11.92 mmol), compound **1**(251 mg, 0.2 mmole), $Pd_2(dba)_3$ (10 mg, 0.01 mmol), and $P(o\text{-}tyl)_3$ (17 mg, 0.05 mmol) were added in 150 ml round bottomed flask. The mixture was vacummed and then backfilled with nitrogen for three times. 50 ml THF were added and refluxed for 10hr. The reaction solution was concentrated by evaporation and the residue was purified by column chromatography (silicon, hexane/dichloromethane (2:1)) to yield a dark purple solid (7.03 g, 99%). 1H NMR (400MHz, CDCl3): δ 9.15(d, *J*=8.4Hz, 2H), 7.32-7.18(m, 4H), 7.01(s, 2H), 6.92(s, 4H), 3.69(d, *J*=6.9Hz, 4H), 2.78(t, *J*=7.7Hz, 4H), 2.62(t, *J*=7.7Hz, 4H), 2.00-1.86(m, 2H), 1.76-1.60(m, 8H), 1.45-1.17(m, 88H), 0.93-0.81(m, 24H). $^{13}$C NMR (100 MHz, $CDCl_3$, δ): 169.02, 146.00, 144.10, 141.50, 140.92, 137.35, 135.91, 132.59, 132.06, 130.46, 127.72, 127.51, 121.39, 120.65, 119.10, 104.92, 44.77, 36.80, 32.25, 32.16, 30.86, 30.81, 30.03, 30.00, 29.97, 29.90, 29.73, 29.67, 27.03, 23.03, 14.46. Element analysis: Theory: N(%): 1.88 C(%): 77.46 S(%): 8.62 H(%): 9.89 Found: N(%): 1.98 C(%): 77.98 S(%): 8.61 H(%): 9.93.

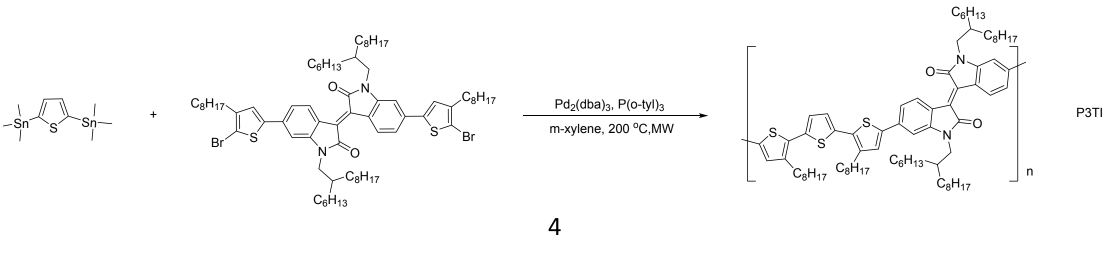
### (E)-6,6'-Bis(5'-bromo-3,4'-dioctyl-[2,2'-bithiophen]-5-yl)-1,1'-bis(2-hexyldecyl)-[3,3'-biindolinylidene]-2,2'-dione (3)



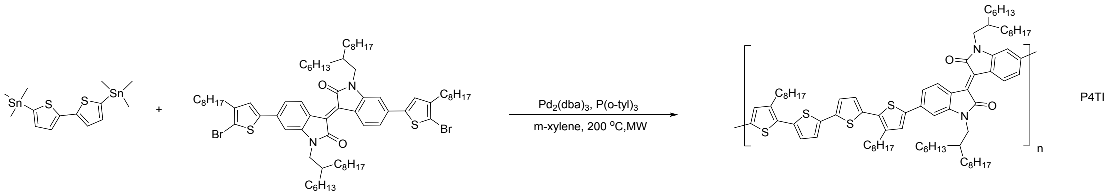
**2** **3**

To a solution of compound **2** (7.03 g, 4.72 mmol) in 50 ml anhydrous THF, *N*-bromosuccinimide (1.68 g, 9.44 mmole) was added separately in one of eight portions with an interval of 15 min. After 10 hr reaction, the reaction solution was evaporated by using rotavapor. The residue was purified by column chromatography (silicon, hexane/dichloromethane (2:1)) to yield a dark purple solid (6.92 g, 89%). 1H NMR (400MHz, CDCl3): δ 9.15(d, *J*=8.4Hz, 2H), 7.35-7.12(m, 4H), 6.91(s, 2H), 6.86(s, 2H), 3.69(d, *J*=6.9Hz, 4H), 2.73(t, *J*=7.7Hz, 4H), 2.57(t, *J*=7.7Hz, 4H), 1.98-1.84(m, 2H), 1.72-1.60(m, 8H), 1.45-1.17(m, 88H), 0.93-0.81(m, 24H). $^{13}$C NMR (100 MHz, $CDCl_3$, δ): 168.94, 145.98, 142.92, 141.99, 141.40, 137.48, 135.75, 132.06, 131.45, 130.53, 127.42, 127.13, 121.50, 119.10, 109.36, 104.88, 44.74, 36.80, 32.15, 30.99, 30.37, 30.08, 30.03, 29.97, 29.85, 29.76, 29.65, 27.04, 23.03, 14.46. Element analysis: Theory: N(%): 1.70 C(%): 70.04 S(%): 7.79 H(%): 8.82 Found: N(%): 1.88 C(%): 70.00 S(%): 7.67 H(%): 8.81.

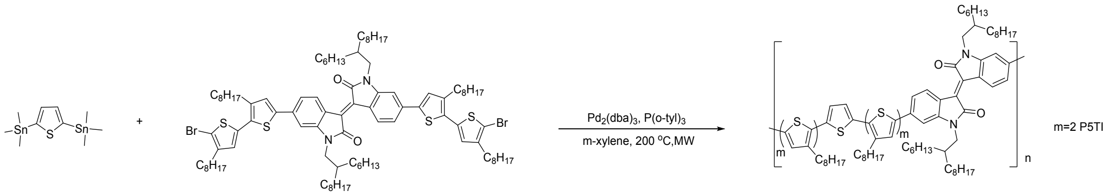
**General synthetic procedure of polymers** Acceptor compound (0.2 mmol) either compound **1** or compound **3** and donor compound (0.2 mmol) either 2,5-bis(trimethylstannyl)thiophene or 5,5'-bis(trimethylstannyl)-2,2'-bithiophene were sealed with $Pd_2(dba)_3$ (6 mg, 0.007 mmol), and $P(o\text{-}tyl)_3$ (10 mg, 0.033 mmol) in a microwave reaction vessel. 4 ml m-xylene was introducing in the vessel by using gas-tight syringe and the reaction was performed at 200 $^{o}$C with 300 W for one hour. After the reaction was complete, the polymer was precipitated in methanol and followed by sequent Soxhlet extraction of methanol and hexane to remove impurities; note, additional THF extraction was applied for P4TI and P6TI. The polymer was finally dried in a vacuum oven to yield the corresponding products.



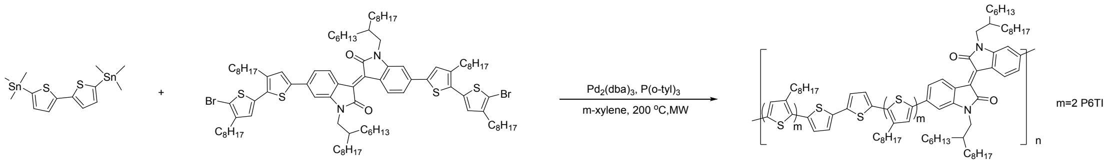
**P3TI** (89%). $^1$H NMR (400MHz, CDCl3): δ 9.50-8.75 (br, 2H), 7.50-7.00 (br, 6H), 6.75-6.25 (br, 4H), 3.75-3.25 (br, 4H), 3.00-2.50 (br, 4H), 2.0-0.5 (br, 92H). GPC: $M_n$ = 48k g/mol, PDI=2.41.



**P4TI** (81%). $^1$H NMR (400MHz, CDCl3): δ 9.50-8.75 (br, 2H), 7.50-7.00 (br, 8H), 6.75-6.25 (br, 4H), 3.75-3.25 (br, 4H), 3.00-2.50 (br, 4H), 2.0-0.5 (br, 92H). GPC: $M_n$ = 26k g/mol, PDI=2.08.



**P5TI** (80%). $^1$H NMR (400MHz, CDCl3): δ 9.50-8.75 (br, 2H), 7.50-7.00 (br, 10H), 6.75-6.25 (br, 4H), 3.75-3.25 (br, 4H), 3.00-2.50 (br, 4H), 2.0-0.5 (br, 122H). GPC: $M_n$ = 28k g/mol, PDI=2.17.



**P6TI** (78%). $^1$H NMR (400MHz, CDCl3): δ 9.50-8.75 (br, 2H), 7.50-7.00 (br, 12H), 6.75-6.25 (br, 4H), 3.75-3.25 (br, 4H), 3.00-2.50 (br, 4H), 2.0-0.5 (br, 122H). GPC: $M_n$ = 35k g/mol, PDI=1.81.

**Device Fabrication.**

In order to optimize the performance of polymers:$PC_{71}BM$ photovoltaic devices, polymer:$PC_{71}BM$ hybrid solution in different weight ratios, solvents, additives and concentrations were tested. For P3TI:$PC_{71}BM$ and P5TI:$PC_{71}BM$ photovoltaic devices, we prepared the hybrid solution with the blending ratio of 1:1.5 (wt/wt) at 1.86wt% concentration in o-DCB with 3 vol% of DIO. For P4TI:$PC_{71}BM$ system, the hybrid solution was prepared with the blending ratio of 1:1.5 (wt/wt) at 0.89wt% concentration in the solvent combination of CF and o-DCB (1:1 vol/vol). For P6TI:$PC_{71}BM$ system, the hybrid solution was prepared with the blending ratio of 1:1.5 (wt/wt) at 1.86wt% concentration in CB with 3 vol% of CN. All samples dissolved in chlorobenzene (CB) or 1,2-dichlorobenzene(o-DCB) as major solvent are stirred at 70°C for 48 hours. Moreover, the samples dissolved in chloroform (CF) or used CF in the solvent combination are stirred at 50°C for 48 hours. The isoindigo based polymer solar cells were fabricated with the conventional configuration of ITO/PEDOT:PSS/polymer:$PC_{71}BM$/Ca/Al. First, the transparent electrode ITO (Luminescence Technology Corp., 10Ω) glass was cleaned sequentially in detergent, TL-1($NH_3$:$H_2O_2$:$H_2O$ = 1:1:5), methanol, isopropanol and then applied to UV-ozone treatment for 15 minutes. Then poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Baytron P VP AI 4083)was filtered through 0.20μm PVDF filter and spin-coated at 5000rpm for 60 seconds on the cleaned ITO glass as hole transport layer. Afterward, the PEDOT:PSS film was baked at 140$^{o}$C for 20 minutes for removing the remaining moisture. Subsequently, the polymer:$PC_{71}BM$ hybrid solution was spin-coated over the PEDOT:PSS layer at 1200rpm for 60s as photoactive layer and dried overnight in the glove box. Finally, 50nm calcium and 100 nm cathode aluminum were thermally evaporated through a shadow mask under the pressure of 5 x $10^{-6}$torr to form a device with 0.046 $cm^2$ active area. For device characterization, AM 1.5 solar simulator, which has 100 mW/$cm^2$ input power to illuminate the devices, was perform and voltage source meter was utilized to measure the J-V characteristic curves of the devices.

**Density Functional Theory Calculation.**

Molecular modeling of oligomeric versions of the PnTI series was performed using hybrid density functional theory (DFT). The calculations were carried out using Gaussian ’09 and GaussView 5 was used for visualization. For ground state optimizations, the B3LYP/6-31G* level was used. Molecular orbitals were calculated as a single point ground state energy B3LYP/6-311G(d,p) with tight convergence.

**Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS) Measurements.**

GIWAXS measurements were performed by using Beamline 17-A at NSRRC, Taiwan to investigate the crystallinity of different polymer:PC71BM films. The samples were prepared by spin-coated the hybrid solution on the silicon substrates with 1cm x 1cm pre-cleaned by ultrasonic treatment in detergent, TL-1(NH3:H2O2:H2O = 1:1:5), methanol, and isopropanol. The films were illuminated by X-rays at an incidence angle of about 0.2$^{o}$, which is above the critical angle of the blend films.

**Hole Mobility.**

To determine the hole mobility of all polymers, space charge limited current (SCLC) model by selecting high work function materials ITO and Au as electrodes for the diode was used. From the plot of $J^{0.5}$ vs. V, hole mobility of polymer can be deuced from

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

where J is the current density. For polymer, the relatively permittivity $\varepsilon_r$ is generally equal to 3, $\varepsilon_0$is the permittivity of free space, which is equal to 8.85 x $10^{-12}$($C^2$/J m), μ is the carrier mobility, $V_{eff}$ is effective potential drop inside the active materials and L is the film thickness. The film thickness is 100nm, 100nm, 80nm, 200nm for P3TI:$PC_{71}BM$, P4TI:$PC_{71}BM$, P5TI:$PC_{71}BM$, P6TI:$PC_{71}BM$, respectively.

**Table S1.** Comparison of the current density from J-V curves and IPCE results.

| Polymer | $J_{sc}$(mA/$cm^2$) | Integrated $J_{sc}$ from IPCE(mA/$cm^2$) |
|---|---|---|
| **P3TI** | 13.78 | 13.80 |
| **P4TI** | 13.90 | 13.22 |
| **P5TI** | 8.83 | 8.58 |
| **P6TI** | 16.24 | 15.71 |

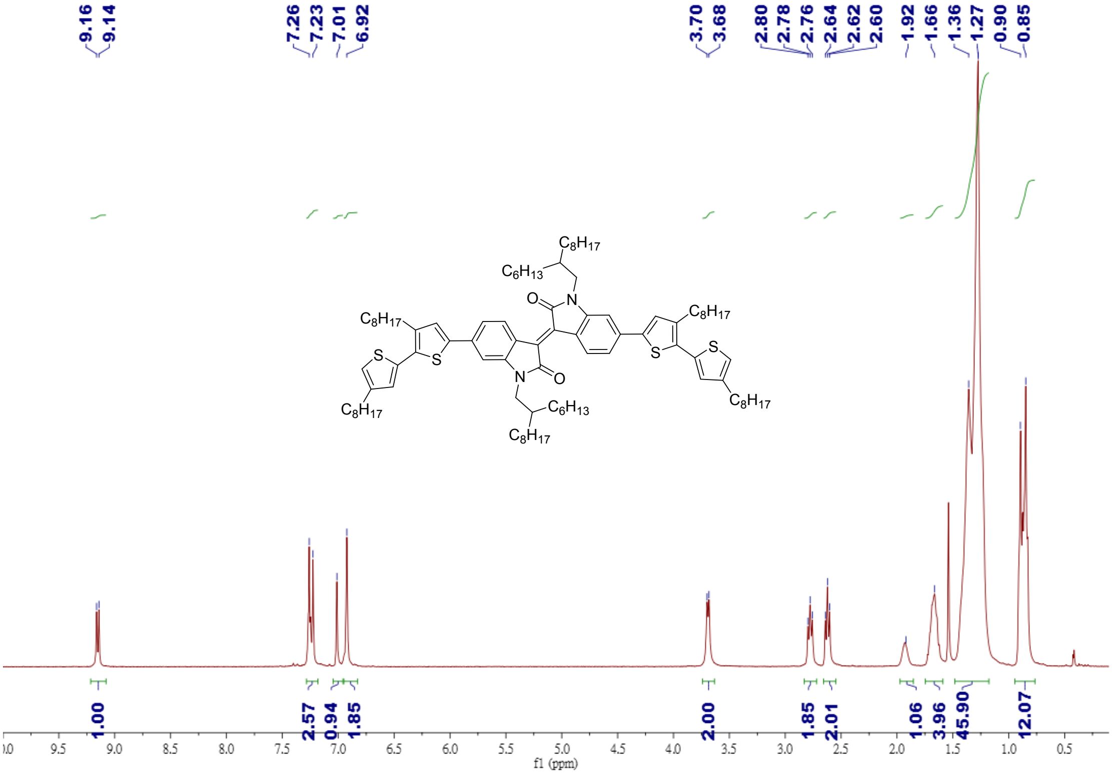


**Fig. S1** $^1$H NMR spectrum of (E)-6,6'-Bis(3,4'-dioctyl-[2,2'-bithiophen]-5-yl)-1,1'-

bis(2-hexyldecyl)-[3,3'-biindolinylidene]-2,2'-dione **(2)**

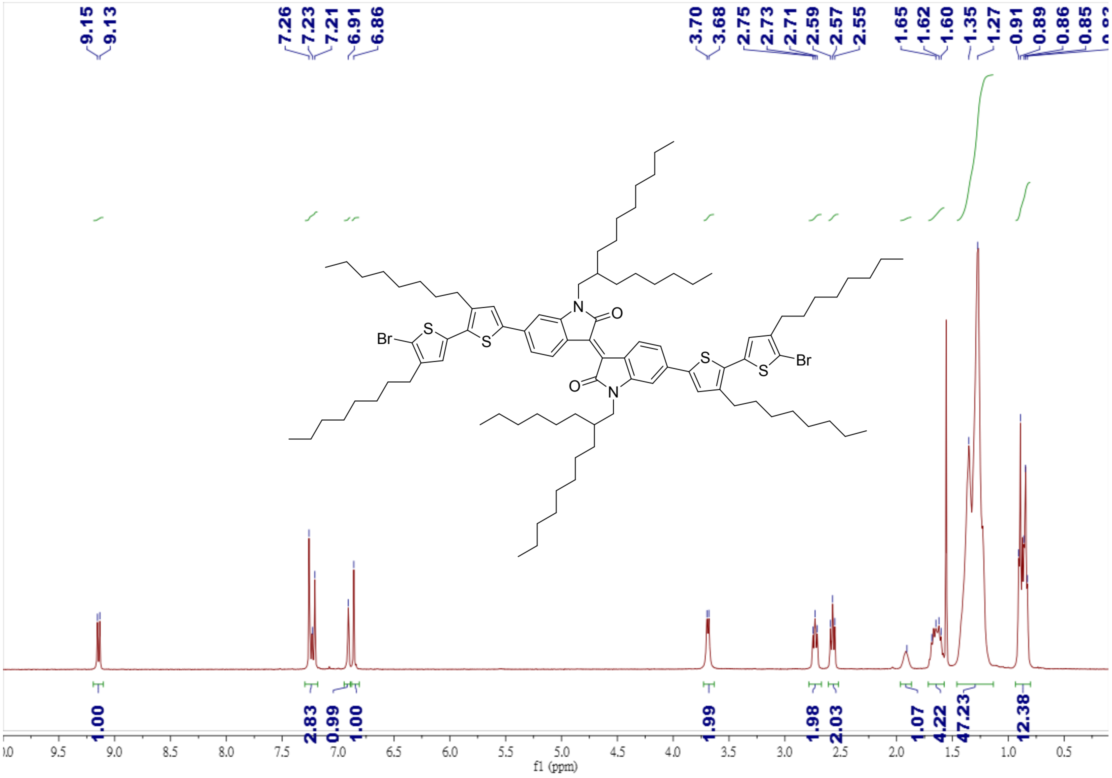


**Fig. S2** ${}^{1}$H NMR spectrum of (E)-6,6'-Bis(5'-bromo-3,4'-dioctyl-[2,2'-bithiophen]-5-yl)-1,1'-bis(2-hexyldecyl)-[3,3'-biindolinylidene]-2,2'-dione **(3)**

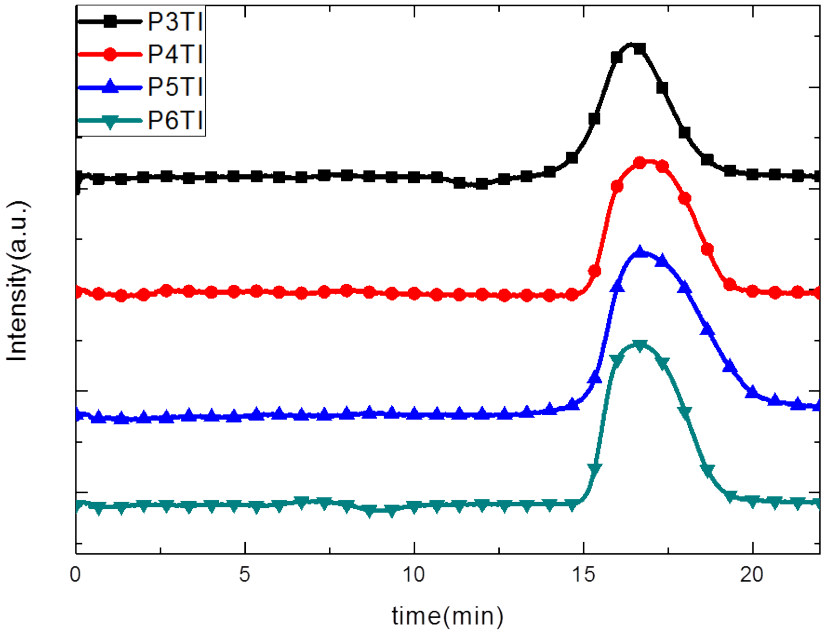


**Fig. S3** HT-GPC traces of PnTI. 1,2,4-trichlorobenzene is used as eluent and the working temperature is at 135°C. The molecular weights and molecular weight distribution were calculated by using monodisperse polystyrenes as calibration standards.

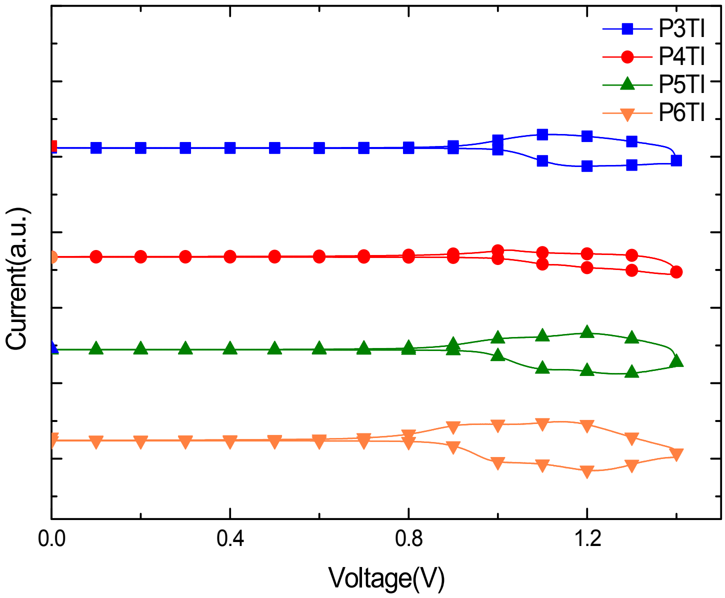


**Fig. S4** Cyclic voltammograms of P3TI, P4TI, P5TI, and P6TI films cast on a ITO electrode in $CH_3CN$ solution with $0.1 molL^{-1}$ $Bu_4NPF_6$.

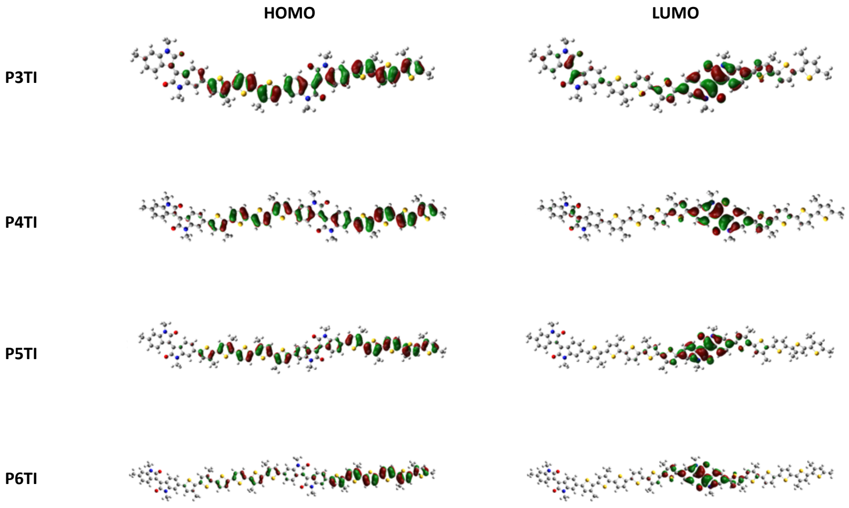


**Fig. S5** Calculated HOMO (left) and LUMO (right) frontier orbitals of P3TI, P4TI, P5TI and P6TI with two repeating units.

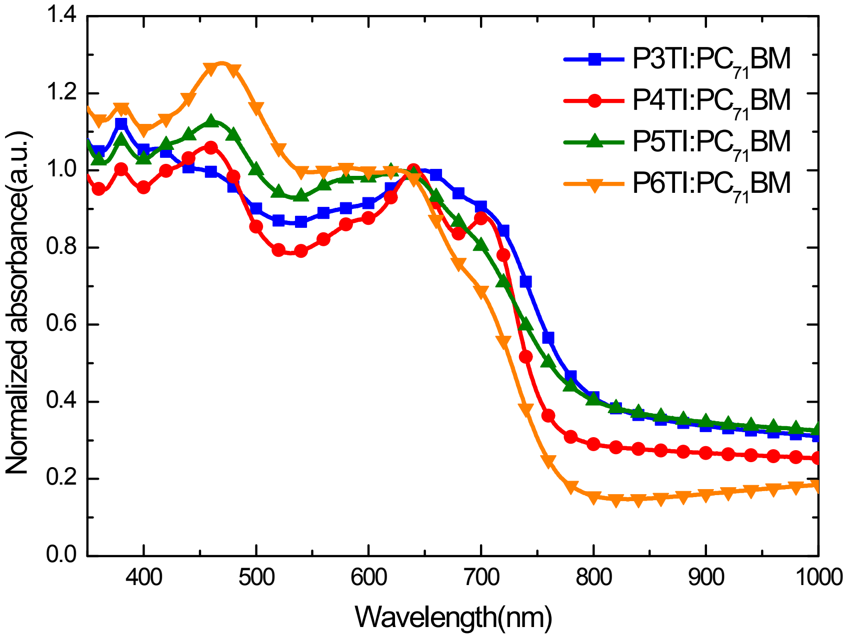


**Fig. S6** UV-Vis absorption spectra of optimized polymer:PC$_{71}$BM (1:1.5) blend films.

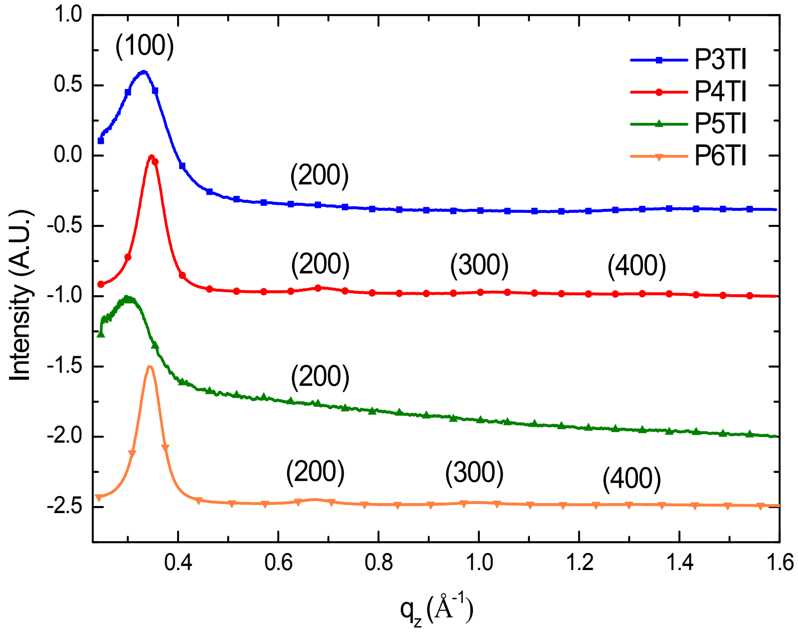


**Fig. S7** Out-of-plane linecuts of GI-WAXS profiles of (a) P3TI, (b)P4TI, (c)P5TI, and (d)P6TI.

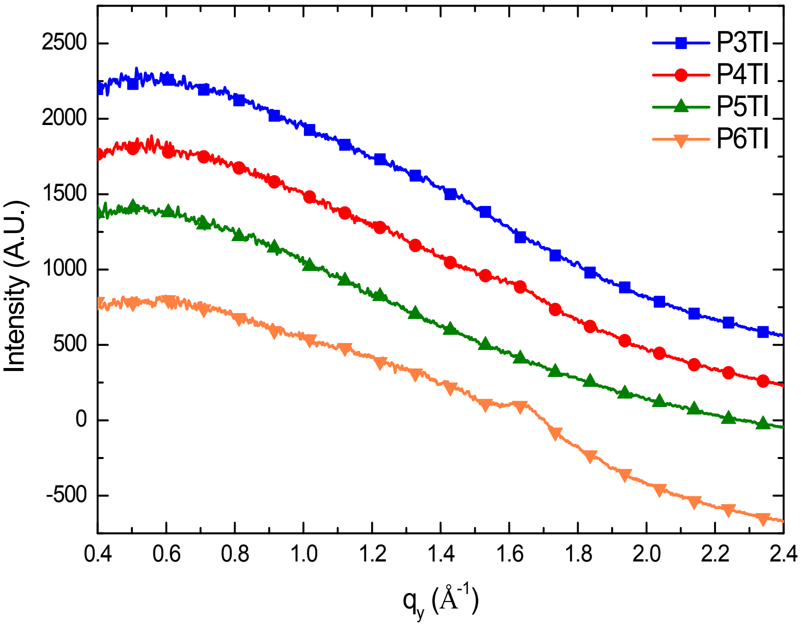


**Fig. S8** In-plane linecuts of GI-WAXS profiles of (a) P3TI, (b)P4TI, (c)P5TI, and (d)P6TI.

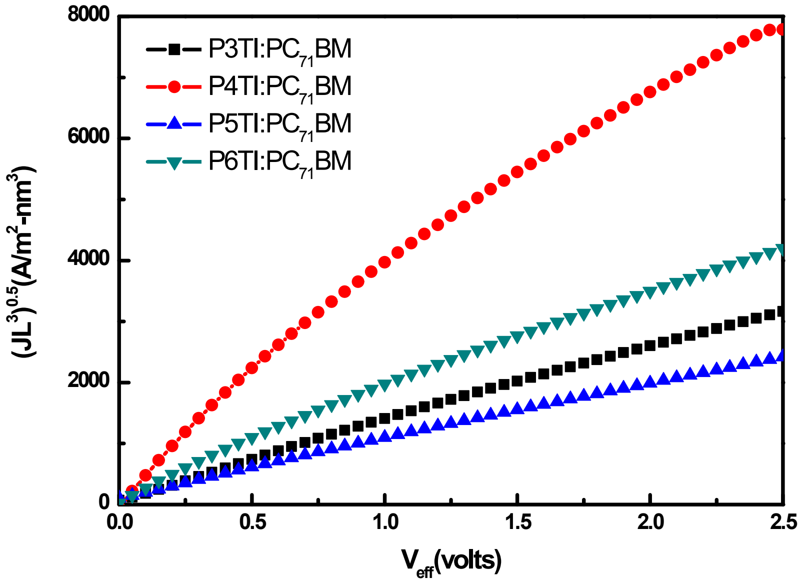


**Fig S9.** Dark current density-effective voltage characteristics of hole single carriers in PnTI:PC$_{71}$BM thin film cast from their optimal conditions.

## Reference

1. J. G. Mei, K. R. Graham, R. Stalder and J. R. Reynolds, *Org Lett*, 2010, **12**, 660-663.
2. E. G. Wang, Z. F. Ma, Z. Zhang, K. Vandewal, P. Henriksson, O. Inganas, F. L. Zhang and M. R. Andersson, *J. Am. Chem. Soc.*, 2011, **133**, 14244-14247.