Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

# Supporting Information

## Narrow Bandgap Conjugated Polymers based on a High-Mobility Polymer Template for Visibly Transparent Photovoltaic Devices

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## 1. General methods

Ultraviolet-Visible (UV-Vis) absorption spectra were recorded on a DU-800 spectrometer. Nuclear magnetic resonance (NMR) spectra were obtained on Varian 500 MHz spectrometer. Gel permeation chromatography (GPC) was performed in chloroform ($CHCl_3$) on a Waters 2690 Separation Module equipped with a Waters 2414 Refractive Index Detector and a Waters 2996 Photodiode Array Detector. Molecular weights were calculated relative to linear PS standards. Cyclic voltammetry (CV) measurements were conducted using a standard three-electrode configuration under an argon atmosphere. A three-electrode cell equipped with a glassy carbon working electrode, an Ag wire reference electrode and a Pt wire counter-electrode. The measurements were performed in absolute acetonitrile with tetrabutylammoniumhexafluorophosphate (0.1 M) as the supporting electrolyte at a scan rate of 100 mV/s. Polymer films for CV test were drop-casted onto the glassy carbon working electrode from a 5 mg/mL chloroform solution. The absolute energy level of ferrocene/ferrocenium ($Fc/Fc^+$) to be 4.8 eV below vacuum.

## 2. Synthesis

4,8-Bis(3,5-didecyl)thiophen)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane), Benzo[1,2-*b*:4,5-*b*]bis-2-bromo-4,4'-dihexyl-4*H*-silolo[3,2-*b*]thiophene) were purchased from SunaTech Inc. Tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$], Tris(dibenzylideneacetone)dipalladium (0) [$Pd_2dba_3$] and tri-*o*-tolylphopine (P-(*o*-tol)$_3$) were purchased from Strem Chemicals Inc. Compoundbenzo[1,2-b:4,5-b]bis(2-trimethylstannyl-4,4'-dihexyl-4H-silolo[3,2-b]thiophene) (Bis-SiIDT-tin)[1] were prepared by methods similar to those reported in the literature. All the solvent were distillated before used.

**Synthesis of M1**:

A 20 mL reaction vial was charged with Bis-SiIDT-tin (500 mg, 0.520 mmol, 1.0 eq), 4,7-Dibromo-BT (620 mg, 2.05 mmol, 4.0 eq), $Pd(PPh_3)_4$ (80 mg, 0.069mmol, 0.10eq), and dry toluene (5 mL) were added to a 2-5 mL microwave tube in the nitrogen atmosphere glovebox. The tube was sealed and subjected to the following reaction conditions in the microwave reactor: 80 °C for 2 min, 110 °C for 2 min, 140 °C for 5 min and 160 °C for 40 min. After the reaction was cooled to room temperature, the crude product was purified by column chromatography using hexane as an eluent to yield **M1** as dark red solid (550 g, 60 % yield). $^1H$ NMR ($CDCl_3$, 400 MHz,$\delta$) 8.16 (s, 2H), 7.88 (d, 2H), 7.76 (d, 2H), 7.71 (s, 2H), 1.55-1.40 (m, 8H), , 1.40-1.20 (m, 24H), 1.10-0.98 (m, 8H), 0.90-82 (m, 12H).

**Synthesis of M2**:

A 20 mL reaction vial was charged with Bis-SiIDT-tin (500 mg, 0.520 mmol, 1.0 eq), 4,7-Dibromo-FBT (380 mg, 1.18 mmol, 2.25 eq), $Pd(PPh_3)_4$ (80 mg, 0.069mmol, 0.10eq), and dry toluene (5 mL) inside a dry nitrogen box. The reaction vial was then sealed using a Teflon®cap and moved out of the dry box. The reaction mixture was stirred at 90°C in a conventional oil bath for 72 h. The resulting mixture was first passed through a short silica gel column by using chloroform as eluent. After the chloroform solution was concentrated to dryness, a second purification step via column chromatography (10~30% DCM in hexanesgradient) was needed to give **M2** (450 mg, 50%) as a dark red powder.$^1$H NMR ($CDCl_3$, 400 MHz, $\delta$) 8.18 (s, 2H), 7.77 (d, 2H), 7.73 (s, 2H), 1.57-1.41 (m, 8H), 1.35-1.31 (m, 8H), 1.26-1.23 (m, 16H), 1.10-0.99 (m, 8H), 0.86-83 (m, 12H).

**Synthesis of M3**:

A 20 mL reaction vial was charged with Bis-SiIDT-tin (500 mg, 0.520 mmol, 1.0 eq), 4,7-Dibromo-PT (380 mg, 1.18 mmol, 2.25 eq), $Pd(PPh_3)_4$ (80 mg, 0.069mmol, 0.10eq), and dry toluene (5 mL) were added to a 2-5 mL microwave tube in the nitrogen atmosphere glovebox. The tube was sealed and subjected to the following reaction conditions in the microwave reactor: 80 °C for 2 min, 110 °C for 2 min, 140 °C for 5 min and 160 °C for 40 min. After the reaction was cooled to room temperature, the crude product was purified by column chromatography using 10~30% DCM in hexanesgradient as an eluent to yield **M3** as dark purple solid (600 mg, 70 % yield). $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$) 8.74 (s, 2H), 8.66 (s, 2H), 7.78 (s, 2H), 1.55-1.44 (m, 8H), 1.35-1.33 (m, 8H), 1.26-1.23 (m, 16H), 1.10-1.03 (m, 8H), 0.85-82 (m, 12H).

**Synthesis of PBT, PFT and PPT:**

In a 50 mL reaction tube, M1-M3 (0.1 mmol), Bis-BDT-tin (124 mg, 0.1 mmol) tri(o-tolyl)phosphine (10 mg) and $Pd_2(dba)_3$ (5 mg) were dissolved in 5/0.5 mL dry toluene/DMF under argon. After stirring at 110 °C for 24 h, the mixture was cooled to room temperatures and precipitated in methanol (100 mL). The precipitate was filtered and washed with methanol (24 h) and hexane (24 h) successively in a Soxhlet apparatus to remove oligomers and catalyst residue. Finally, the polymer was extracted with chloroform (24 h). The chloroform fraction was concentrated and precipitated in methanol. The precipitate was filtered and dried in vacuum at 80 °C overnight. **PBT**: obtain as dark purple solid (170 mg, 85%), GPC: $M_n$ = 29 000 g mol$^{-1}$, PDI = 1.60. **PFT**: obtain as dark purple fiber (165 mg, 80%), GPC: Mn = 36 000 g mol$^{-1}$, PDI = 1.80. **PPT**: obtain as dark purple fiber (175 mg, 83%), GPC: $M_n$ = 32 000 g mol$^{-1}$, PDI = 1.50.

Reference

1. J. A. Love, I. Nagao, Y. Huang, M. Kuik, V. K. Gupta, C. J. Takacs, J. E. Coughlin, L. Qi, T. S. van der Poll, E. J. Kramer, A. J. Heeger, T.-Q. Nguyen, G. C. Bazan, *J. Am. Chem. Soc.* 2014, **136**, 3597.

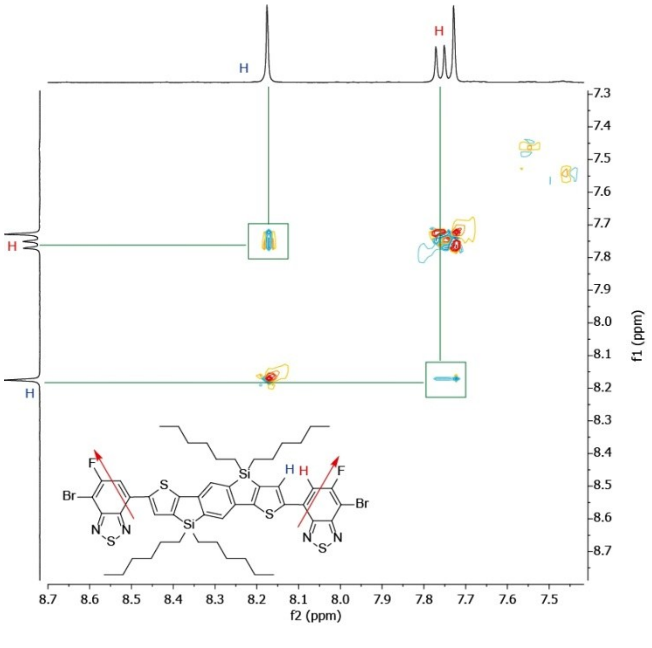


**Figure S1** Aromatic region of 2D $^1$H-$^1$H NOESY NMR spectrum of **3** (left) and **4** (right) in $CDCl_3$ at room temperature with a concentration of ca.35 mg/mL. Crosspeaks indicates the spatial interaction between Hydrogens, due to fast rotation of the C-C single bond between two aromatic units.

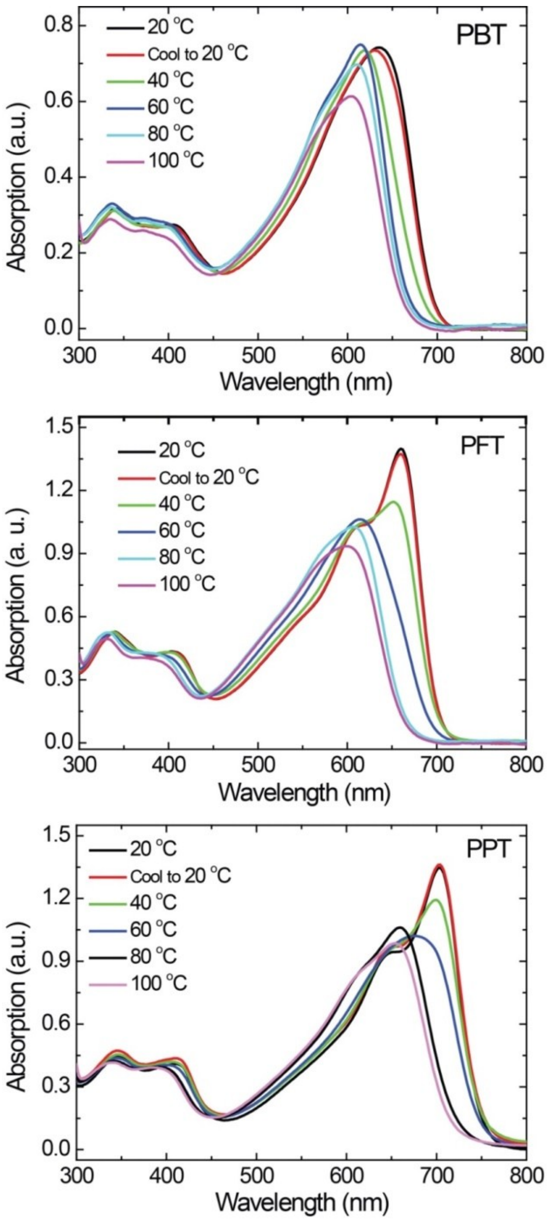


**Figure S2.** Temperatures-dependent absorption spectra of PBT, PFT and PPT in chlorobenzene (0.01 mg/mL).

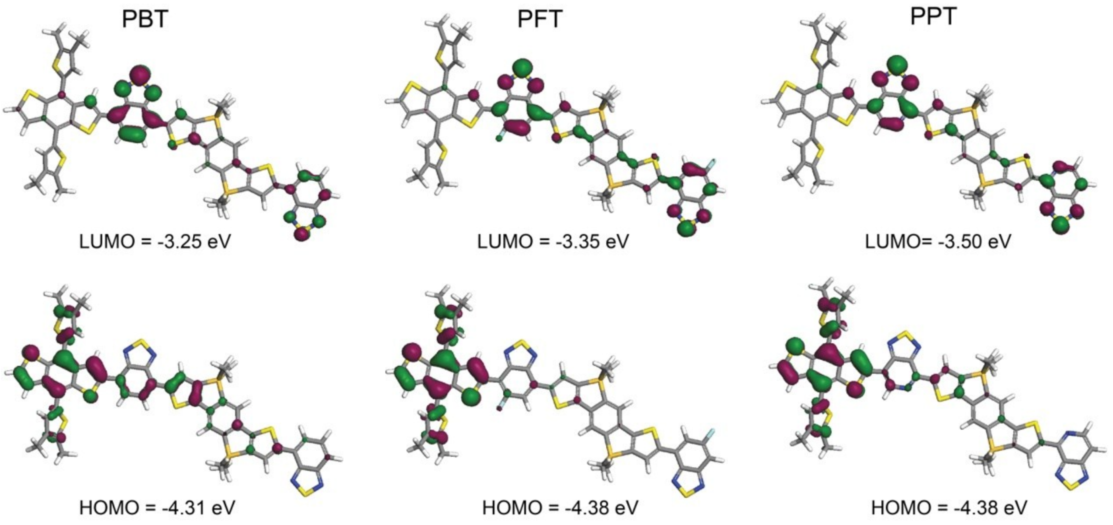


**Figure S3.** Optimized molecular orbital surfaces of the LUMO and HOMO of PBT, PFT and PPT.

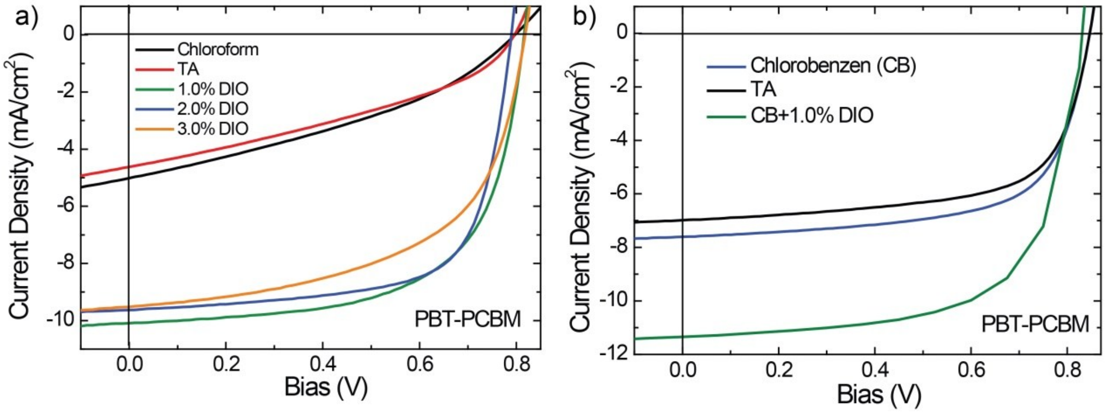


**Figure S4.** $J$–$V$ curves of the optimal PBT-PC$_{61}$BM solar cell devices processed from chloroform (a) and chlorobenzene (b).

**Table S1.** Optimized devices performance based on PBT-PC$_{61}$BM blends.

| Polymer | Solvent | Ratio (w/w) | $V_{oc}$ [V] | $J_{sc}$ [mA/cm$^2$] | *FF* | *PCE* *(%)* |
|---|---|---|---|---|---|---|
| PBT | CF | 1/2 | 0.80 | 5.01 | 0.37 | 1.44 |
| PBT | TA | 1/2 | 0.80 | 4.62 | 0.37 | 1.33 |
| PPT | +1.0% DIO | 1/2 | 0.81 | 10.08 | 0.68 | 5.56 |
| PBT | +2.0% DIO | 1/2 | 0.79 | 9.63 | 0.69 | 5.20 |
| PBT | +3.0% DIO | 1/2 | 0.82 | 9.52 | 0.60 | 4.74 |
| PBT | CB | 1/2 | 0.84 | 7.60 | 0.66 | 4.22 |
| PBT | TA | 1/2 | 0.84 | 6.98 | 0.66 | 3.87 |
| PBT | +1.0% DIO | 1/2 | 0.80 | 11.10 | 0.70 | 6.22 |

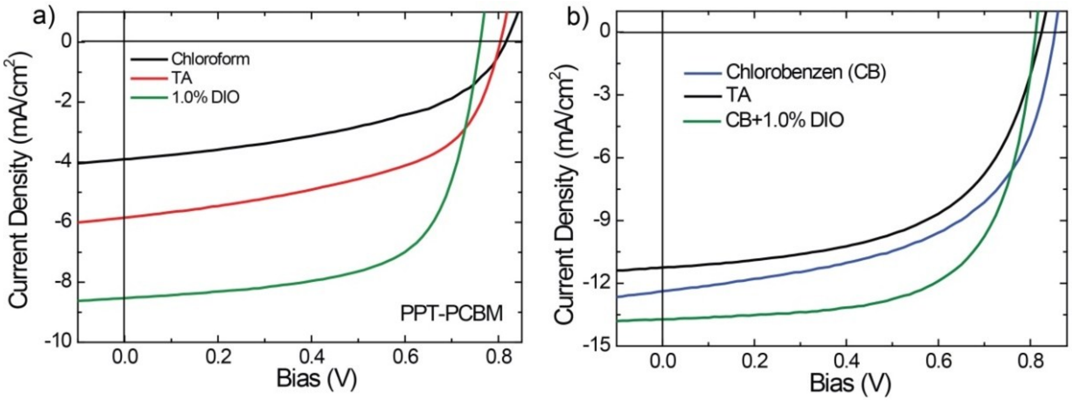


**Figure S5.** *J*–*V* curves of the optimal PPT-PC$_{61}$BM solar cell devices processed from chloroform (a) and chlorobenzene (b).

**Table S2.** Optimized devices performance based on PPT/PC$_{61}$BM blends.

| Polymer | Solvent | Ratio (w/w) | $V_{oc}$ [V] | $J_{sc}$ [mA/cm$^2$] | *FF* | *PCE (%)* |
|---|---|---|---|---|---|---|
| PBT | CF | 1/2 | 0.81 | 3.89 | 0.46 | 1.45 |
| PPT | TA | 1/2 | 0.80 | 5.98 | 0.53 | 2.49 |
| PPT | +1.0% DIO | 1/2 | 0.75 | 8.52 | 0.66 | 4.20 |
| PPT | CB | 1/2 | 0.85 | 12.38 | 0.55 | 5.79 |
| PPT | TA | 1/2 | 0.82 | 11.25 | 0.56 | 5.17 |
| PPT | +1.0% DIO | 1/2 | 0.81 | 13.72 | 0.66 | 7.25 |

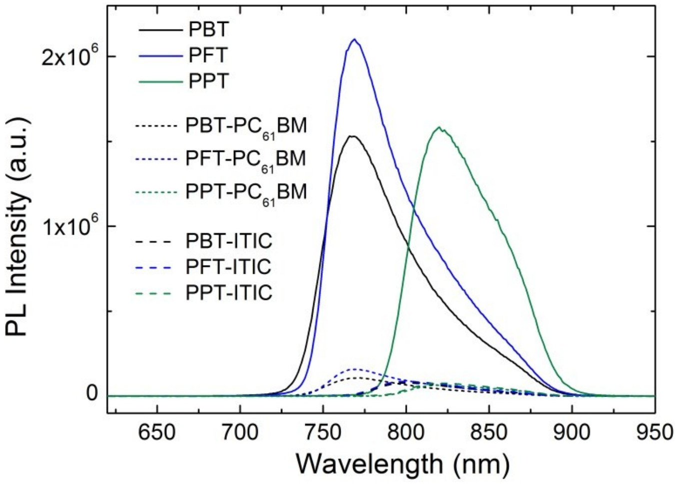
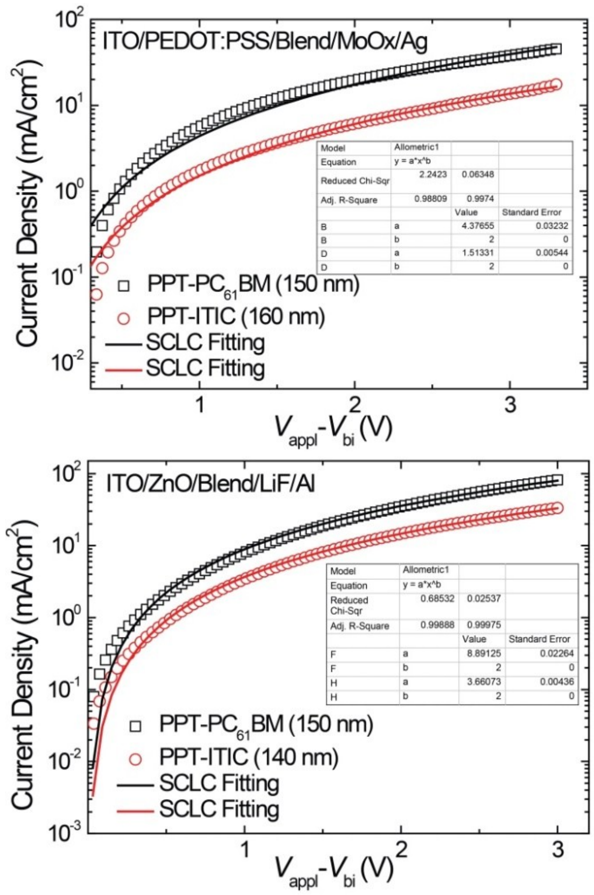


**Figure S6.** Photoluminescence (PL) spectra of neat polymer, polymer-PC$_{61}$BM and polymer-ITIC blends.



| | | | |
|---|---|---|---|
| Model | Allometric1 | | |
| Equation | y = a*x^b | | |
| Reduced Chi-Sqr | 2.2423 | 0.06348 | |
| Adj. R-Square | 0.98809 | 0.9974 | |
| | | Value | Standard Error |
| B | a | 4.37655 | 0.03232 |
| B | b | 2 | 0 |
| D | a | 1.51331 | 0.00544 |
| D | b | 2 | 0 |

| | | | |
|---|---|---|---|
| Model | Allometric1 | | |
| Equation | y = a*x^b | | |
| Reduced Chi-Sqr | 0.68532 | 0.02537 | |
| Adj. R-Square | 0.99888 | 0.99975 | |
| | | Value | Standard Error |
| F | a | 8.89125 | 0.02264 |
| F | b | 2 | 0 |
| H | a | 3.66073 | 0.00436 |
| H | b | 2 | 0 |

**Figure S7.** *J-V* curves and SCLC fit of PPT-PC61BM and PTP8-ITIC hole-only (up) and electron-on diodes (down) devices.

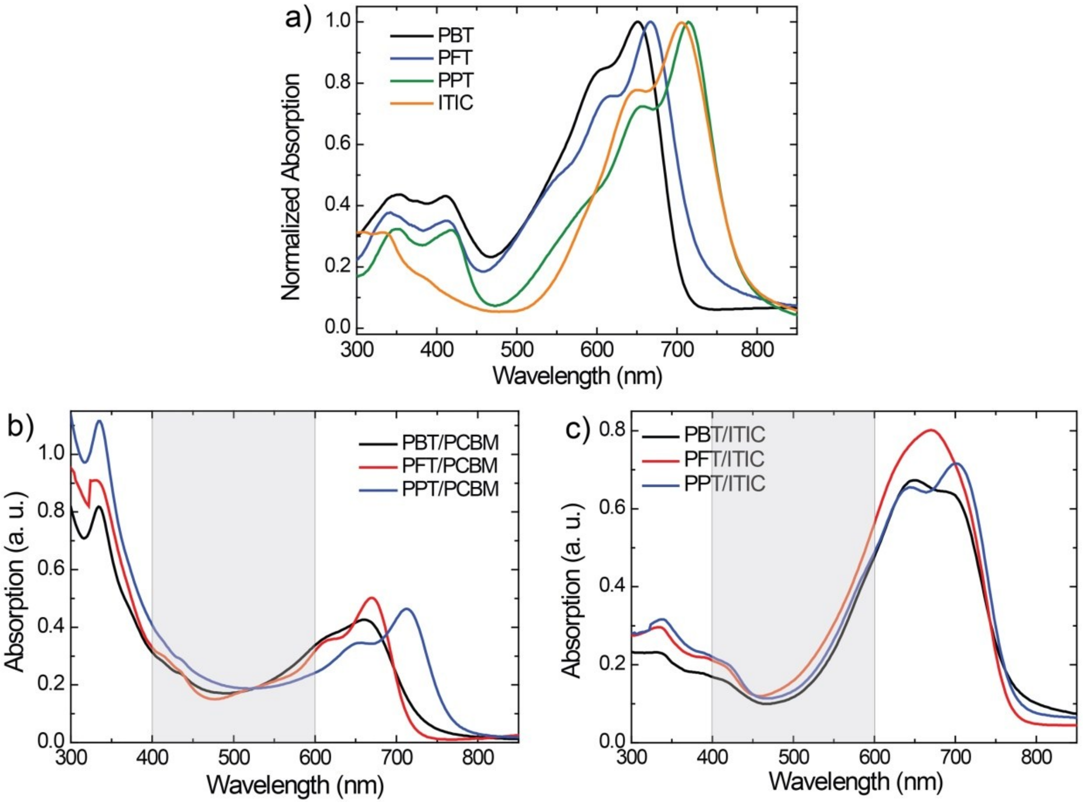


**Figure S8.** Absorption spectra of polymer and ITIC thin films (a), polymer-PC$_{61}$BM blend films (b) and polymer-ITIC blend films processed from optimal conditions.

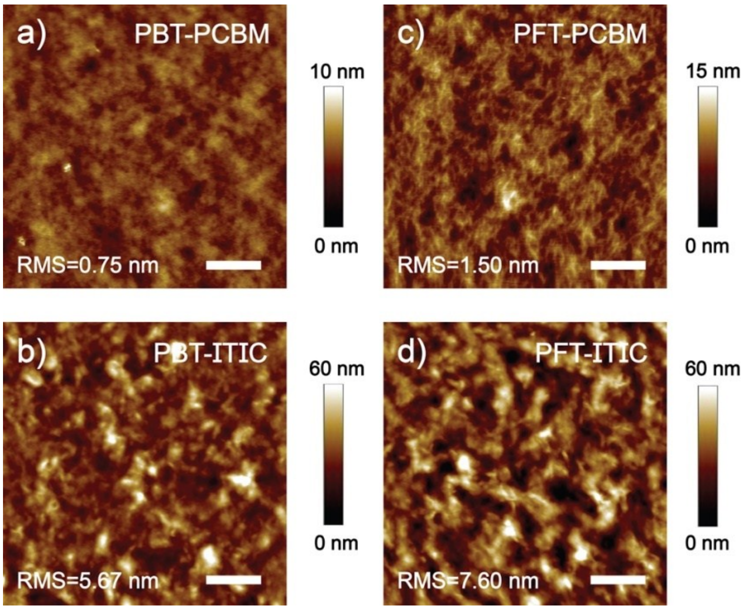


**Figure S9.** AFM height images of PBT-PC$_{61}$BM (a), PBT-ITIC (b), PFT-PC$_{61}$BM (c) and PFT-ITIC (d) blends processed from optimal conditions.

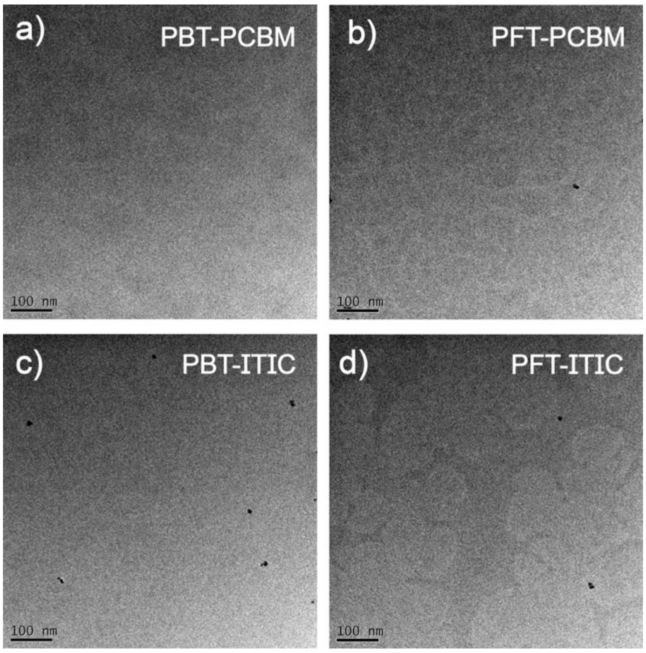


**Figure S10.** TEM images of PBT-PC$_{61}$BM (a), PBT-ITIC (b), PFT-PC$_{61}$BM (c) and PFT-ITIC (d) blends processed from optimal conditions.

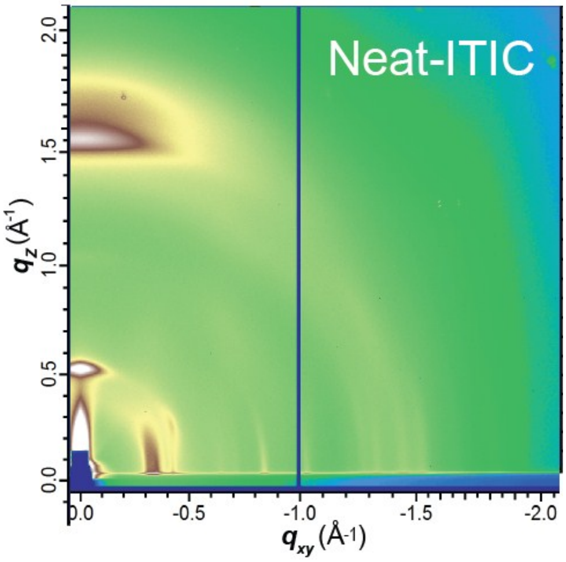


**Figure S11.** 2d-GIWAXS patterns of ITIC thin films.