Electronic Supplementary Information

Distinction between the PTB7-Ths Prepared from $Pd(PPh_3)_4$ and $Pd_2(dba)_3$/P-(o-tol)$_3$ Catalyzed Stille Coupling Polymerization and Resultant Photovoltaic Performance

Jianhong Gao,[a] Wei Wang,[a] Shoujie Zhang, [a] Shengqiang Xiao,[a] Chun Zhan,[a] Mingyan Yang,[a]*
Xinhui Lu,[b] Wei You*[a,c]*

[a] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, P. R. China E-mail: shengqiang@whut.edu.cn

[b] Department of Physics, Chinese University of Hong Kong, Hong Kong, P. R. China E-mail: xhlu@phy.cuhk.edu.hk

[c] Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, USA Email: wyou@unc.edu

1. Materials

The monomer of (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-*b*:4,5-*b′*]dithiophene-2,6-diyl)bis(trimethylstannane) (**BDTT**) was synthesized according to the reported method.[1] The acceptor monomer of 2-ethylhexyl-4,6-dibromo-3-fluorothieno[3,4-b]thiophene-2-carboxylate (**FTT**) was purchased from Suna Tech Inc and directly used. [6,6]-Phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$, >99%, EL device grade) was purchased from Solenne. The sol-gel of ZnO solution was prepared with zinc acetate dihydrate (Aldrich, 99.9%, 1.05 g) and Ethanolamine (Aldrich, 99.5%, 0.28g) dissolved in 2-methoxyethanol (Aldrich, 99.8%, 10mL) under vigorous stirring for 12 h in air.[2] All other chemicals were purchased from J&K and Energy Chemicals.

2. Instruments and Methods

All ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III-HD-500 MHz spectrometer in $CDCl_3$ at 298 K, unless specified otherwise. Chemical shifts (δ values) were recorded in units of ppm relative to tetramethylsilane (TMS) as an internal standard. The mass spectroscopy of compounds was performed on API 2000 Finnigan Trace MS or Bruker Biflex III MALDI-TOF mass spectrometer. The molecular weight of the polymer was determined by gel permeation chromatography (GPC) on a PL-GPC 220 apparatus, using 1,2,4-trichlorobenzene as the eluent at 150 ^{o}C and calibrated with polystyrene standards. Thermogravimetric analysis (TGA) was carried out on a NETZSCH syncthermogravimetric analyzer (STA449F3) at a heating rate of 10 ^{o}C min^{-1} under nitrogen. UV-vis absorption spectra of the solutions in o-DCB and films spin-coated on the precleaned glass were taken on a Shimadzu UV-1800 spectrophotometer. The photoluminescence (PL) spectrum of films spin-coated on precleaned quartz glasses were recorded on a Fluoro Max-3-P spectrometer. Cyclicvoltammogram (CV) measurements were carried out in a solution of 0.1 M tetrabutylammonium hexalfluorophosphate (Bu_4NPF_6) with anhydrous acetonitrile as the supporting electrolyte on a CHI 660D electrochemical analyzer using a standard three-electrode configuration, with a platinum disk as the working electrode, a platinum wire as the counter electrode and a $Ag/AgNO_3$ (0.01 M $AgNO_3$ in the supporting electrolyte) electrode as the reference electrode at a scan rate of 80 mV s^{-1} at room temperature. Ferrocene is used as internal standard to calculate the frontier orbital energy levels of the polymers. Raman spectroscopy measurements were carried out for polymer thin films on a Renishaw inVia microscope. The excitation source was a 514 nm (Ar ion) laser and the spectra were obtained with a laser power of ~ 0.9 mW and an acquisition time of 60 s in N_2.

3. Preparation of PTB7-Th-L

To a 50 mL of round-bottom flask was introduced (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-*b*:4,5-*b′*]dithiophene-2,6-diyl)bis(trimethylstannane) (180.9 mg, 0.2 mmol), 2-ethylhexyl-4,6-dibromo-3-fluorothieno[3,4-b]thiophene-2-carboxylate (94.4 mg, 0.2 mmol) under N_2 before $Pd_2(dba)_3$ (5.5 mg, 0.006 mmol), tri(*o*-tolyl)phosphine (10.9 mg, 0.036 mmol) and anhydrous chlorobenzene (6.0 mL) were added. The round-bottom flask was then heated at 140 ^{o}C for 48 hours. After cooling down to room temperature, the mixture was added into 100 mL of methanol dropwisely. The precipitate was collected by filtration and extracted in a Soxhlet with methanol, acetone, hexane, dichloromethane sequentially. The final product in dichloromethane fraction was then concentated, reprecipitated into 80 mL of methanol, filtered and dried under vacuum (158.0 mg, yield 85%, M_n = 12.4 kg mol^{-1}, PDI = 2.8). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.21-8.31(br, 4.1 H), 6.68-7.08 (br, 2.2 H), 3.87-4.71 (br, 1.9 H), 2.68-3.25 (br, 4.0 H), 0.75-1.93 (br, 46.0 H).

4. Preparation of PTB7-Th-H

To a 50 mL of round-bottom flask was introduced (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-*b*:4,5-*b′*]dithiophene-2,6-diyl)bis(trimethylstannane) (180.9 mg, 0.2 mmol), 2-ethylhexyl-4,6-dibromo-3-fluorothieno[3,4-b]thiophene-2-carboxylate (94.4 mg, 0.2 mmol) before being transfered to a glovebox where $Pd(PPh_3)_4$ (12.0 mg, 0.01 mmol) and the mixed solvent (5 mL of toluene and 1 mL of DMF) were added in. The mixture was then stirred at reflux for 32 hr. The polymerization proceeded for additional 12 hours after adding 2-bromothiophen (15 μL) and 2-trimethyltin-thiophene (45 μL) as end-capping agents. After the resulting solution was cooled down to room temperature, it was then poured into methanol. The precipitate was collected by filtration and extracted by methanol, acetone, hexane, dichloromethane and chloroform sequentially. The chloroform fraction was then concentated, reprecipitated into 80 mL of methanol, filtered and dried under vacuum to obtain the final product (108.0 mg, yield 58%, $M_n = 22.6$ kg mol^{-1}, PDI = 2.1). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.48-8.20 (br, 4.2 H), 6.40-7.20 (br, 2.2 H), 4.00-4.60 (br, 2.0 H), 2.38-3.55 (br, 4.0 H), 0.45-1.85 (br, 46.0 H).

5. Supplementary figures

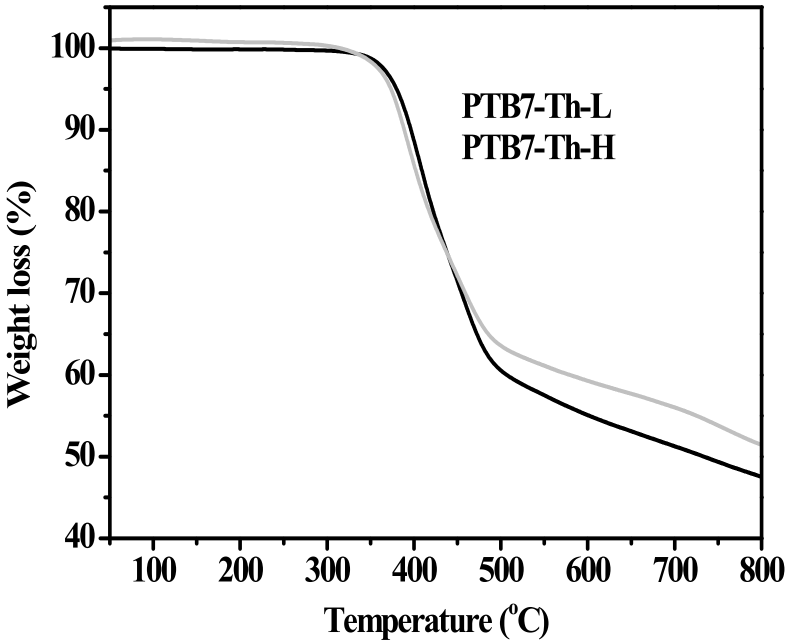

Fig. S1 TGA curves of **PTB7-Th-L** and **PTB7-Th-H** at a heating rate of 10 °C min^{-1} under N_2.

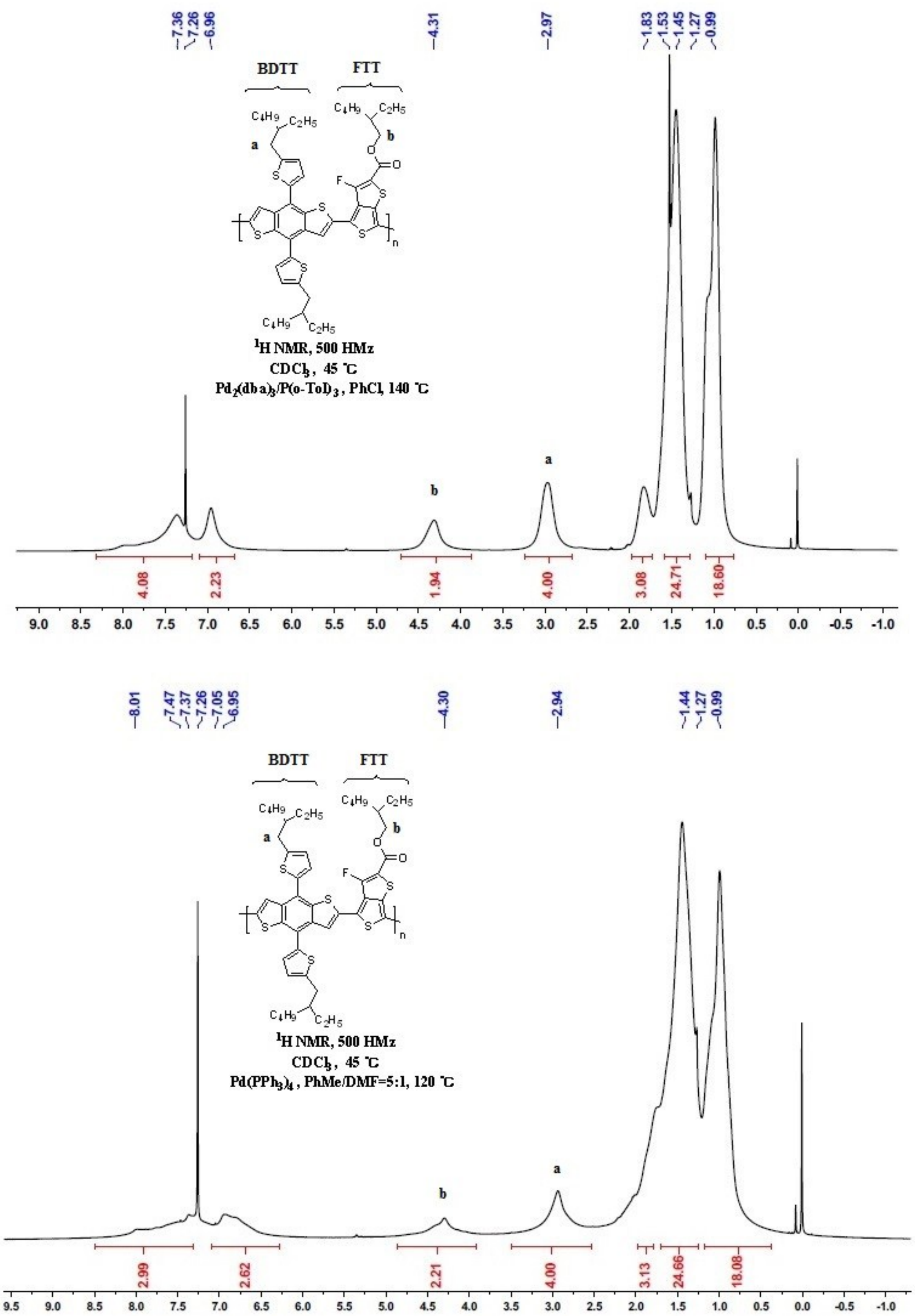

Fig. S2 ^{1}H-NMR Spectroscopy of **PTB7-Th-L** (up) and **PTB7-Th-H** (bottom) in CDCl$_3$.

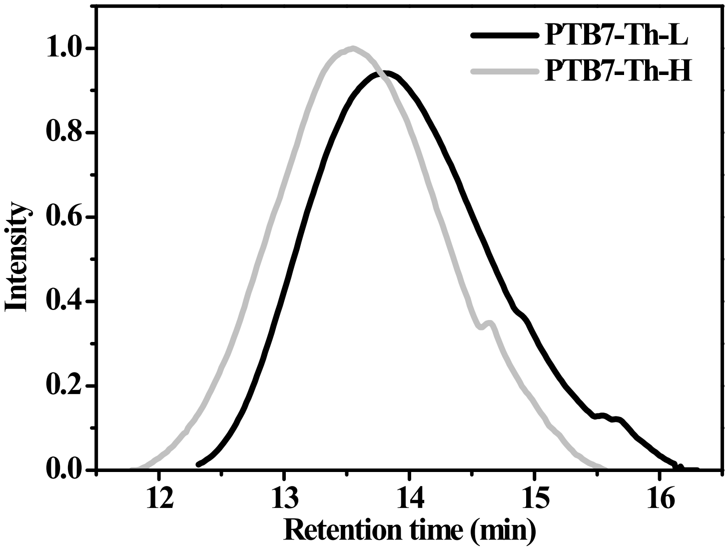

Fig. S3 High temperature GPC chromatograms for **PTB7-Th-L** and **PTB7-Th-H** eluted by 1,2,4-trichlorobenzene at 150 °C.

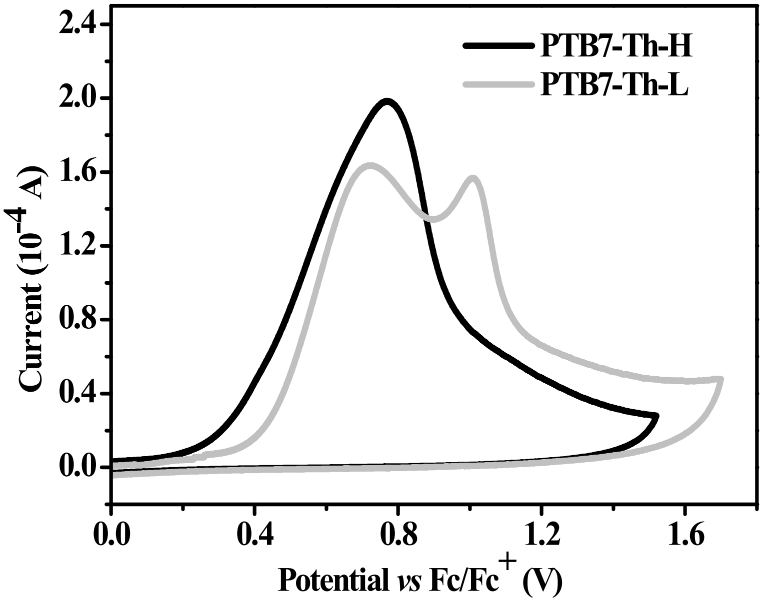

Fig. S4 Cyclic voltammograms of the polymer of **PTB7-Th-L** and **PTB7-Th-H** in thin film (drop cast from 2 mg mL^{-1} chloroform solution) at a scan rate of 100 mV S^{-1}.

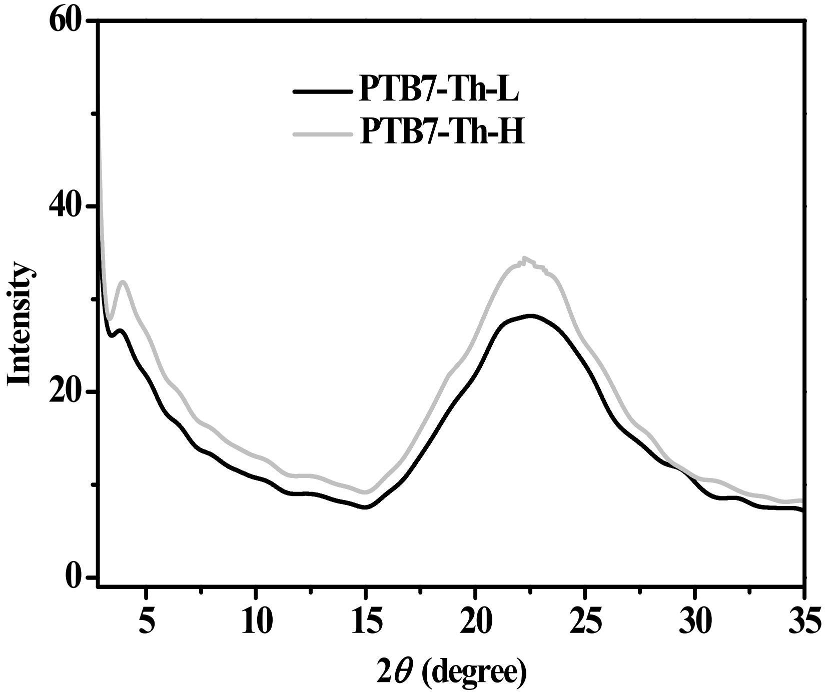

Fig. S5 Powdery XRD profiles of **PTB7-Th-L** and **PTB7-Th-H** films

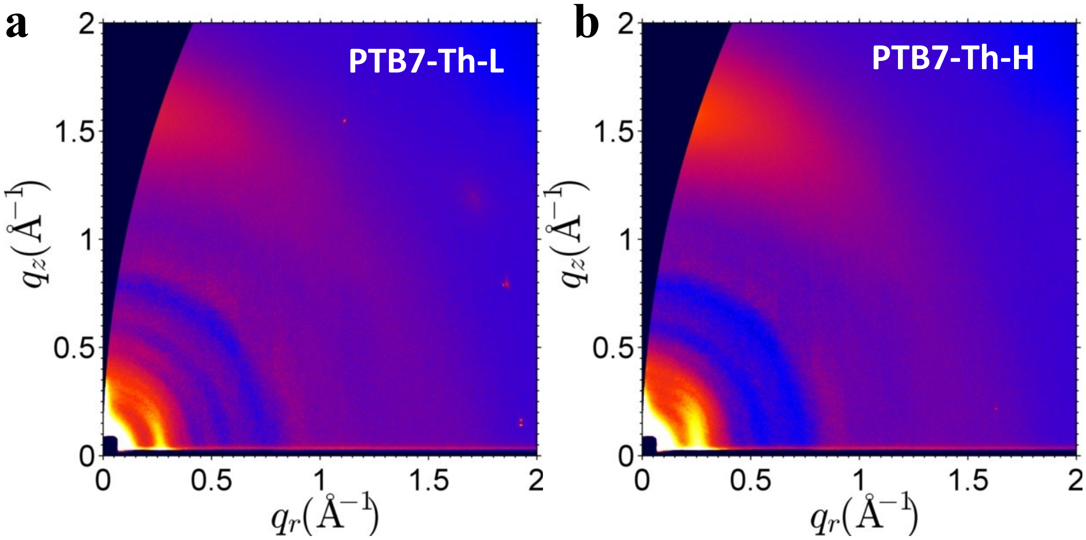

Fig. S6 GIWAXS patterns of neat films of **PTB7-Th-L** (a) and **PTB7-Th-H** (b).

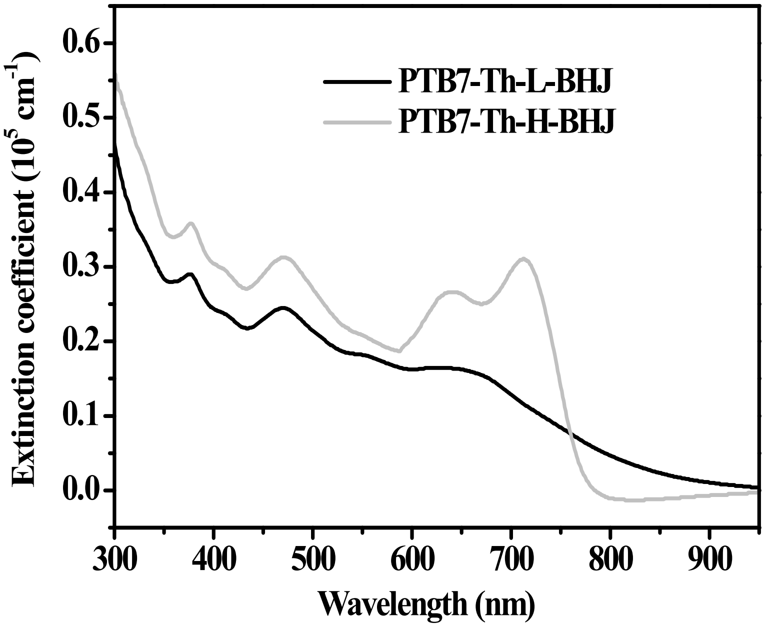

Fig. S7 The absorption spectra of the optimized BHJ blend films with **PTB7-Th-L** and **PTB7-Th-H** respectively.

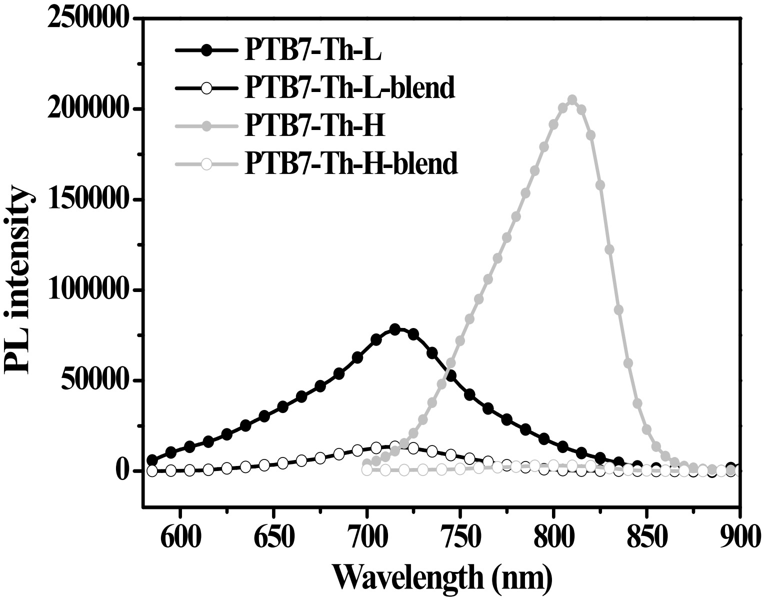

Fig. S8 Photoluminescence spectra of pure polymer in film (with similar thickness to the corresponding BHJ blends) and polymer:$PC_{71}BM$ blend (2:3, w/w) films for **PTB7-Th-L** and **PTB7-Th-H** (excited at 580 nm and 688 nm respectively).

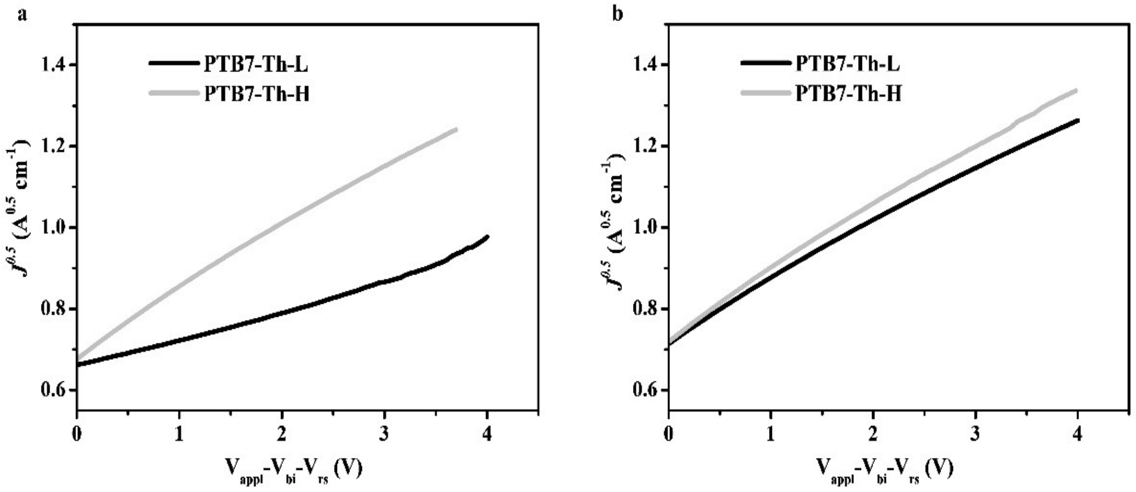

Fig. S9 $J^{0.5}$ *vs* V_{appl}-V_{bi}-V_{rs} plots for a) hole-only and b) electric-only devices of **PTB7-Th-L** and **PTB7-Th-H.**

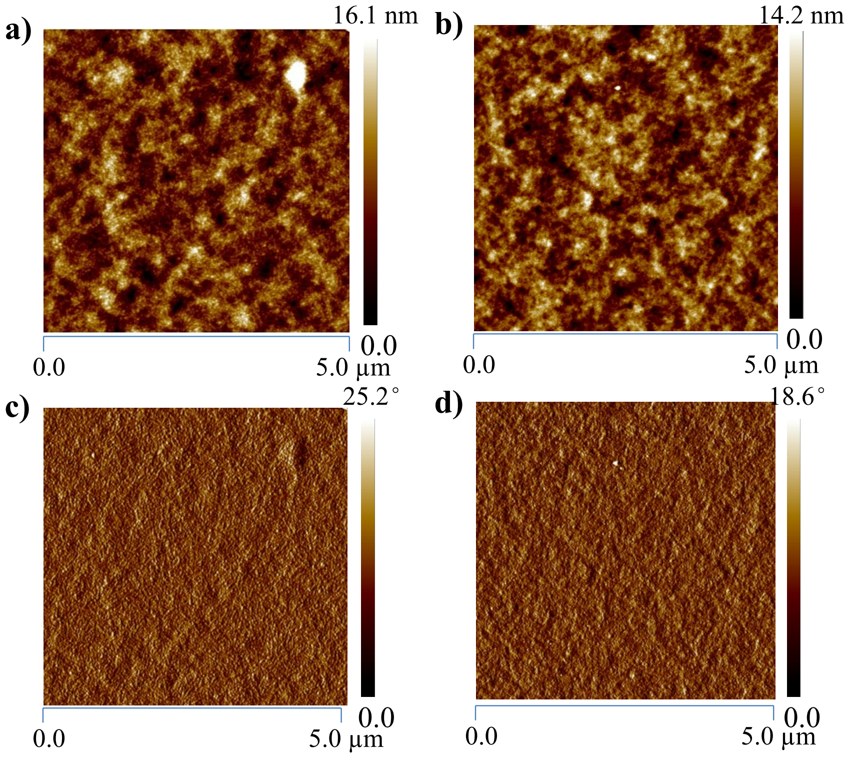

Fig. S10 Tapping-mode AFM height (a and b) and phase (c and d) images of **PTB7-Th-L**:$PC_{71}BM$ and **PTB7-Th-H**:$PC_{71}BM$ blends respectively.

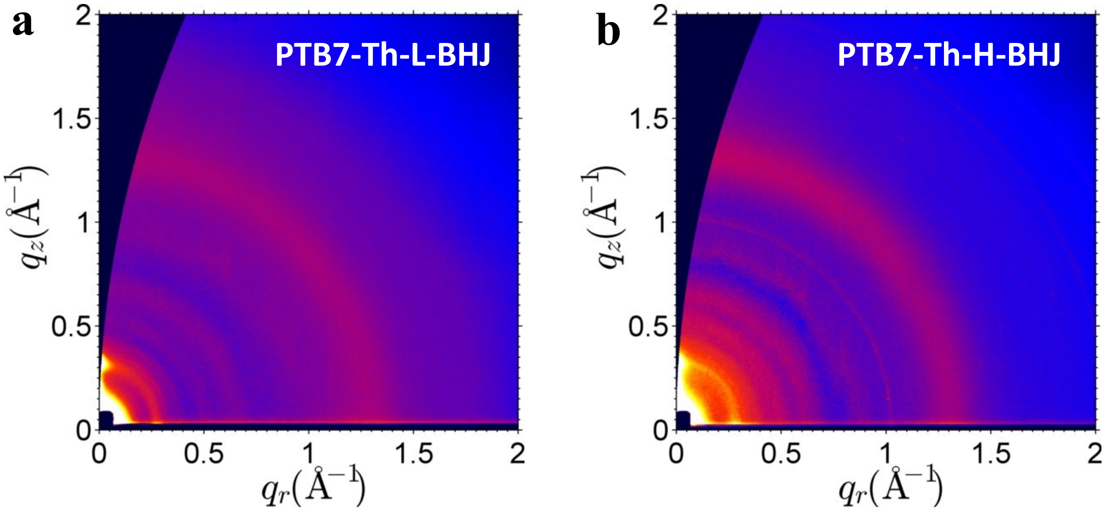

Fig. S11 GIWAXS patterns of the **PTB7-Th-L**:PC$_{71}$BM BHJ blend (a) and the **PTB7-Th-H**:PC$_{71}$BM BHJ blend (b).

6. References

[1] Liao, S.-H.; Jhuo, H.-J.; Cheng, Y.-S.; Chen, S.-A. Fullerene Derivative-Doped Zinc Oxide Nanofilm as the Cathode of Inverted Polymer Solar Cells with Low-Bandgap Polymer (PTB7-Th) for High Performance, Adv. Mater. **2013**, 25, 4766-4771.

[2] Sun, Y.; Seo, J. H.; Takacs, C. J.; Seifter, J.; Heeger, A. J. Inverted Polymer Solar Cells Integrated with a Low-Temperature-Annealed Sol-Gel-Derived ZnO Film as an Electron Transport Layer, *Adv. Mater.* **2011**, 23, 1679-1683.