Electronic Supplementary Information for

2-D Moiety Modified Terpolymer Acceptors with Reduced Molecular Planarity and Crystallinity: Improved Performance and Stability for All-Polymer Solar Cells

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Materials and characterizations

All solvents were purchased from Sigma Aldrich Co., Energy Chemical Co., Alfa Aesar without further purification. PTB7-Th was purchased from Solarmer Materials Inc., PBDB-T and PDCBT were purchased from Vizu Chem (Shanghai). *N*,*N′*-bis(2-octyl-1-dodecyl)-2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic acid bisimide (NDI unit), 5,5′-bis(trimethylstannyl)-2,2′-bithiophene (T2 unit) and 8-Bis[5-(2-ethylhexyl)-2-thienyl]benzo[1,2-*b*:4,5-*b*']dithiophene (BDT unit) were purchased from Suna Tech.

^{1}H NMR spectra were recorded on a Bruker DMX-400 spectrometer in deuterochloroform using tetramethylsilane (TMS; δ=0 ppm) as an internal standard. The molecular weights of the polymers acceptors were estimated by gel permeation chromatography (GPC) on Agilent PL-GPC-220 using *o*-dichlorobenzene as the eluent at 120^{o}C with polystyrenes as the internal standards. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit at a heating rate of 10^{o}C min^{-1} from 25 to 350^{o}C, under argon. Ultraviolet-visible (UV–vis) absorption spectra of solution in chloroform and thin film on a quartz substrate were measured using Shimadzu UV-2500 recording spectrophotometer. The simulated chemical geometry of the polymer monomers was conducted using the Gaussian 09 program package. The electrochemical cyclic voltammetry was conducted on a CHI voltammetric analyzer, in a 0.1 mol L^{-1} acetonitrile solution of tetrabutylammonium hexafluorophosphate (n-Bu$_4$NPF$_6$) at a potential scan rate of 100 mV s^{-1}. The conventional three electrode configuration consists of a platinum working electrode, a platinum wire counter electrode, and an Ag/AgCl wire pseudo-reference electrode. The polymer sample was coated on the platinum sheet of working electrode. The reference electrode was checked versus ferrocenium-ferrocene (Fc$^+$/Fc) as internal standard as recommended by IUPAC (the vacuum energy level: 24.8 eV). All the solutions were deaerated by bubbling nitrogen gas for a few minutes prior to the electrochemical measurements. HOMO energy levels were calculated from the equation of E_{HOMO}=-($E_{\mathrm{onset(ox)}}$+4.8) eV, and LUMO from E_{LUMO}=-($E_{\mathrm{onset(red)}}$+4.8) eV. *J-V* curves of the all-PSCs were measured on a computer-controlled Keithley 2400 Source Measure Unit. Oriel Sol3A Class Solar Simulator (model, Enlitech SS-F5-3A) with a 450 W xenon lamp and an air mass 1.5 filter was used as the light source. The light intensity was calibrated to 100 mW cm^{-2} by a silicon reference cell. EQE spectra was measured by Solar Cell Spectral Response Measurement System QE-R3-011 (Enli Technology, Taiwan). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. The contact angle measurements were performed through KRUSS DSA1005 contact angle analyzer. Distilled deionized water and diiodomethane were employed as probe liquids. The surface energy were calculated via Owens-Wendt model: $\gamma_L(1+\cos\vartheta)=2[(\gamma_d^S\times\gamma_d^L)^{1/2}+(\gamma_p^S\times\gamma_p^L)^{1/2}]$, where the superscripts γ_d and γ_p stand for the dispersion and polar components of the surface energy, as well as *L* and *S* refer to the probe liquid and film sample, respectively. Blend film morphologies were characterized via Bruker Dimension ICON atomic force microscopy. GIWAXs were carried out at the SAXs/WAXs beamline of the Australian Synchrotron. The ITO substrates were cleaned in the same method with device fabrication section and the polymer films were spin-coated the same ways as the active layer of the devices onto PEDOT:PSS buffer layer. Samples were analyzed with an X-ray energy of 11 keV and a range of incident angles from Ω=0.02–0.35 in 0.005 increments to allow signal optimization near the critical angle of the polymer film but below the critical angle of the substrate. Data from GIWAXs experiments were analyzed using a customized version of NIKA 2D based in IgorPro.

Polymerization of polymer acceptors

The polymerizing method for all polymer acceptors were similar. 5,5'-Bis(trimethylstannyl)-2,2'-bithiophene (98.4 mg, 0.2 mmol), *N*,*N'*-bis(2-octyl-1-dodecyl)-2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic acid bisimide (197.1 mg, 0.2 mmol), and the third monomer, 8-Bis[5-(2-ethylhexyl)-2-thienyl]benzo[1,2-*b*:4,5-*b*']dithiophene (BDT unit) was added with feed ratio 0, 5, 10 or 20 mol% together with anhydrous toluene (5 mL) and DMF (1.25 mL) were added to a 50 mL Schlenk bottle and purged with argon for 15 min. Then, 10 mg (4.3 mmol%) $Pd(PPh_3)_4$ was added to the reaction container. After flushing under argon for another 20 min, the reaction mixture was placed in an oil bath and stirred at 120^{o}C for 12 h. The mixture was cooled to room temperature and poured into methanol (400 mL); then, the product was filtered with a Soxhlet thimble, where methanol, hexane, and chloroform (CF) were used for Soxhlet extraction. Finally, the extraction from chloroform was concentrated and precipitated with methanol again before drying under vacuum to get dried solid.

Fabrication of all-PSCs devices

All-PSCs in conventional structure of ITO/PEDOT:PSS/active layer/PDINO/Al were fabricated. ITO (patterned indium tin oxide) glass was cleaned in an ultrasonic bath with acetone and isopropanol solvents, and treated in an ultraviolet-ozone chamber for 30 min. A thin film (30 nm) of PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate), Baytron PVP AI 4083) was spin-coated onto the ITO glass at 3500 rpm and dried subsequently at 150^{o}C for 15 min in air. Then the substrates were transferred to a nitrogen glove box, where the active layers were spin-coated onto the PEDOT:PSS layer. For PBDB-T system, the PBDB-T:polymer acceptors (2:1, w/w) mixed CB solution with total concentration of 18 mg mL^{-1} were spin-coated at 2500 rpm with 1.5% (v/v) DIO as the solvent additive followed by thermal annealing at 120^{o}C for 10 min. And for the devices with PTB7-Th as donor material, PTB7-Th:polymer acceptor (2:1, w/w, 15 mg mL^{-1}) blend in CB solution was spin-casting at 2000 rpm with 1.5% (v/v) DIO as the solvent additive, and then annealed at 120^{o}C for 10 min. In addition, for PDCBT-based devices, the PDCBT:polymer acceptor (2:1, w/w) was dissolved in CF solution without any solvent additive in a total concentration of 9 mg mL^{-1}. Then the blend was spin-coated onto PEDOT:PSS layer at 900 rpm, followed by thermal annealing at 130^{o}C for 10 min. The film thickness of different blend films based on PBDB-T, PTB7-Th and PDCBT exhibited film thickness around 95, 120 and 140 nm. After the preparation of active layers, methanol solution of PDINO at a concentration of 1.0 mg mL^{-1} was deposited upon the active layer at 3000 rpm to afford a PDINO cathode buffer layer with thickness of ca. 10 nm. An aluminum (*approx*. 100 nm) layer was subsequently evaporated onto the surface of the PDINO layer under vacuum (*approx*. 8×10^{-5} Pa) to form the negative electrode.

On the other side, the inverted device configuration with structure of ITO/ZnO/active layer/MoO_3/Ag was employed in device stability measurements. ZnO was prepared according to literature reported procedures[1] and deposited through spin-coating onto ITO glass at 4000 rpm followed by thermal treatment at 200°C for 1 h. The thickness of ZnO layer was calculated as 40 nm. Afterwards, the active layer was spin-coated. Finally, a layer of ca. 8 nm MoO_3 and then a Ag layer of ca. 100 nm were evaporated subsequently under high vacuum.

Fabrication of hole- and electron-only devices for SCLC measurements

Hole and electron mobility were measured using the space charge limited current (SCLC) method. The hole-only devices with the device structure of ITO/PEDOT:PSS/active layer/Au were used to measure the hole mobility and the electron-only devices were fabricated with the configuration of ITO/ZnO/active layer/PDINO/Al. And the processing details of blend films were same with the fabricating conditions of all-PSCs. The thickness of active layers and buffer layers was measured with stylus profiler (KLA Tencor P-7). The hole and electron mobilities were calculated by Mott–Gurney equation.

Reference in Supporting Information

1. Y. Sun, J. H. Seo, C. J. Takacs, J. Seifter and A. J. Heeger, *Adv. Mater.*, 2011, **23**, 1679-1683.

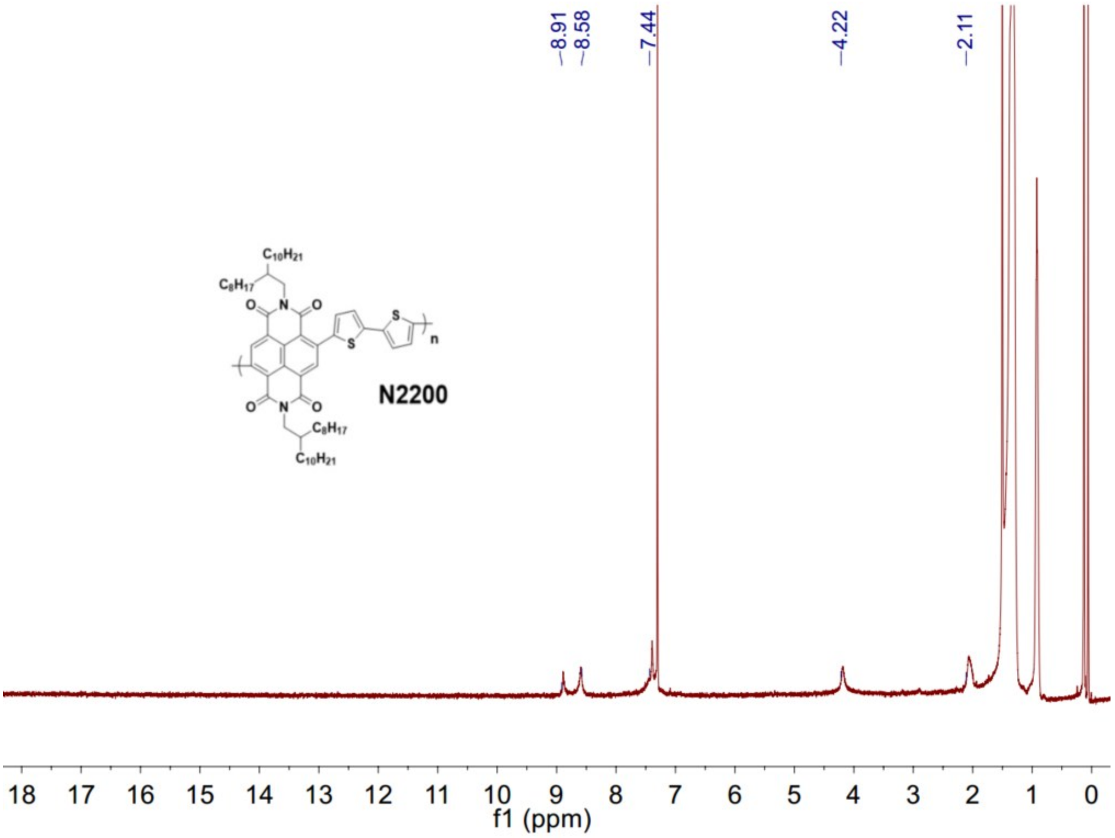

Figure S1. The ^{1}H NMR spectra of N2200.

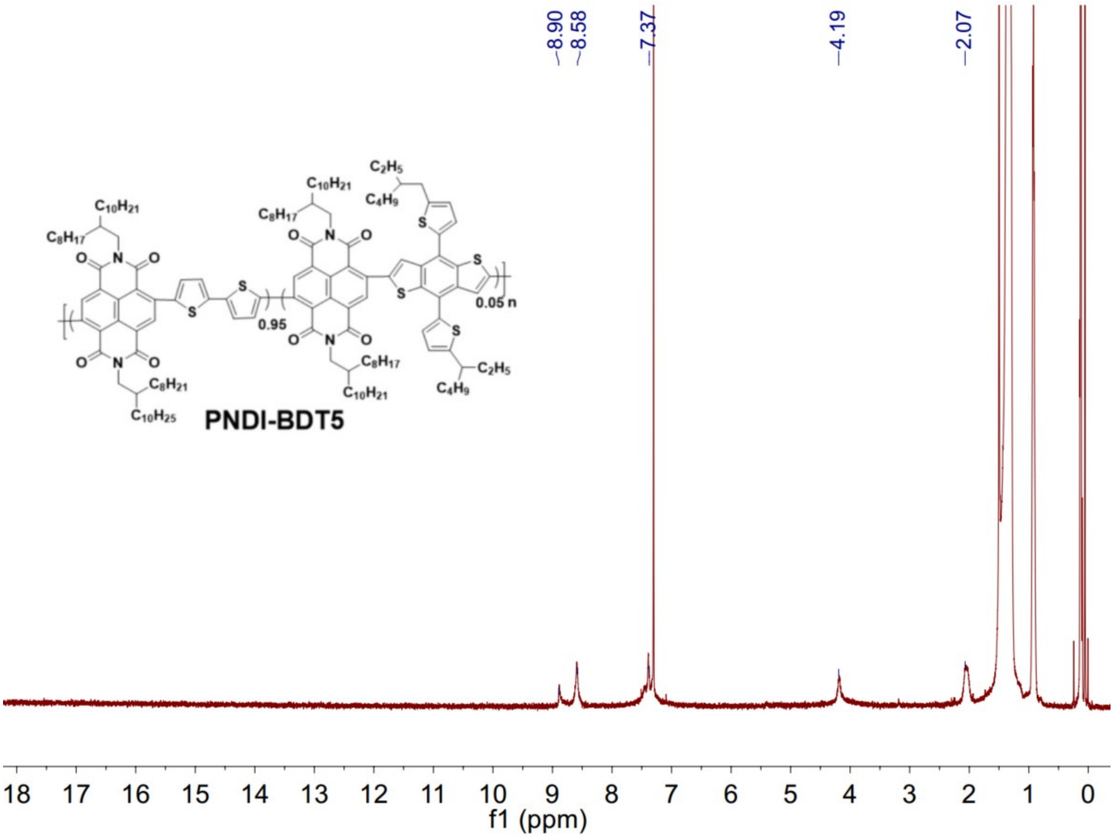

Figure S2. The ^{1}H NMR spectra of PNDI-BDT5.

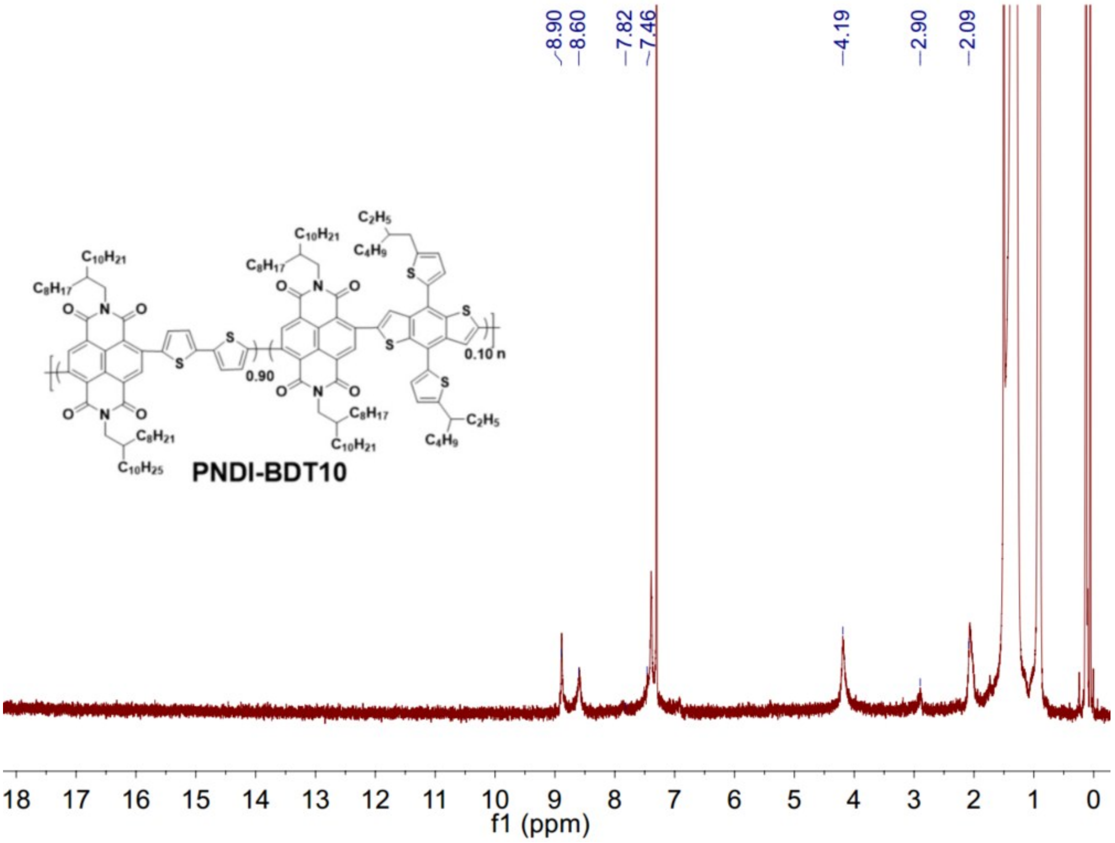

Figure S3. The ^{1}H NMR spectra of PNDI-BDT10.

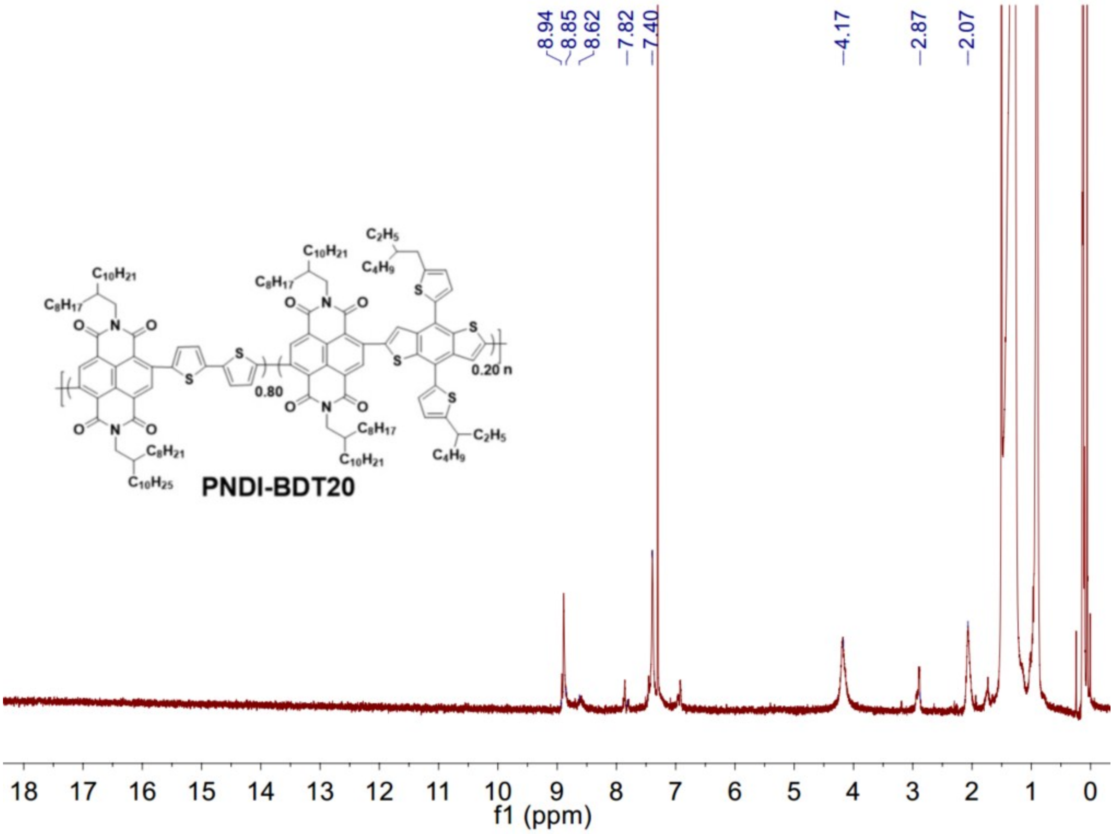

Figure S4. The ^{1}H NMR spectra of PNDI-BDT20.

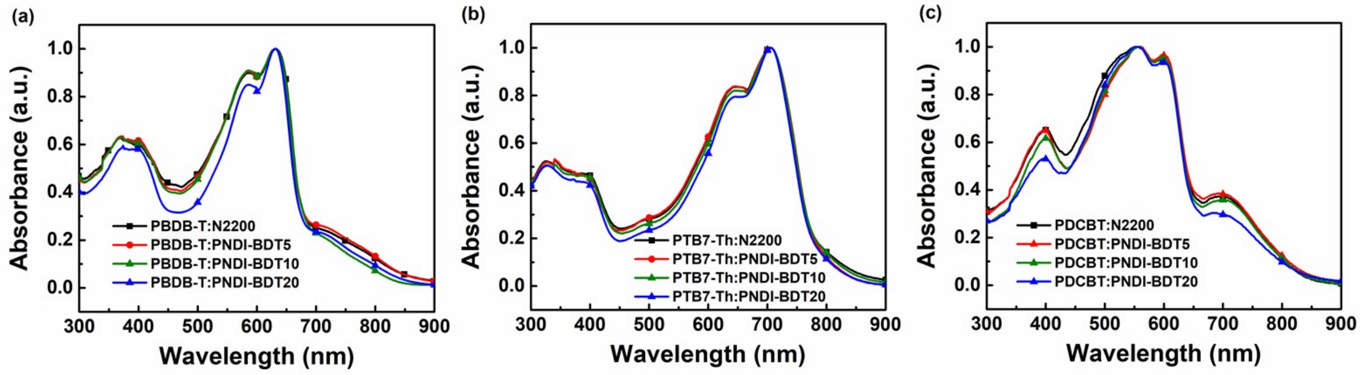

Figure S5. UV-vis absorption spectra of different donor:acceptor blends in film state.

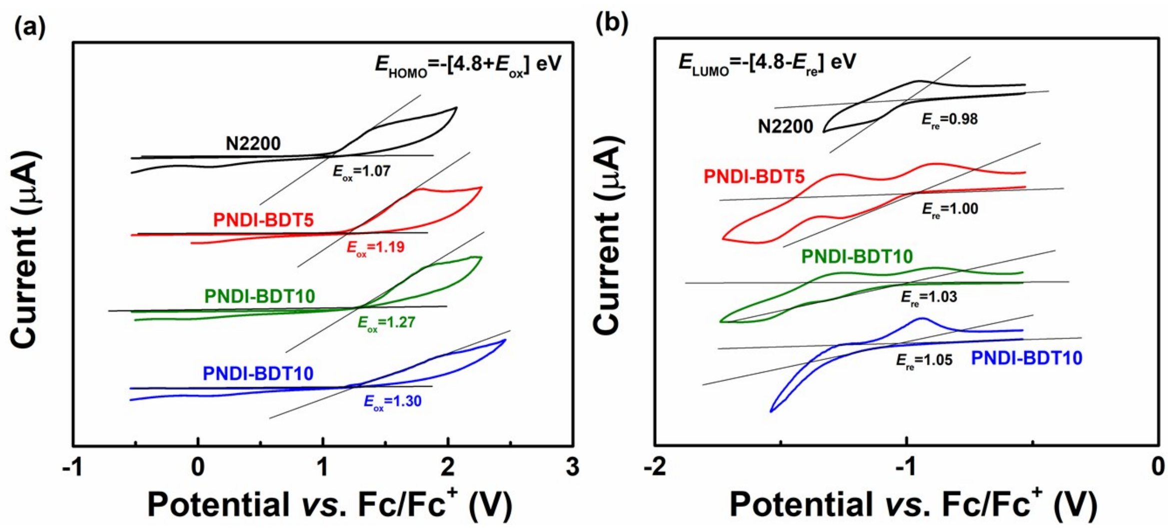

Figure S6. Cyclic voltammograms of the oxidation (a) and reduction (b) curves for N2200 and PNDI-BDTx polymers.

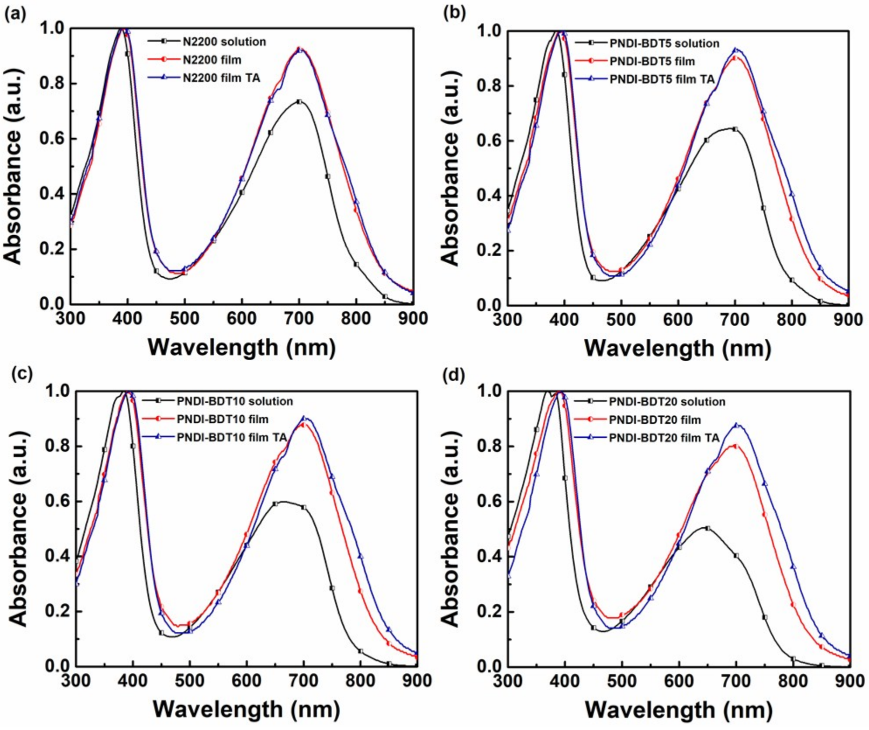

Figure S7. Comparison of UV-vis absorption spectra profiles of different polymer acceptors in different conditions.

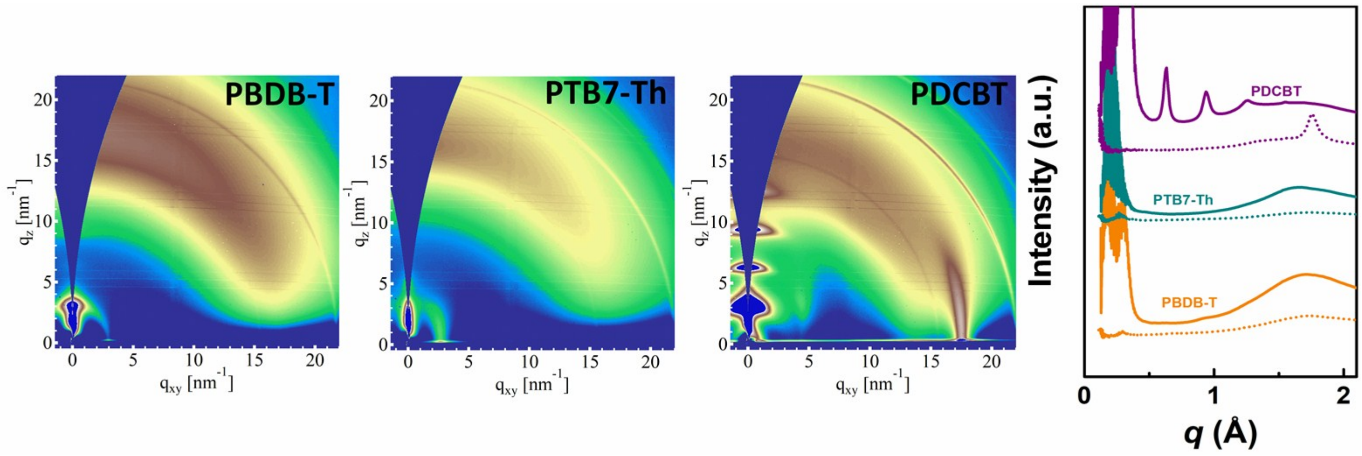

Figure S8. 2D-GIWAXs patterns and 1D line-cuts profiles of three different donors (solid line: out-of-plane, dot line: in-plane).

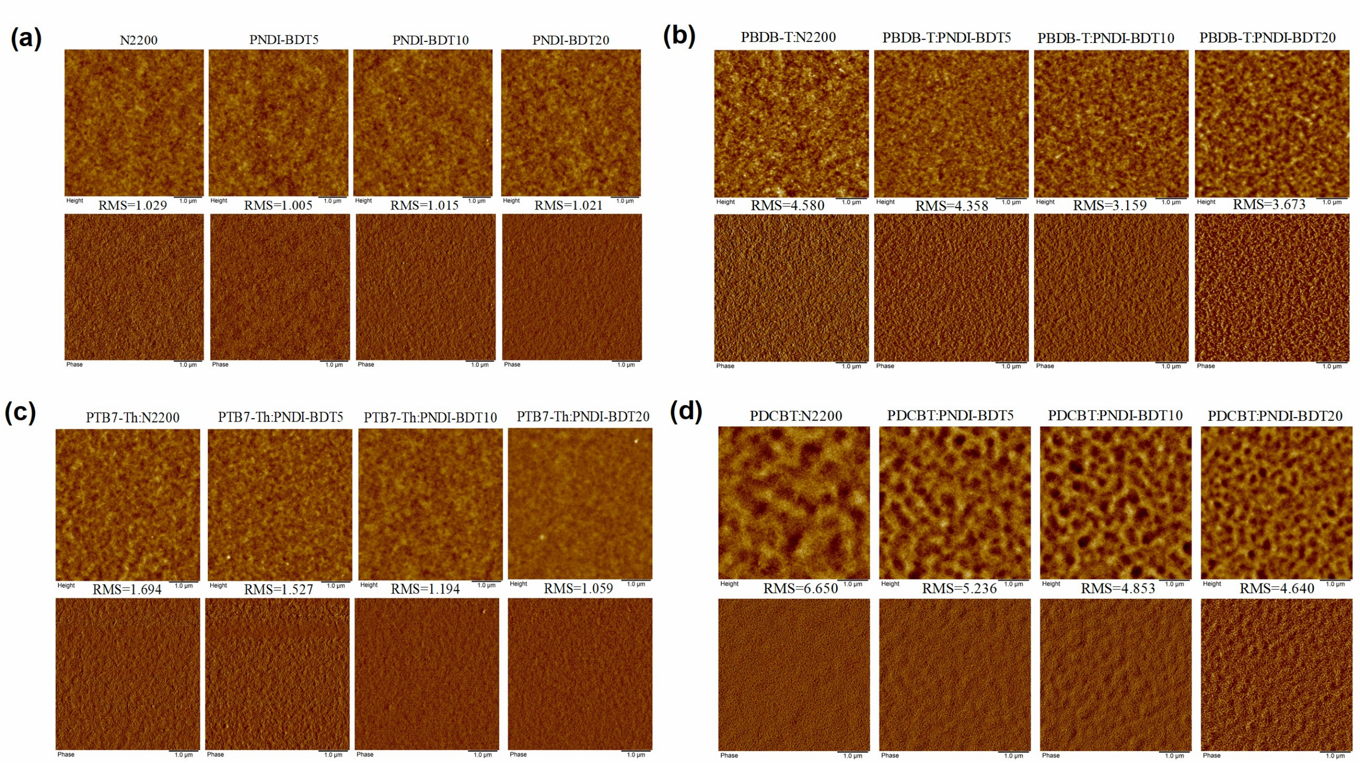

Figure S9. AFM height and phase images of polymer acceptor neat films (a), PBDB-T:polymer acceptor blends (b), PTB7-Th:polymer acceptors blends (c) and PDCBT:polymer acceptors blends (d) as well as the corresponding RMS values.

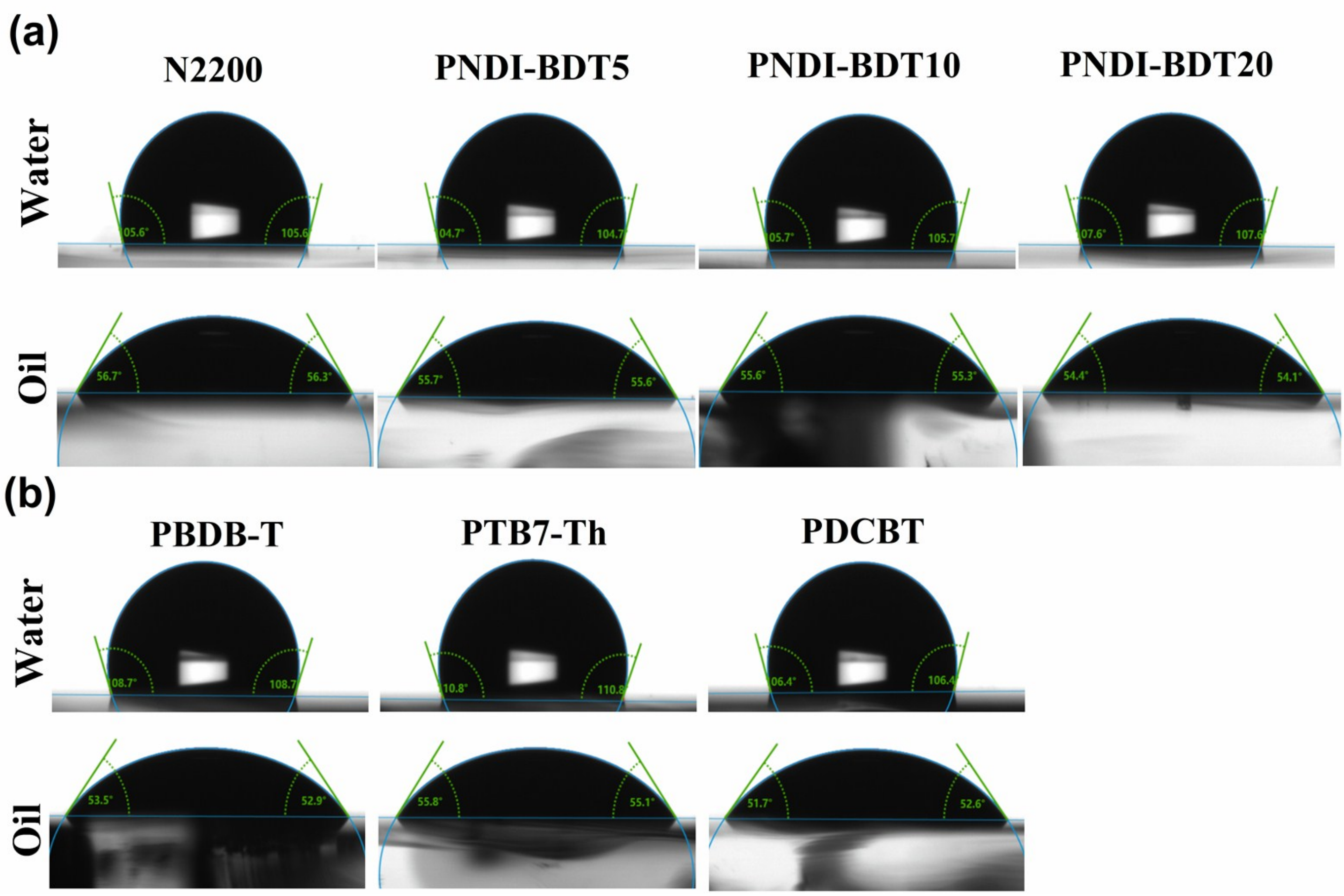

Figure S10. Images of the surface contact angel measurements of corresponding neat films.

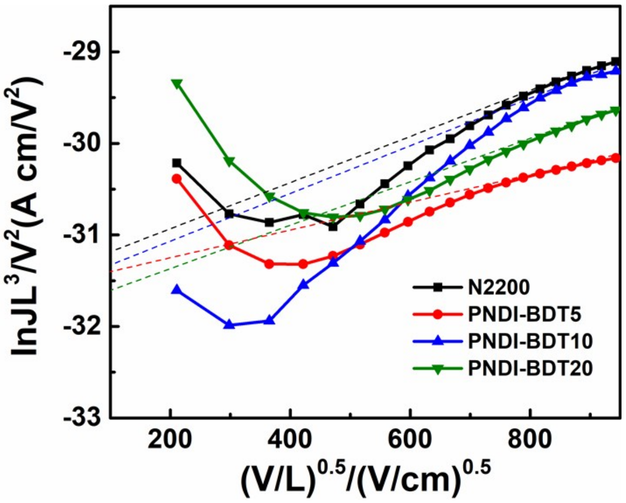

Figure S11. *J-V* curves fitted by SCLC methods for electron-only devices based on different polymer acceptors.

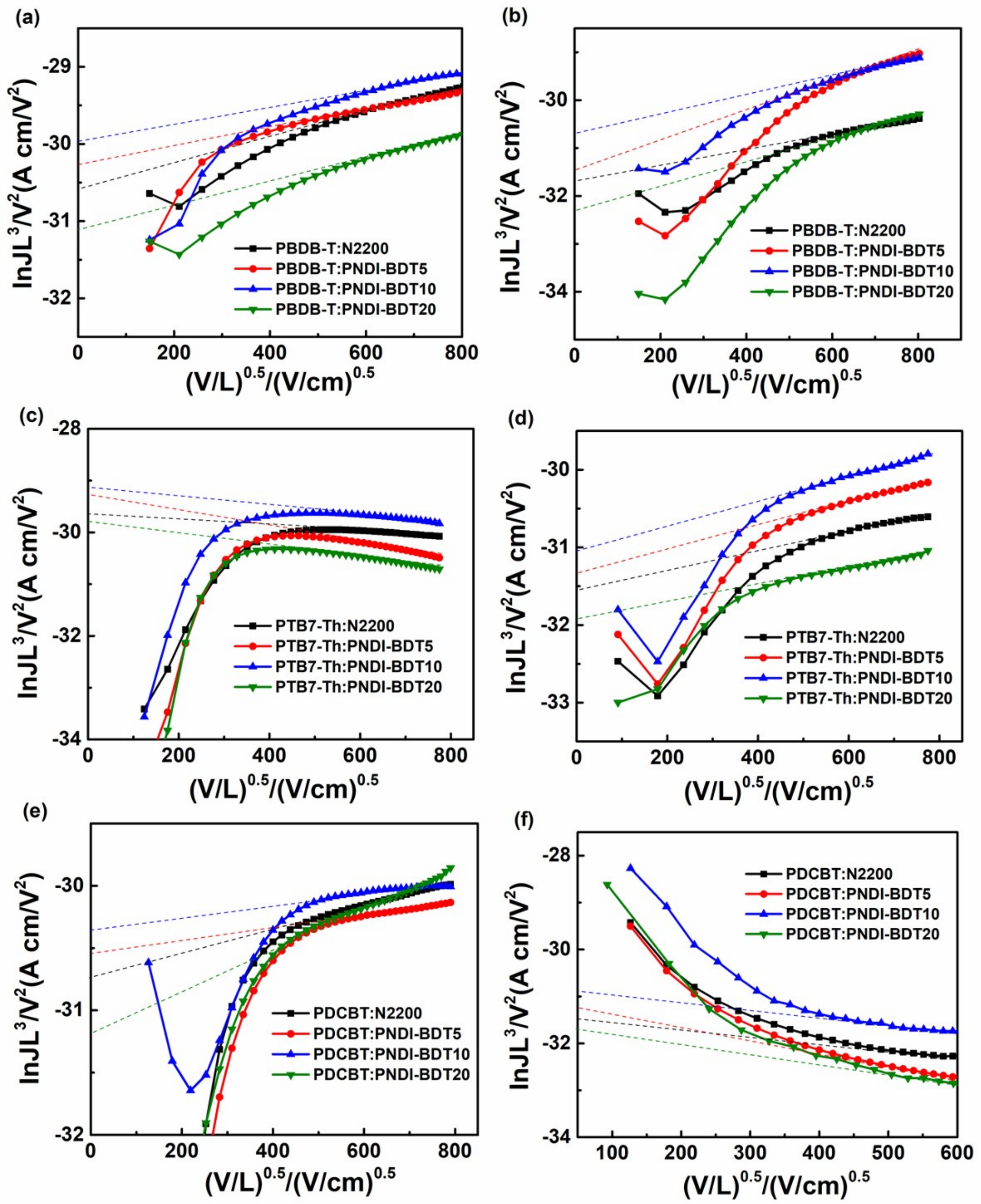

Figure S12. *J*-*V* curves fitted by SCLC methods for the measurements of hole and electron mobilities of different donor:acceptor blends.

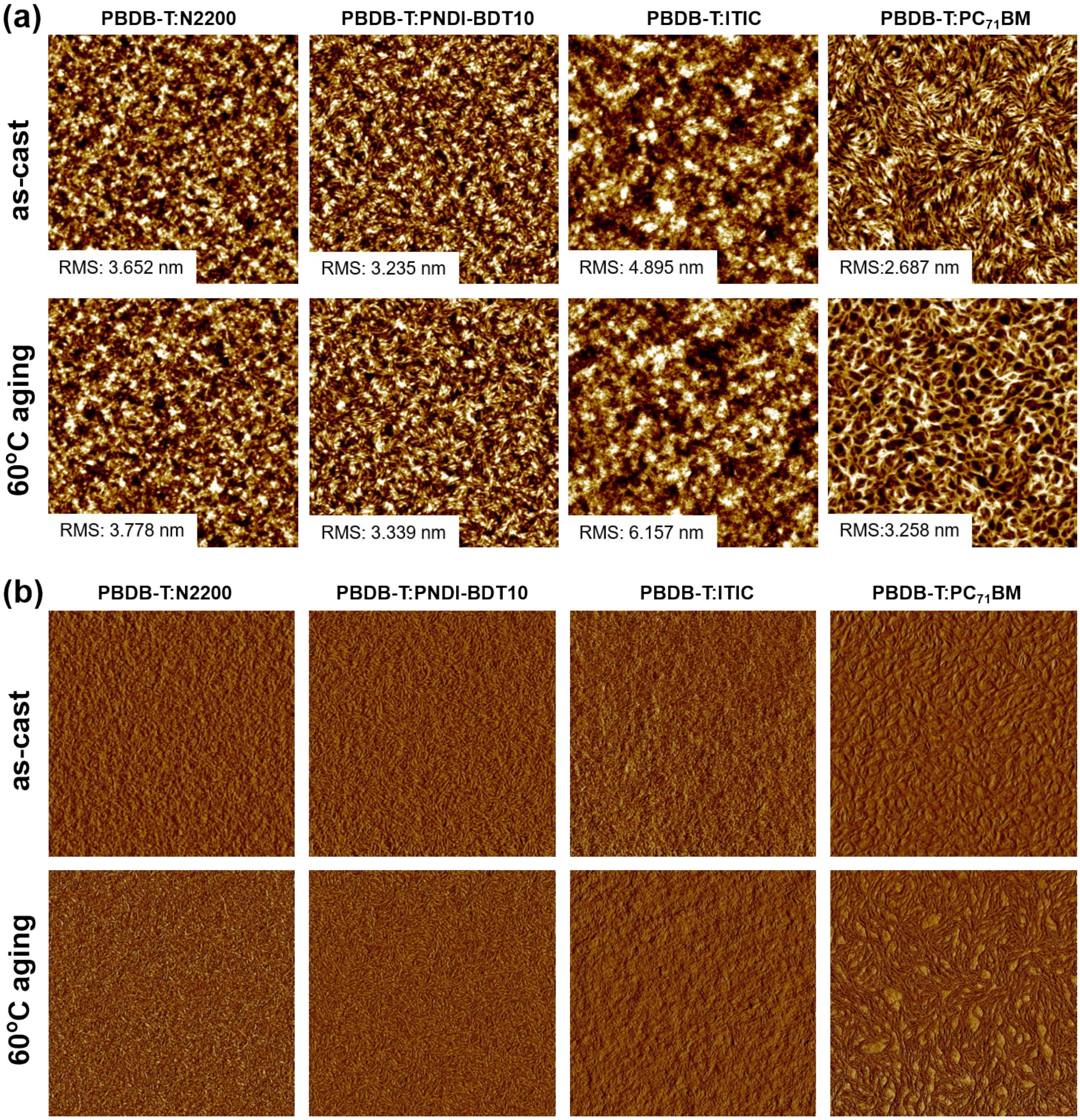

Figure S13. AFM height images (a) and phase images (b) of different typed blend films with or without 60^{o}C-annealing.

Table S1. The data calculated from contact angle measurements.

Film surface	$\vartheta_{\mathrm{water}}$ [º]	ϑ_{oil} [º]	r_{d} [mJ m^{-2}]	r_{p} [mJ m^{-2}]	r [mJ m^{-2}]
PBDB-T	108.7	53.2	32.48	0.069	32.549
PTB7-Th	110.8	55.4	31.36	0.14	31.500
PDCBT	106.4	52.2	33.04	0.014	33.054
N2200	105.6	56.5	30.59	0.012	30.602
PNDI-BDT5	104.7	55.6	31.06	0.025	31.085
PNDI-BDT10	105.7	55.4	31.17	0.0045	31.175
PNDI-BDT20	107.6	54.3	31.84	0.018	31.858

Table S2. The electron mobilities of different polymer acceptors.

Polymer acceptor	μ_{e} [cm^2 V^{-1} s^{-1}]
N2200	9.83×10^{-5}
PNDI-BDT5	7.89×10^{-5}
PNDI-BDT10	8.46×10^{-5}
PNDI-BDT20	6.39×10^{-5}