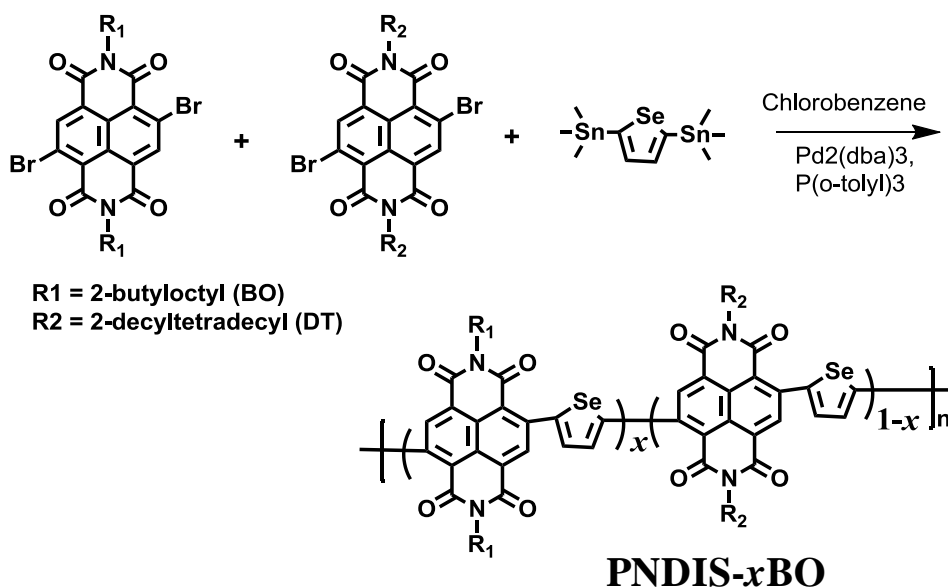


## Supporting Information

### Side Chain Engineering of *n*-Type Conjugated Polymer Enhances Photocurrent and Efficiency of All-Polymer Solar Cells

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**Figure S1.** Synthesis of NDI-selenophene random copolymers: PNDIS-10BO, PNDIS-30BO, and PNDIS-50BO by Stille coupling copolymerization.

**Materials:** 4,9-Dibromo-2,7-bis(2-decyltetradecyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8-tetraone was purchased from Suna Tech and all other chemicals were purchased from Sigma-Aldrich and TCI America. 4,9-Dibromo-2,7-bis(2-butyloctyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8-tetraone and 2,5-bis(trimethylstannyl)selenophene were synthesized according to the known literature procedures.<sup>S1</sup>

**2,5-Dibromoselenophene.** Selenophene (5 g, 0.038 mol) was added into a 250 mL round-bottom flask and purged with argon before adding 100 mL of chloroform. Afterward, NBS (13.575 g, 0.076 mol) was added portionwise. After stirring the mixture overnight at room temperature in the dark, the reaction was quenched by adding water. The crude product was

extracted with chloroform, and purified by column chromatography with 100 % hexane. Slightly yellow oil was obtained and used in next step without further purification. 2,5-Dibromoselenophene (7.5 g, 68.3 %), <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.02 (2H).

**2,5-Bis(trimethylstannyl)selenophene.** 2,5-Dibromoselenophene (2 g, 6.92 mmol) was added into a 250 mL round-bottom flask. Under argon atmosphere, 50 mL THF was then added. The mixture was cooled to -78 °C in a dry ice bath and 2.5 M butyllithium solution in hexane (6.1 mL, 15.23 mmol) was added dropwise. After stirring the mixture for an hour at -78 °C, 1 M trimethyltinchloride solution in THF (15.9 mL, 15.9 mmol) was added in one portion at -78 °C. Dry ice bath was removed after 5 min and the mixture was warmed up to room temperature. After stirring overnight at room temperature, the reaction mixture was poured into water and extracted with diethyl ether 2 times. The organic phase was dried with anhydrous sodium sulfate and the solvent was evaporated by vacuum rotary evaporator. After recrystallization in MeOH, yellow crystals were obtained and subsequently used in polymerization. 2,5-Bis(trimethylstannyl)selenophene (500 mg, 15.8 %), <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.72 (2H), 0.3 - 0.48 (18H); m.p. 118 °C.

**Poly{[N,N'-bis(2-decyltetradecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-selenophene}** (**PNDIS**). 4,9-Dibromo-2,7-bis(2-decyltetradecyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8-tetraone (500 mg, 0.456 mmol), 2,5-bis(trimethylstannyl)selenophene (208.1 mg, 0.456 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (8.34 mg, 0.0091 mmol) and P(*o*-tolyl)<sub>3</sub> (11.1 mg, 0.0365 mmol) were added into a 100 mL three-neck round-bottom flask. The flask equipped with a condenser was then degassed and filled with argon three times. Afterwards, 21 mL of chlorobenzene was added and degassed and filled with argon three times. The reaction mixture was refluxed for 72 h under argon. After cooling down to room temperature, the polymerization mixture was poured and stirred into 200 mL methanol and 5 mL hydrochloric acid solution for 3 h. The polymer precipitated out as a dark reddish purple solid and was filtered using a filter paper. The polymer was purified by Soxhlet

extraction with methanol, hexane, and acetone. GPC:  $M_w = 44.4$  kDa,  $M_n = 36.8$  kDa, PDI = 1.2; TGA:  $T_d = 414$  °C.

***Poly{([N,N'-bis(2-decyltetradecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-selenophene)-ran-([N,N'-bis(2-butyloctyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-selenophene)}*** (***PNDIS-10BO***, ***PNDIS-30BO***, and ***PNDIS-50BO***). Three monomers, 4,9-dibromo-2,7-bis(2-decyltetradecyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8-tetraone, 4,9-dibromo-2,7-bis(2-butyloctyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8-tetraone, and 2,5-bis(trimethylstannyl)selenophene, with Pd<sub>2</sub>(dba)<sub>3</sub> (2 mol%) and P(*o*-tolyl)<sub>3</sub> (8 mol%) were added into a 100 mL three-neck round-bottom flask. The flask equipped with a condenser was then degassed and filled with argon three times. Afterwards, chlorobenzene was added and degassed one time. The reaction mixture was refluxed for 72 h under argon, and cooled down to room temperature. The polymerization mixture was poured into 200 mL methanol and 5 mL hydrochloric acid solution and stirred for 3 h. The polymer precipitated out as a solid and was filtered using a filter paper. The polymer was purified by Soxhlet extraction with methanol, hexane, and acetone sequentially. ***PNDIS-10BO***, GPC:  $M_w = 50.5$  kDa,  $M_n = 44.8$  kDa, PDI = 1.1; TGA:  $T_d = 384$  °C; ***PNDIS-30BO***, GPC:  $M_w = 61.8$  kDa,  $M_n = 48.9$  kDa, PDI = 1.3; TGA:  $T_d = 394$  °C; ***PNDIS-50BO***, GPC:  $M_w = 72.2$  kDa,  $M_n = 41.7$  kDa, PDI = 1.7; TGA:  $T_d = 403$  °C.

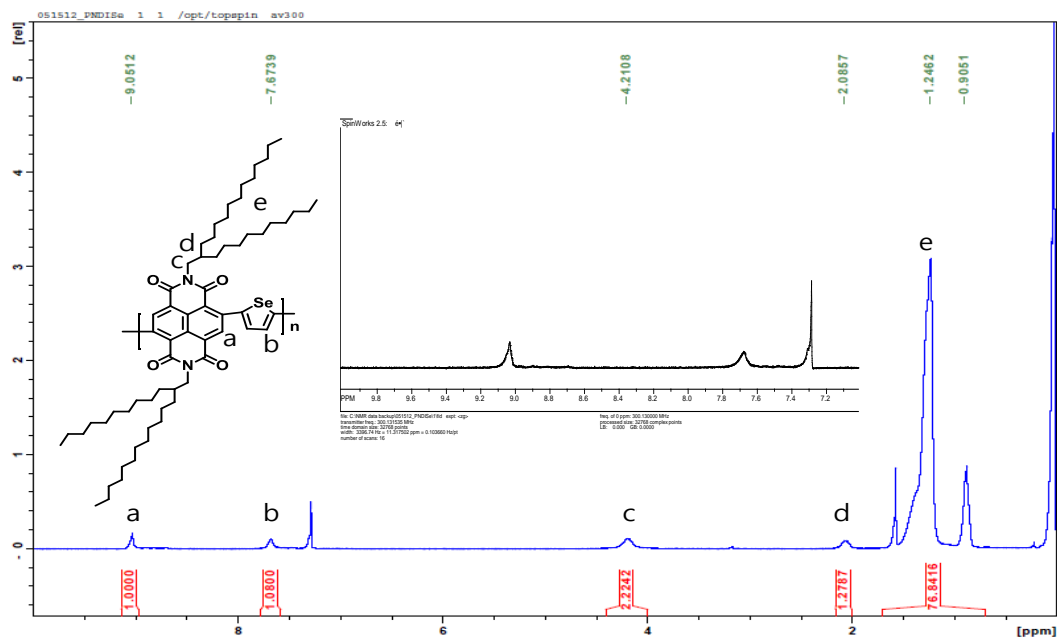


Figure S2.  $^1\text{H}$  NMR spectrum of PNDIS.

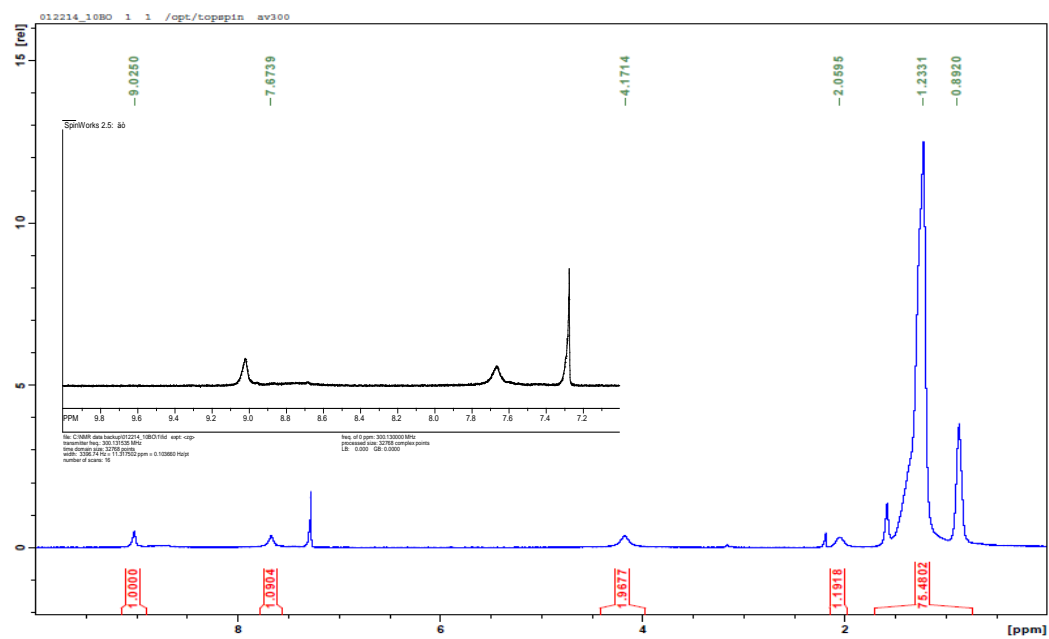
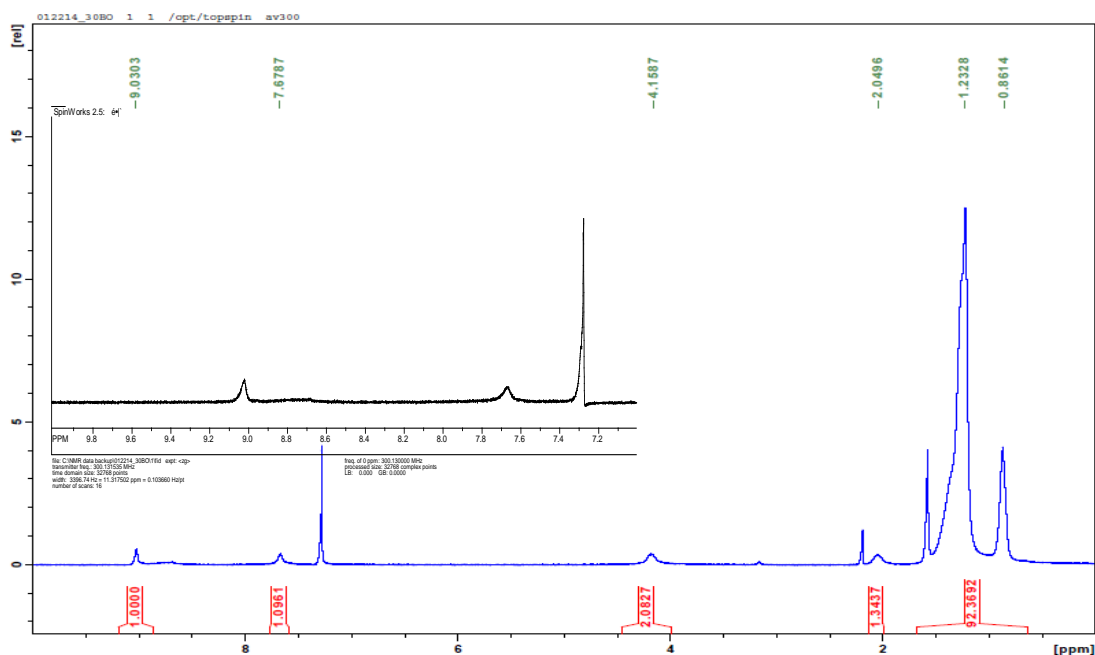
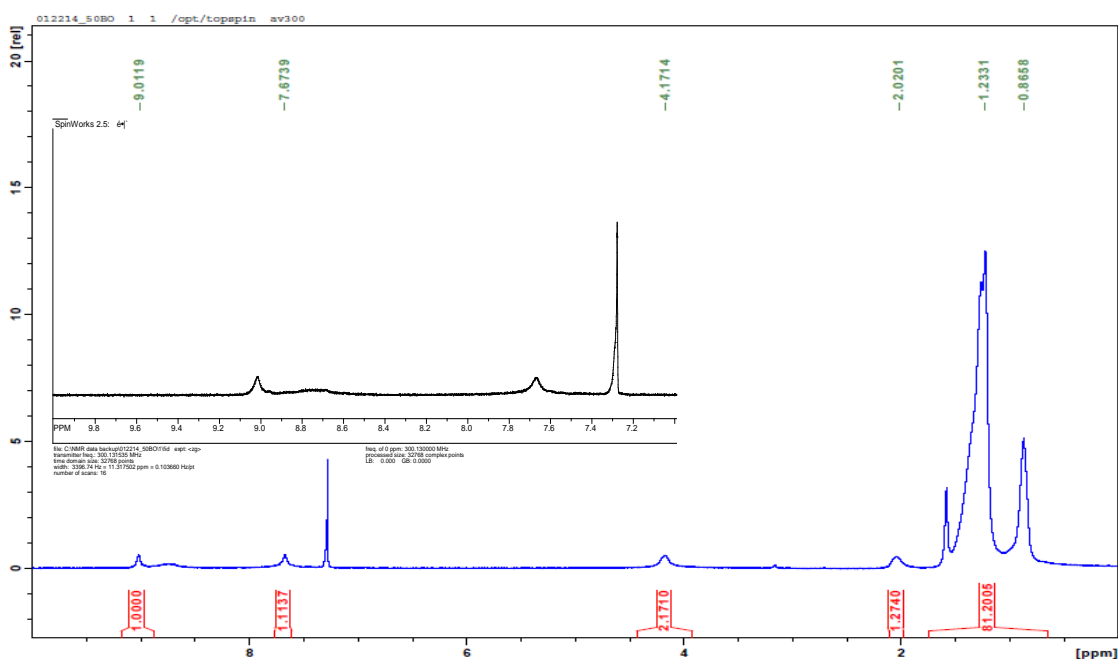


Figure S3.  $^1\text{H}$  NMR spectrum of PNDIS-10BO.



**Figure S4.**  $^1\text{H}$  NMR spectrum of PNDIS-30BO.



**Figure S5.**  $^1\text{H}$  NMR spectrum of PNDIS-50BO.

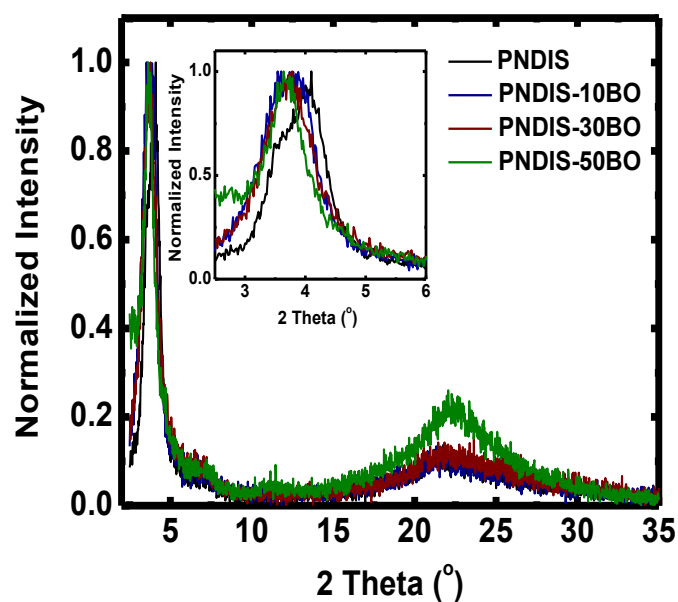
**Characterization:** The structure and physical properties of the new polymers were investigated by  $^1\text{H}$  NMR, gel permeation chromatography (GPC) analysis, thermogravimetric analysis (TGA) and X-ray diffraction (XRD).  $^1\text{H}$  NMR spectra at 300 MHz were recorded on a Bruker-AF300 spectrometer to verify the molecular structure, and the molecular weight was

measured using GPC Model 120 (DRI, PLBV400HTViscometer) against polystyrene standards in chlorobenzene at 60 °C. Thermal stability of the polymers was tested on a TA Instruments Q50 TGA at a heating rate of 20 °C per minute under nitrogen gas flow.

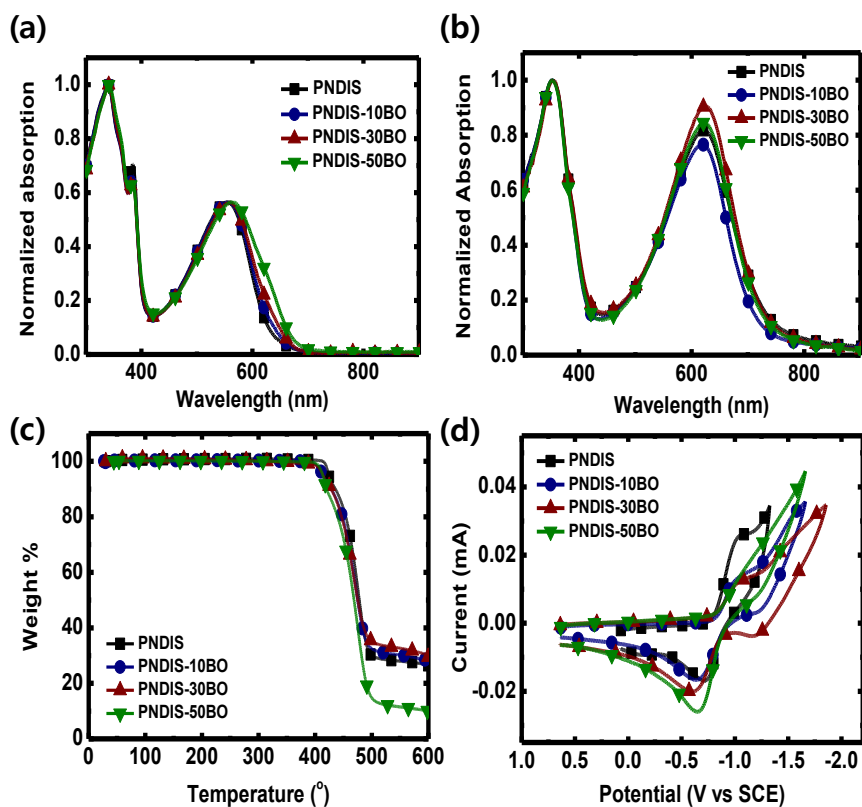
Electrochemical properties of the polymers were investigated by cyclic voltammetry (CV). CV experiments were done on an EG&G Princeton Applied Research potentiostat/galvanostat (model 273A) in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) in acetonitrile at a scan rate of 20 mV/s. Platinum wires were used as counter and working electrodes, and  $\text{Ag}/\text{Ag}^+$  (Ag in 0.1 M  $\text{AgNO}_3$  solution, Bioanalytical System, Inc.) was used as a reference electrode. Ferrocene/ferrocenium was used as an internal standard, and the reference potential was converted to the saturated calomel electrode (SCE) scale. The samples for CV were prepared by dip-coating the copolymer solutions in chloroform onto Pt wires.

Optical absorption spectra of the polymers were measured on a Perkin-Elmer model Lambda 900 UV/vis/near-IR spectrophotometer. Solution and solid state absorption spectra were obtained from dilute ( $10^{-6}$  M) polymer solutions in chloroform and as thin films on glass substrates, respectively.

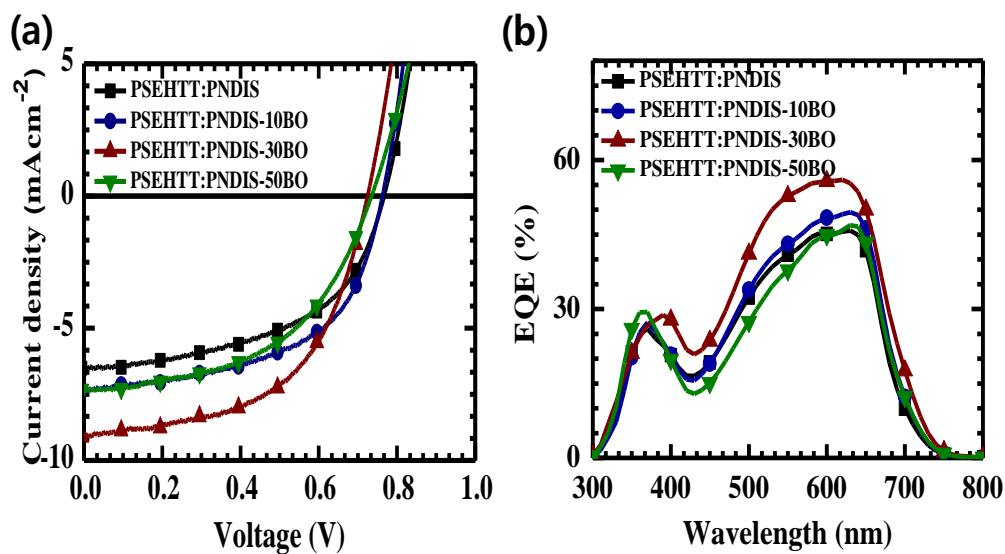
X-ray diffraction patterns were obtained from Bruker F8 power XRD with a  $\text{Cu K}\alpha$  radiation as a X-ray source, and the solid samples were prepared by drop-casting of highly concentrated polymer solutions (20 mg/mL) in chloroform onto glass substrates with annealing at 200 °C for 30 minutes.



**Figure S6.** X-ray diffraction (XRD) patterns of PNDIS (black), PNDIS-10BO (blue), PNDIS-30BO (red), and PNDIS-50BO (green).



**Figure S7.** UV-vis absorption spectra in solution (a) and in thin film (b), (c) TGA thermograms, and (d) cyclic voltammograms.



**Figure S8.** *J-V* curves (a) and EQE spectra (b) of all-polymer solar cells.

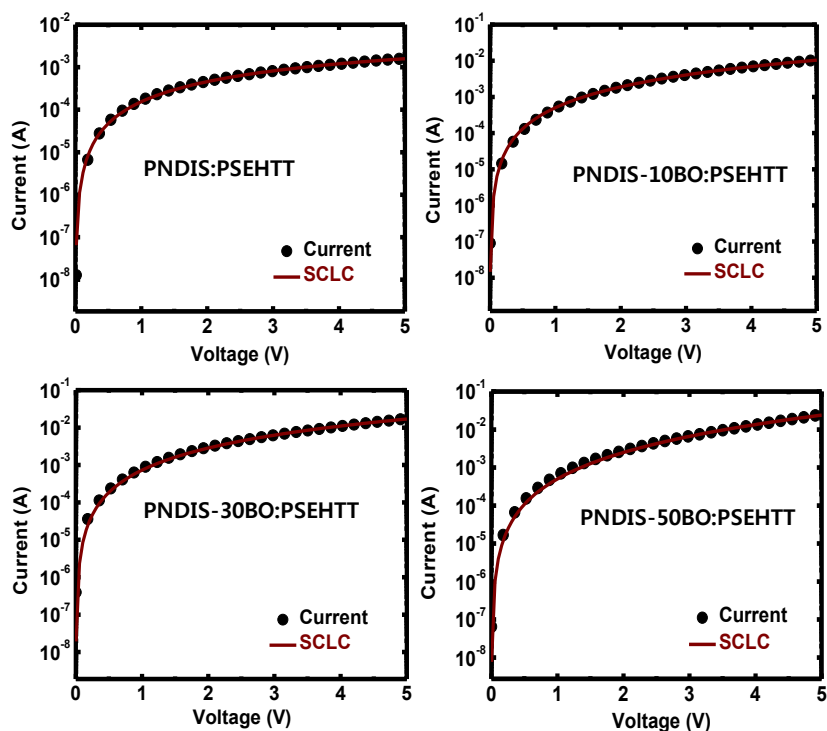
**Table S1.** Molecular Weight of *n*-Type Polymers and Donor Polymer Investigated.

Polymer	$M_n$ [kDa]	$M_w$ [kDa]	PDI
PSEHTT	34.3	128.1	3.7
PNDIS	36.8	44.4	1.2
PNDIS-10BO	44.8	50.5	1.1
PNDIS-30BO	48.8	61.8	1.3
PNDIS-50BO	41.7	72.2	1.7

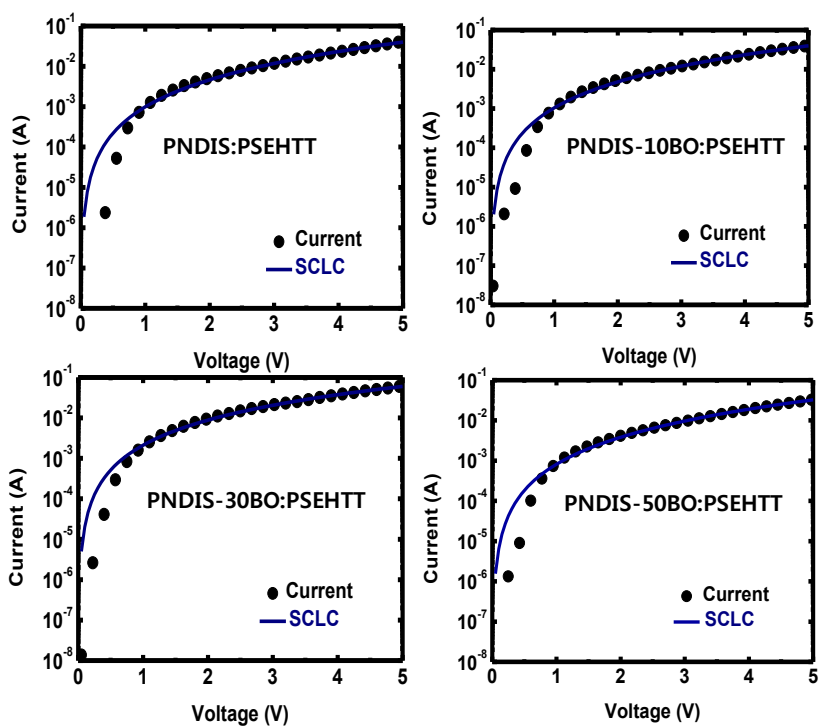
**Table S2.** X-ray Diffraction Data and the Mean Crystalline Domain Size (*L*) of Polymers.

Polymer	(100) [°]	(010) [°]	$d_{100}$ [Å]	$d_{010}$ [Å]	<i>L</i> [nm]
PNDIS	3.99	21.52	22.14	4.12	8.4
PNDIS-10BO	3.76	21.92	23.46	4.05	8.5
PNDIS-30BO	3.71	22.22	23.79	3.99	8.8
PNDIS-50BO	3.67	22.64	24.03	3.92	13.3

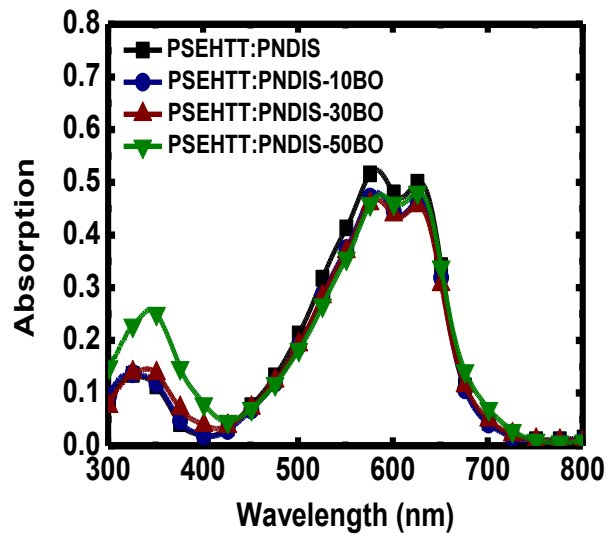




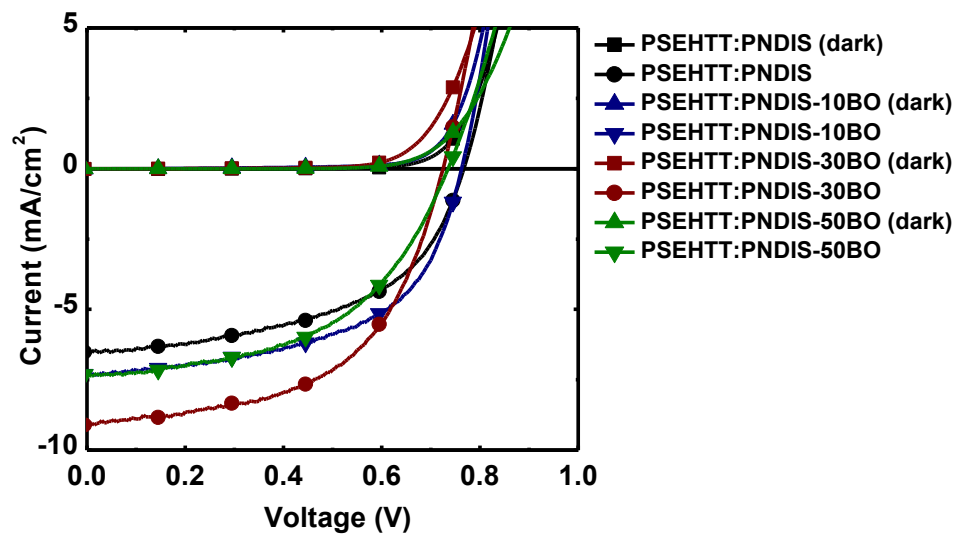
**Figure S9.** Current ( $J$ ) – voltage ( $V$ ) characteristics and space-charge-limited current (SCLC) fittings of devices measured in ambient conditions. Electron-only SCLC devices: ITO/ZnO/blend/LiF/Al.



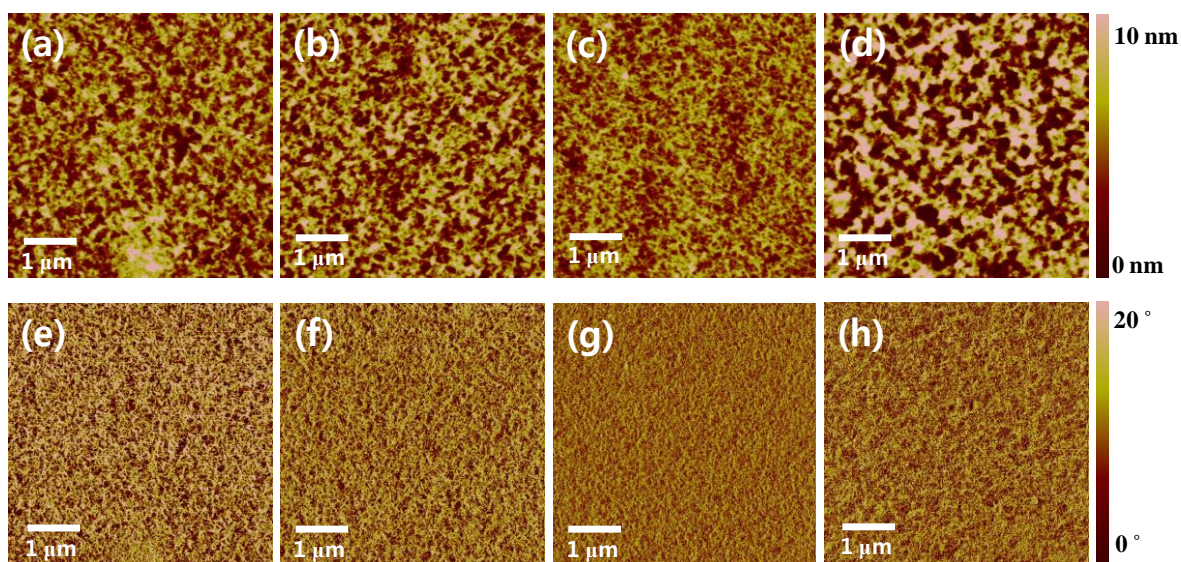
**Figure S10.** Current ( $J$ ) – voltage ( $V$ ) characteristics and space-charge-limited current (SCLC) fittings of devices measured in ambient conditions. Hole-only SCLC devices: ITO/PEDOT:PSS/blend/Au.



**Figure S11.** UV-vis absorption spectra of all-polymer BHJ solar cells.



**Figure S12.** Current ( $J$ ) – voltage ( $V$ ) characteristics of all polymer BHJ solar cells from 1:1.5 wt/wt blend of PSEHTT:PNDIS, PSEHTT:PNDIS-10BO, PSEHTT:PNDIS-30BO, and PSEHTT:PNDIS-50BO under illumination with the corresponding dark current density.



**Figure S13.** AFM height and corresponding phase images ( $5\ \mu\text{m}\times 5\ \mu\text{m}$ ) of the surfaces of BJJ solar cells: (a, e) PSEHTT:PNDIS; (b, f) PSEHTT:PNDIS-10BO; (c, g) PSEHTT:PNDIS-30BO; and (d, h) PSEHTT:PNDIS-50BO.

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