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A synergetic effect of alkyl-thiophene π-bridge and side chain modification on device performances for stable all-polymer solar cells with high PCE

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Materials

1,3-dibromo-5-octyl-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione **1** (purity: >98%), 2,6-bis(trimethyltin)-4,8-bis-[5-(2-ethylhexyl)thiophen-2-yl]benzo[1,2-*b*:4,5-*b*]dithiophene **M2** (purity: >98%), 2,6-bis(trimethyltin)-4,8-bis-[4,8-bis-(5-dodecylsulfanylthiophen-2-yl)]benzo[1,2-*b*:4,5-*b*]dithiophene **M3** (purity: >98%), 4,9-dibromo-2,7-bis-(2-hexyldecyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone **M4** (purity: >98%), 2,5-bistrimethylstannanylselenophene **M5** (purity: >98%) and (9,9-dioctyl-2,7-fluorene)-alt-(9,9-bis(3-(*N,N*-dimethylamino)propyl)-2,7-fluorene were purchased from Derthon. Tributyl (4-hexylthiophen-2-yl)-stannane **2** (purity: >98%) was purchased from suna tech inc. $Pd(PPh_3)_4$, *N*-bromosuccinimide (NBS), $Pd_2(dba)_3$, $P(o\text{-}tol)_3$, PEDOT:PSS (Baytron PVP A1 4083), phenylboronic acid, bromobenzene were purchased from J&K Scientific Ltd. All solvents (*N,N*-dimethylformamide (DMF), petroleum ether, dichloromethane, toluene, chloroform, methanol, acetone and hexane) were purchased from Sinopharm and must be distilled in order to exclude water and oxygen in the reaction. Our previous work reported the synthesis of reference donor PBDT(T)TPD, and acceptors P(NDI2OD-T) and P(NDI2OD-Se) [1].

Synthesis (shown in Scheme S1)

1,3-bis-(4-hexylthiophen-2-yl)-5-octyl-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione（3）

Under nitrogen atmosphere, compound 1 (0.1 g, 0.24 mmol), 2 (0.25 g, 0.55 mmol), and $Pd(PPh_3)_4$ (5 mol%) were mixed in 3 mL of toluene. The mixture was heated to reflux for 24 h. Subsequently, the reaction was cooled to room temperature, and the solvent was removed by rotary evaporation. Then, the raw product was purified by silica gel chromatography using petroleum ether/dichloromethane(2:1), and compound 3 was obtained as yellow solid (yield:0.14 g, 98 %).^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.87 (d, 2H), 7.02 (d, 2H), 3.73-3.56 (m, 2H), 2.70 -2.51 (m, 4H), 1.72-0.64 (m, 37H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 162.94, 145.18, 137.02, 132.38, 131.32, 128.28, 123.77, 38.83, 32.13, 30.70, 29.65, 29.52, 29.49, 29.43, 28.80, 27.24, 22.93, 14.37. Elemental analysis: Calcd for $C_{34}H_{47}NO_2S_3$ (%): C, 68.30, H, 7.92, N, 2.34. Found (%): C, 67.71, H, 7.78, N, 2.12. Mass (m/z) [M^+]: Calcd for $C_{34}H_{47}NO_2S_3$ 597.94. Found 597.21.

1,3-bis-(5-bromo-4-hexylthiophen-2-yl)-5-octyl-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione（M1）

Under nitrogen atmosphere, compound 3 (0.14 g，0.24 mmol) was dissolved into 20 mL of DMF,

Then, NBS (0.15 g，0.84 mmol) was added into the flask in one portion, and the reactant was stirred at 80 ^{o}C for 24 h. 50 mL of water was added into the flask, and the product was extracted by chloroform. After removing the solvent by rotary evaporation, the product was purified by silica gel chromatography by using Petroleum ether/dichloromethane (2:1) as eluent. Compound M1 was obtained as yellow solid (yield: 0.11g, 58 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm} 7.63 (s, 2H), 3.69-3.58 (m, 2H), 2.64 -2.52 (m, 4H), 1.76 – 0.73 (m, 37H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_{ppm} 162.61, 143.96, 135.62, 132.09, 130.47, 128.49, 113.76, 38.91, 32.13, 29.96, 29.89, 29.75, 29.61, 29.52, 29.46, 28.76, 27.25, 22.93, 14.38. Elemental analysis: Calcd for $C_{34}H_{45}Br_2NO_2S_3$ (%): C, 54.04, H, 6.00, N, 1.85. Found (%): C, 54.34, H, 6.10, N, 1.81. Mass (m/z) [M^+]: Calcd for $C_{34}H_{45}Br_2NO_2S_3$ 755.73. Found 754.45.

Synthesis of polymer **PBDT(T)-HT-TPD**

M1 (0.065 g, 0.11 mmol), M2 (0.10 g, 0.11 mmol), $Pd_2(dba)_3$ (2 mol%), and P(o-tol)$_3$ (8 mol%) were dissolved into 3 mL of toluene/DMF (5:1) in a single-neck round-bottom flask under nitrogen atmosphere. The mixture was heated to reflux for 48 h. After end-capping by sequential addition of phenylboronic acid for 12 h and bromobenzene for 6 h, the mixture was cooled to room temperature and precipitated from methanol (200 mL). The solid was sequentially purified via Soxhlet extraction using methanol, acetone, hexane, and chloroform. The chloroform fraction was concentrated. The pure polymer **PBDT(T)-HT-TPD** was obtained by re-precipitation from methanol and drying under vacuum for 24 h as dark-black solid with a yield of 76.6%. GPC: M_n=17.9 kg/mol, M_w=52.1kg/mol, PDI=2.91.^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10-6.80 (br, 8H, ArH), 4.00-3.50 (br, 2H,), 3.0-2.02 (br, 8H), 2.00-0.81 (br, 67H).

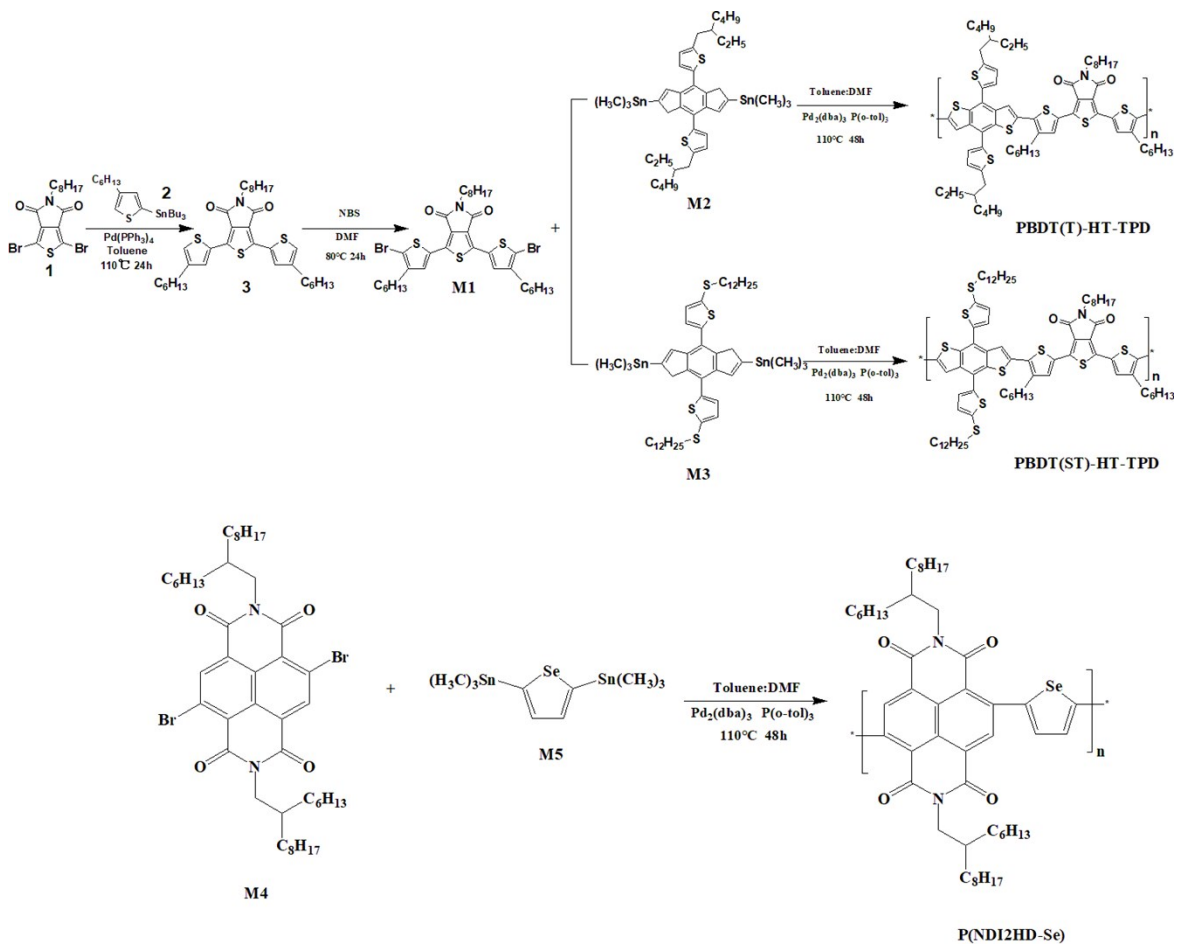
PBDT(ST)-HT-TPD was synthesized according to the foregoing general polymerization method, except compound M3 instead of compound M2. The pure polymer **PBDT(ST)-HT-TPD** as dark-black solid with a yield of 75.6%. GPC: M_n=19.1 kg/mol, M_w=65.9 kg/mol, PDI=3.45. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.15-6.70 (br, 8H, ArH), 4.00--2.05 (br, 10H), 2.03-0.72 (br, 83H).

Synthesis of polymer **P(NDI2HD-Se)**

M4 (0.10 g, 0.11 mmol), M5 (0.052 g, 0.11 mmol), $Pd_2(dba)_3$ (2 mol%), and P(o-tol)$_3$ (8 mol%) were mixed into 3 mL of toluene/DMF (5:1) under nitrogen atmosphere. The mixture was stirred at

110℃ for 48 h, and the reaction was sequentially sealed end by adding phenylboronic acid for 12 h and bromobenzene for 6 h. After cooling down to room temperature, and the raw product was precipitated into 200 mL of methanol. The solid was sequentially purified via Soxhlet extraction using methanol, acetone, hexane, and chloroform. The chloroform fraction was concentrated. The pure polymer **P(NDI2HD-Se)** was obtained by re-precipitation from methanol and drying under vacuum for 24 h as blue-black solid with a yield of 84.6%. GPC: M_n=22.8 kg/mol, M_w=41.0 kg/mol, PDI=1.80. ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm) 9.02-8.50 (br, 2H, ArH), 7.80-7.00 (br, 2H, ArH), 4.2 (s, 4H -CH_2-), 2.05-1.95 (br, 2H), 1.80-0.80 (br, 60H).

The GPC curves and ^{1}HNMR spectra of above polymers are shown in Fig S1 and Fig S2.



Scheme S1 Synthetic routes of the monomers and polymers

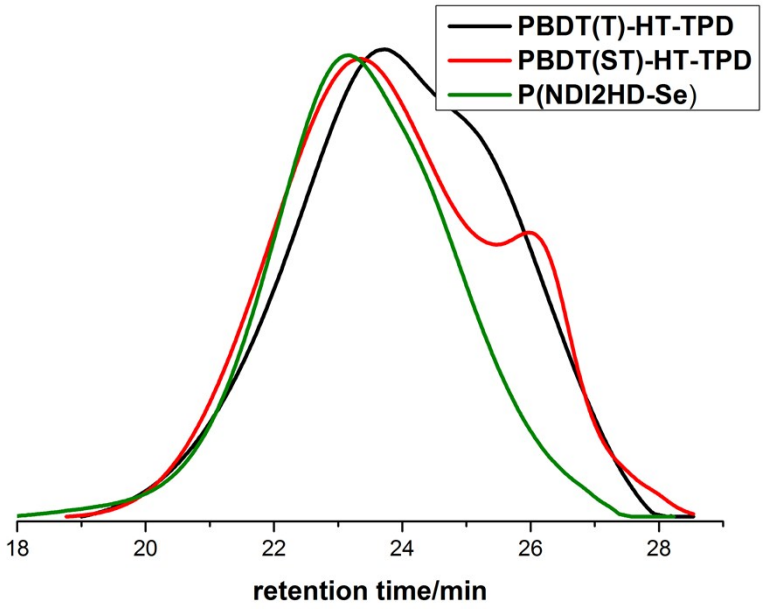
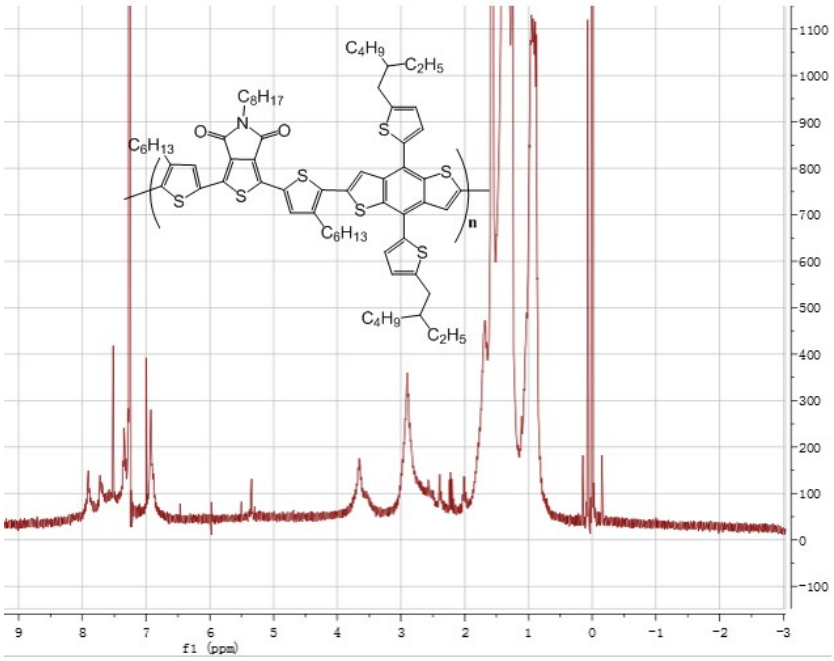
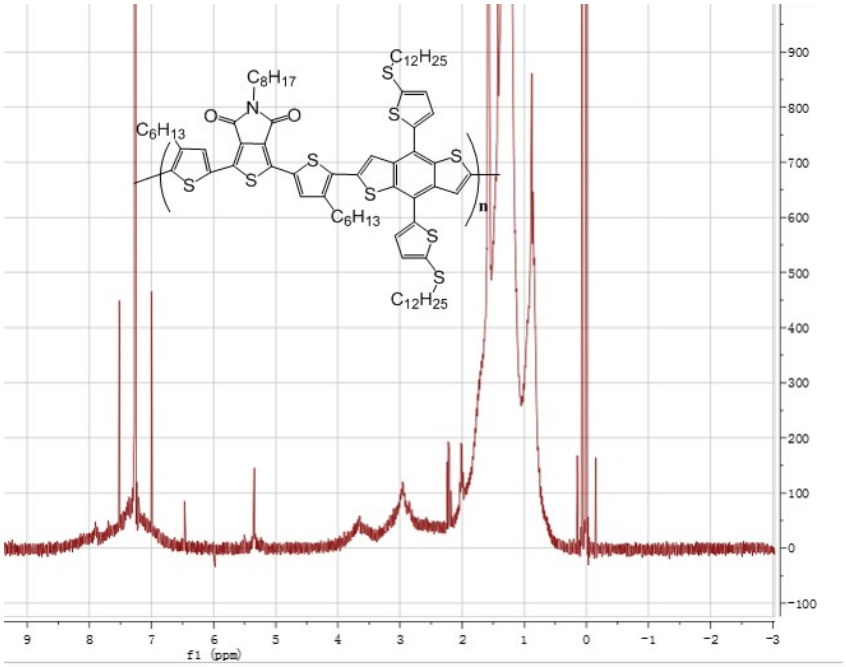


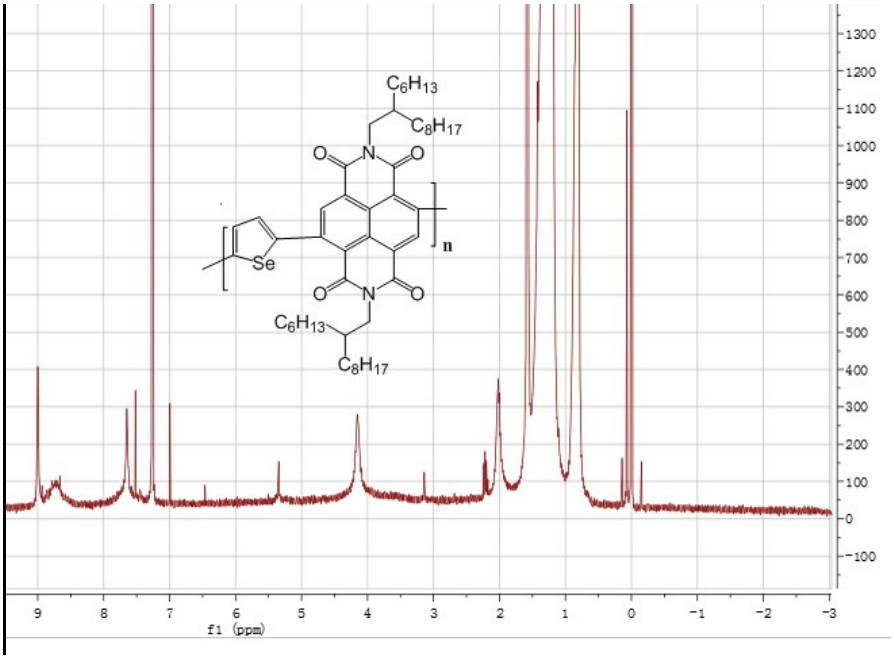
Fig S1 GPC curves of polymers



PBDT(T)-HT-TPD



PBDT(ST)-HT-TPD



P(NDI2HD-Se)

Fig S2 ^{1}H NMR spectra of polymers

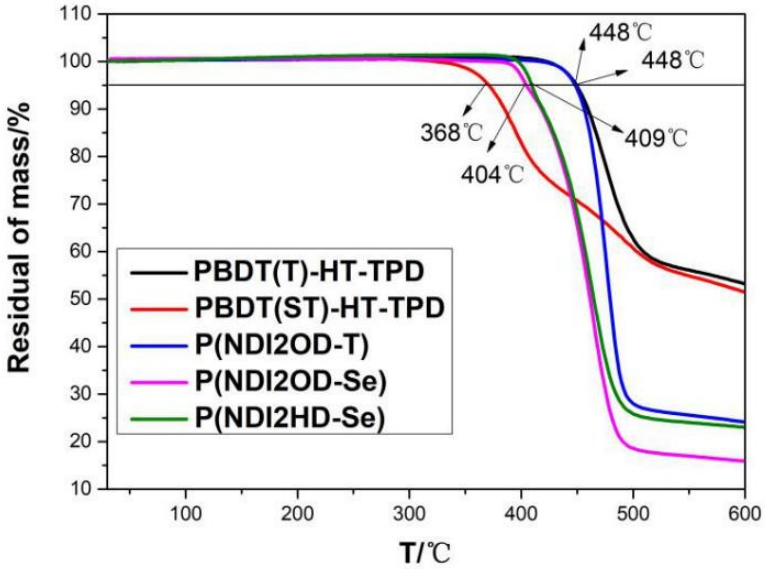


Fig. S3 TGA curves of Polymers

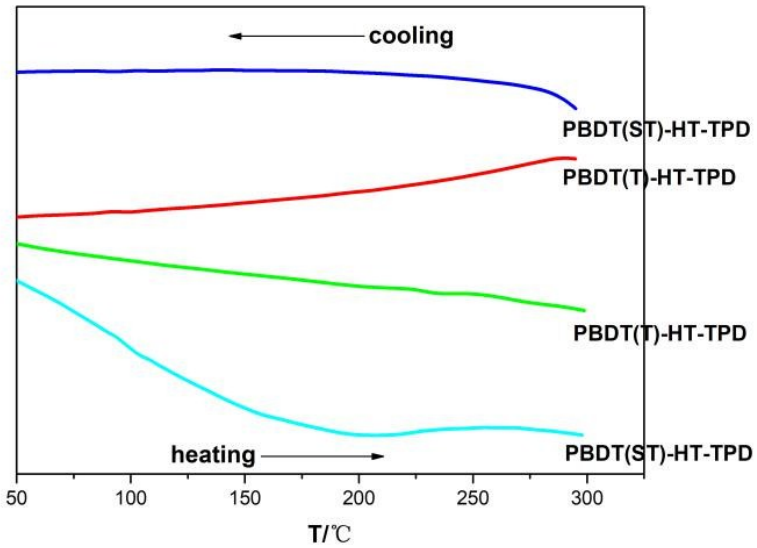


Fig. S4 DSC curves of PBDT(T)-HT-TPD and PBDT(ST)-HT-TPD, measured with a scan rate of 10 ^{o}C/min

Table. S1 the optimization condition of PSCs based on polymer blend

Polymer	C（mg/mL）	Ratio	Solvent	Speed(r/m)	Cathode buffer layer
PBDT(T)-HT-TPD:P(NDI2OD-T)	12	1.5:1	CF+0.5%DIO	2500	NO
PBDT(T)-HT-TPD:P(NDI2OD-Se)	12	1.5:1	CF+0.75%DIO	2500	NO
PBDT(T)-HT-TPD:P(NDI2HD-Se)	12	1.5;1	CF+0.75%DIO	2500	NO
PBDT(ST)-HT-TPD:P(NDI2OD-T)	12	1.5:1	CF+0.5%DIO	2500	NO
PBDT(ST)-HT-TPD:P(NDI2OD-Se)	12	1.5:1	CF+0.5%DIO	2500	NO
PBDT(ST)-HT-TPD:P(NDI2HD-Se)	12	1.5:1	CF+0.5%DIO	2500	NO

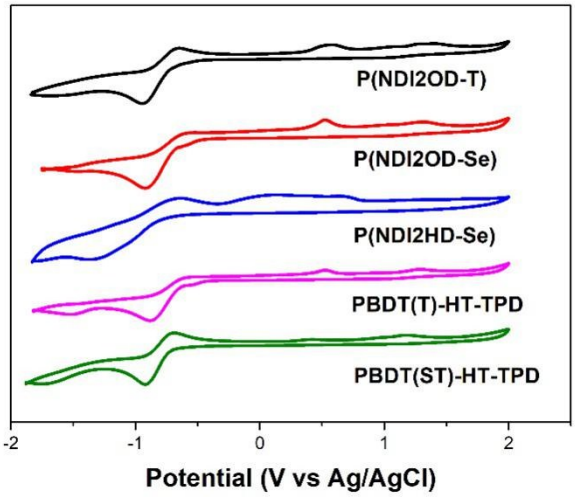


Fig.S5 CV curves of polymers

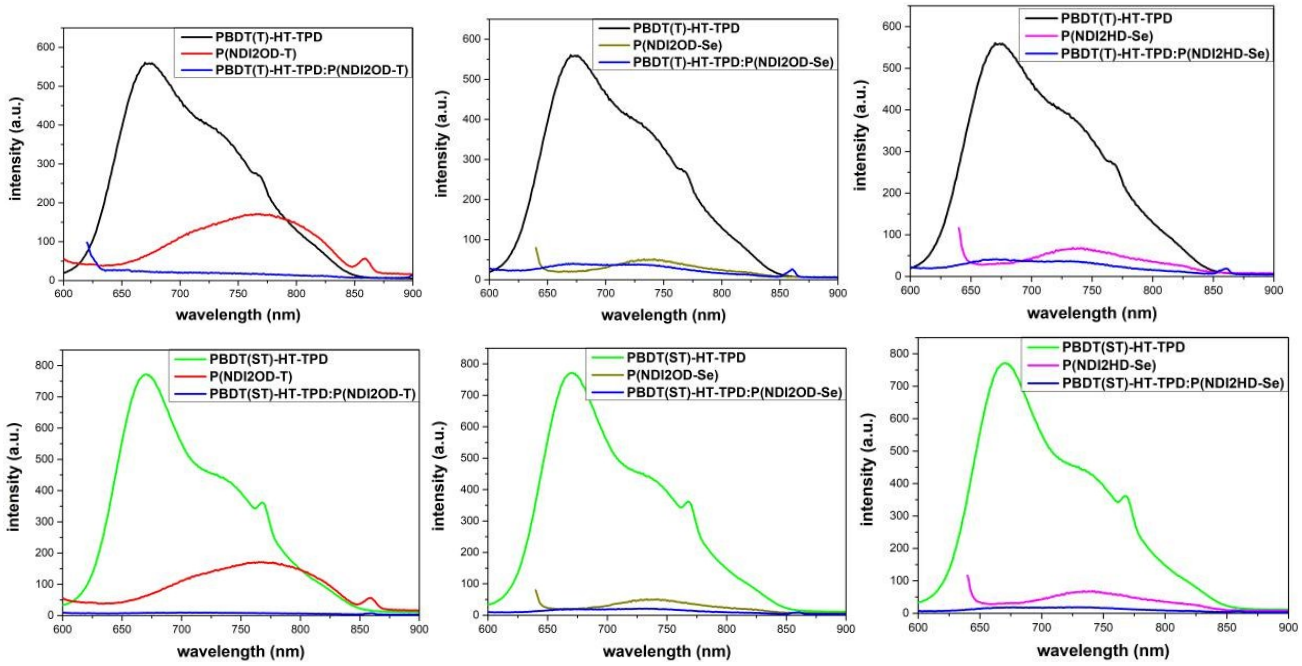


Fig.S6 The PL spectra of the neat polymer and blend films.

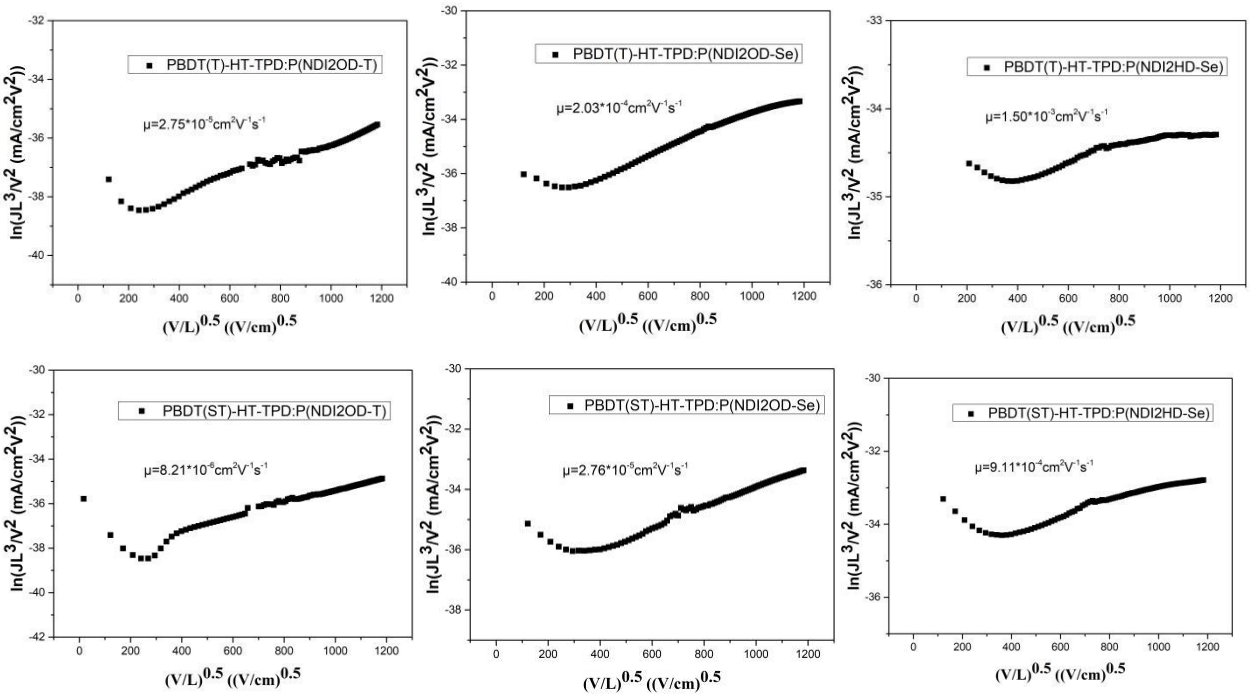


Fig.S7-1 The electron mobility of PBDT(T)-HT-TPD and PBDT(ST)-HT-TPD/ acceptors blends by SCLC

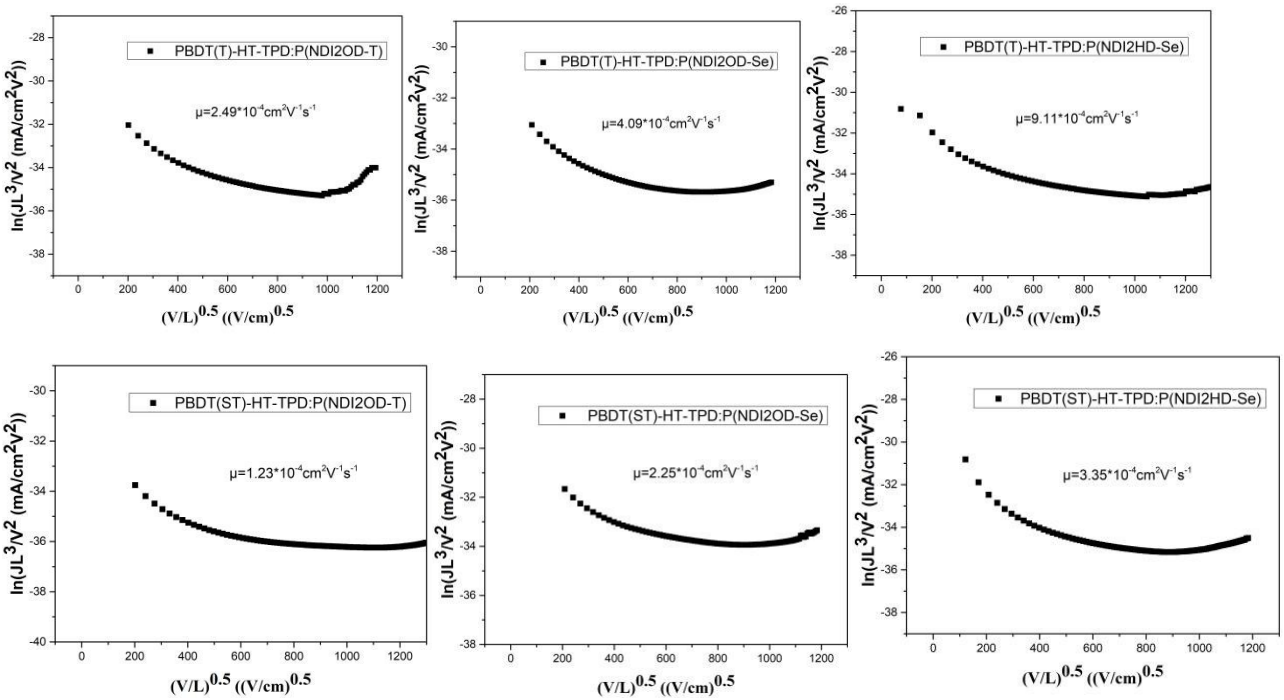


Fig.S7-2 The hole mobility of PBDT(T)-HT-TPD and PBDT(ST)-HT-TPD/ acceptors blends by SCLC

Table S2 Photovoltaic parameters of the PSCs based on PBDT(T)TPD:accetors[a]

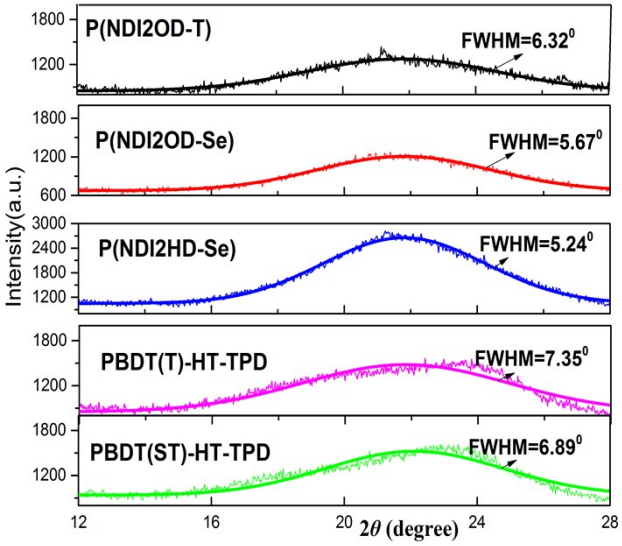
Polymer donors	Polymer acceptors	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	μ_e (cm^{2}V^{-1}s^{-1})	μ_h (cm^{2}V^{-1}s^{-1})	μ_h/μ_e
PBDT(T) TPD	P(NDI2OD-T)	1.03	3.71	47.50	1.81	$7.49*10^{-5}$	$2.76*10^{-6}$	0.04
	P(NDI2OD-Se)	1.04	8.56	53.01	4.71	$2.49*10^{-4}$	$4.10*10^{-5}$	0.16

a :The device structure of ITO/PEDOT:PSS/Polymer blend/Ca/Al .

Table S3 Summary of key parameters extracted from the XRD curves for the neat polymers and polymers blends [a].

Sample	Lamellar stacking (100) peak		π-π stacking (010) peak	
	lamellar stacking [Å]	Coherence length[a] [nm]	π-π stacking [Å]	Coherence length[b] [nm]
PBDT(T)-HT-TPD neat	20.70	3.46	4.05	1.10
PBDT(ST)-HT-TPD neat	24.50	3.92	4.00	1.18
P(NDI2OD-T) neat	21.52	6.92	4.12	1.28
P(NDI2OD-Se) neat	21.10	9.23	4.11	1.43
P(NDI2HD-Se) neat	20.00	9.94	4.08	1.54
PBDT(T)-HT-TPD:P(NDI2OD-T) blend	20.80	4.34	4.09	1.16
PBDT(T)-HT-TPD:P(NDI2OD-Se) blend	20.50	4.85	4.05	1.30
PBDT(T)-HT-TPD:P(NDI2HD-Se) blend	19.30	5.64	3.99	1.36
PBDT(ST)-HT-TPD:P(NDI2OD-T) blend	22.40	4.14	4.11	1.12
PBDT(ST)-HT-TPD:P(NDI2OD-Se) blend	22.00	4.32	4.09	1.20
PBDT(ST)-HT-TPD:P(NDI2HD-Se) blend	20.80	4.47	4.08	1.25
PBDT(T)TPD neat	23.85	7.43	3.70	1.20
PBDT(T)TPD:P(NDI2OD-Se) blend	22.06	5.80	4.08	1.38

[a]: the mean size of crystalline domains (L_c) was also calculated using the Scherrer equation from lamellar stacking peak [2], $L_c = K\lambda/\beta cos\theta$, where K is shape factor (0.9), λ is X-ray wavelength (1.54 Å), and $\beta$is the full-width-at-half-maximum (FWHM) value (rad) of stacking peak. [b]: L_c was calculated using the Scherrer equation from π-π stacking (010) peak.



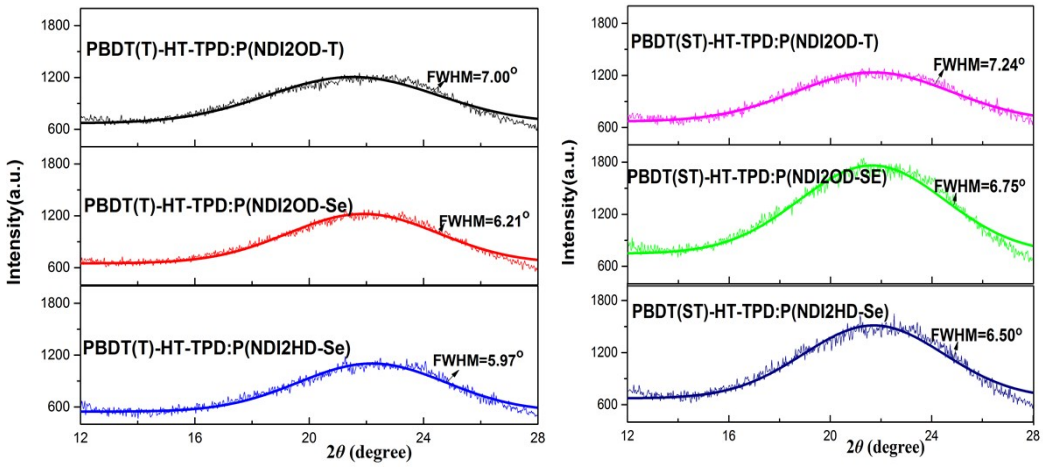


Figure S8-1 The magnified XRD curves of polymer neat and blend films with Gaussian fitting lines

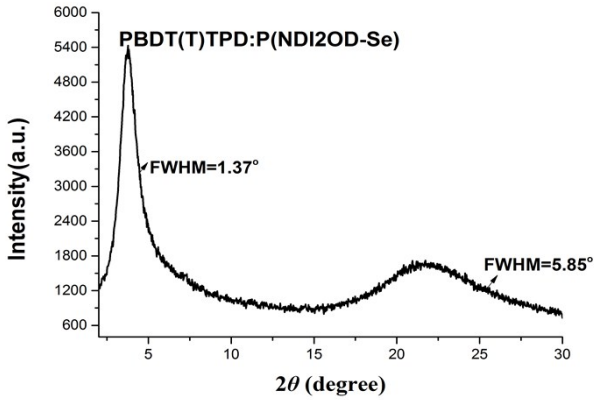


Figure S8-2 The XRD curve of PBDT(T)TPD:P(NDI2OD-Se) blend (reference)

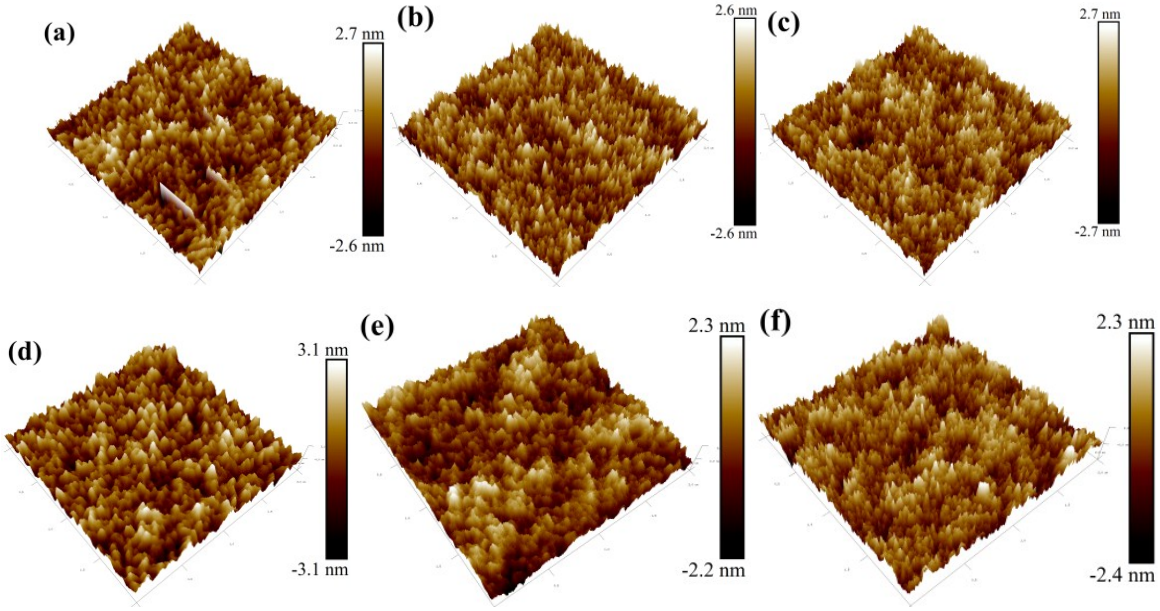


Figure S9 AFM 3D image of blends (a): PBDT(T)-HT-TPD:P(NDI2OD-T) (b): PBDT(T)-HT-TPD:P(NDI2OD-Se) (c): PBDT(T)-HT-TPD:P(NDI2HD-Se) (d): PBDT(ST)-HT-TPD:P(NDI2OD-T) (e): PBDT(ST)-HT-TPD:P(NDI2OD-Se) (f): PBDT(ST)-HT-TPD:P(NDI2HD-Se)

Reference:

[1] T. Zhang, M. Lu, W. Wang, W. Lv, J. Cui, W. Feng and Q. Ling, *Dyes & Pigments*, 2017, **146**, 169-177.

[2] A. L. Patterson, *Phys. Rev.*, 1939, **56**, 978-982.