Supporting Information

Open-Circuit Voltage Modulations on All-Polymer Solar Cells by Side Chain Engineering on 4,8-Di(thiophen-2-yl)benzo[1,2-*b*:4,5-*b*′]dithiophene-Based Donor Polymers

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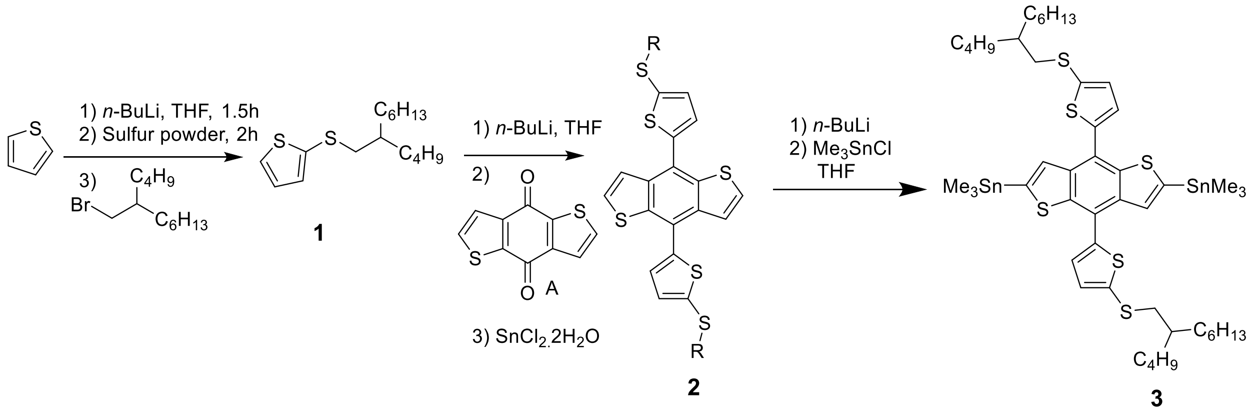
1. Synthesis of monomers

All starting materials, reagents and monomers such as (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b*']dithiophene-2,6-diyl)bis(trimethylstannane) (BDT) and 1,3-bis(5-bromothiophen-2-yl)-5,7-bis(2-ethylhexyl)-4*H*,8*H*-benzo[1,2-*c*:4,5-*c*']dithiophene-4,8-dione (BDD) were purchased from commercial sources and used without further purification. (4,8-bis(5-((2-butyloctyl)thio)thiophen-2-yl)benzo[1,2-*b*:4,5-*b*']dithiophene-2,6-diyl)bis(trimethylstannane) (BDTS) (Scheme S1), ((2,6-bis(trimethylstannyl)benzo[1,2-*b*:4,5-*b*']dithiophene-4,8-diyl)bis(thiophene-5,2-diyl))bis(tributylsilane) (BDTSi) (Scheme S2) and 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(dodecyloxy)benzo[*c*][1,2,5]thiadiazole (TBT) were synthesized by modifying procedures reported in the literature.[1-4]

Scheme S1. Synthetic routes of (4,8-bis(5-((2-butyloctyl)thio)thiophen-2-yl)benzo[1,2-*b*:4,5-*b*']dithiophene-2,6-diyl)bis(trimethylstannane) (BDTS)



2-((2-Butyloctyl)thio)thiophene (1)

2.5 M *n*-BuLi in hexanes (20 mL, 50 mmol) was added dropwise to a solution of thiophene (4.2 g, 50 mmol) in dry THF (100 mL) at 0 ºC under nitrogen atmosphere and stirred for 1.5 h. Then sulfur powder (1.6 g, 50 mmol) was added in one portion to the reaction mixture and stirred at 0 ºC for additional 2 h. Then 5-(bromomethyl)undecane (12.5 g, 50 mmol) was added dropwise and stirred at room temperature overnight. The mixture was then poured into ice-cold water which contained NH_4Cl and extracted with diethyl ether and dried over anhydrous $MgSO_4$. The residue obtained after removal of diethyl ether was passed through a column of silica gel using hexane as eluent to afford **1** (11 g, 78%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (1H, *dd*, *J* = 4.6, 0.84 Hz), 7.08 (1H, *dd*, *J* = 3.2, 0.84 Hz), 6.94 (1H, *dd*, *J* = 4.6, 3.2 Hz), 2.81 (2H, *d*, *J* = 6.4 Hz), 1.66 – 1.51 (1H, *q*), 1.32 – 1.18 (16H, *m*), 0.98 – 0.85 (6H, *t*, *J* = 6.7 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.01, 132.57, 128.42, 127.29, 44.15, 37.62, 32.86, 32.55, 31.85, 29.55, 28.73, 26.48, 22.95, 22.68, 14.12, 14.10.

4,8-Bis(5-((2-butyloctyl)thio)thiophen-2-yl)benzo[1,2-*b*:4,5-*b′*]dithiophene (2)

2-((2-Butyloctyl)thio)thiophene (11 g, 38.66 mmol) was dissolved in dry THF (60 mL) under nitrogen atmosphere and the solution was allowed to cool to 0 ºC. Then 2.5 M n-BuLi in hexanes (15.5 mL, 38.75 mmol) was added dropwise and the mixture was stirred at room temperature for 1 h. Then benzo[1,2-*b*:4,5-*b′*]dithiophene-4,8-dione (3.03 g, 13.75 mmol) in THF (20 mL) was added to the solution and heated at 50 ºC for 1 h. After cooling to 0 ºC $SnCl_2.2H_2O$ (22.2 g, 98.38 mmol) in 10% HCl (30 mL) was added and the mixture was stirred at room temperature overnight. Then it was poured in to water and extracted with diethyl ether. The diethyl ether was removed and the residue was passed through a column of silica gel using hexane as eluent to afford **2** (7 g, 66.6%) as brownish liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (2H, *d*, *J* = 5.72 Hz), 7.47 (2H, *d*, *J* = 5.72 Hz), 7.32 (2H, *d*, *J* = 3.80 Hz), 7.21 (2H, *d*, *J* = 3.80 Hz), 2.94 (4H, *d*, *J* = 6.20 Hz), 1.70 (2H, *q*), 1.53 – 1.22 (32H, *m*), 0.96 – 0.84 (12H, *m*).

^{13}C NMR (100 MHz, CDCl$_3$) δ 142.12, 138.98, 137.62, 136.49, 132.48, 128.32, 127.84, 123.61, 123.10, 43.97, 37.82, 32.94, 32.62, 31.87, 29.60, 28.77, 26.54, 22.96, 22.68, 14.14, 14.13.

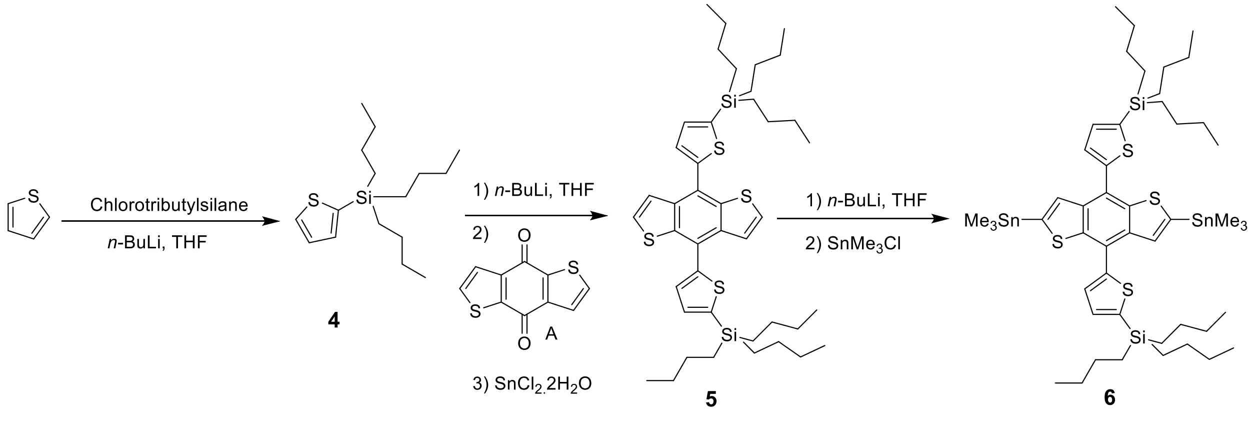
(4,8-Bis(5-((2-butyloctyl)thio)thiophen-2-yl)benzo[1,2-*b*:4,5-*b′*]dithiophene-2,6-diyl)bis(trimethylstannane) (3)

To a solution of compound **2** (1 g, 1.3 mmol) in THF (20 mL) at –78 °C, 2.5 M *n*-BuLi in hexanes (1.4 mL, 3.5 mmol) was added dropwise and stirred for 1 h at –78 °C. Then Me$_3$SnCl (1 M in hexane, 4 mL, 4 mmol) was added dropwise and stirred at room temperature overnight. Then the mixture was poured in to water, extracted with diethyl ether and dried over anhydrous MgSO$_4$. The solvent was removed and the product was recrystallized (twice) from isopropyl alcohol to yield **3** (830 mg, 59.3%) as a yellow solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.64 (2H, *s*), 7.33 (2H, *d, J* = 3.64 Hz), 7.21 (2H, *d, J* = 3.64), 2.94 (4H, *d*, *J* = 6.40 Hz), 1.71 (2H, *q*), 1.45 – 1.25 (32H, *m*), 0.88 (12H, *m*), 0.50 – 0.29 (18H, *m*).

^{13}C NMR (100 MHz, CDCl$_3$) δ 143.25, 142.98, 142.95, 137.27, 137.03, 132.49, 130.72, 128.19, 121.91, 44.01, 37.79, 32.92, 32.58, 31.81, 29.57, 28.72, 26.47, 22.93, 22.66, 14.11, 14.09, –8.33.

Scheme S2. Synthetic routes of ((2,6-bis(trimethylstannyl)benzo[1,2-b:4,5-*b′*]dithiophene-4,8-diyl)bis(thiophene-5,2-diyl))bis(tributylsilane) (BDTSi)



Tributyl(thiophen-2-yl)silane(4)

To a solution of thiophene (4.2 g, 50 mmol) in dry THF (60 mL) at was added dropwise 2.5 M *n*-BuLi in hexanes (20 mL, 50 mmol). The mixture was stirred at –78 °C for 1 h and allowed to warm to room temperature and stirred for 1 h. The mixture was then cooled to –78 °C and chlorotributylsilane (11.7 g, 50 mmol) was added, and the mixture was stirred overnight at room temperature, extracted with diethyl ether and washed with water and brine and dried. After the solvent was removed, the residue was passed through a column of silica gel using hexane as eluent to obtain pure tributyl(thiophen-2-yl)silane. (12 g, 85%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (1H, *dd*, *J* = 4.6, 0.84 Hz,), 7.27 (1H, *dd*, *J* = 3.2, 0.84 Hz), 7.21 (1H, *dd*, 4.6, 3.2 Hz), 1.36 (10H, *m*), 0.91 (8H, *m*), 0.83 (9H, *m*).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.32, 134.44, 130.24, 127.91, 26.83, 25.99, 13.92, 13.37.

4,8-Bis(5-(tributylsilyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b*']dithiophene (5)

To a solution of tributyl(thiophen-2-yl)silane (**4**) (12.5 g, 44.3 mmol) in THF (60 mL) at –78 °C under nitrogen atmosphere was added 2.5 M n-BuLi in hexanes (18 mL, 44.3 mmol). The mixture was kept at –78 °C for 1 h and stirred for 2 h at room temperature. Then benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (3.3 g, 15 mmol) was added quickly and the mixture was stirred for 2 h at 50 °C and cooled to room temperature. Then, $SnCl_2.2H_2O$ (26.6 g, 118 mmol) in 10% HCl (50 mL) was added and the mixture was stirred overnight. It was then extracted with diethyl ether, washed with water and brine, and the solvent was removed. The residue was passed through a column of silica gel using hexane as eluent to obtain compound **5** (7.4 g, 65%) as a light yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (2H, *d*, *J* = 5.68 Hz), 7.55 (2H, *d*, *J* = 3.40 Hz), 7.45 (2H, *d*, *J* = 5.68 Hz), 7.34 (2H, *d*, *J* = 3.40 Hz), 1.45 – 1.32 (24H, *m*), 0.94 – 0.83 (30H, *m*).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.01, 139.42, 139.42, 136.58, 134.76, 129.06, 127.50, 124.25, 124.29, 26.64, 26.02, 13.77, 13.19.

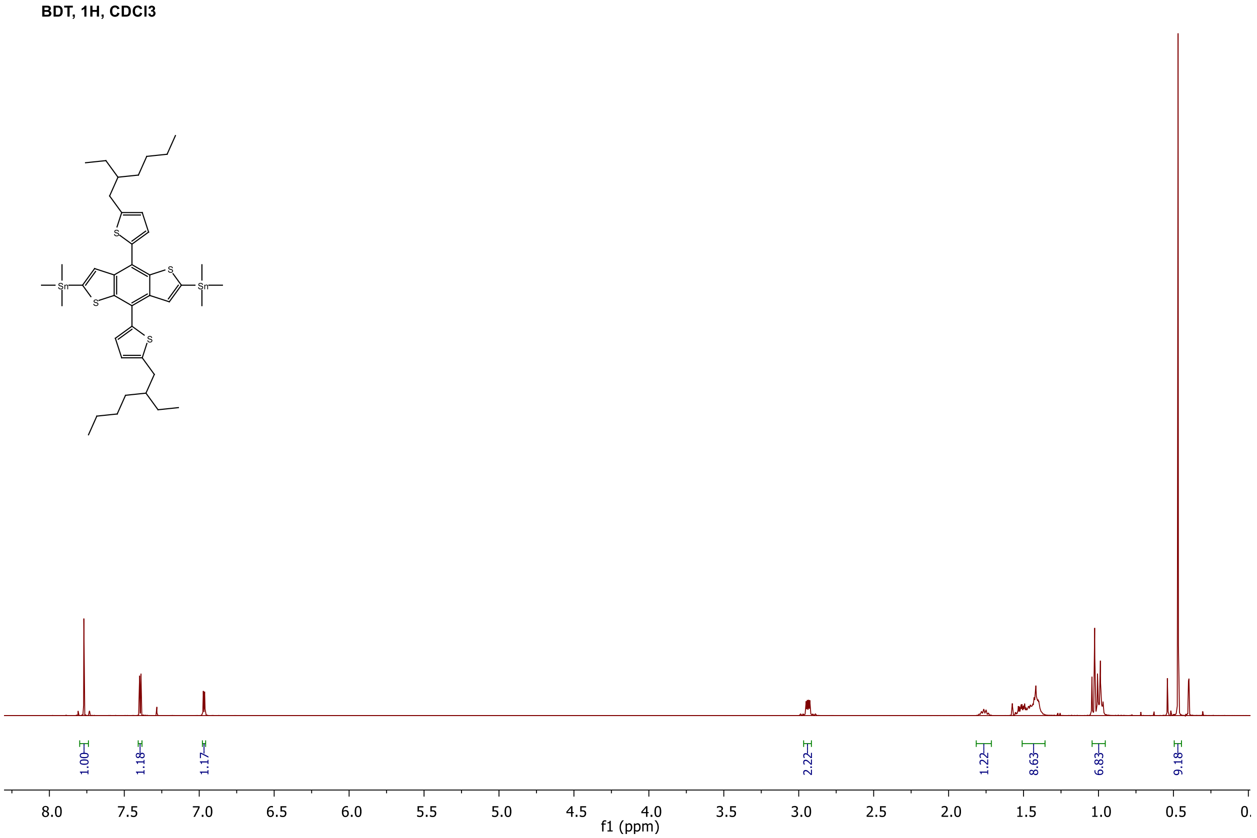
((2,6-Bis(trimethylstannyl)benzo[1,2-b:4,5-b']dithiophene-4,8-diyl)bis(thiophene-5,2-diyl))bis(tributylsilane) (6)

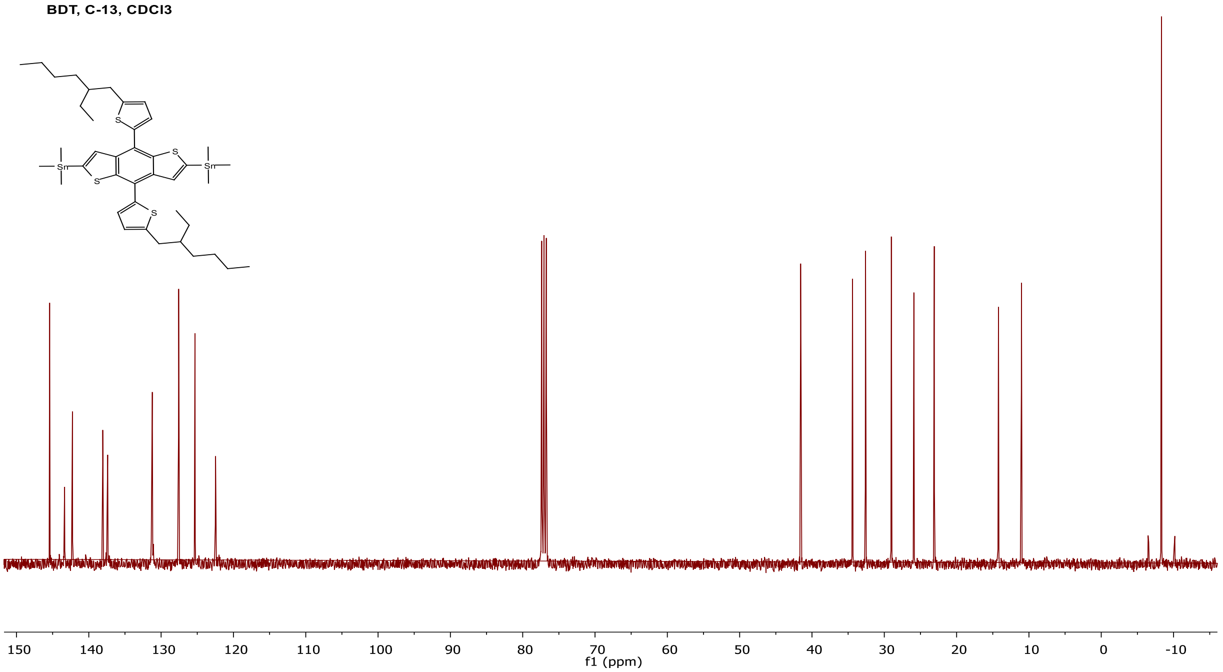
To a solution of compound **5** (1.5 g, 2 mmol) in THF (30 mL) at –78 °C was added dropwise 2.5 M *n*-BuLi in hexanes (2 mL, 5 mmol) and stirred for 1 h and allowed to warm to room temperature and stirred for additional 2 h. Then Me_3SnCl (6 mL of 1 M in hexane, 6 mmol) was added dropwise and the mixture was stirred at room temperature overnight. It was then poured in to water, extracted with diethyl ether, dried over anhydrous $MgSO_4$ and the solvent was removed. The residue was recrystallized (twice) from isopropyl alcohol to yield compound **6** (1.5 g, 70%) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (2H, *s*), 7.59 (2H, *d*, *J* = 3.40 Hz), 7.35 (2H, *d*, *J* = 3.40 Hz), 1.47 – 1.33 (20H, *m*), 0.96 – 0.81 (34H, *m*), 0.38 (18H, *s*).

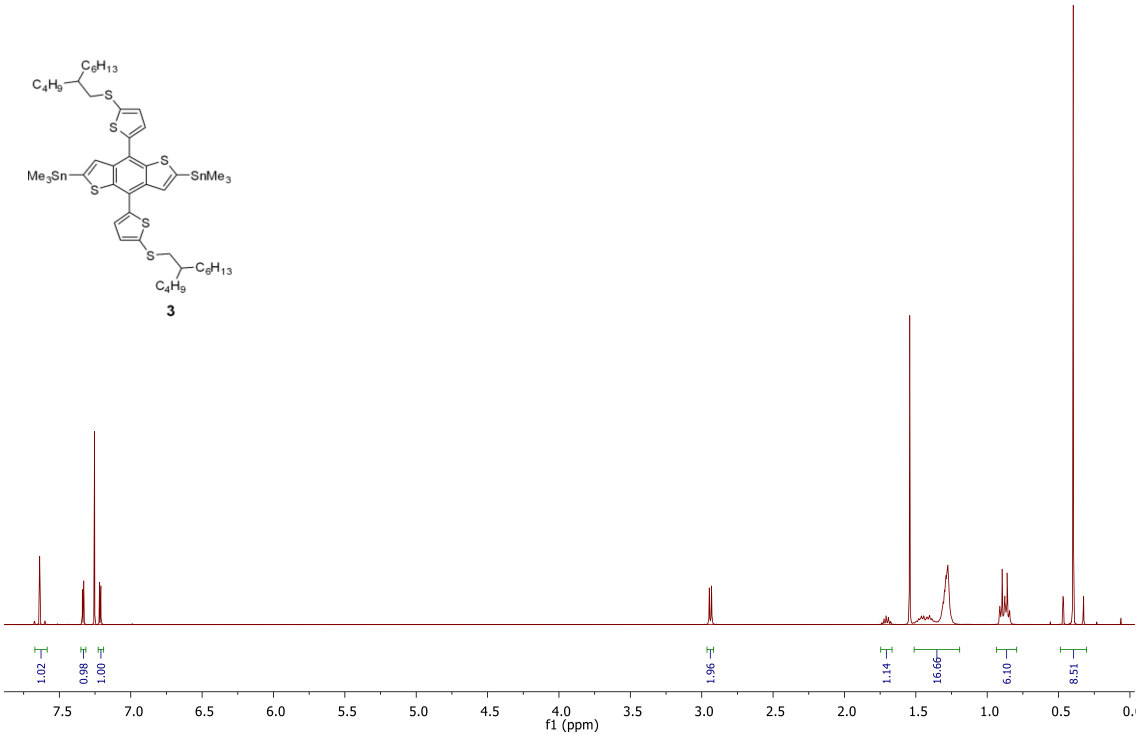
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.68, 143.11, 142.27, 138.63, 137.19, 134.71, 131.18, 128.83, 122.27, 26.67, 26.06, 13.80, 13.23, –8.40.

2. NMR spectra of the monomers

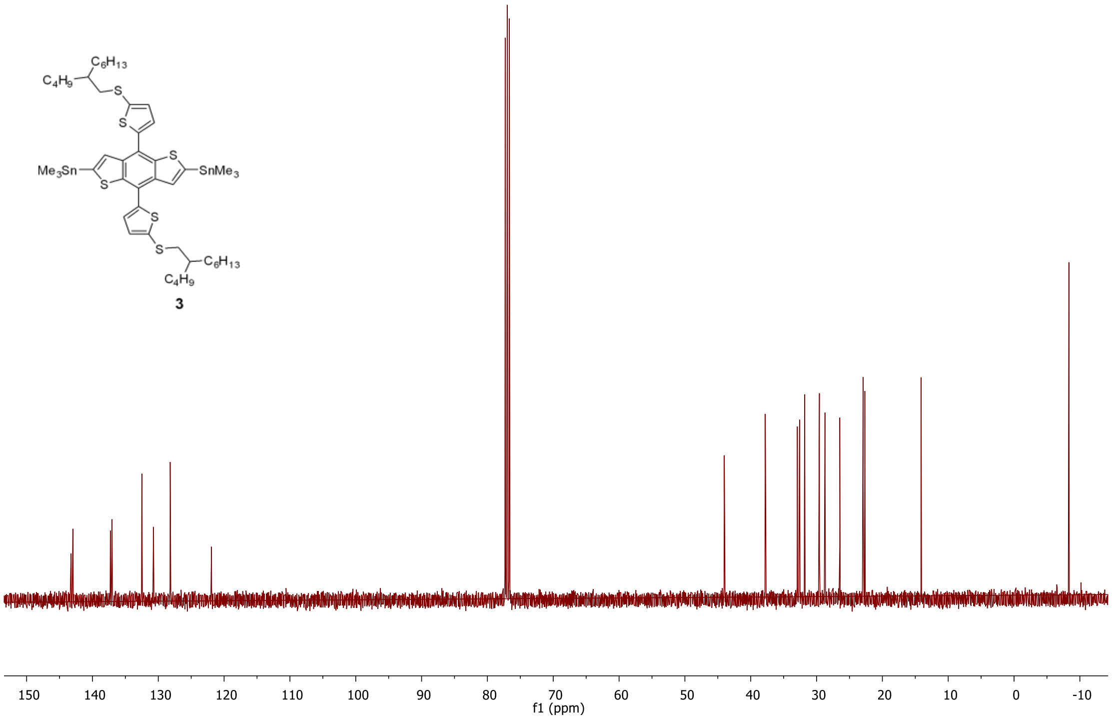




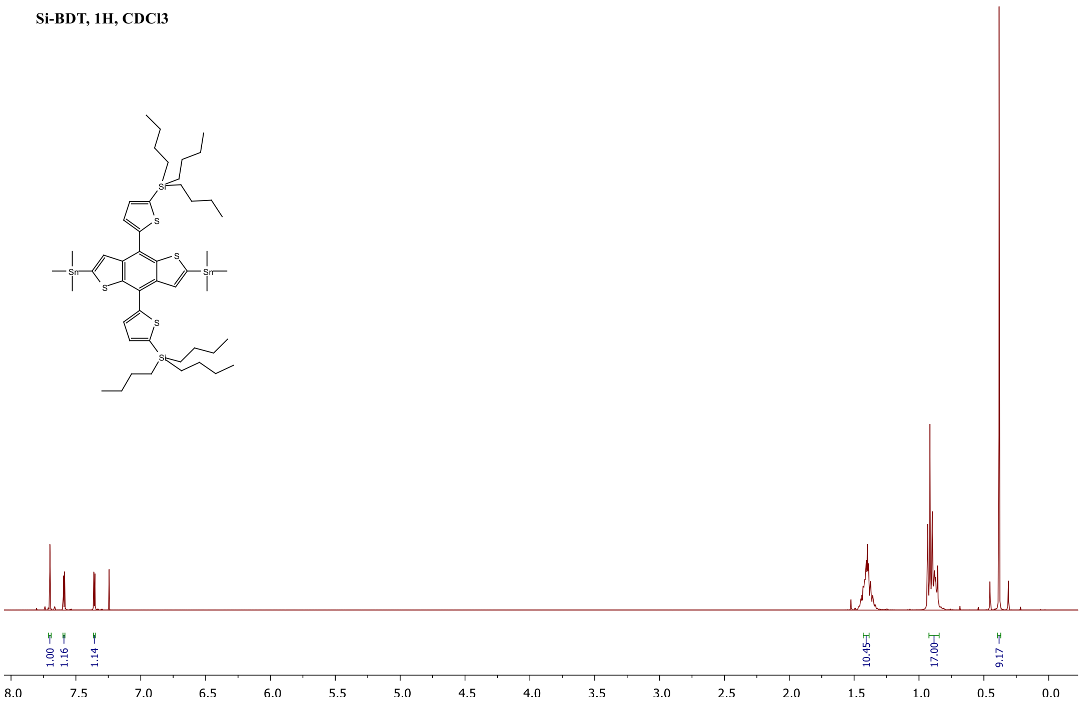
S-BDT , 1H, CDCl3



S-BDT , C-13, CDCl3



Si-BDT, 1H, CDCl3



Si-BDT, C-13, CDCl3

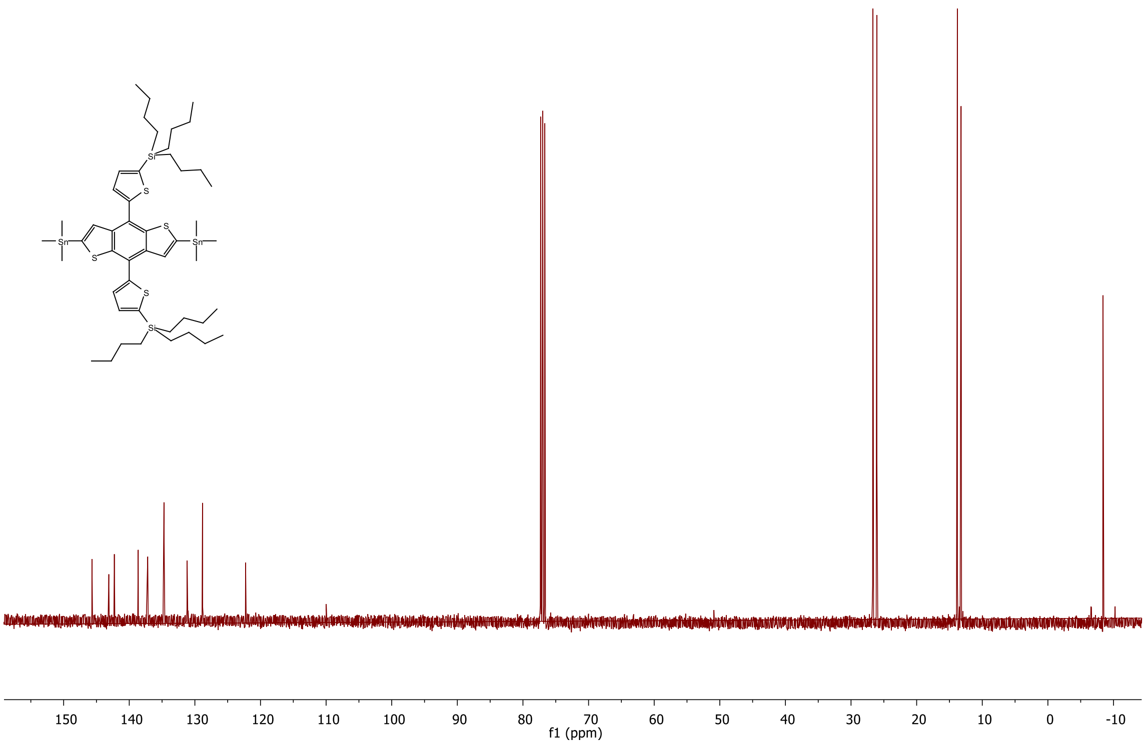
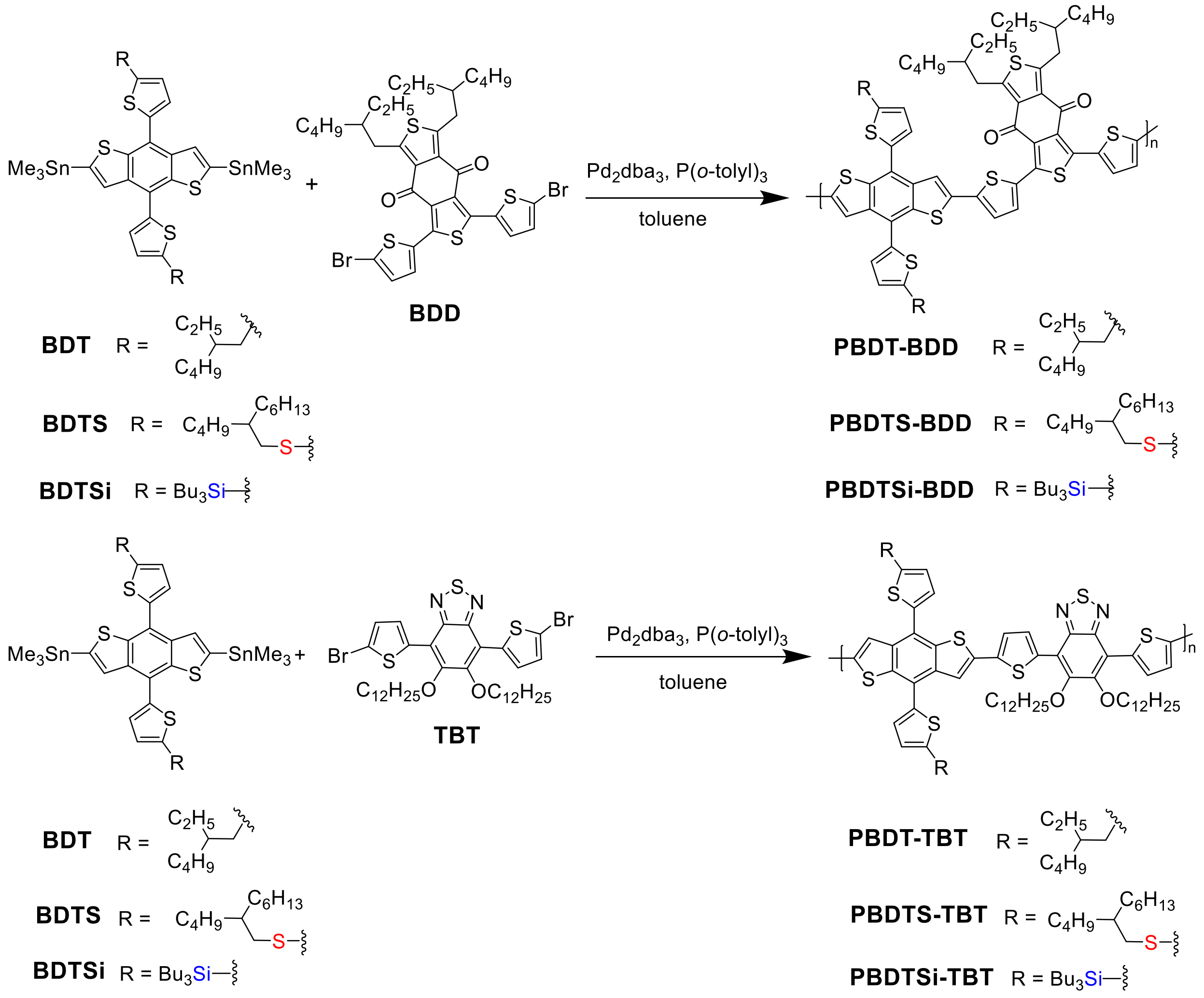


Figure S1. ^{1}H and ^{13}C NMR spectra of the donor monomers.

3. Syntheses of polymers

Scheme S3. Syntheses of the polymers



General procedure for polymerization

In a dry 25 mL flask, the donor (BDT-based) monomer (0.2 mmol), the acceptor (BDD- or TBT-based) monomer (0.2 mmol), $Pd_2(dba)_3$ (0.004 mmol) and P(*o*-Tol)$_3$ (0.0016 mmol) were dissolved in anhydrous toluene (10 mL) under nitrogen atmosphere. The reaction mixture was vigorously stirred at 110 ºC. Table 1 shows the reaction times for the preparation of the different polymers. 2-Bromothiophene and tributyl(thiophen-2-yl)stannane were added into the solution as end cappers. After cooling to room temperature, the polymer was precipitated by pouring the solution into acetone, filtered through a Soxhlet thimble, and then subjected to Soxhlet extraction with acetone, diethyl ether and chloroform. The chloroform fraction was purified by passing it though a short silica gel column and then precipitated from acetone. Finally, the copolymer was obtained by filtration through a 0.45 μm Teflon filter and dried under vacuum at 40 °C overnight.

4. Yields of polymerization reactions and molecular weights of polymers

Table S1. Yields of the polymerization reactions and molecular weights of the polymers

Polymer	Yield (%)	Number Average Molecular weight (*kDa*)	Polydispersity index (M_w/M_n)
PBDT-BDD	78	92.0	2.3
PBDTS-BDD	83	38.4	2.8
PBDTSi-BDD	96	60.0	2.4
PBDT-TBT	73	36.1	2.6
PBDTS-TBT	66	53.0	2.5
PBDTSi-TBT	93	76.4	2.4

5. TGA and DSC measurements

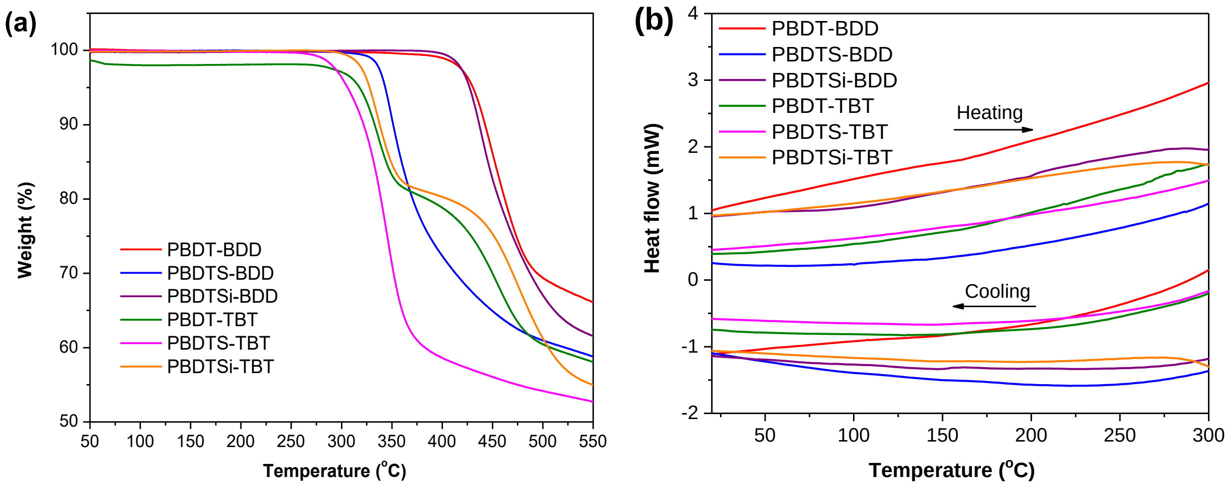


Figure S2. (a) TGA and (b) DSC plots of the donor polymers.

6. Temperature-dependent absorption measurements

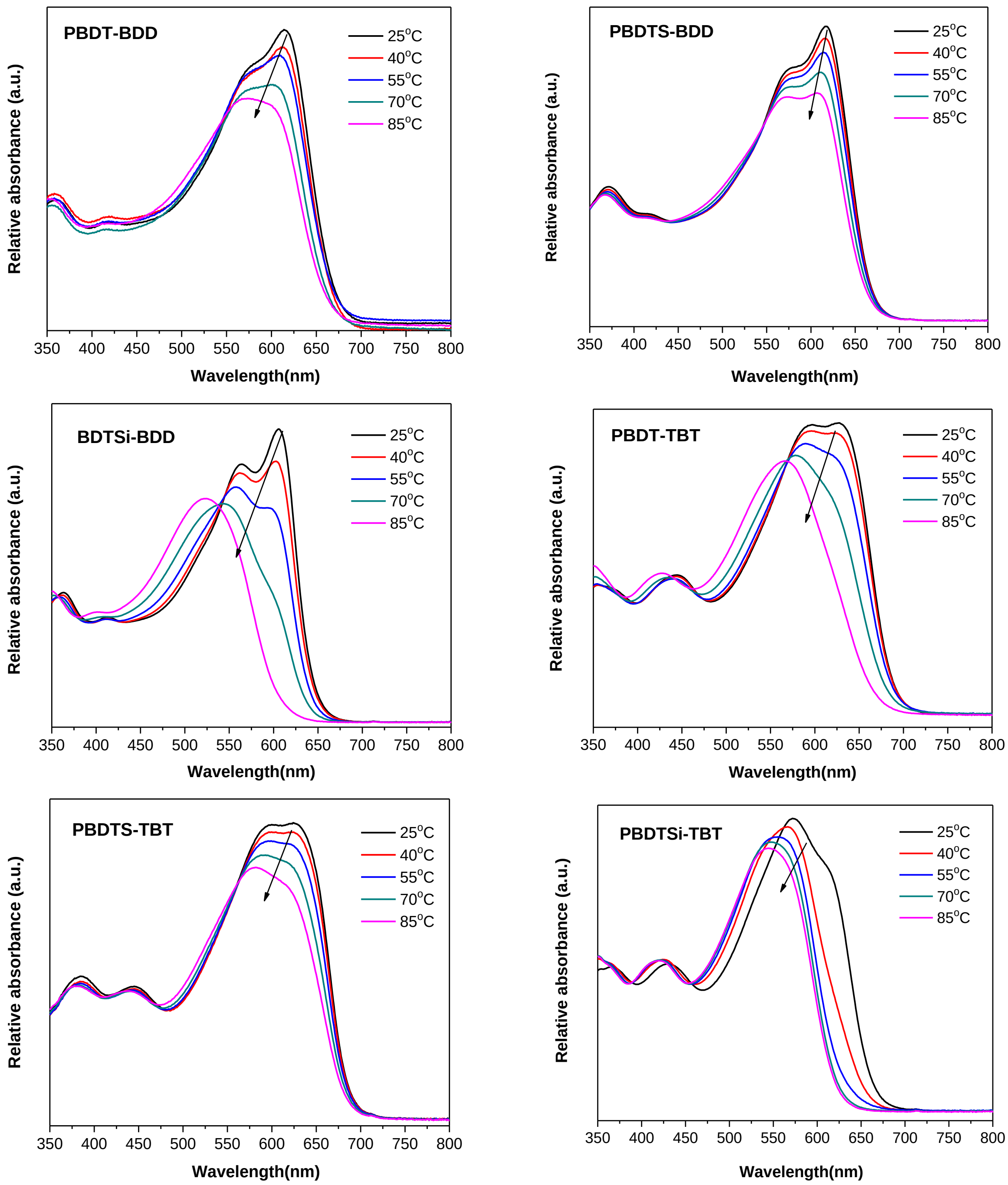


Figure S3. Temperature-dependent absorption spectra of the polymers.

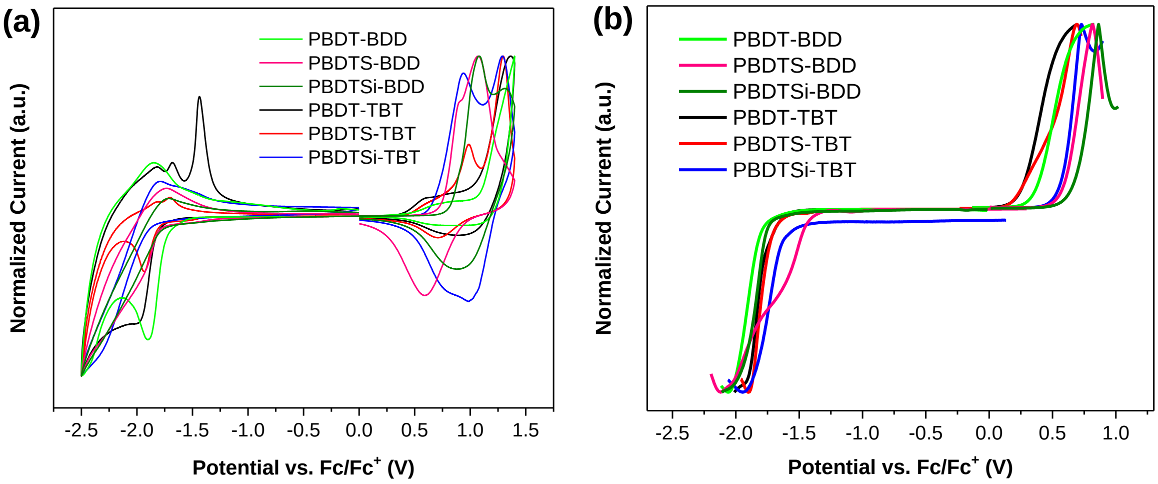
7. Electrochemical measurements

The energy levels of all polymers were determined from both cyclic voltammetry (CV) and square wave voltammetry (SWV) measurements. The HOMO and LUMO levels were estimated from the onsets of oxidation and reduction potentials in the CV measurements, and the peaks of oxidation and reduction potentials in the SWV measurements, by setting the oxidative peak potential of Fc/Fc^+ *vs.* the normal hydrogen electrode (NHE) to 0.63 V, and the NHE *vs.* the vacuum level to 4.5 V.[5]

The energy levels were calculated according to the formula:

HOMO = $-(E_{ox} + 5.13)$ eV and LUMO = $-(E_{red} + 5.13)$ eV

where the E_{ox} and E_{red} were determined from the oxidation and reduction onset potentials relative to ferrocene/ferrocenium (Fc/Fc^+) redox couple for the CV measurements, respectively. The E_{ox} and E_{red} were determined from the oxidation and reduction peak potentials relative to ferrocene/ferrocenium (Fc/Fc^+) redox couple for the SWV measurements, respectively.



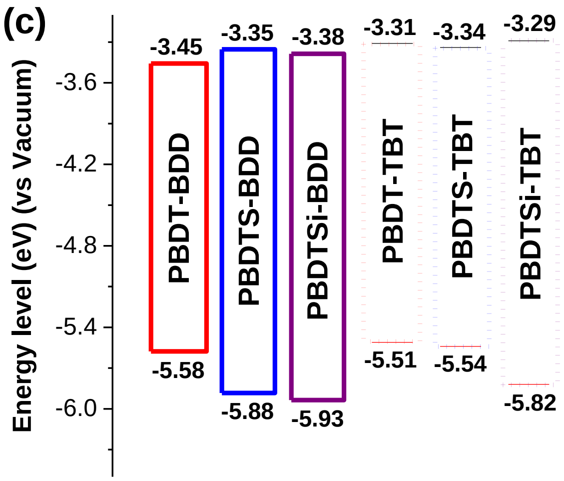


Figure S4. (a) Cyclic voltammograms of the donor polymers (b) Square wave voltammograms of the donor polymers (c) Energy level diagram calculated from cyclic voltammetry measurements.

8. Optimization of the device fabrication of all-PSCs

Table S2. Photovoltaic performances of the PBDT-BDD:PNDI-T10 all-PSCs under different D:A ratios and rotation speeds of spin-coating [a].

Blend ratio	rpm	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
1.5:1	800	0.88	5.3	0.48	2.2
	1000	0.89	6.1	0.50	2.7
	1500	0.89	6.8	0.60	3.6
	2000	0.89	7.0	0.61	3.8
	2500	0.88	5.4	0.64	3.1
1:1	800	0.90	7.2	0.43	2.8
	1000	0.90	8.8	0.45	3.6
	1500	0.90	9.5	0.54	4.6
	2000	0.90	10.5	0.59	5.6
	2500	0.90	9.8	0.58	5.1
1:1.5	800	0.88	3.6	0.50	1.6
	1000	0.88	4.2	0.51	1.9
	1500	0.88	4.8	0.58	2.4
	2000	0.89	5.3	0.62	2.9
	2500	0.88	5.0	0.61	2.7

[a] device structure: ITO/PEDOT:PSS (40 nm)/PBDT-BDD:PNDI-T10/LiF (0.6 nm)/Al (90 nm)

9. Electron (μ_e) and hole (μ_h) mobilities

The electron (μ_e) and hole (μ_h) mobilities of the active layers were measured by space charge limited current (SCLC) method using hole-only device with configuration of ITO/PEDOT:PSS/active layer/MoO_3/Al, and electron-only device configuration of ITO/ZnO/active layer/LiF/Al.

The mobility of the blend films was calculated by using the Mott–Gurney equation.

$$J = \frac{9\varepsilon_o \varepsilon_r \mu_h (V^2)}{8L^3}$$

where, J is current density, ε is the dielectric constant (assumed to be 3), ε_o is the free space permittivity, d is the thickness of the active layer and $V–V_{bi}$ is the effective voltage. The mobility μ was calculated from the slope of the $J^{1/2}–V$ curve.

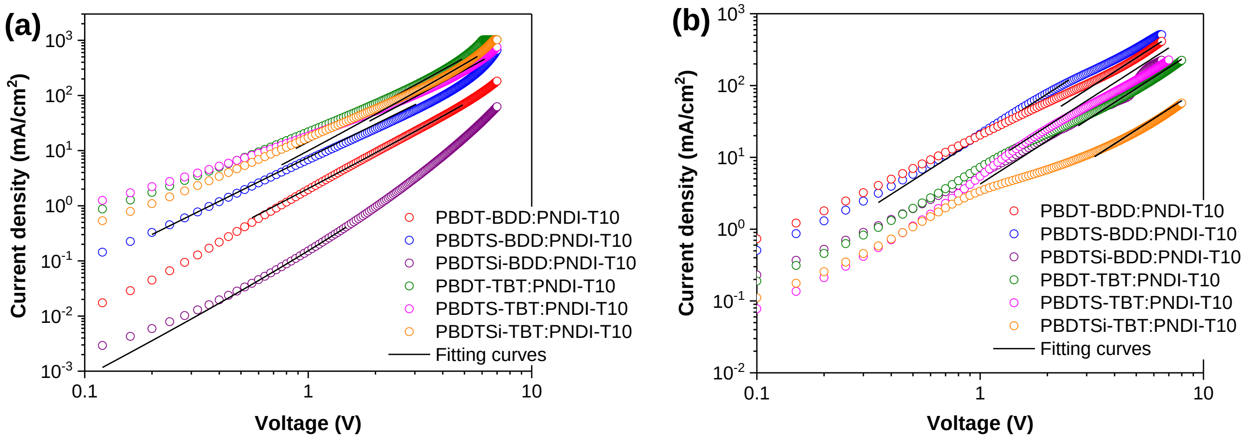


Figure S5. Current density–voltage and SCLC fitting curves of the blends with (a) the hole-only device structure of ITO/PEDOT:PSS/active layer/MoO_3/Al, and (b) the electron-only device structure of ITO/ZnO/active layer/LiF/Al.

10. References

1. Cui, C.; Wong, W.-Y.; Li, Y., Improvement of Open-Circuit Voltage and Photovoltaic Properties of 2D-Conjugated Polymers by Alkylthio Substitution. *Energy Environ. Sci* **2014,** *7* , 2276-2284.
2. Bin, H.; Gao, L.; Zhang, Z.-G.; Yang, Y.; Zhang, Y.; Zhang, C.; Chen, S.; Xue, L.; Yang, C.; Xiao, M.; Li, Y., 11.4% Efficiency Non-Fullerene Polymer Solar Cells with Trialkylsilyl Substituted 2D-Conjugated Polymer as Donor. *Nat. Commun.* **2016,** *7*, 13651.
3. Helgesen, M.; Gevorgyan, S. A.; Krebs, F. C.; Janssen, R. A. J., Substituted 2,1,3-Benzothiadiazole- and Thiophene-Based Polymers for Solar Cells − Introducing a New Thermocleavable Precursor. *Chem. Mater.* **2009,** *21*, 4669-4675.
4. Bouffard, J.; Swager, T. M., Fluorescent Conjugated Polymers that Incorporate Substituted 2,1,3-Benzooxadiazole and 2,1,3-Benzothiadiazole Units. *Macromolecules* **2008,** *41*, 5559-5562.
5. Cardona, C. M.; Li, W.; Kaifer, A. E.; Stockdale, D.; Bazan, G. C., Electrochemical Considerations for Determining Absolute Frontier Orbital Energy Levels of Conjugated Polymers for Solar Cell Applications. *Adv. Mater.* **2011,** *23*, 2367-2371.