Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Significant influence of benzothiophene ring substitution position on photovoltaic performance of benzodithiophene-based donor polymers

Hua Tan,[a,b]* Hongyi Tan,[a] Xiangjun Zheng,[a,b] Jia Yang,[a] Junting Yu,[c]* and Weiguo Zhu[a]*

[A] *School of Materials Science and Engineering, Jiangsu Key Laboratory of Environmentally Friendly Polymeric Materials, Jiangsu Engineering Laboratory of Light-Electricity-Heat Energy-Converting Materials and Applications, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Changzhou University, Changzhou 213164, Jiangsu, P. R. China*

[b] *College of Chemistry, Key Lab of Environment-Friendly Chemistry and Application in Ministry of Education, Xiangtan University, Xiangtan 411105, Hunan, P. R. China*

[c] *Key Laboratory of Theoretical Organic Chemistry and Functional Molecule, Ministry of Education, College of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan 411201,Hunan, P. R. China*

**To whom correspondence should be addressed. Email:*

(H. T.) tanhua815@126.com

(J. Y.) yujuntingtt@163.com

(W. Z.) zhuwg18@126.com

Content

1. General experimental information on materials and characterizations.

2. Devices Fabrication and Characterizations

3. Supplementary figures and tables

Figure S1. TGA plots of PBDTBTs-BDD and PBDTTBs-BDD with a heating rate of 20 ° C min-1 under N2 atmosphere.

Figure S2. Normalized absorption spectra of PBDTBTs-BDD and PBDTTBs-BDD in a chloroform solution.

Figure S3. Cyclic voltammetry curves of PBDTBTs-BDD and PBDTTBs-BDD.

Figure. S4-S16. The detail optimal data of PBDTBTs-BDD and PBDTTBs-BDD-based BHJ solar cells.

Figure S17. XRD patterns of the PBDTBTs-BDD and PBDTTBs-BDD pristine solid powder.

1. General experimental information on materials and characterizations.

All manipulations were performed under dry nitrogen flow. All reagents were obtained from Aldrich and directly used without further purification. NMR spectra were carried on a Bruker AVANCE-III 400 Spectrometer using tetramethylsilane as a reference in deuterated chloroform solution at 298 K. UV-Vis absorption spectra were recorded on a HP-8453 UV visible system. MALDI-TOF mass spectrometric measurements were performed on Bruker Bifiex III MALDI-TOF. TGA was tested with a TA Q600 thermogravimetric analyzer. Cyclic voltammetry was carried out on a CHI660A electro-chemical work station in a three-electrode cell dipped in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution calibrated with a ferrocene/ferrocenyl couple (Fc/Fc^+) under nitrogen protection at a scan rate of 100 mV s^{-1} and room temperature (RT). In this three-electrode cell, a platinum rod, platinum wire and Ag/AgCl were used as a working electrode, counter electrode and reference electrode, respectively. The morphology of blend films were investigated by an atomic force microscopy (AFM) on a Veeco, DI Multimode NS-3D apparatus in a tapping mode under normal air condition at RT.

Synthesis of (4,8-bis(2-((2-ethylhexyl)thio)benzo[b]thiophen-5-yl)- benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (BDTBTs).

4,8-bis(2-((2-ethylhexyl)thio)benzo[b]thiophen-5-yl)benzo[1,2-b:4,5-b']dithiophene (1.05 g, 1.41 mmol) was dissolved in 40 ml of THF and added to a 50 ml three-necked flask. At -78 ℃, n-BuLi (3.52 mmol, 2.2 mL) was added dropwise under nitrogen protection for 1 hour. After Adding trimethyltin chloride (1.0 M, 4.2 mL) to the reaction system and returning to room temperature for 2 h. After concentration by rotary evaporation, the crude product was purified by recrystallization. ^{1}H NMR (400 MHz, CDCl$_3$, δ/ppm) 8.04 (s, 2H), 7.95 (d, *J* = 8.0Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.41 (dd, *J* = 12.0, 12.0 Hz, 4H), 3.05 (d, *J* = 4.0 Hz, 4H), 1.71 (dd, *J*=8.0, 16.0 Hz, 2H), 1.51 (tt, 10H), 1.35 (s, 8H), 0.94 (q, *J* = 8.0 Hz, 14H), 0.53 – 0.26 (m, 18H). ^{13}C NMR (101 MHz, CDCl$_3$, δ/ppm) 142.75, 142.33, 140.83, 140.37, 139.63, 137.19, 136.39, 130.65, 128.74, 126.90, 125.73, 123.57, 122.18, 42.16, 39.20, 32.16, 28.75, 25.41, 23.01, 14.13, 10.77. MS (MALDI-TOF) of $C_{48}H_{62}S_6Sn_2$ for $[M]^+$: 1068.80 ; found: 1069.70. Yield 73.4%.

Synthesis of PBDTBTs-BDD

To a 50 ml three-necked flask was added BDTBTs (300 mg, 0.28 mmol) , BDD (215 mg, 0.28 mmol) and Pd(PPh$_3$)$_4$ (18 mg, 0.016 mmol), anhydrous toluene (10 mlL). The mixture was then degassed by nitrogen for 30 min at room temperature. Then the solution was heated to reflux and stirred for 40 min under an nitrogen atmosphere. After cooling to room temperature, the solution was added dropwise into methanol. The precipitate was collected by filtration and extracted by Soxhlet extraction with methanol and hexanes to remove oligomers and catalyst. The residue was dissolved in chloroform at 90 °C and then transferred to a chromatographic column containing a short path of silica. The column was flushed with chloroform. The polymer was precipitated from methanol and dried under vacuum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13–6.66 (br, 14H), 3.38–2.86 (br, 6H), 2.09–0.214 (br, 68H). PBDTBTs-BDD. Yield: 25.9%.

Synthesis of (4,8-bis(6-((2-ethylhexyl)thio)benzo[b]thiophen-2-yl)- benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (BDTTBs).

4,8-bis(5-((2-ethylhexyl)thio)benzo[b]thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (2.17 g, 2.93 mmol) was dissolved in 40 mL of THF and added to a 100 mL three-necked flask. At -78 ℃, n-BuLi (7.0 mmol, 4.5 mL) was added dropwise under nitrogen protection for 2 hour. After Adding trimethyltin chloride (1.0 M, 8.8 mL) to the reaction system and returning to room temperature for 6 h. After concentration by rotary evaporation, the crude product was purified by recrystallization. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm) 7.93 (s, 2H), 7.86 (d, J = 8.0Hz, 2H), 7.64 (d, J = 20.0 Hz, 4H), 7.45 (dd, 2H), 3.04 (d, J = 8.0 Hz, 4H), 1.67 (dd, J=8.0, 16.0 Hz, 2H), 1.51 (tt, 10H), 1.35 (s, 8H), 0.94 (q, 12H), 0.53 – 0.26 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$, δ/ppm) 143.66, 141.73, 140.66, 138.21, 137.57, 133.84, 130.68, 126.69, 124.54, 124.13, 122.44, 39.10, 32.40, 28.82, 25.62, 22.97, 14.14, 10.81. MS (MALDI-TOF) of $C_{48}H_{62}S_6Sn_2$ for [M]+: calcd. 1068.80 ; found: 1068.65. Yield 79.8%.

Synthesis of PBDTTBs-BDD

To a 50 ml three-necked flask was added BDTTBs (301 mg, 0.28 mmol) , BDD (216 mg, 0.28 mmol) and $Pd(PPh_3)_4$ (6 mg, 0.005 mmol), anhydrous toluene (15 ml). The mixture was then degassed by nitrogen for 30 min at room temperature. Then the solution was heated to reflux and stirred for 5 h under an nitrogen atmosphere. After cooling to room temperature, the solution was added dropwise into methanol. The precipitate was collected by filtration and extracted by Soxhlet extraction with methanol and hexanes to remove oligomers and catalyst. The residue was dissolved in chloroform at 90 °C and then transferred to a chromatographic column containing a short path of silica. The column was flushed with chloroform. The polymer was precipitated from methanol and dried under vacuum. ^1H NMR (400 MHz, $CDCl_3$) δ 8.10–5.66 (br, 14H), 3.46–2.67 (br, 6H), 2.15–0.26 (br, 68H). PBDTTBs-BDD. Yield 27.9%.

2. General experimental information on materials and characterizations.

Bulk heterojunction solar cells were fabricated with the following conventional structure: ITO/PEDOT:PSS/active layer/PFN-Br/Al. ITO substrates were cleaned and then dried in an oven at 85℃ for 12 hours. The PEDOT:PSS precursor was spin-coated at 2000 r.p.m. onto the ITO surface and thermal annealed (200 °C) for 60 min in air, and the thickness of PEDOT:PSS films are about 30 nm. Then the PEDOT:PSS-coated substrates were transferred into a nitrogen-filled glove box. A 16.0 mg mL^{-1} chloroform solution of PBDTBTs-BDD:ITIC, PBDTBs-BDD:ITIC and PBDTTBs-BDD:Y6 (1:1 weight ratio) was spin-coated at 2000 r.p.m. And a 17.6 mg mL^{-1} chloroform solution of PBDTBTs-BDD: Y6 (1:1.2 weight ratio) was spin-coated at 2000 r.p.m. The active layer thermal annealed (100 °C for PBDTBTs-BDD:ITIC, 100℃ for PBDTTBs-BDD: ITIC, 100 ℃ for PBDTBTs-BDD:Y6 and 90 ℃ for PBDTTBs-BDD: Y6) for 10 min. Then evaporated 5 nm thick PFN-Br and 100 nm thick Al on the active layer. The current density-voltage (*J*-*V*) characteristics of the devices under illumination of AM 1.5 G solar simulator (Newport, 100 mW cm^{-2}, calibrated by a silicon reference cell) were measured on a computer-controlled Keithley 2420 Source Measure Unit. The external quantum efficiencies (EQE) of solar cells were analyzed using a certified Newport incident photon conversion efficiency (IPCE) measurement system (Model 66902). The hole mobilities of blend films were investigated by employing the hole-only devices with a structure of ITO/PEDOT:PSS/active layer/MnO_3/Al. The electron mobilities of blend films were performed in the electron-only devices with a structure of ITO/ZnO/active layer/Ca/Al.

3. Supplementary figures and tables

Figure S1

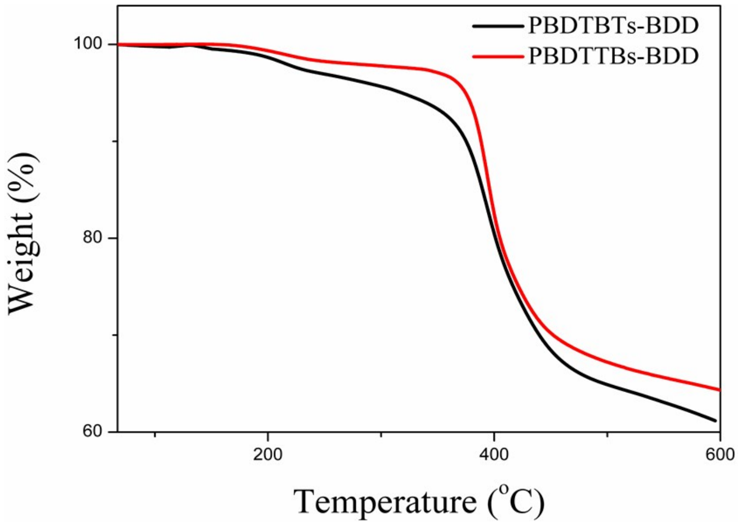


Figure S2

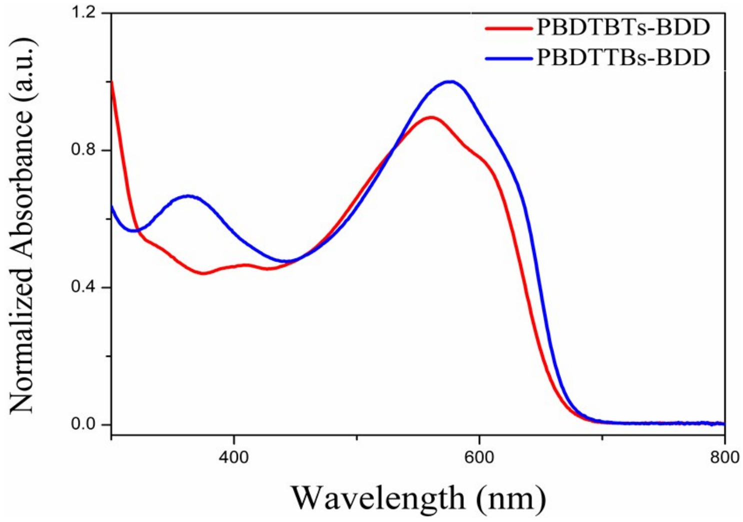


Figure S3

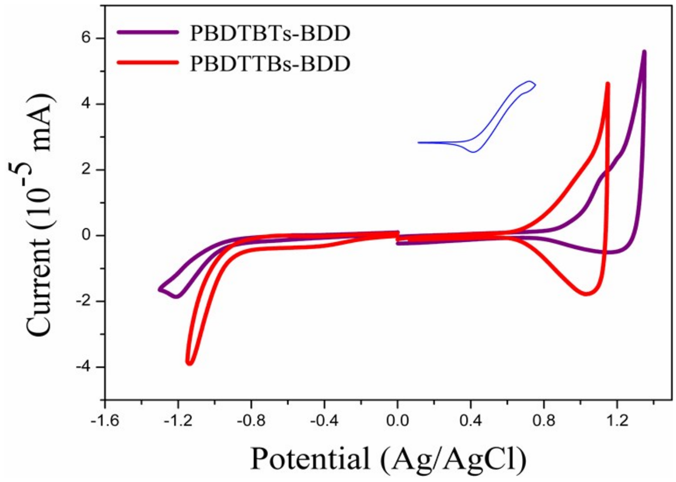

PBDTBTs-BDD
PBDTTBs-BDD
Current (10^{-5} mA)
6
4
2
0
-2
-4
-1.6
-1.2
-0.8
-0.4
0.0
0.4
0.8
1.2
Potential (Ag/AgCl)

Figure S4

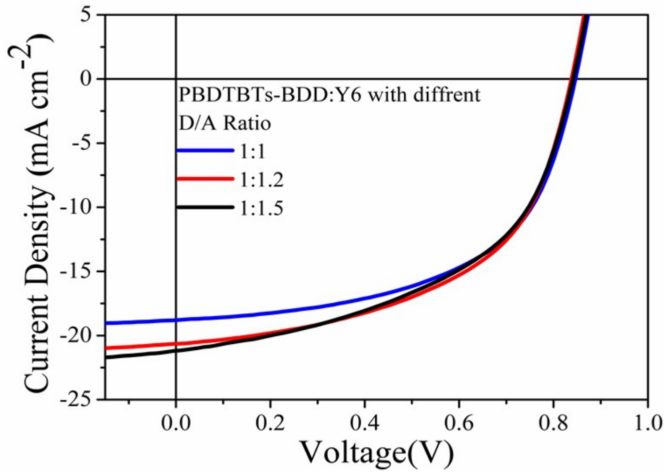


Table S1. Photovoltaic properties of the PSCs based on PBDTBTs-BDD:Y6 with different D/A Ratio.

		V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%]
D/A	1:1	0.85	18.75	56.24	8.91
	1:1.2	0.84	20.56	53.54	9.22
	1:1.5	0.84	21.09	50.45	8.93

solvent: CF .

Figure S5

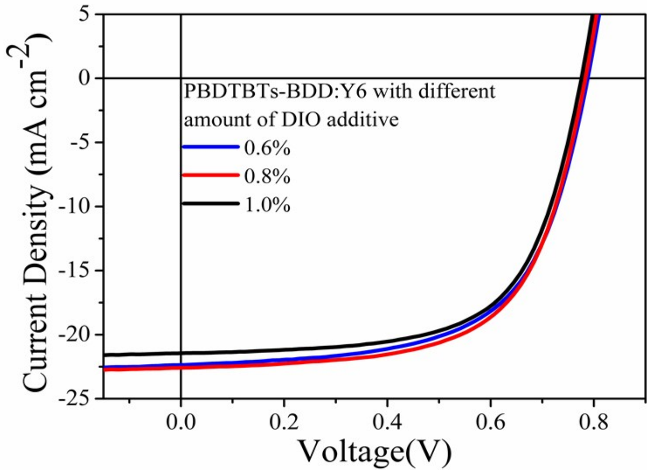


Table S2. Photovoltaic properties of the PSCs based on PBDTBTs-BDD:Y6 with different amount of DIO additive.

		V_{OC} [V]	J_{SC} [mA cm^{-2}]	*FF* [%]	PCE [%]
DIO	0.6%	0.79	22.33	61.97	10.90
	0.8%	0.78	22.56	63.27	11.17
	1.0%	0.77	21.25	64.91	10.65

Figure S6

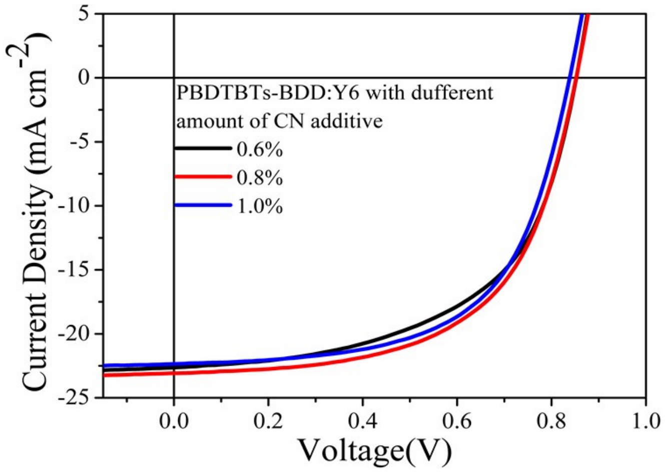


Table S3. Photovoltaic properties of the PSCs based on PBDTBTs-BDD:Y6 with different amount of CN additive.

		V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%]
CN	0.6%	0.85	22.56	56.30	10.82
	0.8%	0.85	22.76	60.06	11.61
	1.0%	0.84	22.32	60.21	11.26

Figure S7

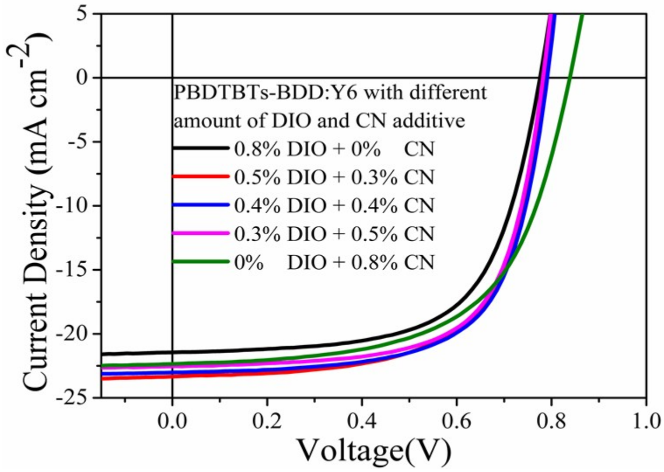


Table S4. Photovoltaic properties of the PSCs based on PBDTBTs-BDD:Y6 with different amount of DIO and CN additive.

DIO	CN	V_{OC} [V]	J_{SC} [mA cm^{-2}]	*FF* [%]	PCE [%]
0.8%	0%	0.78	22.56	63.27	11.17
0.5%	0.3%	0.79	23.31	64.79	11.86
0.4%	0.4%	0.79	23.00	66.43	12.07
0.3%	0.5%	0.79	22.52	66.94	11.79
0%	0.8%	0.85	22.76	60.06	11.61

Figure S8

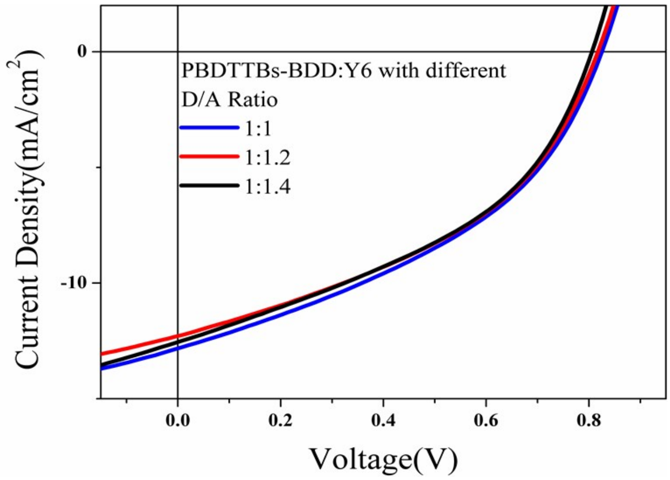


Table S5. Photovoltaic properties of the PSCs based on PBDTTBs-BDD:Y6 with different D/A Ratio.

		V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%]
D/A	1:1	0.82	12.81	40.97	4.32
	1:1.2	0.81	12.26	49.20	4.22
	1:1.4	0.80	12.54	41.69	4.20

Figure S9

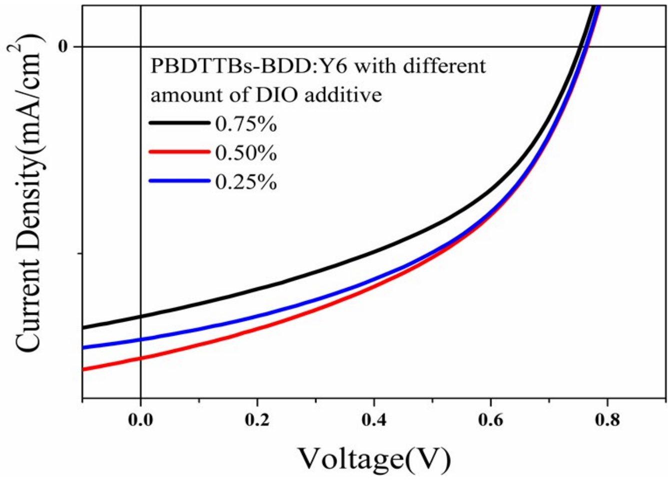


Table S6. Photovoltaic properties of the PSCs based on PBDTTBs-BDD:Y6 with different amount of DIO additive.

DIO	V_{OC} [V]	J_{SC} [mA cm^{-2}]	*FF* [%]	PCE [%]
0.25%	0.76	14.11	46.67	5.02
0.5%	0.76	15.03	44.64	5.12
0.75%	0.75	13.03	44.62	4.37

Figure S10

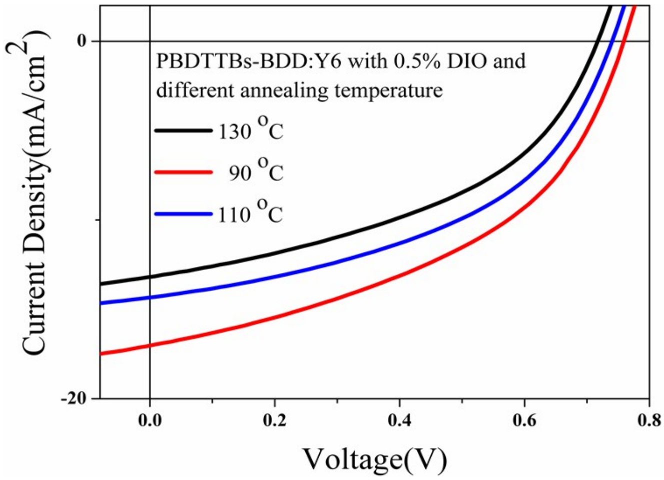


Table S7. Photovoltaic properties of the PSCs based on PBDTTBs-BDD:Y6 with different annealing temperature.

Temperature (°C)	V_{OC} [V]	J_{SC} [mA cm^{-2}]	*FF* [%]	PCE [%]
90	0.76	16.97	45.19	5.81
110	0.74	14.28	47.18	4.98
130	0.72	13.14	44.97	4.23

Figure S11

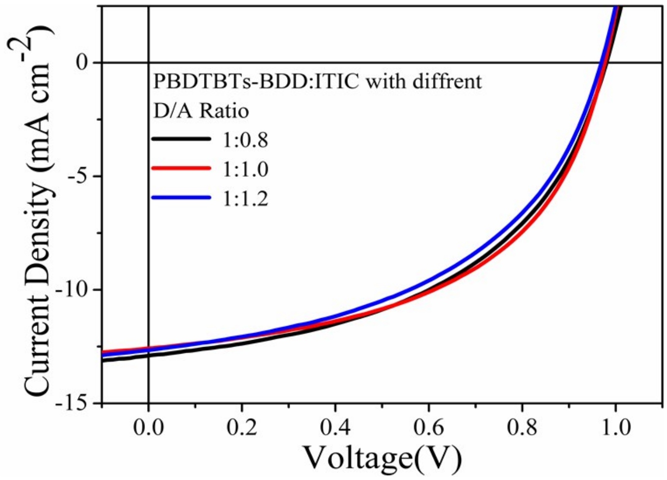
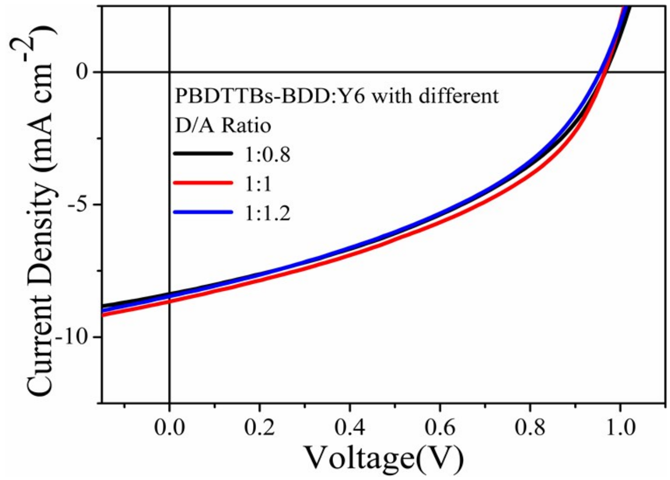


Table S8. Photovoltaic properties of the PSCs based on PBDTBTs-BDD:ITIC with different D/A Ratio.

		V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%]
D/A	1:1	0.98	12.89	48.92	6.17
	1:1.2	0.98	12.57	51.58	6.33
	1:1.4	0.97	12.64	48.04	5.88

Figure S12



DIO	V_{OC}	J_{SC}	*FF*	PCE
	[V]	[mA cm^{-2}]	[%]	[%]
0.6%	0.96	12.37	57.88	6.89

0.8%	0.96	11.98	61.75	7.05
1.0%	0.95	11.77	60.51	6.75

Table S9. Photovoltaic properties of the PSCs based on PBDTBTs-BDD:ITIC with different amount of DIO additive.

Figure S13

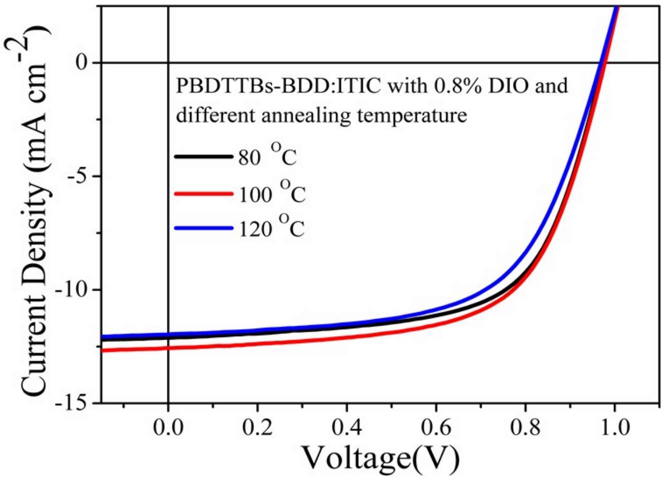


Table S10. Photovoltaic properties of the PSCs based on PBDTBTs-BDD:ITIC with different annealing temperature.

Temperature (°C)	V_{OC}	J_{SC}	*FF*	PCE
	[V]	[mA cm^{-2}]	[%]	[%]

80	0.98	12.09	45.19	5.81
100	0.98	12.55	63.28	7.76
120	0.97	11.95	61.45	7.11

Figure S14

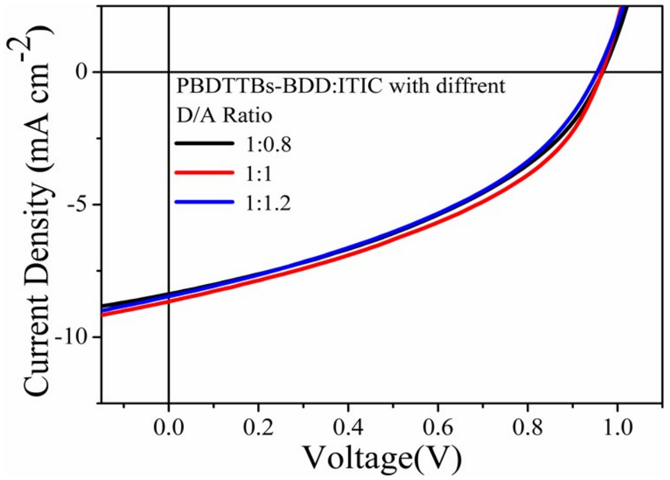


Table S11. Photovoltaic properties of the PSCs based on PBDTTBs-BDD:ITIC with different D/A Ratio.

	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%]

	1:0.8	0.96	8.36	40.23	3.24
D/A	1:1.0	0.96	8.64	41.41	3.45
	1:1.2	0.95	8.46	39.89	3.21

Figure S15

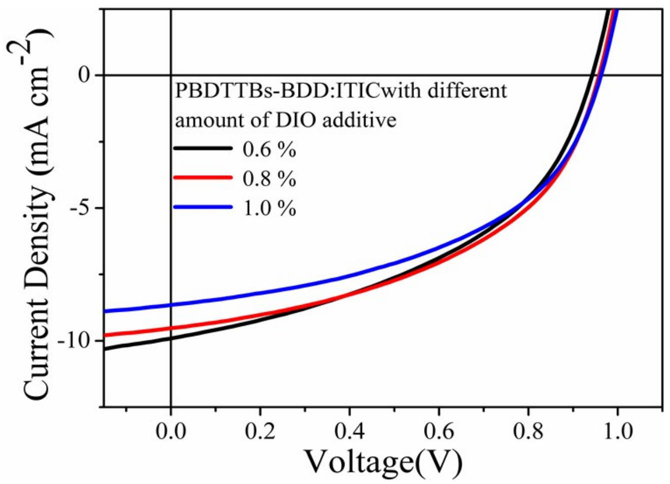


Table S12. Photovoltaic properties of the PSCs based on PBDTTBs-BDD:ITIC with different amount of DIO additive.

DIO	V_{OC} [V]	J_{SC} [mA cm^{-2}]	*FF* [%]	PCE [%]
0.6%	0.94	10.07	44.72	4.23
0.8%	0.96	9.50	47.67	4.33
1.0%	0.96	8.62	48.36	4.01

Figure S16

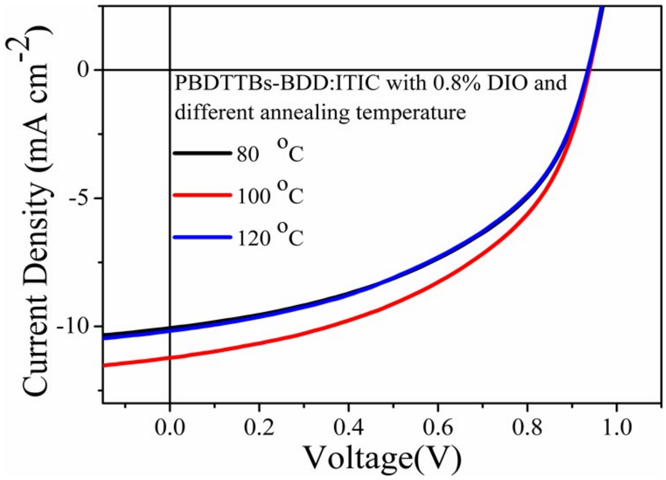


Table S13. Photovoltaic properties of the PSCs based on PBDTTBs-BDD:ITIC with different annealing temperature.

Temperature (°C)	V_{OC} [V]	J_{SC} [mA cm^{-2}]	*FF* [%]	PCE [%]
80	0.94	10.03	47.64	4.47
100	0.94	11.18	48.13	5.04
120	0.93	10.14	46.90	4.44

Figure S17.