Supporting Information

Simultaneous Enhancement of Performance and Insensitivity to Active Layer Thickness for OPVs by Functionalizing π-spacer's Side Chain

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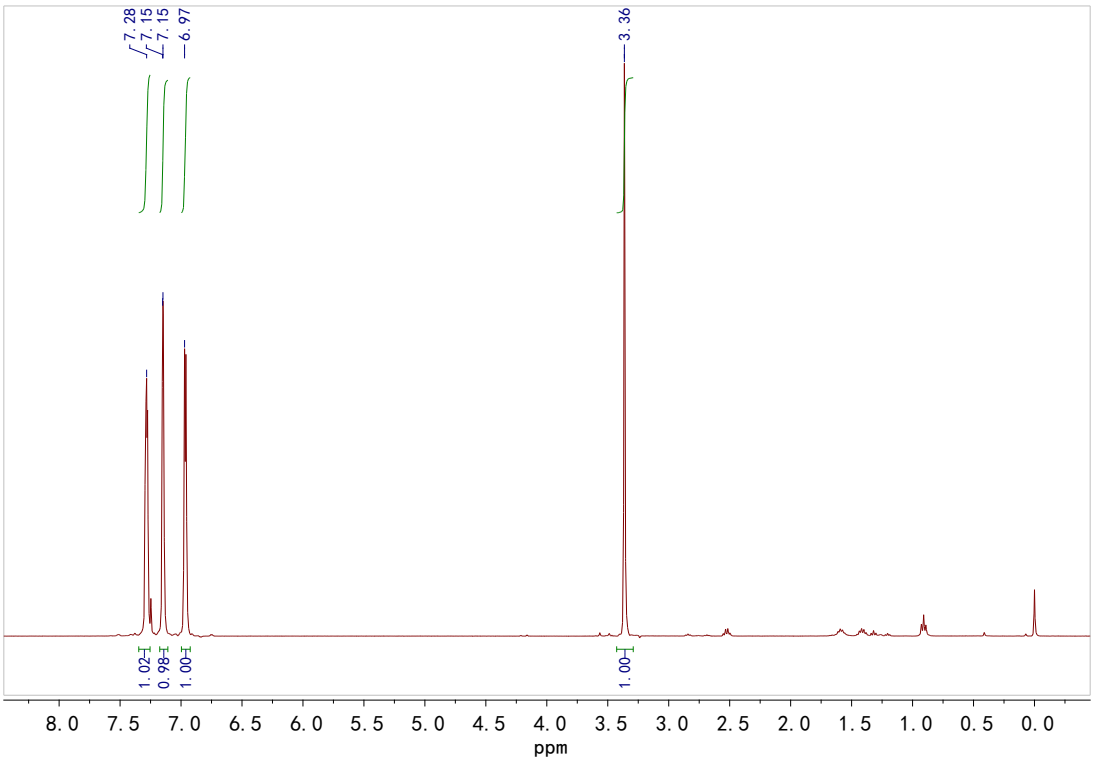

Fig. S1 ^{1}H NMR spectrum of compound 1 in $CDCl_3$ at room temperature.

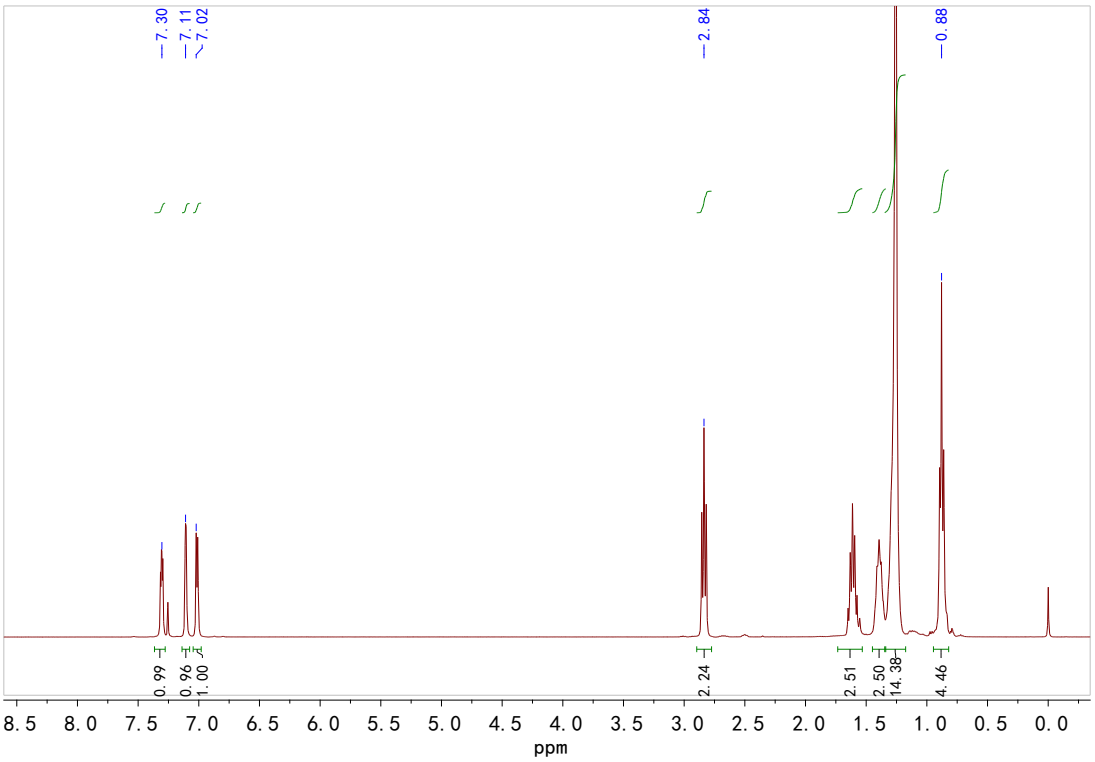

Fig. S2 ^{1}H NMR spectrum of compound 2 in $CDCl_3$ at room temperature.

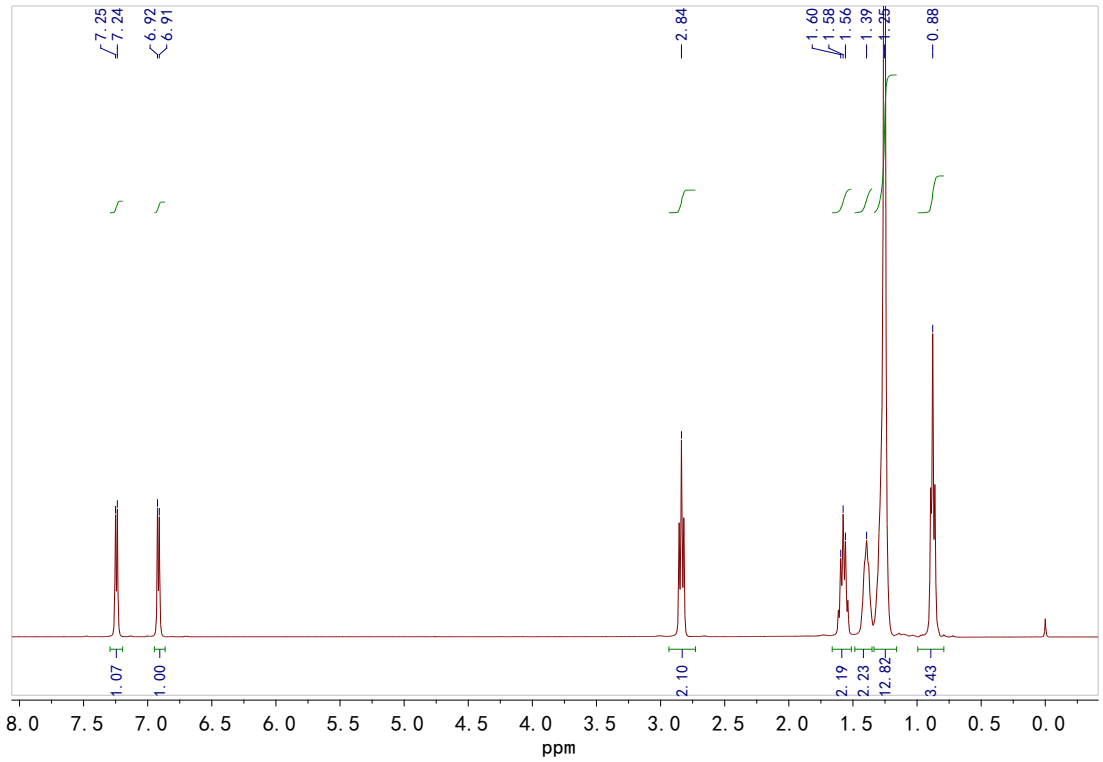

Fig. S3 ^{1}H NMR spectrum of compound 3 in $CDCl_3$ at room temperature.

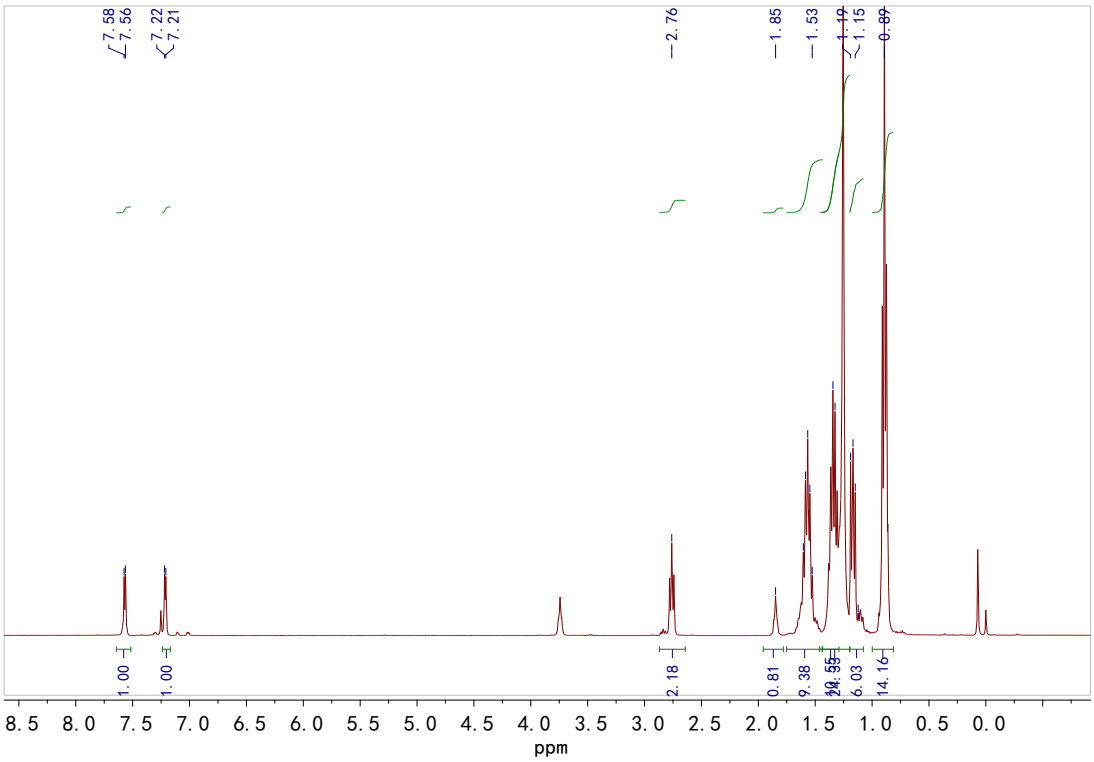

Fig. S4 ^{1}H NMR spectrum of compound 4 in $CDCl_3$ at room temperature.

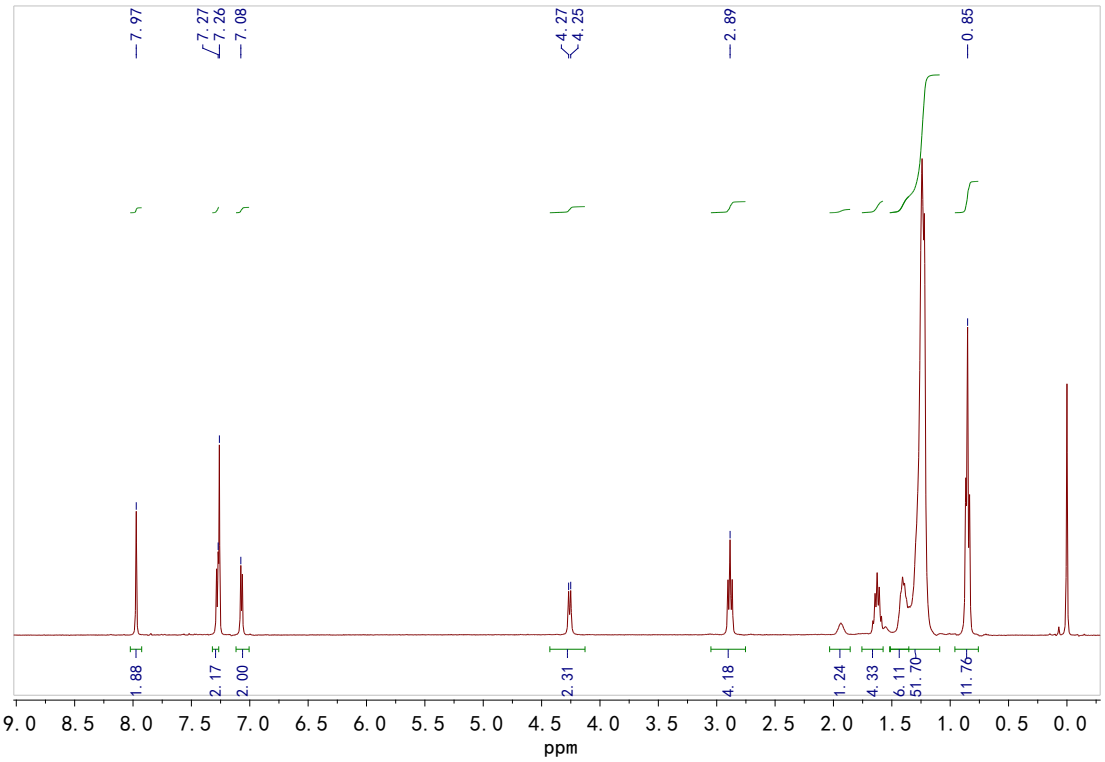

Fig. S5 ^{1}H NMR spectrum of compound 5 in $CDCl_3$ at room temperature.

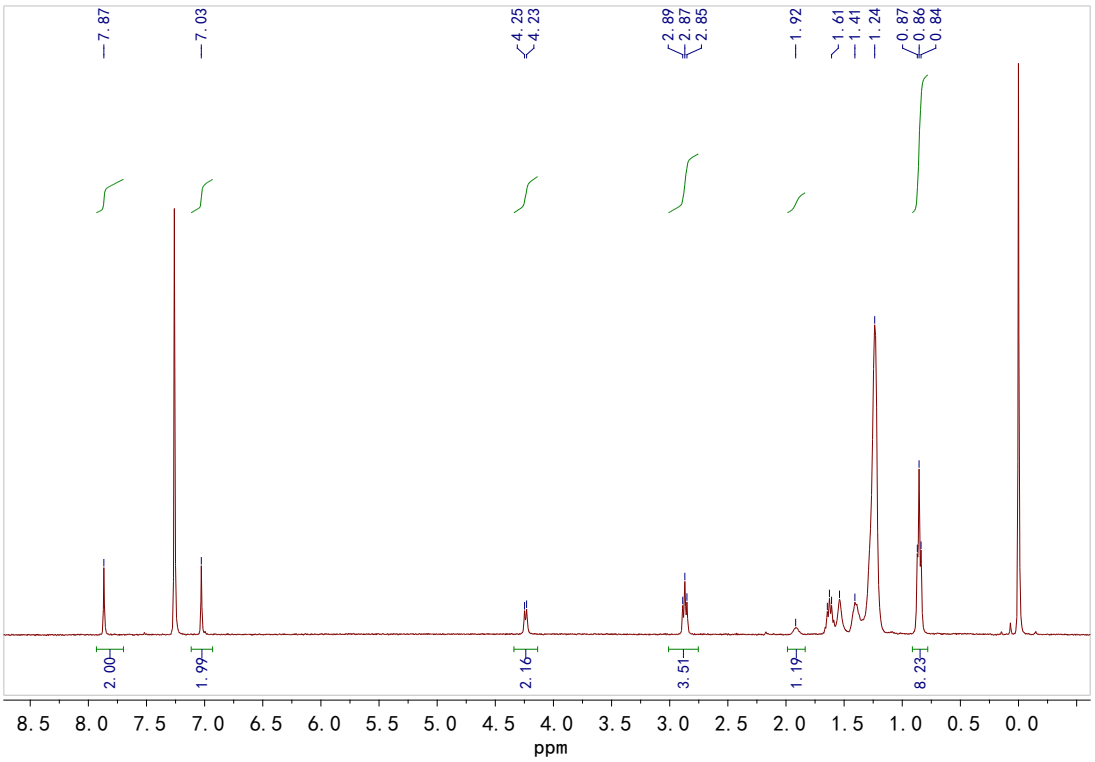

Fig. S6 ^{1}H NMR spectrum of compound 6 in $CDCl_3$ at room temperature.

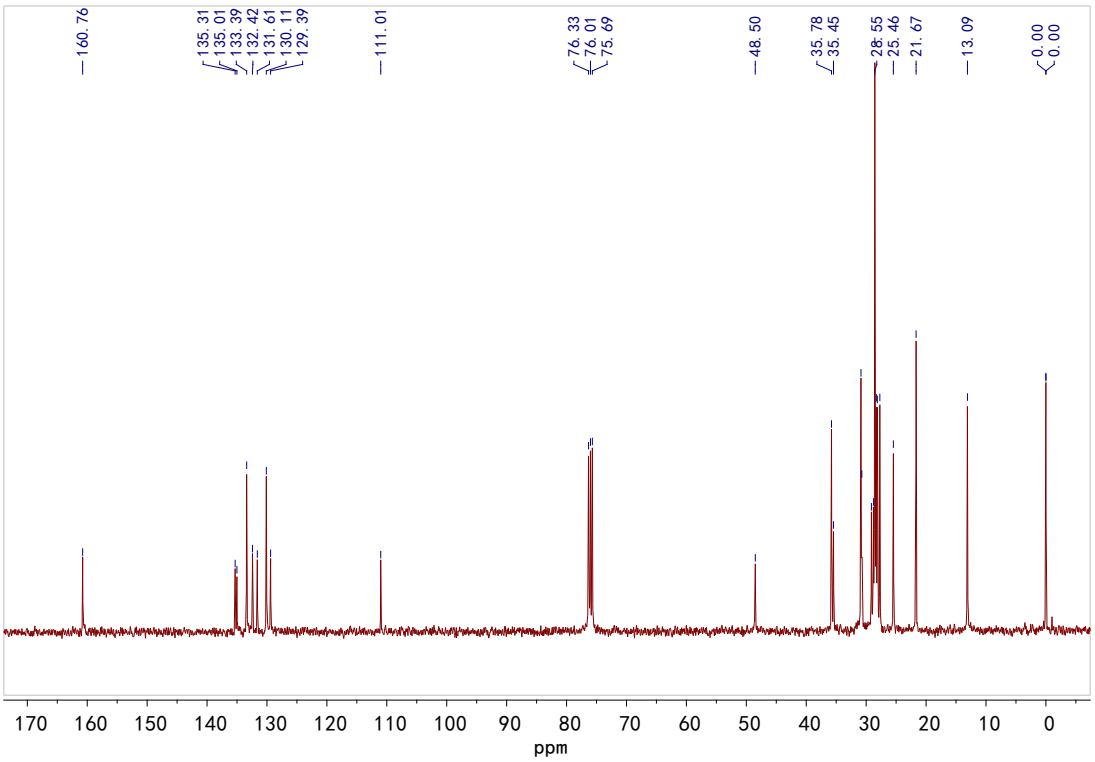

Fig. S7 ^{13}C NMR spectrum of compound 6 in $CDCl_3$ at room temperature.

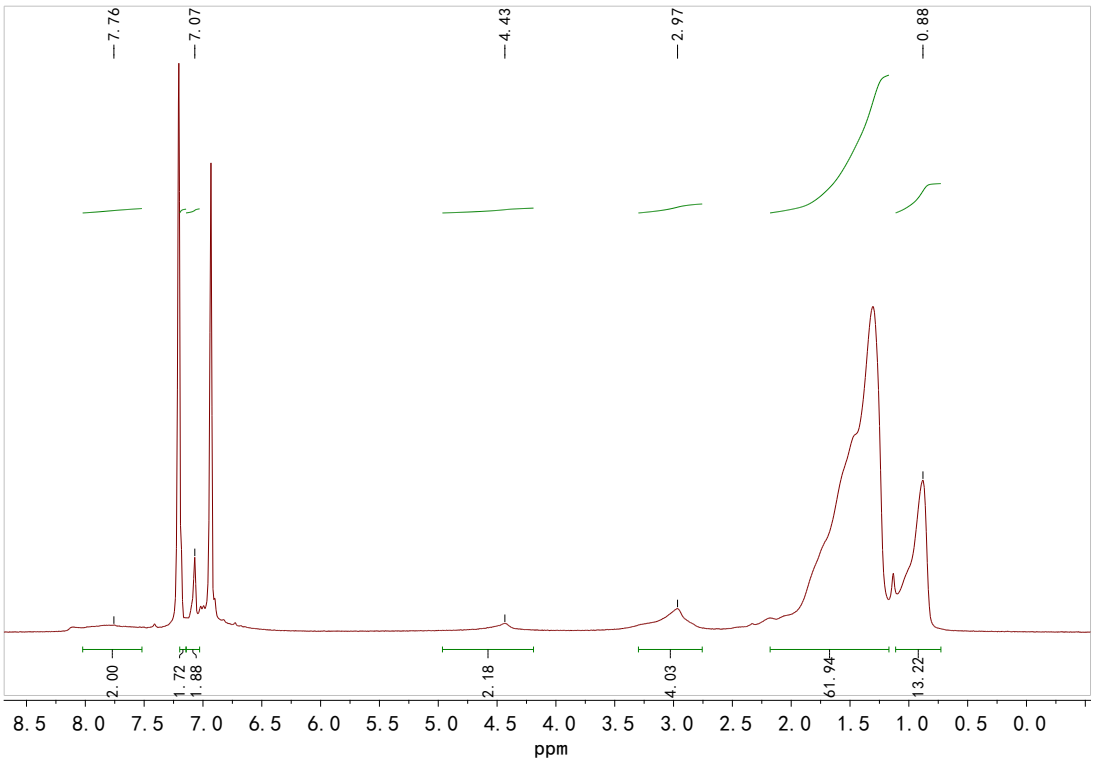

Fig. S8 ^{1}H NMR spectrum of polymer PBTI3T-S in 1,2-Dichlorobenzene-d4 at 100 ^{o}C.

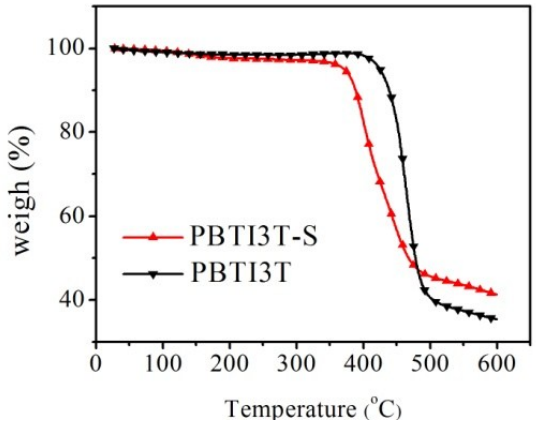

Fig. S9 TGA plots of PBTI3T-S and PBTI3T with a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

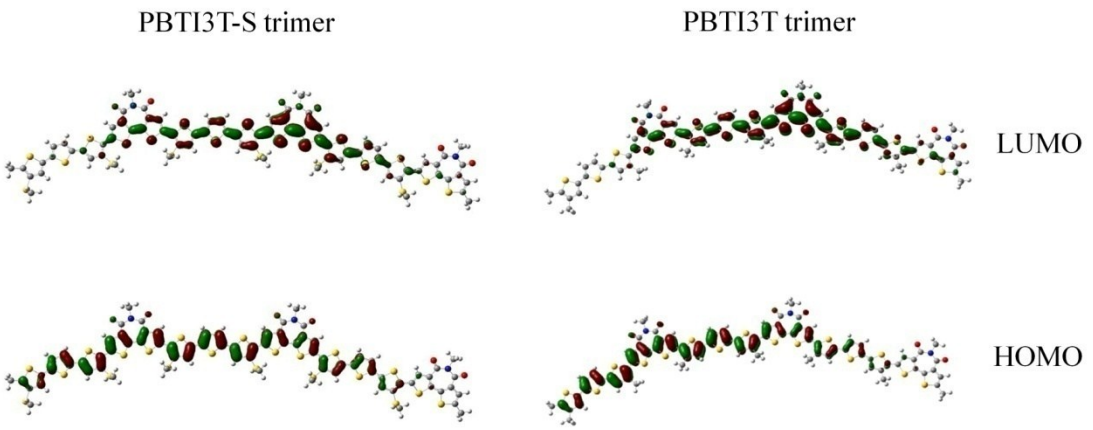

Fig. S10 B3LYP/6-31G** electronic density contours for PBTI3T-S trimer and PBTI3T trimer.

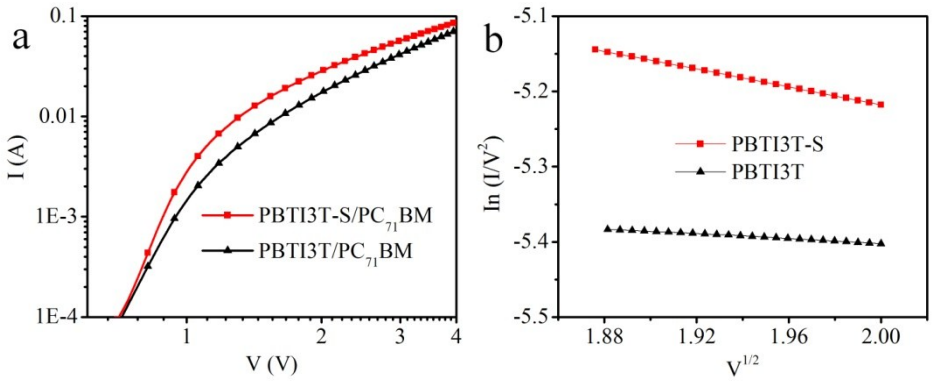

Fig. S11 (a) Hole-only *I–V* curves of PBTI3T-S/$PC_{71}BM$ and PBTI3T/$PC_{71}BM$ blend films. (b) Linear fits for the plots of ln(I/V^2) versus $V^{1/2}$ based on the SCLC model.

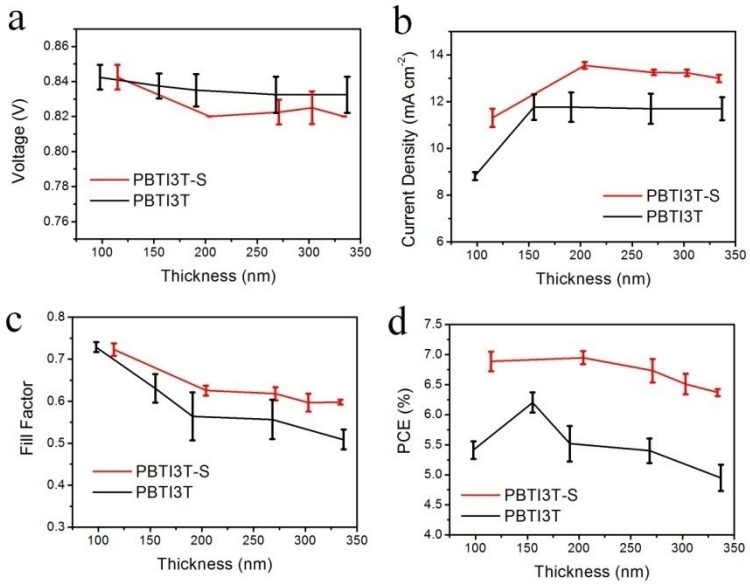

Fig. S12 The variations of film thickness with (a) open circuit voltage, (b) short-circuit current, (c) fill factor and (d) power conversion efficiency.

Table S1 Device characteristics of PBTI3T-S:$PC_{71}BM$ PSCs with different DIO ratios. PBTI3T-S:$PC_{71}BM$ = 1:1 (w/w), chlorobenzene as solvent and DIO (v/v) as processing additive.

DIO Ratio （%, v/v)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE[a] (%)	Thickness （nm）
0	0.90	6.00	51.43	2.78 (2.48)	90
1	0.84	11.68	64.08	6.29 (6.06)	144
2	0.84	11.36	69.13	6.60 (6.51)	138
3	0.84	11.50	62.30	6.02 (5.79)	141

[a]Average PCE in parentheses from 8 devices.

Table S2 Device characteristics of PBTI3T-S:$PC_{71}BM$ PSCs with different D:A blend ratios. Chlorobenzene as solvent and 2% DIO (v/v) as processing additive.

D/A Ratio(w/w)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE[a] (%)	Thickness （nm）
2:1	0.88	10.83	53.61	5.11 (4.68)	250
1:1	0.84	11.36	69.13	6.60 (6.51)	144
1:2	0.84	11.31	70.84	6.73 (6.68)	204
1:3	0.82	10.58	62.43	5.42 (5.23)	193
1:4	0.84	9.08	58.91	4.49 (4.44)	199

[a]Average PCE in parentheses from 8 devices.

Table S3 Device characteristics of Polymer:$PC_{71}BM$ PSCs with chloroform as solvent. The devices have the structure ITO/PEDOT:PSS/polymer:$PC_{71}BM$/LiF/Al. 2% DIO (v/v) as processing additive.

Polymer	D/A ratio (w/w)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE[a] (%)	Thickness （nm）
PBTI3T-S	1:1	0.86	11.50	72.00	7.12 (6.72)	105
PBTI3T	1:2	0.84	10.35	73.74	6.41 (6.09)	98

[a]Average PCE in parentheses from 8 devices.