

## Supporting Information

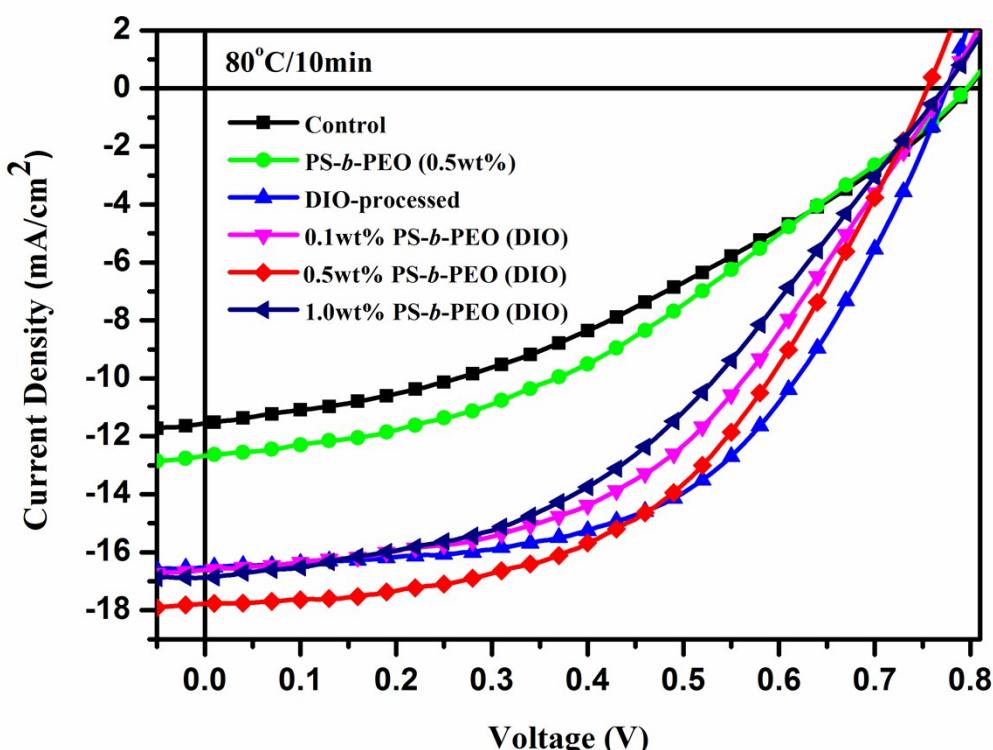
### A block copolymer enhances the efficiency of small-molecule bulk-heterojunction photovoltaics

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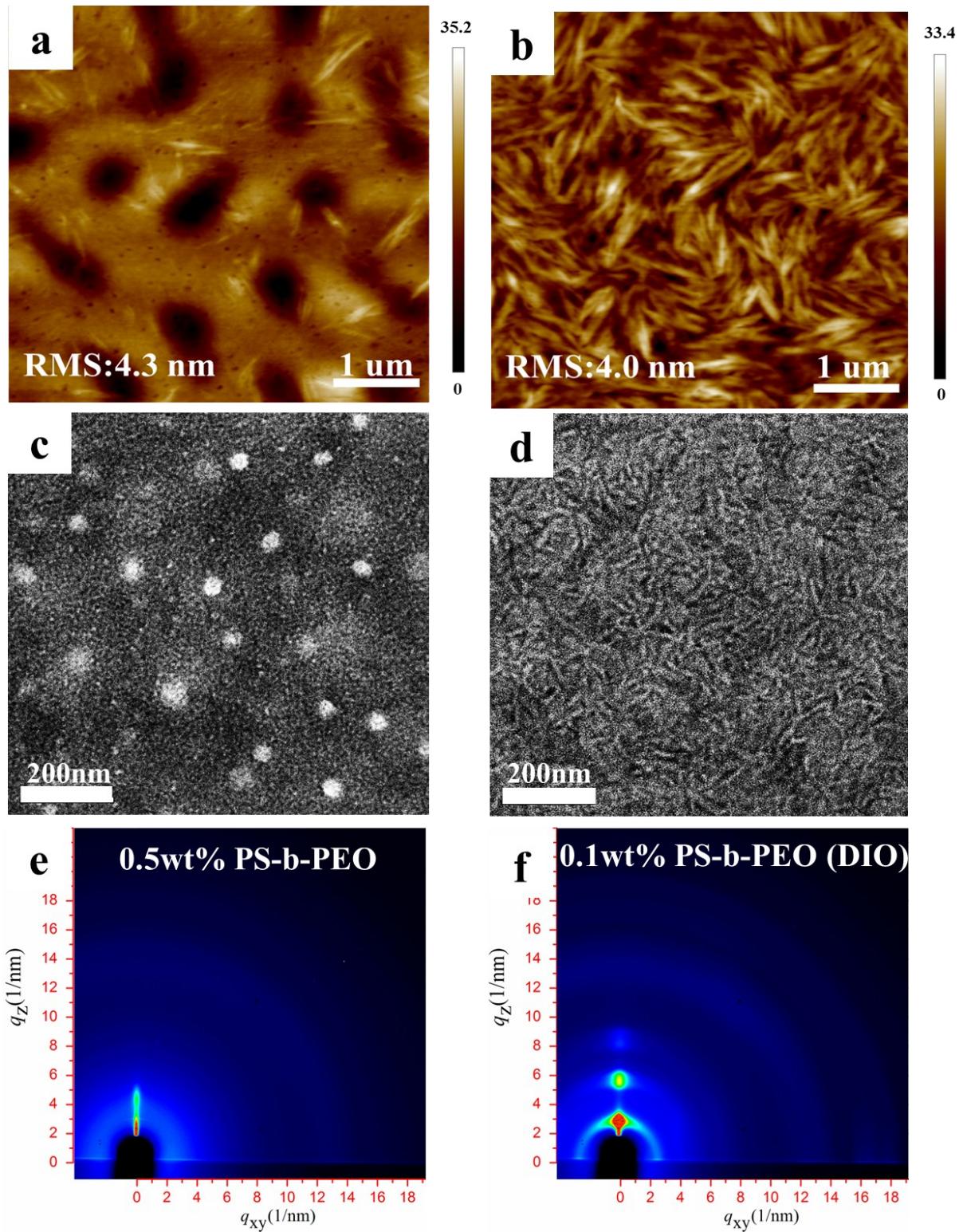
**Table S1** Parameters of devices incorporating p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>:PC<sub>71</sub>BM active layers spin-cast from chlorobenzene solutions containing different amounts of PS-*b*-PEO, with or without the additive DIO, drying for 30 min, and then heating at 80 °C for 10 min under an inert atmosphere to drive off residual solvent.

p-DTS(FBTTh <sub>2</sub> ) <sub>2</sub> :PC <sub>71</sub> BM	V <sub>oc</sub>	J <sub>sc</sub>	FF	η
	[V]	[mA cm <sup>-2</sup> ]	[%]	[%]
Control	0.80 ± 0.01	11.5 ± 0.13	36.9 ± 0.4	3.4 ± 0.11
PS- <i>b</i> -PEO (0.5wt%)	0.80 ± 0.02	12.7 ± 0.08	37.9 ± 0.3	3.8 ± 0.13
DIO-processed	0.78 ± 0.02	16.4 ± 0.07	54.7 ± 0.2	7.0 ± 0.12
0.1wt% PS- <i>b</i> -PEO (DIO)	0.77 ± 0.02	16.5 ± 0.11	48.6 ± 0.3	6.1 ± 0.10
0.5wt% PS- <i>b</i> -PEO (DIO)	0.76 ± 0.01	17.7 ± 0.12	50.9 ± 0.4	6.8 ± 0.11
1.0wt% PS- <i>b</i> -PEO (DIO)	0.77 ± 0.01	16.8 ± 0.10	43.9 ± 0.3	5.6 ± 0.13

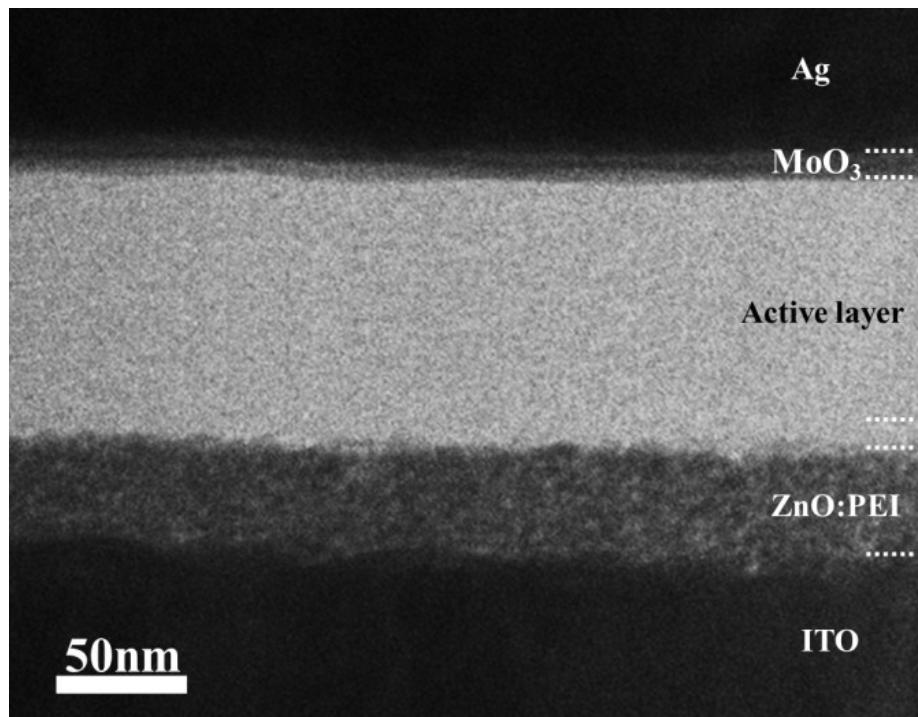
V<sub>oc</sub>: Open-circuit voltage; J<sub>sc</sub>: short-circuit density; FF: fill factor ; η: power conversion efficiency.



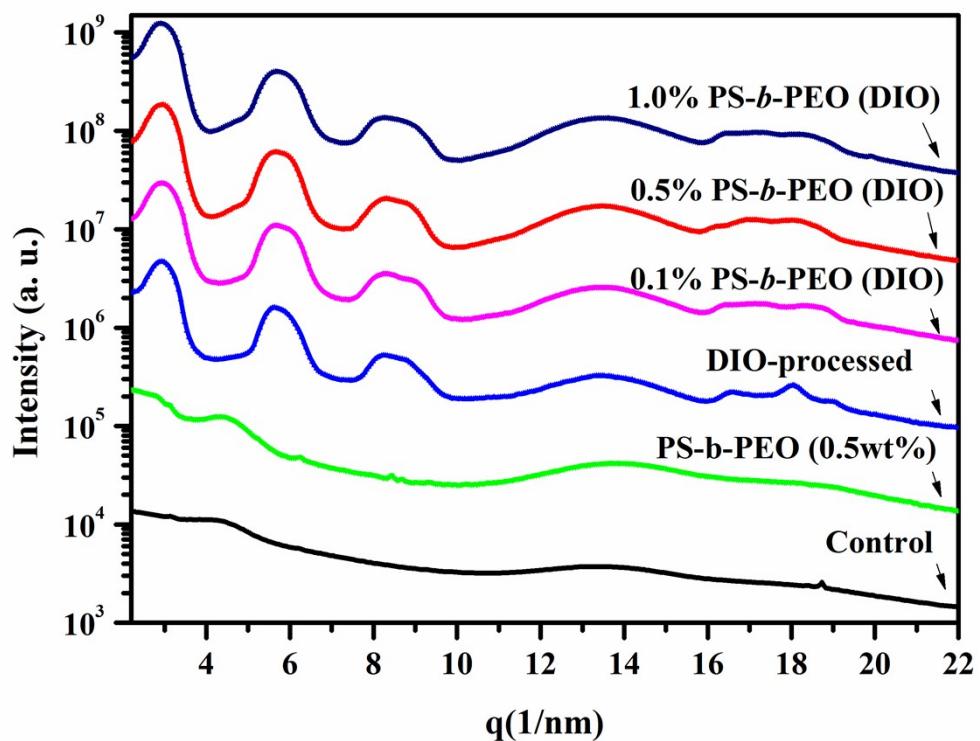
**Fig. S1** J-V characteristics of inverted small-molecule solar cells incorporating p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>:PC<sub>71</sub>BM active layers containing various weight fractions of PS-*b*-PEO, processed with and without the additive DIO, drying for 30 min, and then heating at 80 °C for 10 min under an inert atmosphere to drive off residual solvent.



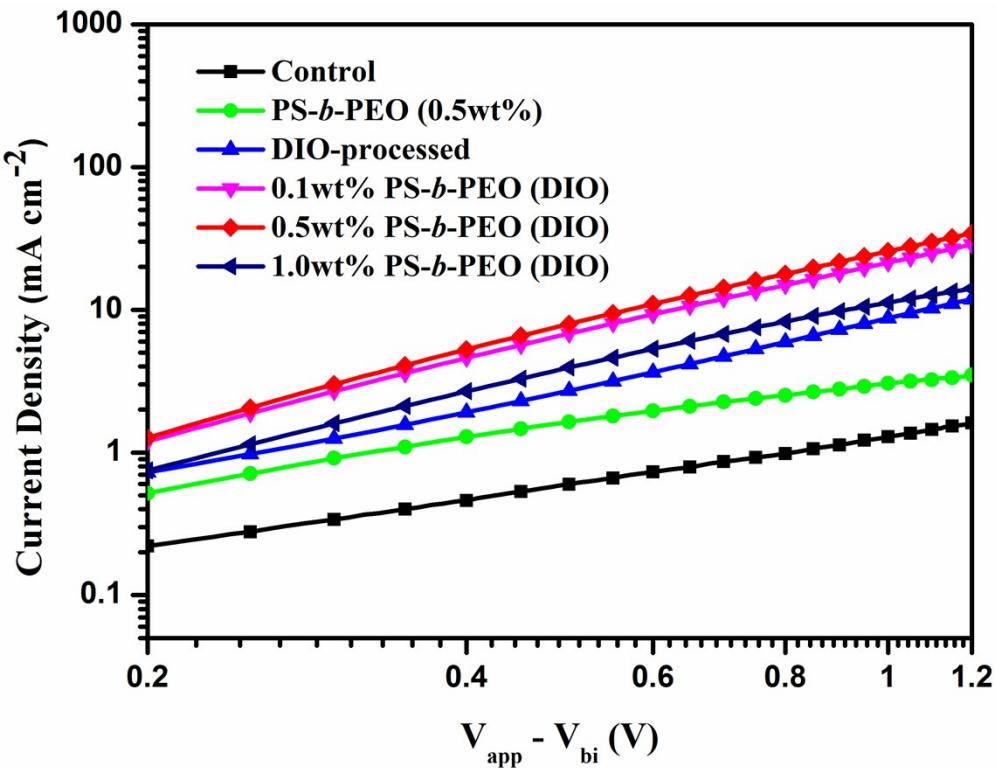
**Fig. S2** (a–b) AFM topographic, (c–d) TEM images and (e–f) 2D GIWAXS patterns of p-DTS( $\text{FBTTh}_2$ )<sub>2</sub>:PC<sub>71</sub>BM films; (a, c, e) 0.5 wt % PS-*b*-PEO without DIO; (b, d, f) 0.1 wt % PS-*b*-PEO with DIO-process.



**Fig. S3** The high-resolution TEM image of the cross-sectional area of the ITO/ZnO:PEI/p-DTS( $\text{FBTTh}_2$ )<sub>2</sub>:PC<sub>71</sub>BM(1.5: 1, w:w):PS-*b*-PEO (0.5 wt %)/MoO<sub>3</sub>/Ag inverted solar cell device structure.



**Fig. S4** GIWAXS out-of-plane profiles of control; 0.5 wt % PS-*b*-PEO; DIO-processed; 0.1 wt % PS-*b*-PEO (DIO); 0.5 wt % PS-*b*-PEO (DIO); 1.0 wt % PS-*b*-PEO (DIO).



**Fig. S5** Current density–electric field log-log plots for hole-only diodes (configuration: ITO/PEDOT:PSS/SMBHJ/MoO<sub>3</sub>/Ag) containing films prepared with or without DIO and PS-*b*-PEO.