

## Supporting Information

### Synergistic optimization of interfacial energy-level alignment and defects passivation toward efficient annealing-free inverted polymer solar cells

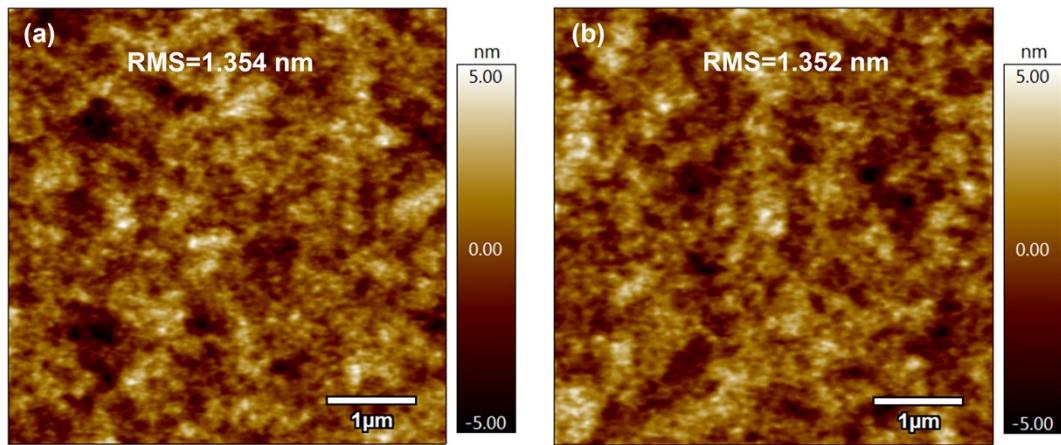
Shuai Huang,<sup>ab</sup> Lian Duan,<sup>\*ab</sup> and Dongdong Zhang,<sup>\*ab</sup>

<sup>a</sup> Key Lab of Organic Optoelectronics and Molecular Engineering of Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, China.

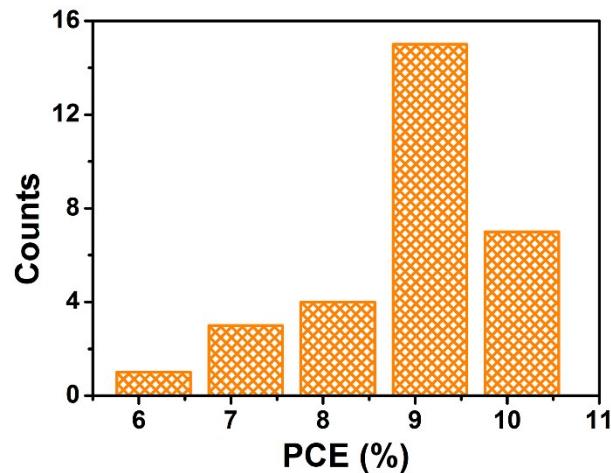
<sup>b</sup> Center of Flexible Electronics Technology, Tsinghua University, Beijing 100084, P. R. China.

\*Corresponding author: Lian Duan, and Dongdong Zhang

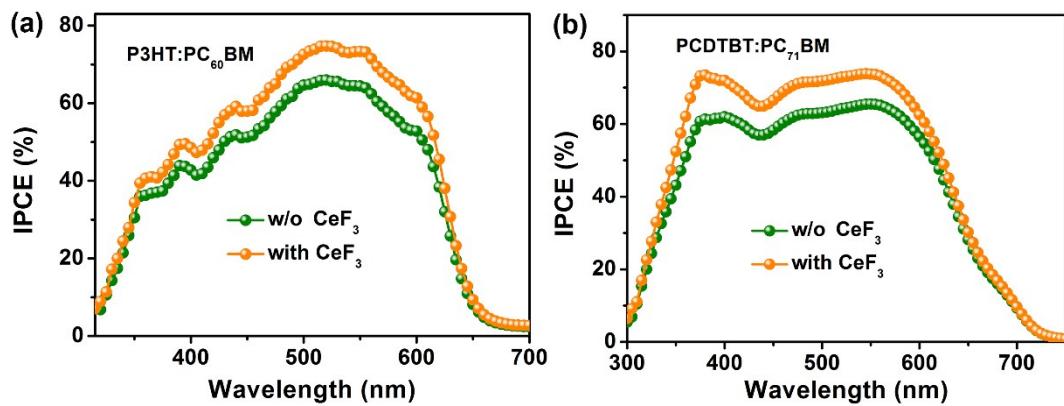
E-mail address: duanl@mail.tsinghua.edu.cn, ddzhang@mail.tsinghua.edu.cn.



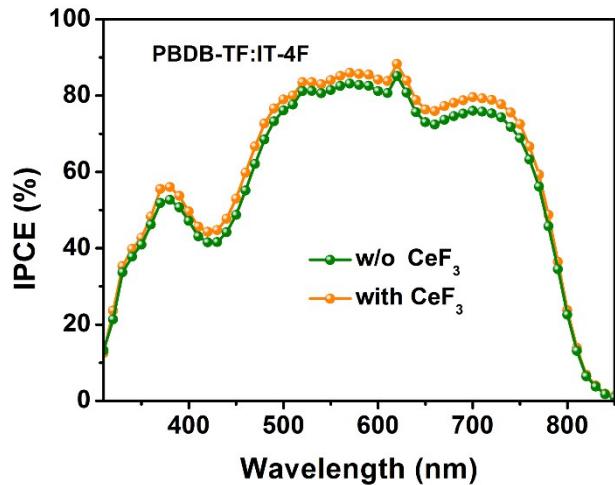
**Fig. S1** AFM images of ITO/ZnO/BHJ and ITO/ZnO/CeF<sub>3</sub>/BHJ films.



**Fig. S2** Histogram of PCE for the CeF<sub>3</sub>-based cells.



**Fig. S3** IPCE spectra of the solar cells based on the (a) P3HT:PC<sub>60</sub>BM and (b) PCDTBT:PC<sub>71</sub>BM active layers.



**Fig. S4** The corresponding IPCE spectra of the PBDB-TF:IT-4F-based PSCs.

**Table S1.** Device parameters extracted from  $J$ - $V$  characteristics.

Active layer	Interfacial layer	$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA cm}^{-2}$ )	FF (%)	PCE (%)	Integrated $J_{sc}$ ( $\text{mA cm}^{-2}$ )
P3HT:PC <sub>60</sub> BM	w/o CeF <sub>3</sub>	0.60	9.12	58.08	3.17	8.64
	with CeF <sub>3</sub> (5 Å)	0.63	10.56	64.13	4.26	9.95
PCDTBT:PC <sub>71</sub> BM	w/o CeF <sub>3</sub>	0.84	10.92	60.13	5.52	10.39
	with CeF <sub>3</sub> (5 Å)	0.89	12.31	63.95	7.02	11.68
PBDB-TF:IT-4F	w/o CeF <sub>3</sub>	0.81	20.58	70.86	11.81	18.67
	with CeF <sub>3</sub> (5 Å)	0.83	21.50	73.88	13.18	19.54