Supporting Information

Efficient Polymer Solar Cells Based on a Copolymer of Meta-alkoxy-phenyl-substituted Benzodithiophene and Thieno[3,4-b]thiophene

Wanbin Li†, Bing Guo†, Chunmei Chang†, Xia Guo†,* Maojie Zhang†,* Yongfang Li†‡*

† Laboratory of Advanced Optoelectronic Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China. *E-mail: mjzhang@suda.edu.cn, guoxia@suda.edu.cn

‡ Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. *E-mail: liyf@iccas.ac.cn

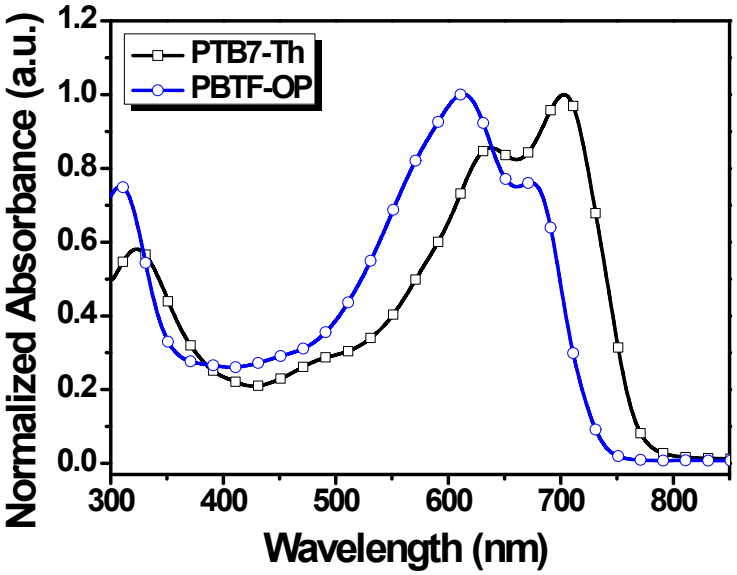


Figure S1. The absorption spectra of polymers in solution.

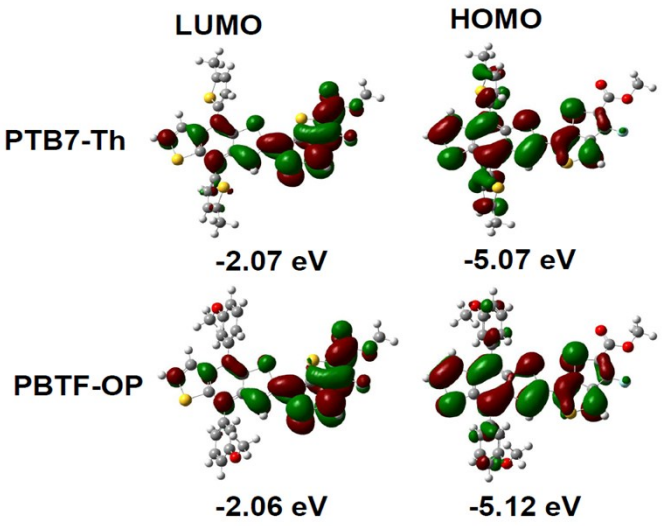


Figure S2. LUMO and HOMO levels for the polymer repeat units. Calculations were carried out by DFT/B3LYP/6-31G level on the polymers with the alkyl side chains replaced by methyl groups to simplify the calculation.

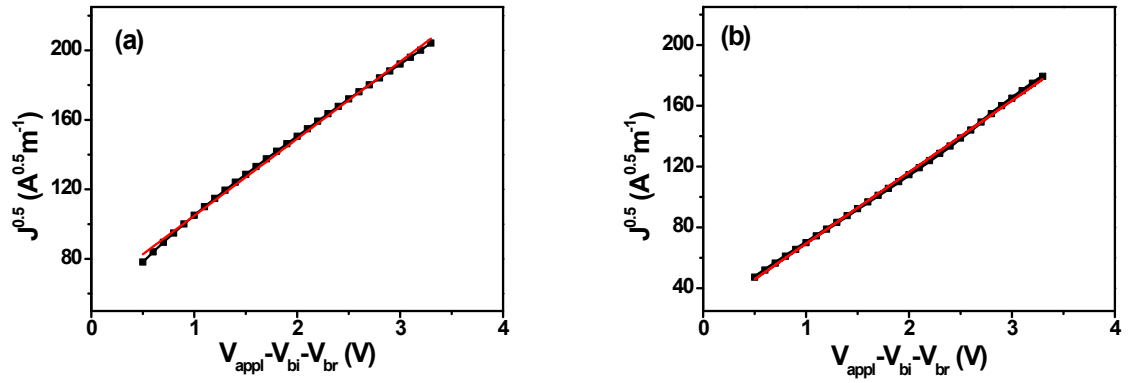


Figure S3. $J^{0.5}$ *vs* V plots for the hole-only diode fabricated with the structure of ITO/PEDOT: PSS/Polymer: $PC_{71}BM$/Au, (a) **PTB7-Th**, (b) **PBTF-OP**. The solid line is the fits of the data points.

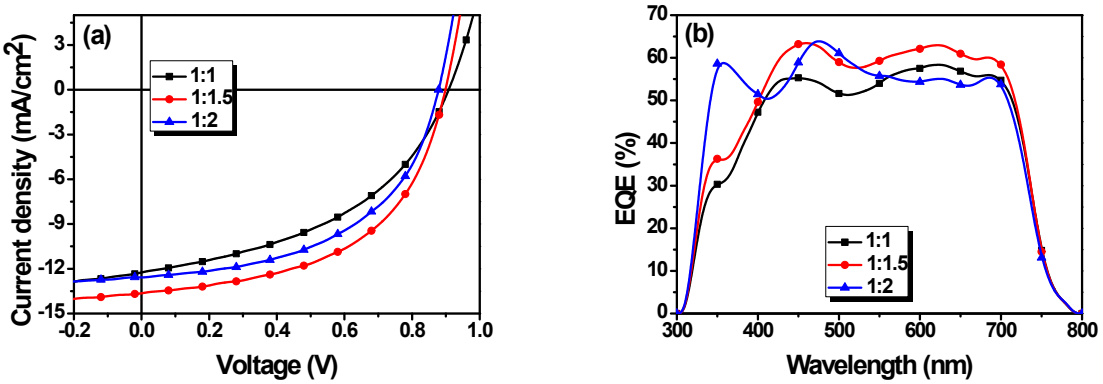
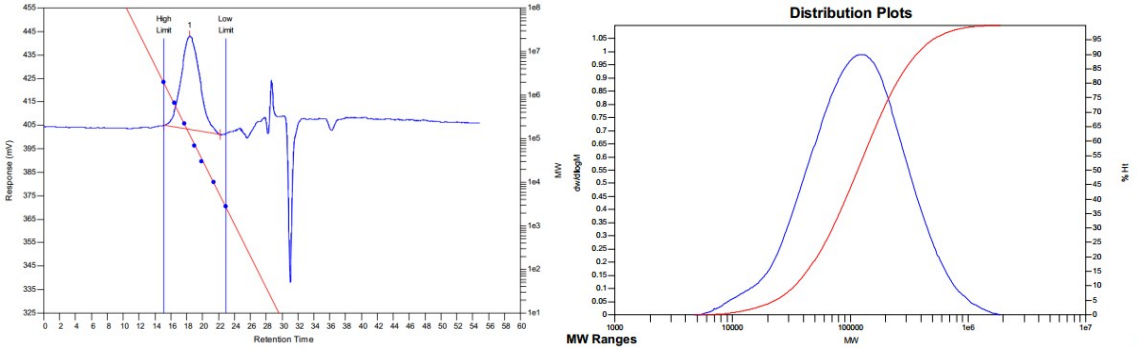
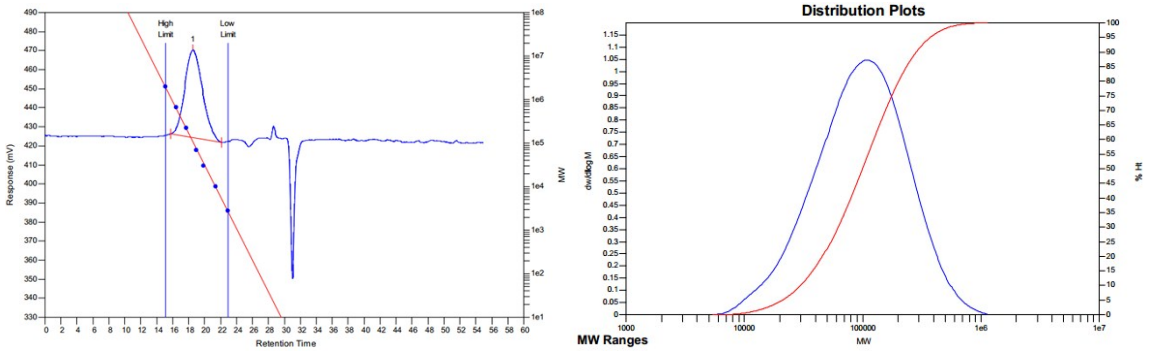


Figure S4. (a) *J-V* characteristics and (b) EQE curves of the PSCs based on the **PBTF-OP**: $PC_{71}BM$ blends with different weight ratios.

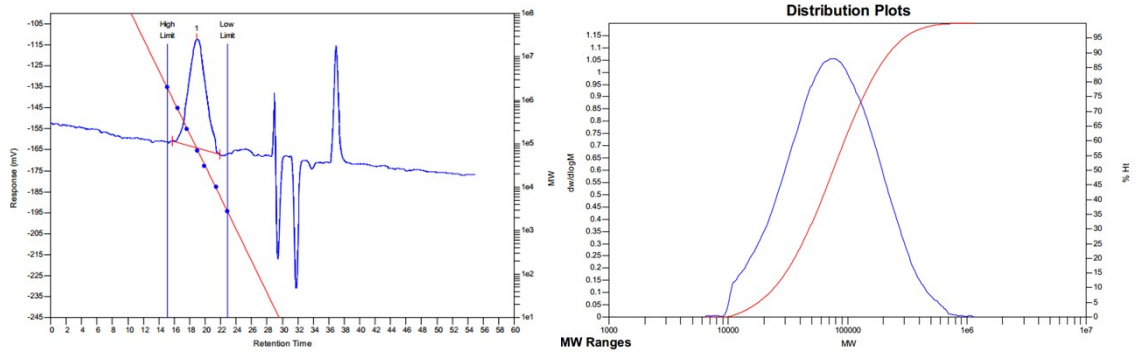
PBTF-OP-1



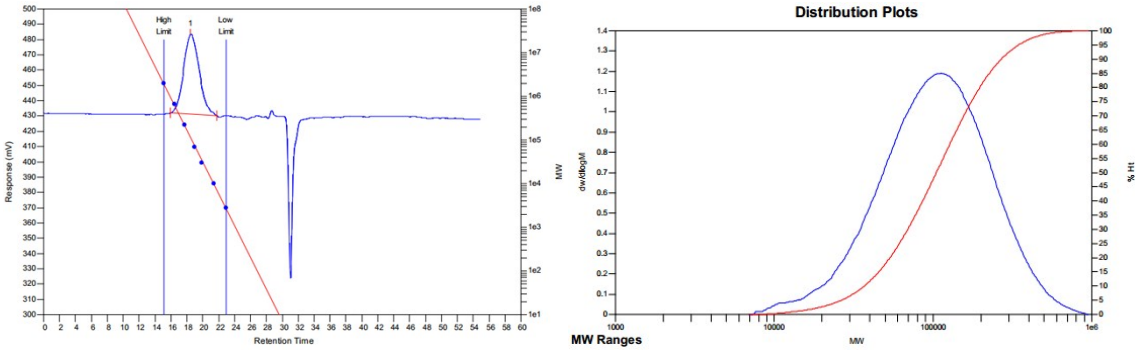
PBTF-OP-2



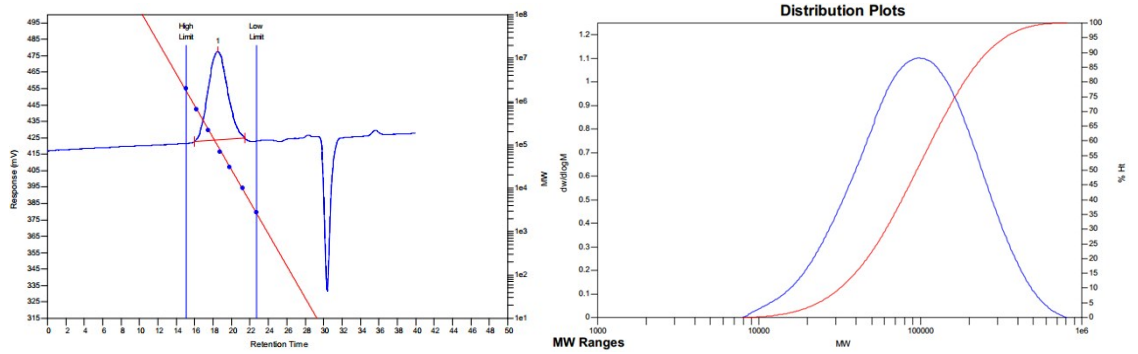
PBTF-OP-3



PTB7-Th-1



PTB7-Th-2



PTB7-Th-3

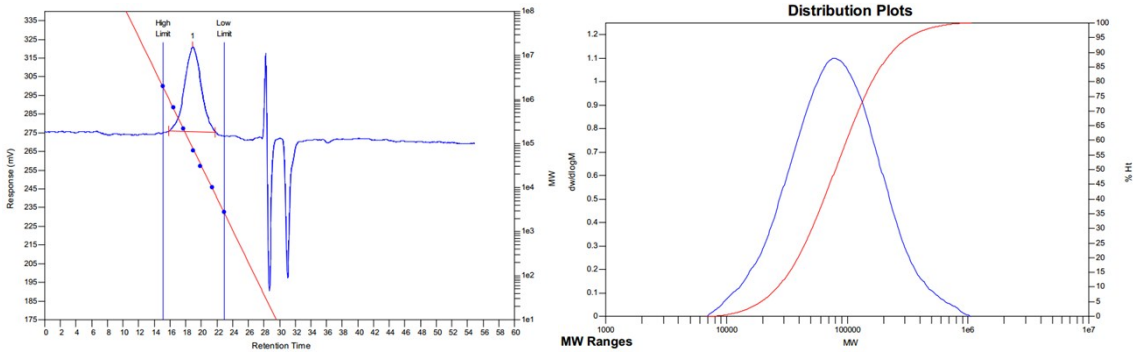


Figure S5. Gel permeation chromatography (GPC) trace of polymers. The molecular weight was evaluated with 1, 2, 4-tricholorobenzene as eluent at 160 °C.

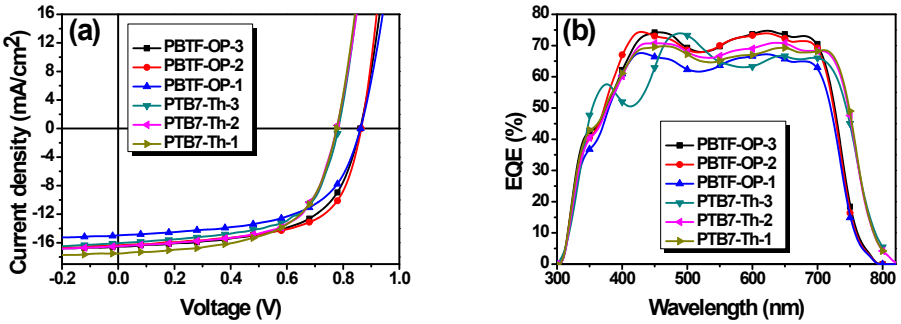


Figure S6. (a) *J-V* curves of the PSCs based on different molecular weight polymer: $PC_{71}BM$ (1:1.5, w/w) under the illumination of AM 1.5G, 100 mW/cm^2; (b) EQE curves of the corresponding devices.

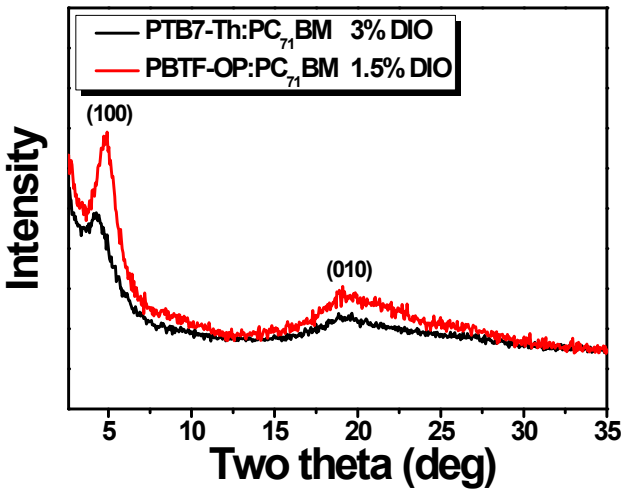


Figure S7. X-ray diffration patterns of polymer:$PC_{71}BM$ with DIO blend films casted from *o*-DCB on Si substrates.

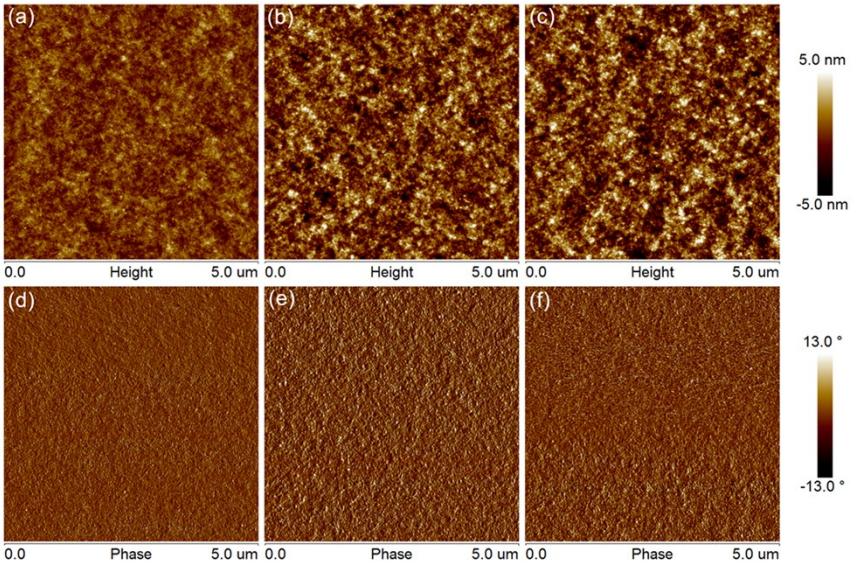


Figure S8. AFM height (top) and phase (bottom) images of **PBTF-OP**: $PC_{71}BM$ blend films: (a) and (d) for **PBTF-OP**: $PC_{71}BM$ without DIO, (b) and (e) for **PBTF-OP**: $PC_{71}BM$ with 1.5% DIO, (c) and (f) **PBTF-OP**: $PC_{71}BM$ with 3% DIO, (image size: 5 μm ×5 μm).

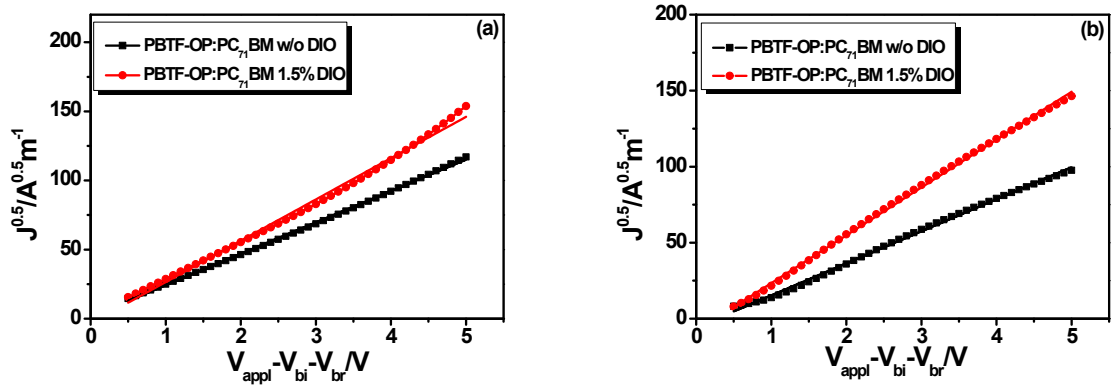


Figure S9. $J^{0.5}$ *vs* V plots and space-charge-limited current (SCLC) fittings of devices. (a) Hole-only SCLC devices: ITO/PEDOT: PSS/blend/ MoO_3/Al with **PBTF-OP**: PC71BM (without or with 1.5% DIO); (b) Electron-only SCLC devices: ITO/ZnO/blend/PFN/Al with **PBTF-OP**: $PC_{71}BM$ (without or with 1.5% DIO)

Table S1. The molecular weight of different batches of polymers and photovoltaic performance of the PSCs based on polymer: $PC_{71}BM$ (1:1.5, w/w) under the illumination of AM1.5G (100 mW/cm^2)

Polymers	M_n (kg/mol)	M_W (kg/mol)	PDI	Conditions	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF* (%)	PCE (%)
PBTF-OP-1	71.4	168.4	2.36	1.5% DIO	0.86	16.6	59.8	8.5
PBTF-OP-2	64.3	134.6	2.09	1.5% DIO	0.86	16.5	63.2	9.0
PBTF-OP-3	52.6	105.1	1.99	1.5% DIO	0.86	15.6	60.4	8.1
PTB7-Th-1	72.9	133.7	1.83	3% DIO	0.78	17.5	59.1	8.1
PTB7-Th-2	66.2	124.2	1.87	3% DIO	0.78	17.1	62.4	8.3
PTB7-Th-3	55.6	112.2	2.01	3% DIO	0.78	16.1	62.1	7.8

Table S2. The charge transport properties of the blend films of PBTF-OP: $PC_{71}BM$ under different conditions.

Conditions	μ_h (cm^2/Vs)	μ_e (cm^2/Vs)	μ_h/μ_e
w/o DIO	2.30×10^{-4}	3.61×10^{-4}	0.63
w 1.5% DIO	5.88×10^{-4}	4.60×10^{-4}	1.27