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Liquid crystal material as the third component for ternary polymer solar cells with efficiency of 10.83% and enhanced stability

Xiaoling Ma[†], Fujun Zhang*[,†], Qiaoshi An[†], Qianqian Sun[†], Miao Zhang[†] , Jianli Miao[†], Zhenghao Hu and Jian Zhang*[,‡]

[†]Key Laboratory of Luminescence and Optical Information, Ministry of Education, Beijing Jiaotong University, 100044, Beijing, People's Republic of China

[‡]School of Material Science and Technology, Guangxi Key Laboratory of Information Materials, Guilin University of Electronic Technology, 1Jinji Road, 541004, Guilin, Guangxi, People's Republic of China

Experimental

The donor polymer (PTB7-Th), small molecule (BTR) and acceptor fullerene derivatives ($PC_{71}BM$) were purchased from 1-Material, Inc. The mixed PTB7-Th:$PC_{71}BM$ (1:1.5, wt/wt) and BTR:$PC_{71}BM$ (1:1.5, wt/wt) powder was respectively dissolved in a mixed solvent (o-dichlorobenzene/chlorobenzene at volume ratio of 1:1) with 3 vol% 1,8-diiodooctane (DIO) to prepare 25 mg/mL binary blend solutions. Ternary blend solutions of PTB7-Th_{1-x}: BTR_x: $PC_{71}BM_{1.5}$ (x represents BTR contents in donors) were prepared by mixing the binary solutions with different volume ratios. PSCs were fabricated on cleaned Indium tin oxide (ITO) coated glass substrates. The substrates were cleaned via sequential sonication in detergent, de-ionized and ethanol and then blow-dried by high-purity nitrogen. All pre-cleaned ITO substrates were treated by oxygen plasma for 1 minute to improve its work function and clearance. For the inverted organic solar cells, the Zinc oxide (ZnO) solution was spin coated on ITO substrates at 4000 rounds per minute (RPM) for 30 s and annealed at 150 °C for 30 minutes in atmospheric air. Then ITO substrates coated with ZnO layer were transferred into a high-purity nitrogen-filled glovebox. The mixed binary and ternary solutions were respectively spin-coated at 1000 RPM for 40 s on top of ZnO layer to prepare the active layers. A thin molybdenum trioxide (MoO_3) layer (10 nm) and a silver (Ag) layer (100 nm) were sequentially deposited by thermal evaporation. For the conventional organic solar cells, Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) solution was spin-coated on ITO substrates at 5000 RPM for 40 s and dried at 150 °C for 10 min in atmospheric air. Then ITO substrates coated with PEDOT:PSS films were transferred into a high-purity nitrogen-filled glovebox. The mixed binary and ternary solutions were respectively spin-coated onto the PEDOT:PSS/ITO substrates at 1000 RPM for 40 s to prepare the active layers. The conjugated poly[(9,9-bis(3-(N,N-dimethylamino)-propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) was dissolved in methanol with the addition of 0.25 vol% acetic acid to prepare a 0.2 mg/mL solution. Then the prepared PFN solutions were spin-coated onto the active layers at 3000 RPM for 40 s. Finally, aluminum (Al) electrode were deposited by thermal evaporation. For each of the organic solar cells,

the contacts were deposited at the vacuum condition of 10^{-4} Pa. The active area is approximately 3.8 mm^2, which is defined by the overlapping area of ITO anode and Al cathode. The device configuration of inverted and conventional organic solar cells is ITO/ZnO (40 nm)/active layer (120 nm)/MnO_3 (10 nm)/Ag (100 nm) and ITO/PEDOT:PSS (40 nm)/active layer(120 nm)/PFN (10 nm)/Al (100 nm), respectively.

The current density-voltage (*J-V*) curves of all the organic solar cells were measured by a Keithley 2400 unit in high-purity nitrogen-filled glovebox. The AM 1.5G irradiation was provided by an XES-40S2 (SAN-EI ELECTRIC Co., Ltd) solar simulator (AAA grade, 70×70 mm^2 photobeam size) with light intensity of 100 mW/cm^2. The external quantum efficiency (EQE) spectra of organic solar cells were measured by a Zolix Solar Cell Scan 100. The absorption spectra of films were measured with a Shimadzu UV-3101 PC spectrometer. Photoluminescence (PL) spectra of films were measured by a HORIBA Fluorolog®-3 spectrofluorometer system. Grazing incidence X-ray diffraction (GIXD) images were measured by a 5-circle Huber diffractometer at the Beijing Synchrotron Radiation Facility (BSRF). A bent triangle silicon crystal was used to select the X-rays of a wavelength of 1.54 Å. A grazing incidence angle of 0.4° was chosen to increase GIXD peak intensity for investigating the crystallinity and orientation that prevail throughout the active layers. Transmission electron microscopy (TEM) images of active layers were obtained by a JEOL JEM-1400 transmission electron microscope operated at 80 kV. Time-resolved transient photoluminescence (TRPL) spectra were obtained using a FluoroCube-01-NL and FluoroCub-NL from Jobin Yvon, and the excitation light was provided by a NanoLED-460 with pulse width < 1.3 ns and power 7 pJ/pulse.

Table S1. Summarize of ternary organic solar cells based on PTB7-Th:$PC_{71}BM$ binary system.

Third Component	Weight Ratio [wt%]	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%]	Ref.
PffBT4T-2OD	0	0.786	17.79	66.61	9.32	1
	15	0.776	19.02	72.62	10.72	
BQR	0	0.8	17.2	69	9.6	2
	15	0.8	19.8	68	10.7	
P-DTS($FBTTH_2$)$_2$	0	0.805	17.53	65.26	9.20	3
	15	0.755	18.44	75.27	10.5	
PDBT-T1	0	0.80	16.20	68.70	8.90	4
	20	0.81	18.0	70.1	10.2	
PDVT-10	0	0.79	17.11	65.10	8.75	5
	0.5	0.78	18.73	69.00	10.08	
PID2	0	0.75	14.29	70.30	7.88	6
	20	0.78	16.68	70.80	9.20	

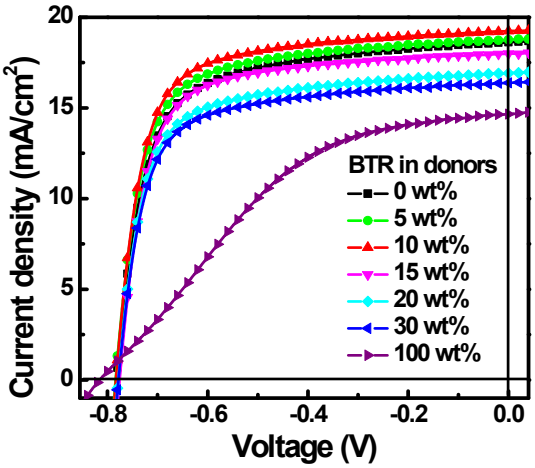

Fig. S1 *J-V* curves of inverted PSCs with different BTR contents in donors under AM 1.5G illumination with light intensity of 100 mW/cm^2.

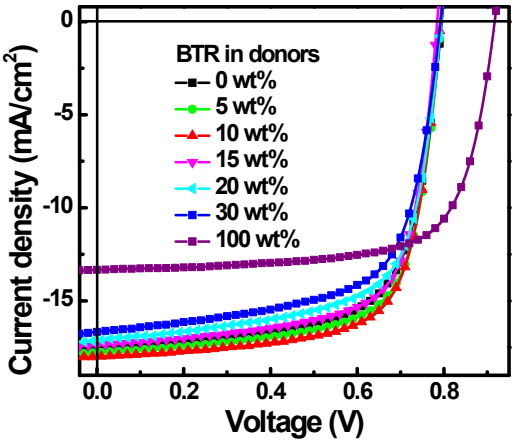

Fig. S2 *J-V* curves of conventional PSCs with different BTR contents in donors under AM 1.5G illumination with light intensity of 100 mW/cm^2.

Table S2. Key photovoltaic parameters of conventional PSCs with different BTR contents in donors.

BTR contents (wt %)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
0	17.56	0.79	68.45	9.49
5	17.78	0.79	70.38	9.88
10	18.01	0.79	71.03	10.11
15	17.39	0.78	69.94	9.48
20	17.12	0.79	67.74	9.16
30	16.66	0.79	65.99	8.69
100	13.33	0.92	71.08	8.72

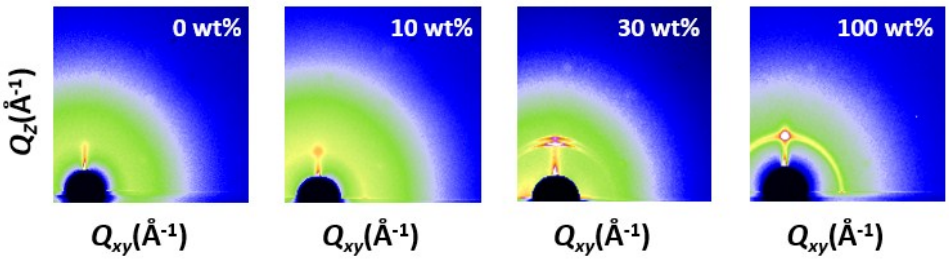

Fig. S3 2D-GIXD patterns of blend films with different BTR contents in donors.

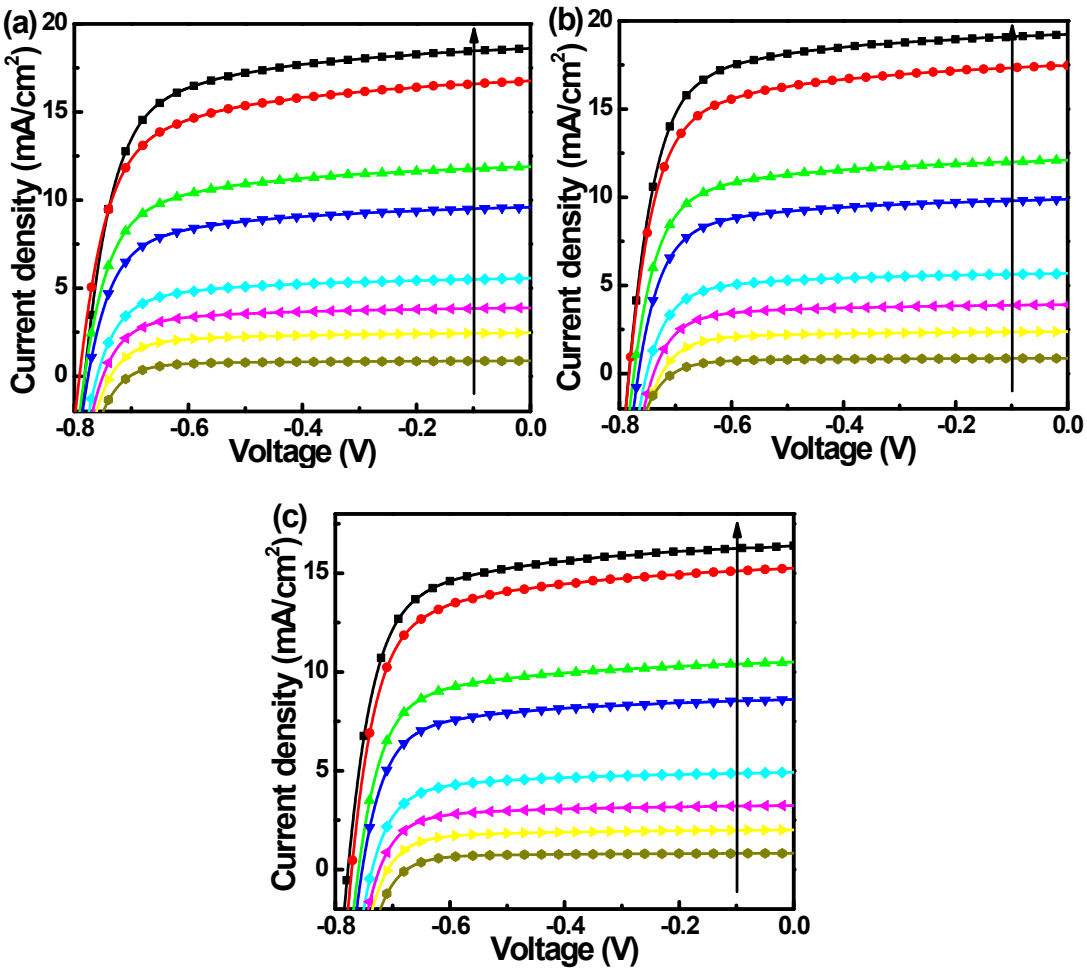

Fig. S4 The *J-V* curves of the PSCs with 0 wt% (a), 10wt% (b), and 30 wt% (c) BTR contents in donors under different light illumination intensity (100, 80, 50, 40, 25, 12.5, 8, 5 mW/cm^2), obtained from standard AM 1.5G (100 mW/cm^2) illumination using a set of neutral optical filters.

Table S3. Key photovoltaic parameters of inverted PSCs with different storage time in high-purity nitrogen-filled glovebox.

Time (hour)	without BTR				10 wt% BTR			
	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
0	18.61	0.78	69.46	10.08	19.23	0.78	72.21	10.83
12	18.16	0.80	66.11	9.61	18.73	0.79	69.78	10.33
36	18.05	0.80	66.74	9.64	18.51	0.79	69.81	10.21

96	17.84	0.80	65.70	9.38	18.39	0.79	68.59	9.97
108	17.61	0.80	65.62	9.24	18.09	0.79	68.80	9.83
156	17.45	0.80	65.57	9.15	18.04	0.79	68.48	9.76
180	17.08	0.81	64.86	8.97	17.78	0.80	67.57	9.61
204	17.44	0.80	65.28	9.11	18.12	0.79	68.17	9.76
300	16.70	0.80	63.03	8.60	17.60	0.79	67.91	9.44
380	16.82	0.79	63.82	8.48	17.36	0.78	67.72	9.17
440	16.22	0.79	62.42	8.00	17.28	0.78	66.23	8.93
512	15.80	0.79	62.15	7.76	17.12	0.78	66.35	8.86

Table S4. Key photovoltaic parameters of conventional PSCs with different storage time in high-purity nitrogen-filled glovebox.

Time (hour)	without BTR				10 wt% BTR			
	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
0	17.56	0.79	68.45	9.49	18.01	0.79	71.03	10.11
12	16.79	0.79	65.97	8.75	17.84	0.79	69.30	9.77
60	15.88	0.79	63.07	7.91	16.61	0.79	67.99	8.92
80	15.40	0.79	62.98	7.66	16.41	0.79	66.14	8.57
152	15.26	0.78	61.09	7.27	16.37	0.79	64.78	8.38
176	14.86	0.79	60.73	7.13	16.26	0.79	62.18	7.99
208	14.84	0.79	59.64	7.00	16.10	0.79	61.73	7.85
280	14.49	0.79	58.35	6.68	15.63	0.79	61.21	7.56
352	14.20	0.79	58.06	6.51	15.45	0.78	60.17	7.25
500	13.78	0.79	57.13	6.22	14.95	0.79	60.12	7.10

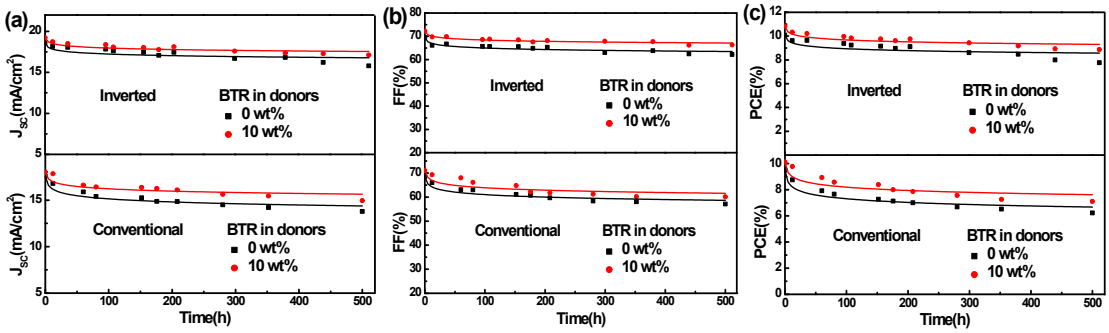

Fig. S5 Photovoltaic parameters as the function of storage time (t) (Scatters: measured values; Solid lines: fitted curves).

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