Supporting Information

Stable large area organic solar cells realized by using random terpolymers donors combined with a ternary blend

Xiaopeng Xu,[a] Zhaozhao Bi,[b] Wei Ma,[b,*] Guangjun Zhang,[a] He Yan,[c,*] Ying Li,[a] and Qiang Peng[a,*]

[a] Key Laboratory of Green Chemistry and Technology of Ministry of Education, College of Chemistry and State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610064, P. R. China

[b] State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, P. R. China

[c] Department of Chemistry and Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration & Reconstruction, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR, 999077

*To whom correspondence should be addressed: Tel: +86-28-86510868; fax: +86-28-86510868; e-mail: msewma@mail.xjtu.edu.cn; hyan@ust.hk; qiangpengjohnny@yahoo.com

1. Materials and methods

Materials: ITCPTC was purchased from Derthon Optoelectronic Materials Science Technology. The terpolymers of PT1, PT3 and PT5, and the small molecular acceptor of meta-TrBRCN were synthesized according to our previously reports.[1,2] All the other chemicals were purchased from Aladdin, Adamas, Sigma-Aldrich, and Alfa Asear Chemical Co., and used without further purification. All solvents were freshly distilled immediately prior to use.

Methods: UV-vis spectra were obtained on a Hitachi U2910 spectrophotometer. The UPS measurements were conducted on a Thermo Scientific ESCALAB 250Xi photoelectron spectroscope. 2D-GIWAXS measurements were performed at beamline 7.3.3 8 at the Advanced Light Source. Samples were prepared on the Si substrates using identical blend solutions as those used in PSC devices. The 10 keV X-ray beam was incident at a grazing angle of 0.12°-0.16°, selected to maximize the scattering intensity from the samples. The scattered X-rays were detected using a Dectris Pilatus 2M photon counting detector. R-SoXS transmission measurements were performed at beamline 11.0.1.2 at the Advanced Light Source (ALS). AFM images were obtained by using a Bruker Inova atomic microscope in tapping mode. Charge carrier mobiltities were tested using the SCLC method, which is described by $J=9\varepsilon_0\varepsilon_r\mu V^2/8L^3$. J is the current density, L is the film thickness of the active layer, μ is the hole or electron mobility, ε_r is the relative dielectric constant of the transport medium, ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1}), V is the internal voltage in device and $V = V_{appl}-V_{bi}-V_a$, where V_{appl} is the applied voltage to the device, V_{bi} is the built-in

voltage and V_a is the voltage drop.

2. Device fabrication and measurement

The patterned tndium tin oxide (ITO, sheet resistance = 15 Ω square^{-1}) glass substrates were sequentionally ultrasonicated with detergent, deionized water, acetone and isopropanol. Then, the ITO glasses were treated with UV for 30 min in a UV-ozone chamber. The zinc oxide (ZnO) precursor solution (diethylzinc solution 2M in toluene, diluted by tetrahydrofuran) was spin-coated on the surface of ITO substrate at a spinning rate of 5000 rpm for 30 s in dry air followed by baked in dried air at 180 °C for 30 min to form a thin ZnO film (~ 30 nm) as an electron extraction layer. The terpolymer:ITCPTC$_x$:meta-TrBRCN$_{(1-x)}$ solution (1:x:(1-x), w/w, 20 mg/mL in chlorobenzene) was prepared and stirred overnight before used and 0.5 v% of DIO was used as the solvent additive. The active blend solution was spin-coated on the top of ZnO layer at a speed of 2000 rpm for 60 s to form a 100 nm thickness of active layer. A molybdenum trioxide (MoO_3, 10 nm) and a silver anode (Ag, 100 nm) were finally deposited onto the top of the active layer in an evaporation chamber under high vacuum ($\leqslant 10^{-6}$ mbar). The device area was exactly fixed at 4.00 mm^2 for small area devices and 1.0 cm^2 for large area devices. The *I-V* characterization was performed on a computer-controlled Keithley 2400 Source under AM1.5G (100 mW cm^{-2}) using a solar simulator (XES-70S1, SAN-EI), which was calibrated by a standard Si solar cell (AK-200, Konica Minolta, INC.). The EQE values were measured with a Newport QE test Model 77890 (Newport Co. Ltd.) during illumination with monochromatic light from a xenon lamp. All fabrication and characterization processes, except for the ZnO

layer preparation and EQE measurements, were conducted in a high purity argon filled glove box (<0.1 ppm O_2 and H_2O).

3. Supplementary figures

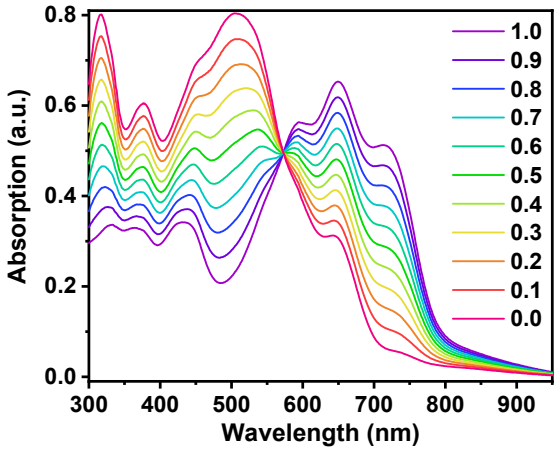

Fig. S1 UV-vis absorption spectra of PT1:ITCPTC$_x$:meta-TrBRCN$_{(1-x)}$ blends.

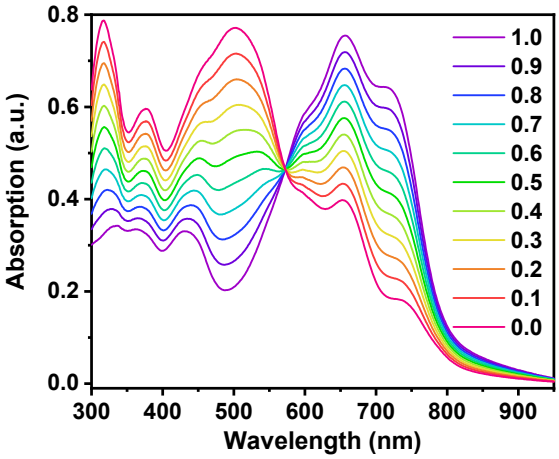

Fig. S2 UV-vis absorption spectra of PT3:ITCPTC$_x$:meta-TrBRCN$_{(1-x)}$ blends.

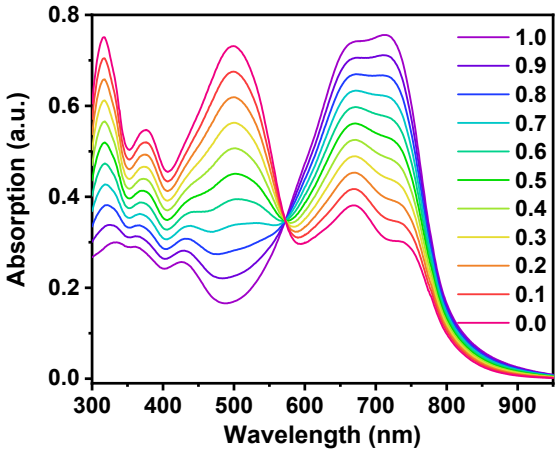

Fig. S3 UV-vis absorption spectra of PT5:ITCPTC$_x$:meta-TrBRCN$_{(1-x)}$ blends.

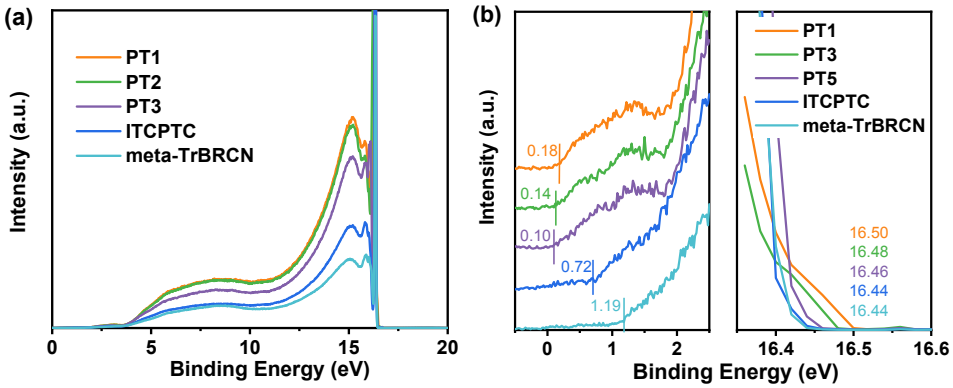

Fig. S4 UPS spectra of the terpolymers and the acceptor materials.

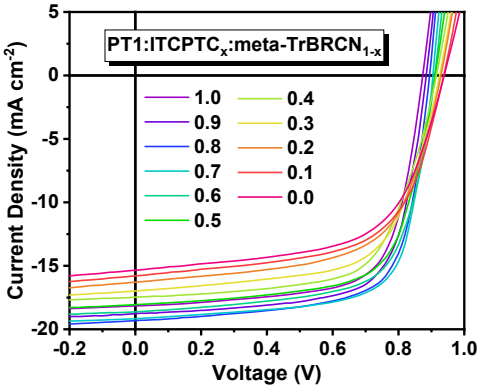

Fig. S5 *J-V* curves of the PT1:ITCPTC$_x$:meta-TrBRCN$_{1-x}$ based ternary blend devices.

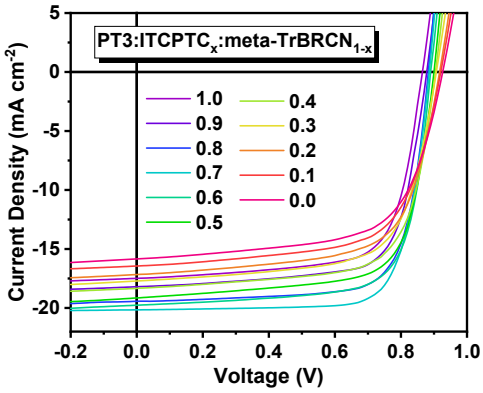

Fig. S6 *J-V* curves of the PT3:ITCPTC$_x$:meta-TrBRCN$_{1-x}$ based ternary blend devices.

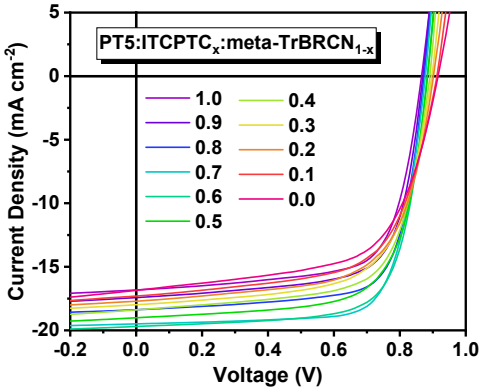

Fig. S7 *J-V* curves of the PT5:ITCPTC$_x$:meta-TrBRCN$_{1-x}$ based ternary blend devices.

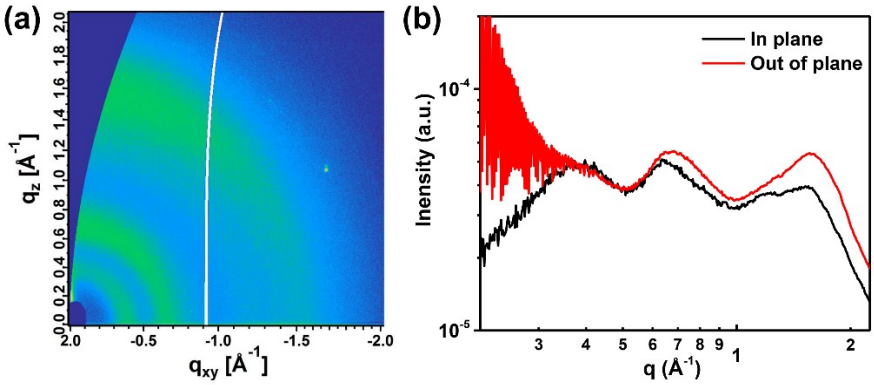

Fig. S8 (a) 2D-GIWAXS pattern of meta-TrBRCN. (b) In-plane and out-of-plane line-cuts.

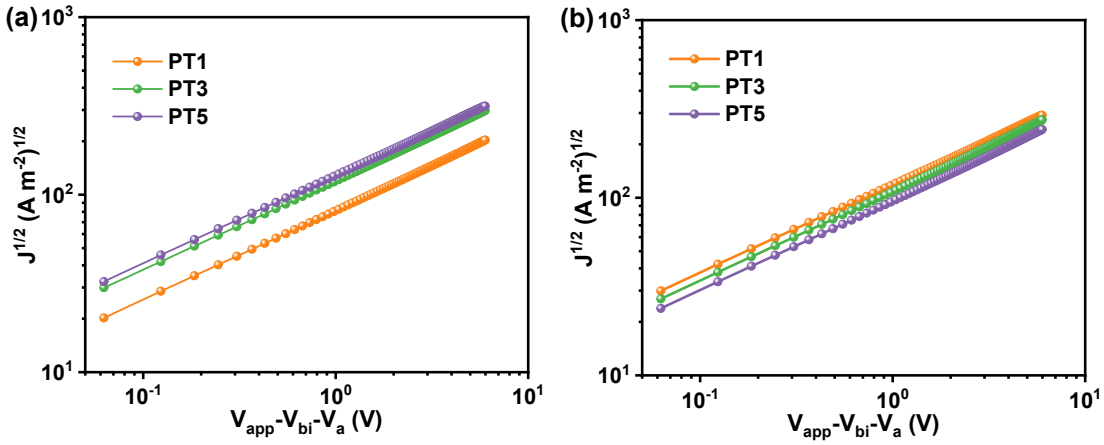

Fig. S9 $J^{1/2}$-V curves of the terpolymer:ITCPTC$_{0.7}$:meta-TrBRCN$_{0.3}$ based ternary blend devices with a hole-only device structure of ITO/PEDOT:PSS/ active layer/MoO_3/Au (a) and an electron-only device structure of Al/active layer/Al (b).

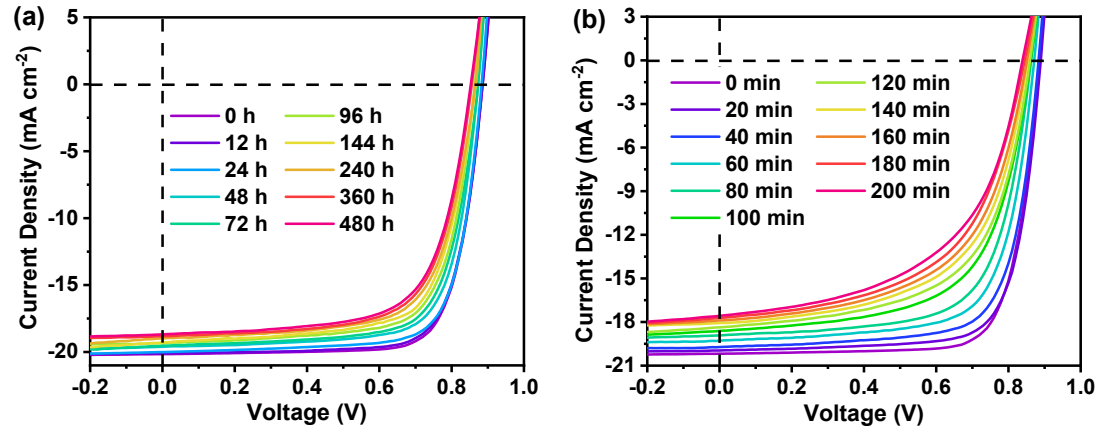

Fig. S10 J-V curves of the PT3:ITCPTC$_{0.7}$:meta-TrBRCN$_{0.3}$ based ternary blend devices (a) stored in nitrogen filled glove box for different times and (b) heated at 120 °C for different times.

4. Supplementary Tables

Table S1 Photovoltaic performances of PT1:ITCPTC$_x$:meta-TrBRCN$_{(1-x)}$ based ternary blend devices under AM 1.5G 100 mW cm^{-2} illumination.

ITCPTC content	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
1.0	0.874 (0.870±0.004)[a]	18.16 (17.74±0.38)	69.4 (68.9±0.5)	11.01 (10.66±0.35)
0.9	0.885 (0.877±0.008)	18.74 (18.40±0.34)	69.7 (69.3±0.4)	11.56 (11.18±0.38)
0.8	0.894 (0.883±0.011)	19.32 (18.99±0.33)	70.1 (69.7±0.4)	12.11 (11.69±0.52)

0.7	0.903 (0.891±0.012)	19.17 (18.87±0.30)	70.9 (70.4±0.5)	12.27 (11.84±0.43)
0.6	0.909 (0.897±0.012)	18.63 (18.28±0.35)	68.0 (67.5±0.5)	11.52 (11.07±0.45)
0.5	0.912 (0.903±0.009)	18.06 (17.69±0.37)	67.3 (66.9±0.4)	11.08 (10.69±0.39)
0.4	0.916 (0.909±0.007)	17.47 (17.13±0.34)	65.1 (64.8±0.3)	10.41 (10.09±0.32)
0.3	0.924 (0.916±0.008)	16.98 (16.59±0.39)	63.9 (63.6±0.3)	10.03 (9.66±0.37)
0.2	0.929 (0.922±0.007)	16.29 (15.93±0.36)	62.1 (61.7±0.4)	9.40 (9.06±0.34)
0.1	0.936 (0.928±0.008)	15.79 (15.42±0.37)	61.8 (61.3±0.5)	9.13 (8.77±0.36)
0.0	0.939 (0.935±0.004)	15.35 (15.00±0.35)	60.7 (60.2±0.5)	8.75 (8.44±0.31)

[a]Average value with standard deviation from 20 devices.

Table S2 Photovoltaic performances of PT3:ITCPTC$_x$:meta-TrBRCN$_{(1-x)}$ based ternary blend devices under AM 1.5G 100 mW cm^{-2} illumination.

ITCPTC content	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
1.0	0.865 (0.861±0.005)[a]	17.49 (17.20±0.29)	70.7 (70.2±0.5)	10.69 (10.40±0.29)
0.9	0.876 (0.867±0.009)	18.20 (17.89±0.31)	72.0 (71.5±0.5)	11.48 (11.06±0.42)
0.8	0.880 (0.875±0.007)	19.43 (19.10±0.33)	74.7 (74.3±0.4)	12.78 (12.39±0.39)
0.7	0.886 (0.879±0.007)	20.16 (19.88±0.28)	76.3 (75.7±0.6)	13.63 (13.23±0.40)
0.6	0.890 (0.885±0.005)	19.76 (19.42±0.34)	73.0 (72.5±0.5)	12.83 (12.46±0.37)
0.5	0.899 (0.891±0.008)	19.15 (18.85±0.30)	71.0 (70.6±0.4)	12.22 (11.85±0.36)
0.4	0.905 (0.897±0.008)	18.34 (18.01±0.33)	69.8 (69.4±0.4)	11.59 (11.21±0.38)
0.3	0.908 (0.903±0.005)	17.72 (17.36±0.36)	67.6 (67.1±0.5)	10.88 (10.52±0.36)
0.2	0.915 (0.909±0.006)	17.17 (16.85±0.32)	66.5 (66.1±0.4)	10.45 (10.12±0.33)
0.1	0.921 (0.915±0.006)	16.44 (16.09±0.35)	65.5 (65.0±0.5)	9.92 (9.57±0.35)
0.0	0.926 (0.921±0.05)	15.84 (15.53±0.31)	64.6 (64.1±0.5)	9.47 (9.24±0.23)

[a]Average value with standard deviation from 20 devices.

Table S3 Photovoltaic performances of PT5:ITCPTC$_x$:meta-TrBRCN$_{(1-x)}$ based ternary blend devices under AM 1.5G 100 mW cm^{-2} illumination.

ITCPTC content	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
1.0	0.865	16.82	69.8	10.15
	(0.857±0.008)[a]	(16.47±0.35)	(69.4±0.4)	(9.08±0.36)
0.9	0.869	17.42	70.6	10.69
	(0.862±0.007)	(17.08±0.34)	(70.3±0.3)	(9.64±0.39)
0.8	0.874	18.38	72.8	11.70
	(0.867±0.007)	(18.08±0.30)	(72.4±0.4)	(10.67±0.37)
0.7	0.877	19.49	74.4	12.72
	(0.872±0.005)	(19.21±0.28)	(73.9±0.5)	(11.79±0.40)
0.6	0.882	19.69	72.2	12.53
	(0.878±0.004)	(19.38±0.31)	(71.9±0.3)	(11.64±0.38)
0.5	0.885	19.01	69.2	11.65
	(0.883±0.003)	(18.66±0.35)	(68.9±0.3)	(10.94±0.39)
0.4	0.891	18.39	68.3	11.19
	(0.888±0.004)	(18.07±0.32)	(67.8±0.5)	(10.50±0.39)
0.3	0.897	17.98	65.7	10.59
	(0.894±0.003)	(17.64±0.34)	(65.3±0.4)	(10.06±0.38)
0.2	0.902	17.71	65.1	10.40
	(0.899±0.004)	(17.34±0.37)	(64.8±0.3)	(9.88±0.37)
0.1	0.910	17.30	63.7	10.03
	(0.904±0.006)	(16.97±0.33)	(63.2±0.5)	(9.52±0.37)
0.0	0.916	16.85	62.3	9.61
	(0.910±0.006)	(16.51±0.34)	(61.9±0.4)	(9.26±0.36)

[a]Average value with standard deviation from 10 devices.

Table S4 Photovoltaic performances for PT3:ITCPTC$_{0.7}$:meta-TrBRCN$_{0.3}$ based ternary blend devices stored in nitrogen filled glove box for different times.

Time (h)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
0	0.886	20.16	76.3	13.63
12	0.886	20.10	75.5	13.44
24	0.883	20.00	75.2	13.28
48	0.873	19.61	73.7	12.61
72	0.873	19.61	71.8	12.29
96	0.867	19.32	71.4	11.96
144	0.866	19.29	70.0	11.70
240	0.864	18.98	68.8	11.28
360	0.856	18.82	68.4	11.02
480	0.853	18.68	67.7	10.79

Table S5 Photovoltaic performances for PT3:ITCPTC$_{0.7}$:meta-TrBRCN$_{0.3}$ based ternary blend devices heated at 120 °C for different times.

Time (min)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
0	0.886	20.18	76.0	13.59
20	0.890	20.00	75.2	13.39
40	0.881	19.71	73.9	12.83
60	0.869	19.28	71.1	11.91
80	0.863	18.92	67.0	10.94
100	0.862	18.62	63.1	10.12
120	0.857	18.37	60.5	9.52
140	0.851	18.07	58.6	9.01
160	0.848	17.89	57.2	8.68
180	0.844	17.71	55.9	8.36
200	0.840	17.60	54.6	8.07

5. References

1 Xu, X. P.; Zhang, G. J.; Zhao, Y. Z.; Liu, J.; Li, Y.; Peng, Q. Highly Efficient Random Terpolymers for Photovoltaic Applications with Enhanced Absorption and Molecular Aggregation. *Chin. J. Polym. Sci.* 2017, **35**, 249-260.

2 Wu, W. L.; Zhang, G. J.; Xu, X. P.; Wang, S. C.; Li, Y.; Peng, Q. Wide Bandgap Molecular Acceptors with a Truxene Core for Efficient Nonfullerene Polymer Solar Cells: Linkage Position on Molecular Configuration and Photovoltaic Properties. *Adv. Funct. Mater.* 2018, **28**, 1707493.