Supporting Information

Employing structural similar acceptor as crystalline modulator to construct high efficiency ternary organic solar cells

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Instruments and measurements

The thermal property of the polymers was measured by thermogravimetric analysis (TGA) in a nitrogen atmosphere at a heating rate of 20 ℃ min^{-1}.The number-average molecular weight (Mn) and polydispersity index (PDI) were measured by gel permeation chromatography (GPC) using THF as the eluent and polystyrene as the internal standard. The molecular weight was obtained by gel permeation chromatography (GPC) using chlorobenzene as the eluent, and the GPC column was kept at 150 °C in order to break the molecular aggregates. UV-vis absorption spectra were performed on Lambda 25 spectrophotometer. Current density-voltage (*J-V*) curves of the solar cells were characterized by a Keithley 2420 source meter. A standard silicon solar cell was used to calibrate the light intensity. The external quantum efficiencies (EQEs) of devices were measured using a certified Newport incident photon conversion efficiency (IPCE) measurement system. Atomic force microscopy (AFM) was performed by tapping mode under an argon atmosphere, using an Agilent 5400 instrument. Transmission electron microscopy (TEM) were performed by a HITACHI H-7650 electron microscope at an accelerate voltage of 100 kV.

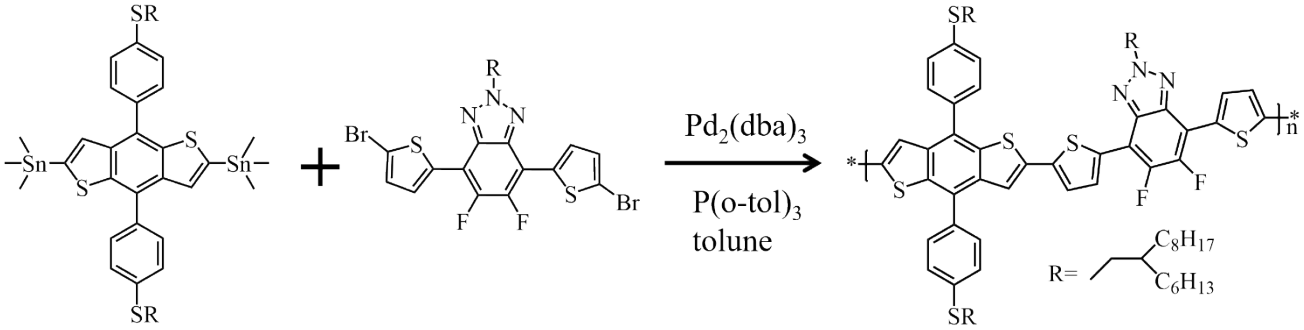
Materials and regiments

The monomer BDTPSSn was synthesized according to the literature[1]. 4,7-bis(5-bromothiophen-2-yl)-5,6-difluoro-2-(2-hexyldecyl)-2H-benzo[d][1,2,3]triazole was purchased from Derthon Optoelectronic Materials Sci. Tech. Co., Ltd. Tetrahydrofuran and toluene are dried over Na/benzophenone and then distilled before use. Other chemicals were all purchased commercially and used as received.

Synthesis of PBTA-PS-PS

Compounds BDTPSSn (118.1 mg,0.1 mmol), FTAZ-Br (70.2 mg, 0.1 mmol), $Pd_2(dba)_3$ (1.8 mg, 0.002 mmol), and $P(o\text{-}tol)_3$ (3.6 mg, 0.012 mmol) were added into a flask. The flask was subjected to three

successive cycles of vacuum followed by refilling with argon. Then, 5mL of dry toluene was added. he reaction mixture was heated to 110 °C carefully for 3 h under argon protection. Then the mixture was cooled to room temperature, and the polymer was precipitated by addition of methanol, filtered, and purified by Soxhlet extraction with methanol, chloroform, and chlorobenzene, respectively. The CB solution was concentrated by evaporation and then precipitated into methanol. The purple solid was filtered to yield the desired polymer PBTA-PS-PS (110 mg, 78% yield). Mn: 32.1 kDa, PDI: 2.76.



Scheme 1. Synthesis route of PBTA-PS-PS.

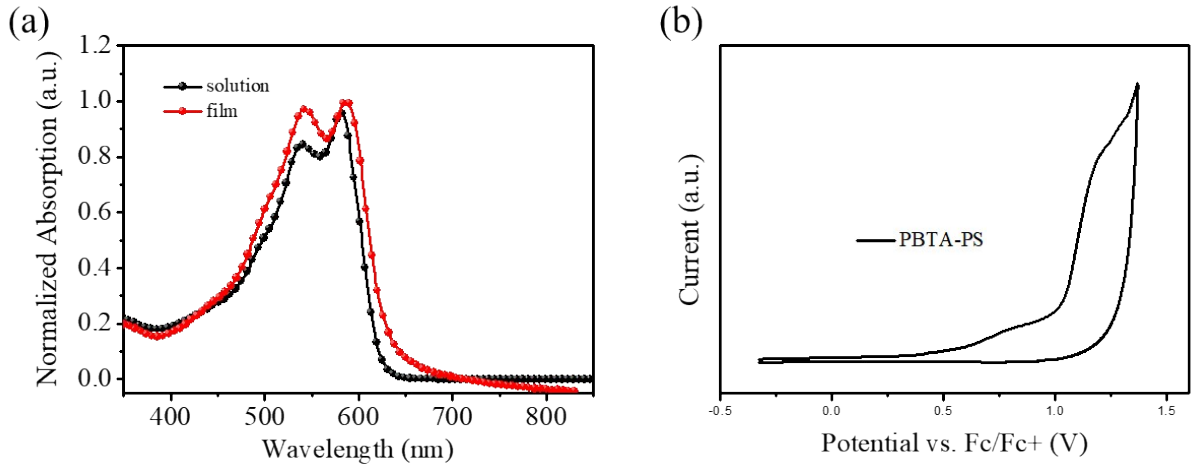


Figure S1. (a) Normalized absorption spectra of PBTA-PS-PS in film and solution states. (b) The cyclic voltammetry graph of PBTA-PS-PS.

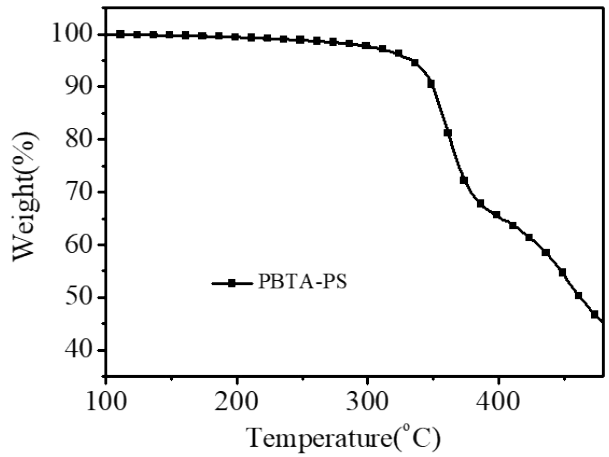


Figure S2. TGA plot of PBTA-PS-PS.

Fabrication and characterization of devices

The binary and ternary polymer solar cells (PSCs) were prepared using the conventional device structure of indium tin oxides (ITO) glass/poly(3,4-ethylenedioxythiopene):poly(styrenesulfonate) (PEDOT:PSS)/PBTA-PS-PS:Acceptors/perylene diimide functionalized with amino N-oxide (PDINO)/Al. The patterned ITO glass was sequentially cleaned in detergent, demonized water, acetone and isopropanol using the ultrasonic cleaning machine. Each step takes 13 mins. Then the ITO substrates were treated with oxygen plasma for 6 mins. The plasma treated ITO substrates were spin coated with PEDOT:PSS (Baytron PVP Al 4083) for about 30 nm followed by annealing at 160 °C for 20 min. Subsequently, the substrates were transferred to a glove box filled with nitrogen. The chlorobenzene (CB) solution (10mg/mL, polymer) of PBTA-PS-PS:ITIC, PBTA-PS-PS:IT-4F and PBTA-PS-PS:ITIC:IT-4F with different weight ratios (1:1, 1:1.2, 1:1.5 for binary solution and 1:1.2:0.1, 1:1.2:0.2, 1:1.2:0.3, 1:1.2:0.4, 1:1.2:0.5 for ternary blend solution) were stirred at room temperature overnight before spin coating. The binary and ternary blend film was spin coated on PEDOT:PSS modified ITO glass to fabricate the active layer (~100 nm) at 1750 rpm for 40 seconds. The ternary blend films were then treated by the solvent vapor annealing (SVA) under CB atmosphere for 10 mins. The PDINO, which serves as the electron-transporting layer, were spin coated onto the active layer at 3000 rpm for 10 s. Finally, the samples were transferred to a vacuum chamber, where Al (30 nm) was deposited in high vacuum (10^{-5} Pa) via a mask that control the active area of 0.1 cm^2. Over 16 devices were

prepared in the same condition. The *J-V* curves of PBTA-PS-PS:ITIC with different weight ratios are shown in Figure S3, the corresponding photovoltaic parameters are summarized in table S1. The *J-V* curves of ternary PSCs with different weight ratios are shown in Figure S4., the detailed photovoltaic parameters are summarized in Table S2. All PSCs were measured under illumination of an AM 1.5G solar light simulator at 100 mW/cm^2. The optimal active layer thickness is about 100 nm.

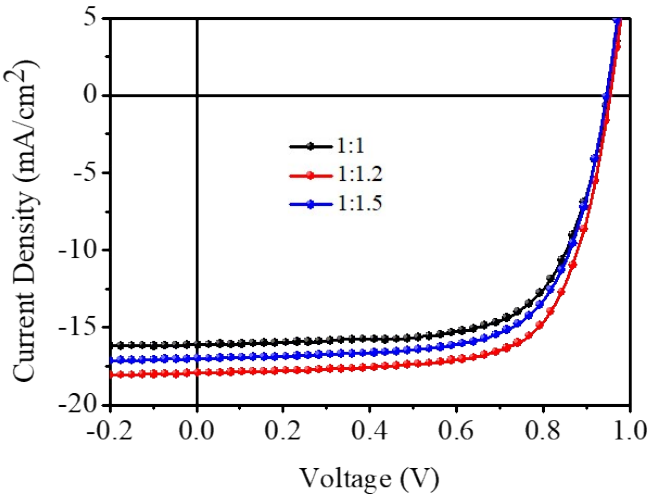


Figure S3. *J-V* curves of ternary PSCs with different PBTA-PS:ITIC weight ratios.

Table S1. Photovoltaic parameters of PSCs with different PBTA-PS:ITIC weight ratios. The average efficiencies and standard deviations were calculated based on 20 cells prepared from different batches.

PBTA-PS:ITIC	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [%]	PCE [%]
1:1	0.94(0.94±0.01)	16.12(15.83±0.23)	67.79(67.02±1.34)	10.27(9.99±0.29)
1:1.2	0.95(0.95±0.01)	17.90(17.70±0.23)	69.59(68.87±1.32)	11.83(11.46±0.39)
1:1.5	0.94(0.94±0.01)	17.01(16.73±0.34)	68.12(66.92±2.79)	10.89(10.67±0.25)

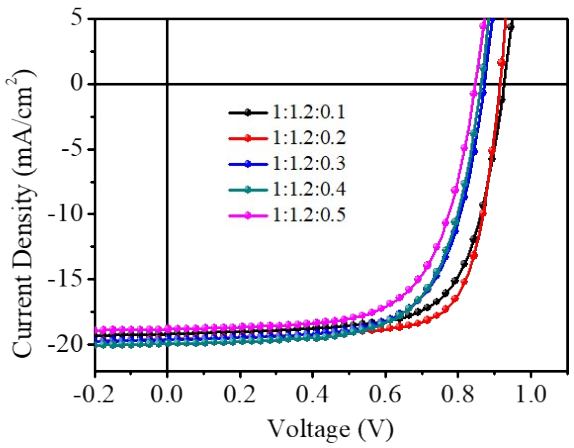


Figure S4. *J-V* curves of ternary PSCs with different PBTA-PS:ITIC:IT-4F weight ratios.

Table S2. Photovoltaic parameters of PSCs with different PBTA-PS:ITIC:IT-4F weight ratios. The average efficiencies and standard deviations were calculated based on 20 cells prepared from different batches.

PBTA-PS:ITIC:IT-4F	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [%]	PCE [%]
1:1.2:0.1	0.93(0.93±0.01)	19.18(19.02±0.21)	69.95(68.17±1.76)	12.47(12.18±0.23)
1:1.2:0.2	0.91(0.91±0.01)	19.60(19.28±0.37)	74.45(73.20±1.54)	13.27(13.09±0.19)
1:1.2:0.3	0.87(0.87±0.01)	19.64(19.32±0.42)	68.07(67.03±0.89)	11.61(11.42±0.18)
1:1.2:0.4	0.85(0.85±0.01)	19.91(19.65±0.34)	67.72(66.45±1.01)	11.33(11.18±0.43)
1:1.2:0.5	0.84(0.84±0.01)	18.81(18.53±0.48)	66.16(65.76±0.98)	10.44(9.97±0.44)

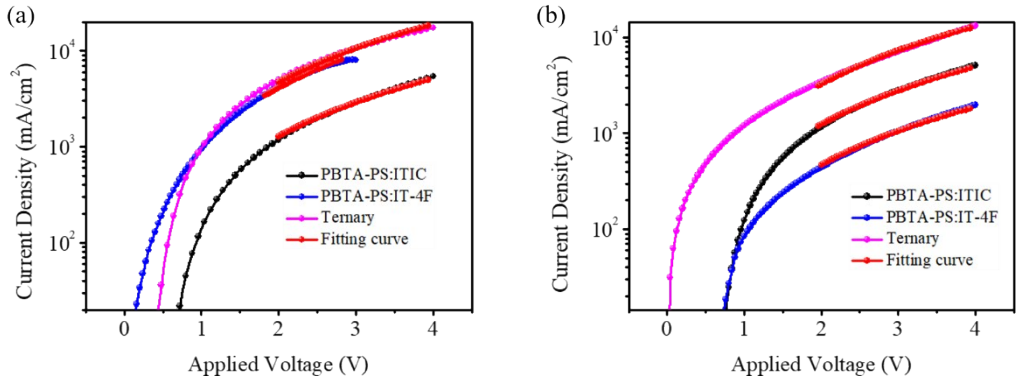


Figure S5. *J-V* curves of (a) electron-only diodes and (b) hole-only diodes.

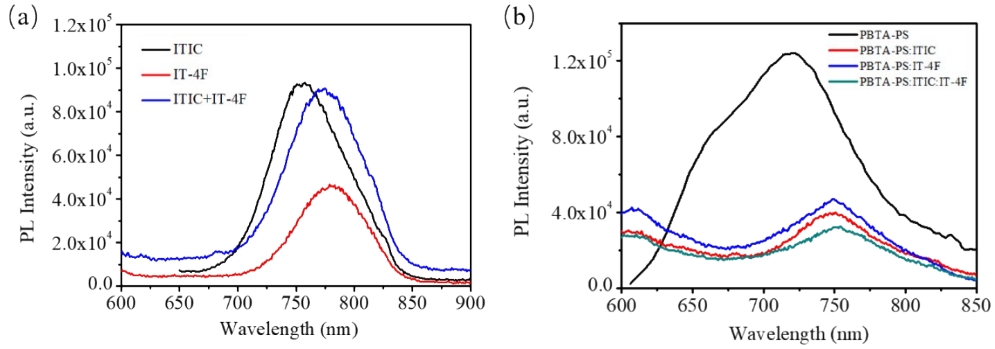


Figure S6. (a) The PL spectra of neat ITIC, IT-4F and ITIC:IT-4F blend films. (b) The PL spectra of neat PBTA-PS-PS film, PBTA-PS-PS:ITIC, PBTA-PS-PS:IT-4F blend film and ternary blend film.

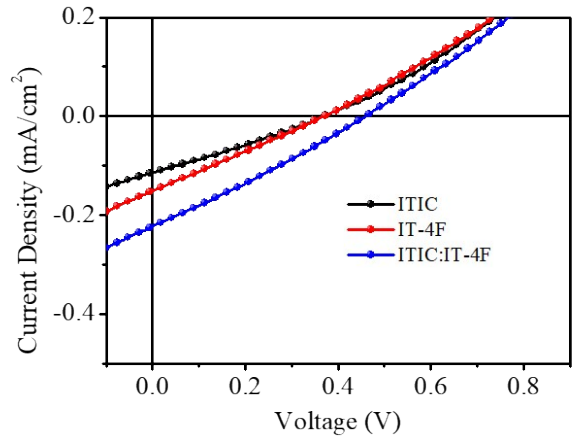


Figure S7. The *J-V* curves of OSCs based on acceptors.

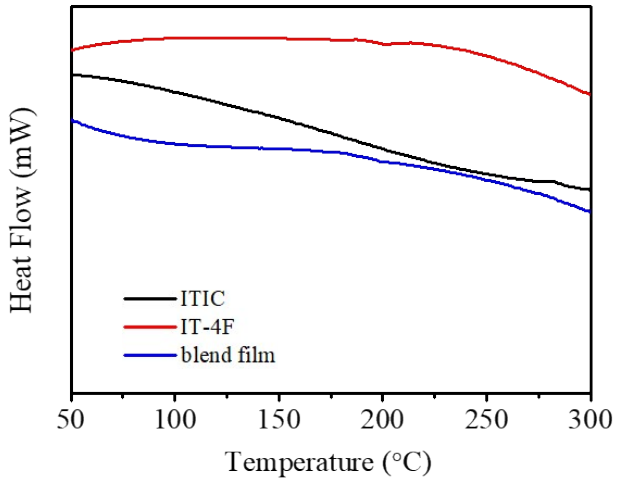


Figure S8. DSC thermograms of neat ITIC, IT-4F and their blend film. The scan range is 50-300°C and the heating rate is 10°C/min.

References

1. G. Huang, J. Zhang, N. Uranbileg, W. Chen, H. Jiang, H. Tan, W. Zhu and R. Yang, *Adv. Energy Mater.*, 2018, **8**, 1702489.