Supporting Information

Simultaneously enhancing the photovoltaic parameters of ternary organic solar cells by incorporating a fused-ring electron acceptor

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1. Experimental section

1.1. Materials

PM6, Y6 were purchased from Solarmer Materials Inc and Derthon Optoelectronics Materials Science Technology Co., Ltd, respectively. BTMe-C8-2F was previously synthesized in our laboratory. PFN-Br was purchased from Suna-Tech Inc. 1-Chloronaphthalene(1-CN) was purchased from Sigmal adrich. Poly-(3,4-ethylenedioxythiophene):poly-(styrenesulphonicacid) (PEDOT:PSS) was supplied by Xi'an Polymer Light Technology Corp. Silver (Ag) was purchased from China New Metal Materials Technology Co., Ltd. All materials were used without further purification. All solvents were purchased from Tianjin Kemiou Chemical

Reagent Co., Ltd and used without further purification.

1.2 Device fabrication and Characterization

The photovoltaic performances of the OSCs were evaluated with a conventional device architecture of ITO/PEDOT:PSS /active layer /PFN-Br /Ag. The ITO patterned glass was carefully washed with used acetone, deionized water, clean acetone, isopropyl alcohol in sequence in the ultrasonic machine and then cleaned for 15 minutes in UV-ozone. The PEDOT:PSS was spin-coated on the ITO glass substrates at 3500 rpm for 35s. Afterwards annealed at 150 ℃ for 15 minutes, then transferred it to the glove box and wait to spin the active layer solution. The active layer solution was prepared the night before according to a certain mass ratio. PM6:Y6 blend and the PM6:Y6:BTMe-C8-2F blend were dissolved in chloroform with a concentration of 13 mg mL^{-1}, 0.5 vol% 1-CN was added as the additive. PM6:BTMe-C8-2F blend was dissolved in chloroform with a concentration of 12 mg mL^{-1}, 1 vol% 1-CN was added as the additive. PM6:Y6 and PM6:Y6:BTMe-C8-2F blends were spin-coated at 1700 rpm for 45s and thermal annealed at 100 ℃ for 10 minutes. PM6:BTMe-C8-2F blend was spin-coated at 1500 rpm for 45s and annealed at 100 ℃ for 10 minutes. The active area of devices is 0.038 cm^{-2}. After the active layer solution spin-casted, PFN-Br (0.5mg/ml in methanol) was spin-coated on top of the active layers at 3500 rpm for 35s to form the electron transporting layer. Finally, the 100 nm thick Ag as the electrode was thermal evaporated under a pressure of 2.2×10^{-4} Pa. The current density voltage (J-V) characteristics for the devices were measured in a glovebox using a Keithley 2400 source meter and an Air Mass 1.5 Global solar simulator (Enlitech,

Taiwan). The irradiation intensity of the light source was calibrated by a standard silicon solar cell with a KG5 filter, modulated a value of 100 mW cm^{-2}. EQE values were tested with a commercial EQE measurement system (Enlitech, QE-R, Taiwan) during illumination with chopped monochromatic light from a xenon lamp.

2. Materials Characterization

The photophysical property was characterized by UV–visible–near infrared spectroscopy (Perkin–Elmer Cary 60 UV–Vis–NIR). The films were prepared by spin-coating donor or acceptor solutions in chloroform atop of quartz substrates.

Photoluminescence (PL) was measured with the PTI QM40 fluorescence spectrophotometer.

The charge transport ability of blend films was tested by the space-charge-limited current (SCLC) method. The structure of electron-only is ITO/ZnO/active layer/PFN-Br/Ag. The structure of hole-only is ITO/PEDOT: PSS/active layer/MoO$_3$/Ag.

The J-V characteristics of the hole-only and electron-only devices were fitted by the Mott-Gurney equation:

$$J = \frac{9}{8}\varepsilon_r\varepsilon_0\mu\frac{V^2}{L^3}$$

Where J is the current density, ε_r is the dielectric permittivity of the active layer, ε_0 is the permittivity of the free space, μ is the mobility, V is the applied voltage, L is the thickness of the active layer. The thickness of each layer was measured by the step profiler (XP-100, AMBIOS). The mobility can be calculated from the slope of the $J^{0.5}$ - V curves.

Contact angle measurements were performed using water and ethylene glycol by sessile drop analysis. Surface energy was calculated by Owens-Wendt-Kaelble's model: $\gamma_L(1 + cos\theta) = 2\left(\sqrt{\gamma_L^d\gamma_S^d} + \sqrt{\gamma_L^p\gamma_S^p}\right)$. The Flory-Huggins interaction parameters(χ) value was calculated by the formula: $\chi_{A:D} = K(\sqrt{\gamma_A} - \sqrt{\gamma_D})^2$.

Atomic force microscopy (AFM) images were measured with a Veeco

multi-mode 8 in a tapping mode.

GIWAXS measurements were carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300K detector. The incidence angle is 0.2^o. The samples for GIWAXS measurements were prepared on silicon substrates by spin coating.
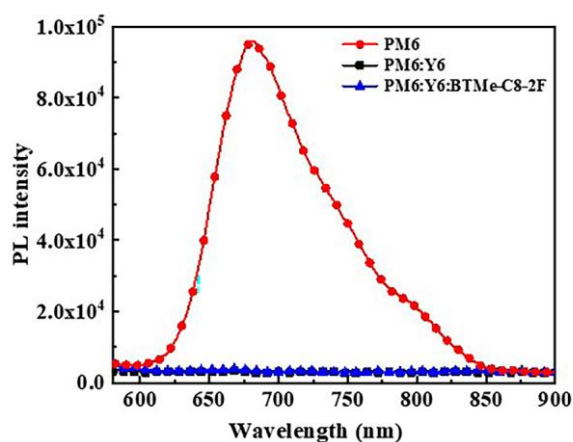
2. Supplementary Figures

Fig. S1 Photoluminescence spectra of PM6 neat film, PM6:Y6 neat film and PM6:Y6:BTMe-C8-2F neat film.
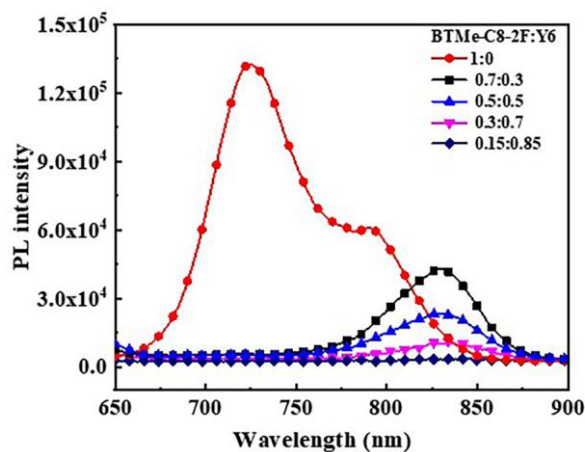

Fig. S2 Photoluminescence spectra of two acceptors based on different weight ratios.
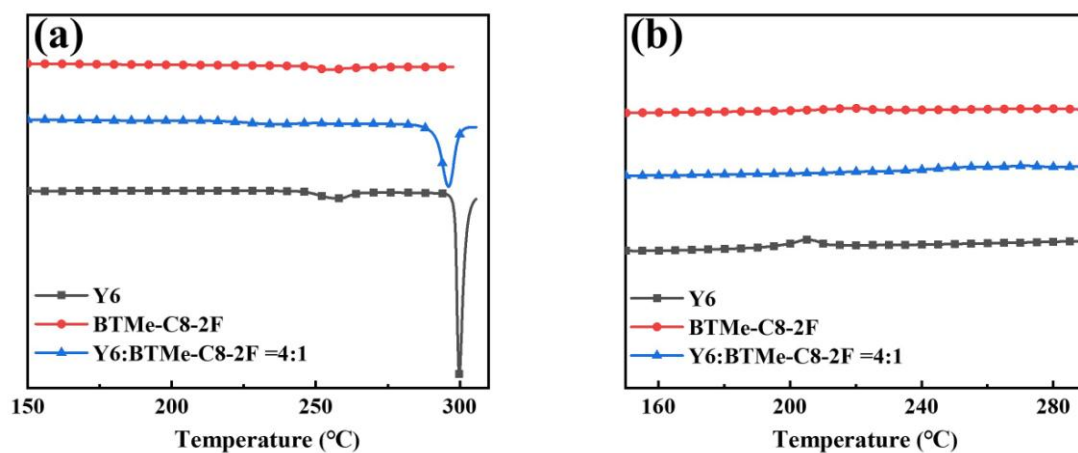
Fig. S3 DSC curves of Y6, BTMe-C8-2F and Y6:BTMe-C8-2F blend (4:1 by weight) (a) in the heating process, (b) in the cooling process.
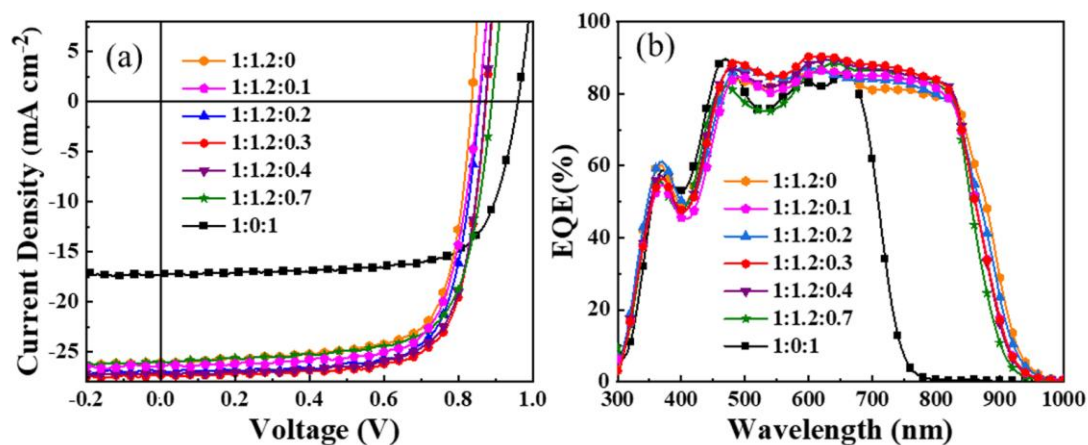

Fig. S4 (a) *J*-V curves of binary OSCs and ternary OSCs with different BTMe-C8-2F contents. (b) EQE spectra of binary and ternary OSCs with different BTMe-C8-2F contents.
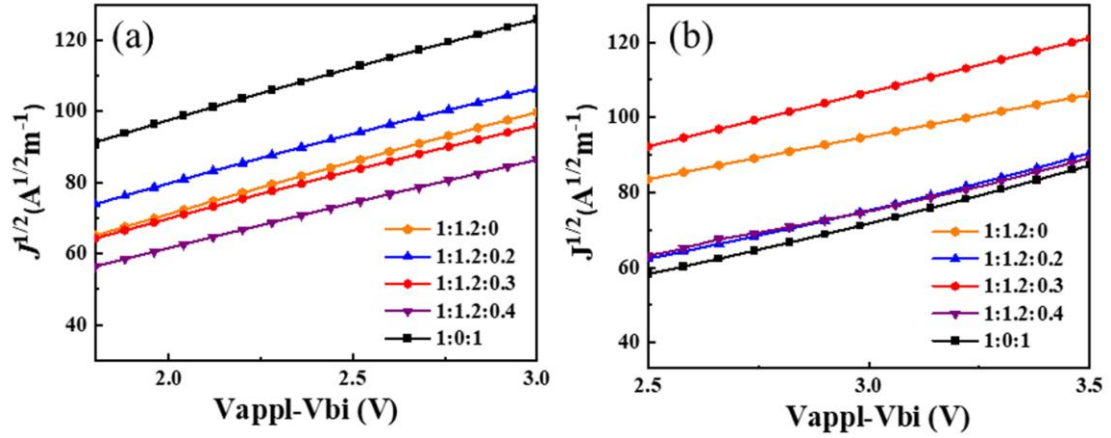
Fig. S5 $J^{0.5}$-V curves of the (a) hole-only and (b) electron-only devices based on ternary OSCs with different weight ratios of BTMe-C8-2F.

4. Supplementary Tables

Table S1 Relevant parameters of contact angles (CA) about PM6, Y6, BTMe-C8-2F pure films.

Film	θ_{Water} (°)	θ_{EG} (°)	γ (mN m^{-1})	χ_{PM6} (k)	χ_{Y6} (k)
PM6	100.50	70.25	30.82	-	0.134
Y6	91.25	65.50	26.89	0.134	-
BTMe-C8-2F	92.50	66.00	27.37	0.102	0.002

Table S2 Data of the Out of plane and In plane peaks analysis of GIWAXS.

PM6:Y6:	Out of plane (010)			In plane (100)		
BTMe-C8-2F	location $[\text{Å}^{-1}]$	d-location $[\text{Å}]$	CCL $[\text{Å}]$	location $[\text{Å}^{-1}]$	d-location $[\text{Å}]$	CCL $[\text{Å}]$
1:1.2:0.2	1.80	3.50	25.45	0.305	20.6	74.83
1:1.2:0.3	1.76	3.57	25.93	0.295	21.3	78.24
1:1.2:0.4	1.78	3.53	24.62	0.295	21.3	72.69

Table S3 Charge mobility of binary and ternary devices.

PM6: Y6: BTMe-C8-2F	μ_h (cm^2 V^{-1} s^{-1})	μ_e (cm^2 V^{-1} s^{-1})	μ_h/μ_e
1:1.2:0	6.52×10^{-4}	5.52×10^{-4}	1.18
1:1.2:0.2	7.07×10^{-4}	6.27×10^{-4}	1.13
1:1.2:0.3	9.62×10^{-4}	9.20×10^{-4}	1.04
1:1.2:0.4	7.23×10^{-4}	6.69×10^{-4}	1.08
1:0:1	6.07×10^{-4}	4.50×10^{-4}	1.35

Table S4 Photovoltaic data based on binary and ternary devices.

PM6: Y6: BTMe-C8-2F	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
1:1.2:0	0.836	26.07	72.76	15.86
1:1.2:0.1	0.854	26.40	72.77	16.61
1:1.2:0.2	0.858	26.96	73.53	17.00
1:1.2:0.3	0.874	27.32	74.05	17.68
1:1.2:0.4	0.878	27.00	73.76	17.48
1:0.2:0.7	0.895	25.97	72.91	16.94
1:0:1	0.961	17.34	71.93	11.98

Table S5 Photovoltaic data based on PM6:Y6:BTMe-C8 = 1:.1.2:0.3 with different thermal annealing temperature.

Annealing temperature (℃)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
/	0.892	26.01	71.21	16.52
80	0.887	26.07	71.65	16.58
100	0.874	27.32	74.05	17.68
120	0.864	26.60	70.22	16.14

Table S6 Photovoltaic data based on PM6:Y6:BTMe-C8 = 1:.1.2:0.3 with different additive ratio.

CN (vol %)	V_{OC} (V)	J_{SC} (mAcm^{-2})	FF (%)	PCE (%)
0	0.883	25.50	70.43	15.86
0.50	0.874	27.32	74.05	17.68
0.75	0.848	25.71	72.18	15.74