Electronic Supplementary Information for:

Over 17% efficiency ternary organic solar cells enabled by two nonfullerene acceptors working in alloy-like model

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Materials and Methods

Instrument. ¹H NMR spectrum was obtained on a Bruker Advance III 400 (400 MHz) nuclear magnetic resonance (NMR) spectroscope. MALDI-TOF MS spectra were measured on a Walters Maldi Q-TOF Premier mass spectrometry. UV-Vis absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Differential scanning calorimetry (DSC) was recorded on a Pekin-Elmer Pyris 1 differential scanning calorimeter. Cyclic voltammetry (CV) was done on a CHI600A electrochemical workstation with Pt disk, Pt plate, and standard calomel electrode (SCE) as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol/L tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6) acetonitrile solution. The CV curves were recorded versus the potential of SCE, which was calibrated by the ferrocene-ferrocenium (Fc/Fc⁺) redox couple (4.8 eV below the vacuum level). The equation of $E_{\text{LUMO/HOMO}} = -e(E_{\text{red/ox}}+4.41)$ (eV) was used to calculate the LUMO and HOMO levels (the redox potential of Fc/Fc⁺ is found to be 0.39 V). Steady state Fluorescence spectra were measured on QM40-LS at room temperature. The transient photoluminescence decay was collected by the TCSPC technique, using a Horiba DeltaFlex modular lifetime measurement system equipped with a diode laser as excitation source ($\lambda =$ 371 nm, pulse width \approx 50 ps, repetition rate = 20.00 kHz). Topographic images of the films were obtained on a VeecoMultiMode atomic force microscopy (AFM) in the tapping mode using an etched silicon cantilever at a nominal load of ~ 2 nN, and the scanning rate for a 10 μm×10 μm image size was 1.5 Hz. Transmission electron microscope (TEM) images were performed on JEOL-1010 at 80 KV accelerating voltage in bright field mode.

Materials. All reagents and solvents, unless otherwise specified, were purchased from commercial sources and were used without further purification. PM6 and Y6 were purchased from Solarmer Inc.

GIWAXS Measurements. 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°.

Device Fabrication and Characterization. Organic solar cells were fabricated on glass substrates commercially pre-coated with a layer of ITO with the conventional structure of ITO/PEDOT:PSS/Active Layer/PFN-Br/Ag. Prior to fabrication, the substrates were cleaned using detergent, deionized water, acetone and isopropanol consecutively for 15 min in each step, and then treated in an ultraviolet ozone generator for 15 min before being spin-coated at 4500 rpm with a layer of 20 nm thick PEDOT:PSS (Baytron P AI4083). After baking the PEDOT:PSS layer in air at 170 °C for 20 min, the substrates were transferred to a glovebox. The active layer was spin coated from 16 mg/mL chloroform solution (D:A = 1:1.2, 0.5%CN) at 3500 rpm for 30 s to form an active layer of around 120 nm. For thick film devices, the control of thickness was realized by changing the total concentration (20 mg/mL for 160 nm, 25 mg/mL for 200 nm, 35 mg/mL for 300 nm, 40 mg/mL for 400 nm, D:A = 1:1.2, 0.5% CN) and the spinning speed was 3500 rpm for 30 s. Then an extra pre-annealing at 100 °C for 10 min was performed. Then a 5 nm thick PFN-Br film was deposited as the cathode buffer layer by the spin-coating of a solution of 0.5 mg/mL PFN-Br in methanol. Finally, the Ag (100 nm) electrode was deposited by thermal evaporation to complete the device with an active area of 4 mm². For a comparison, the device without additive CN in the active layer was fabricated. The non-chlorinated solvent o-xylene was also used instead of chloroform to make the devices.

Inverted devices were fabricated with the structure of ITO/ZnO/Activer Layer/MoO₃/Ag. A thin layer of ZnO was spin coated onto the precleaned ITO-coated glass substrates at 3500 rpm for 60 s and then annealed at 170 °C for 20 min. The substrates were transferred to a glovebox, the active layer was spin coated from 16 mg/mL chloroform solution (D:A = 1:1.2, 0.5% CN) to form an active layer of around 100 nm. Then an extra pre-annealing at 100 °C for 10 min was performed. Finally, a layer of MoO₃ (10 nm) and the Ag (100 nm) electrode were deposited by thermal evaporation to complete the device.

The *J-V* measurement was performed via the solar simulator (SS-F5-3A, Enlitech) along with AM 1.5G spectra whose intensity was calibrated by the certified standard silicon solar cell (SRC-2020, Enlitech) at 100 mV/cm². The external quantum efficiency (EQE) data were obtained by using the solar-cell spectral-response measurement system (RE-R, Enlitech).

The charge carrier mobilities of the binary and ternary blend films were measured using the space-charge-limited current (SCLC) method. Hole-only devices were fabricated in a structure of indium tin oxide (ITO)/PEDOT:PSS/Active Layer/MoO₃/Ag. Electron-only devices were fabricated in a structure of ITO/ZnO/Active Layer/PFN-Br/Al. The device characteristics were extracted by modeling the dark current under forward bias using the SCLC expression described by the Mott-Gurney law:

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu \frac{V^2}{L^3} \qquad (1)$$

Here, $\varepsilon_{\rm r} \approx 3$ is the average dielectric constant of the blend film, ε_0 is the permittivity of the free space, μ is the carrier mobility, L is the thickness of the film, and V is the applied voltage.

Synthesis of BTP-M



BTP-M

To a Schlenk tube were added **Compound 1** (0.1 g, 0.1 mmol), **Compound 2** (0.1 g, 0.5 mmol) and dried CHCl₃ (30 mL). The mixture was frozen with liquid nitrogen, followed by three times of successive vacuum and nitrogen fill cycles, then under the protection of nitrogen, 0.4 mL pyridine was added. The resulting mixture was refluxed at 65 °C for 15 h. After removing the solvent, the residue was purified using silica gel column chromatography with the mixture of petroleum ether and dichloromethane (1:1 ~ 0:1, v/v), yielding a brown solid (85 mg, 60%). ¹H NMR (400 MHz, CDCl₃): δ = 9.10 (s, 2H), 8.54 (d, *J* = 8.1 Hz, 0.7H), 8.46 (s, 1.3H), 7.87 (d, *J* = 7.6 Hz, 1.3H), 7.77 (s, 0.7H), 7.61-7.51 (m, 2H), 4.79 (d, *J* = 7.2 Hz, 4H), 3.21 (s, 4H), 2.57 (d, *J* = 6.1 Hz, 6H), 2.17 (s, 2H), 1.95-1.79 (m, 4H), 1.54-1.43 (m, 4H), 1.41-1.17 (m, 32H), 1.15-0.94 (m, 12H), 0.91-0.74 (m, 12H), 0.67 (t, *J* = 7.2 Hz, 6H). MS (MALDI-TOF): Calcd for C₈₄H₉₄N₈O₂S₅ (M⁺): 1408.03, Found: 1407.96.

Supplementary Figures



Fig. S1 Normalized UV-Vis absorption spectra of BTP-M in chloroform solution and thin film.



Fig. S2 DSC curves of Y6, BTP-M and Y6:BTP-M blend (4:1 by weight) (a) in the heating process, (b) in the cooling process.



Fig. S3 Cyclic voltammograms of BTP-M, Y6, Y6:BTP-M and Fc/Fc⁺. The HOMO and LUMO positions are determined by the point of intersection using two tangent lines at the onsets of oxidation or reduction waves. The equation of $E_{LUMO/HOMO} = -e(E_{red/ox}+4.41)$ (eV) was used to calculate the LUMO and HOMO levels (the redox potential of Fc/Fc⁺ is found to be 0.39 V).



Fig. S4 Normalized UV-Vis absorption spectra of binary and ternary blends with different weight ratios of BTP-M.



Fig. S5 *J-V* curves of binary and ternary (20%) devices with an inverted structure of $ITO/ZnO/Activer Layer/MoO_3/Ag$. The thickness of active layer is ~100 nm.



Fig. S6 *J-V* curves of additive-free binary and ternary (20%) devices with an conventional structure of ITO/PEDOT:PSS/Active Layer/PFN-Br/Ag.



Fig. S7 *J-V* curves of non-chlorinated solvent (*o*-xylene) processed binary and ternary (20%) devices with an conventional structure of ITO/PEDOT:PSS/Active Layer/PFN-Br/Ag.



Fig. S8 Photoluminescence spectra of (a) BTP-M and PM6:BTP-M, (b) Y6 and PM6:Y6 thin films excited at 760 nm.



Fig. S9 (a) *J-V* curve and (b) EQE curve of binary OSCs based on PBDB-T:BTP-M blend. (The optimal fabrication conditions for binary OSCs based on PBDB-T:BTP-M blend are a D/A weight ratio of 1:1, the addition of 0.5% (v/v) CN with a total concentration of 16 mg/mL in chloroform solution and thermal annealing at 100 °C for 10 min)



Fig. S10 Light stability of binary and ternary (20%) devices under 1 sum light (with UV) for encapsulated devices at open-circuit status in ambient air.



Fig. S11 (a) $J^{0.5}$ -V curves of the hole-only devices based on PM6:Y6:BTP-M films with different weight ratios of BTP-M and ternary blends with various thickness. (b) $J^{0.5}$ -V curves of the electron-only devices based on PM6:Y6:BTP-M films with different weight ratios of BTP-M and ternary blends with various thickness.



Fig. S12 Absorption spectra of ternary blend (20%) films with thicknesses varying from 120 nm to 400 nm.



Fig. S13 Dependence of (a) J_{sc} and (b) V_{oc} on light intensity of ternary devices based on PM6:Y6:BTP-M blend with various active layer thickness.



Fig. S14 ¹H NMR spectrum of BTP-M.



Fig. S15 MALDI-TOF mass spectrum of BTP-M.

Supplementary Tables

Table S1 Photovoltaic parameters of different types of devices based on binary and ternary(20%) blends from Fig. S5-S7

Device Type	Blend	$V_{\rm oc}({ m V})$	$J_{\rm sc}$ (mA cm ⁻²)	FF (%)	PCE (%)
Inverted	Binary (0%)	0.829	25.54	72.15	15.21
	Ternary (20%)	0.865	26.59	71.69	16.41
Additive-free	Binary (0%)	0.842	24.53	69.62	14.41
	Ternary (20%)	0.870	24.74	70.47	15.19
o-xylene	Binary (0%)	0.789	8.87	41.83	2.93
solvent	Ternary (20%)	0.831	12.72	62.39	6.61

Table S2 Photovoltaic parameters of OSCs with different acceptor weight ratios of BTP-M and optimal ternary OSCs with different active layer thickness

Active Layer ^a	Thickness (nm)	$V_{\rm oc}\left({ m V} ight)$	$J_{\rm sc}$ (mA cm ⁻²)	FF (%)	PCE (%)
0%	120	0.834 ± 0.008	25.47±0.77	72.71±1.75	15.43±0.12
15%	120	0.862 ± 0.002	25.85±0.53	74.75±0.59	16.62 ± 0.22
20%	120	0.866 ± 0.003	26.86±0.43	72.87±1.01	16.88 ± 0.09
25%	120	0.874 ± 0.003	25.93 ± 0.40	72.33±1.02	16.33±0.06
100%	120	0.976 ± 0.002	8.27±0.24	51.41±0.46	4.15±0.10
20%	160	0.863 ± 0.002	26.58±0.30	68.85±0.55	15.75±0.19
	200	0.863 ± 0.002	26.13±0.52	67.17±1.15	15.10 ± 0.05
	300	0.859 ± 0.003	26.71±0.10	61.74±0.45	14.12 ± 0.08
	400	0.852 ± 0.003	26.53±0.62	57.68±2.13	13.04±0.28

Table S3 Electron and hole mobilities of PM6:Y6:BTP-M films with different weight ratios of BTP-M and ternary blends with various thickness

Sample	$\mu_{\rm h}(\times 10^{-3} {\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1})$	$\mu_{\rm e}(\times 10^{-3} {\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1})$	$\mu_{\rm h}/\mu_{\rm e}$
0%	2.29 ± 0.15	1.83 ± 0.34	1.25
20%	3.38 ± 0.13	1.35 ± 0.61	2.50
100%	0.79 ± 0.44	0.52 ± 0.06	1.53
Ternary 160 nm	3.79 ± 0.10	2.81 ± 0.20	1.35
Ternary 200 nm	9.12 ± 0.81	6.65 ± 0.37	1.96
Ternary 300 nm	2.71 ± 0.07	4.52 ± 0.25	0.60
Ternary 400 nm	2.12 ± 0.05	3.95 ± 0.01	0.69