Supporting Information

18.73% Efficiency Ternary Organic Solar Cells with a Medium Bandgap Acceptor as a Third Component

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Experimental Section

Materials: PM6, IT-M, BTP-eC9, and PFN-Br were purchased from Solarmer Materials (Beijing) Inc. The processing solvents used in the device fabrication processes were purchased from Sigma Aldrich without further purification. PEDOT:PSS (clevios P VP Al 4083) was purchased from H. C. Starck co. Ltd.

Device fabrication: The conventional OSCs with a device architecture of ITO/PEDOT:PSS/Active layer/PFN-Br/Al. Patterned ITO-glass substrates were used as the anode in OSCs. The PEDOT:PSS solutions were spin-coated on the pre-cleaned ITO glass substrates with a spin rate of 5000 rpm for 45 s and then annealed on a hot plate at 150 °C for 15 min in air to obtain uniform films. The concentration of PM6:IT-M:BTP-eC9 with various ratio IT-M in PM6 dissolve in chlorobenzene (CB) solution is 22 mg mL^{-1} and stirred at room temperature for over 3 h and 0.5 vol% 1,8-diiodooctane was added as the additive. The weight ratio of donor:acceptor in OSCs was kept at 1:1.2. The blend solutions were spin-coated onto the ITO/PEDOT:PSS substrates at 3000 rpm for 40 s. The active layers were thermally annealed at 100 °C for 5 min. PFN-Br was dissolved in methanol with the addition of 0.25 vol% acetic acid to prepare a 2 mg mL^{-1} solution. The prepared PEN-Br solution was spin-coated onto the active layers at 5000 rpm for 30 s. Finally, aluminum (Al) electrode was deposited by thermal evaporation. For each of the organic solar cells (OSCs), the contacts were deposited at the vacuum condition of 10^{-4} Pa. The active area is defined as 4.00 mm^2 with a mask.

Characterization: The current density-voltage (*J-V*) characteristics of the solar cells were investigated using a solar simulator (SS-F5-3A, Enlitech) under illumination power of 100 mW cm^{-2} along with AM 1.5G spectra. The light intensity was calibrated by a certified standard silicon solar cell (SRC-2020, Enlitech). The external quantum efficiency (EQE) was characterized by using the solar cell spectral response measurement system (QE-R, Enlitech). Atomic force microscopy (AFM) images were recorded on a Dimension 3100 system (Digital Instruments/Veeco) in tapping mode. The electrochemical impedance spectroscopy (EIS) Nyquist plots were acquired on the CHI660E electrochemical workstation (CH Instruments, Inc.) in the frequency range from 10 Hz to 1 MHz under dark conditions.

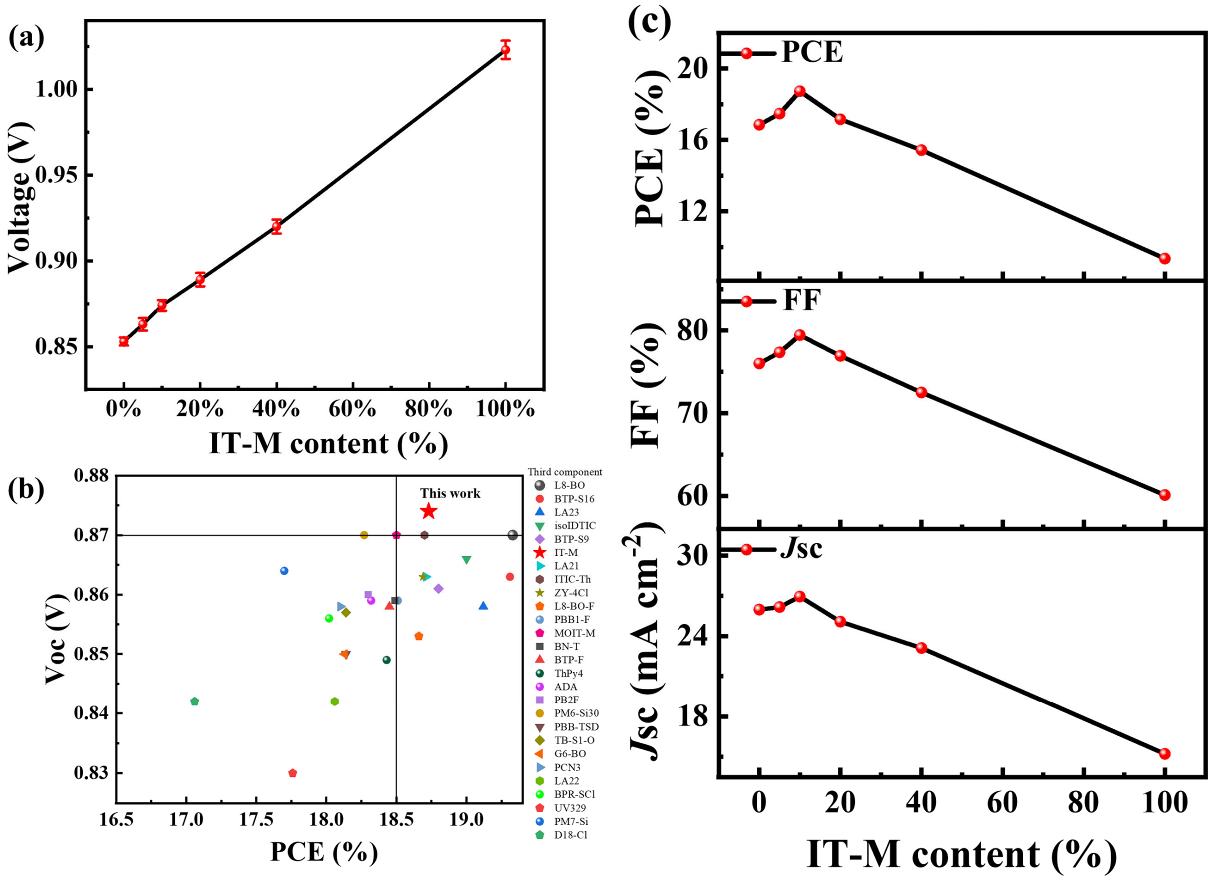

Figure S1. (a) V_{OC} dependence on the IT-M content. (b) Comparison of the V_{OC} of recently reported PM6:BTP-eC9-based ternary OSCs and this work with references listed in Table S4. (c) The J_{SC}, FF and PCE with different IT-M content.

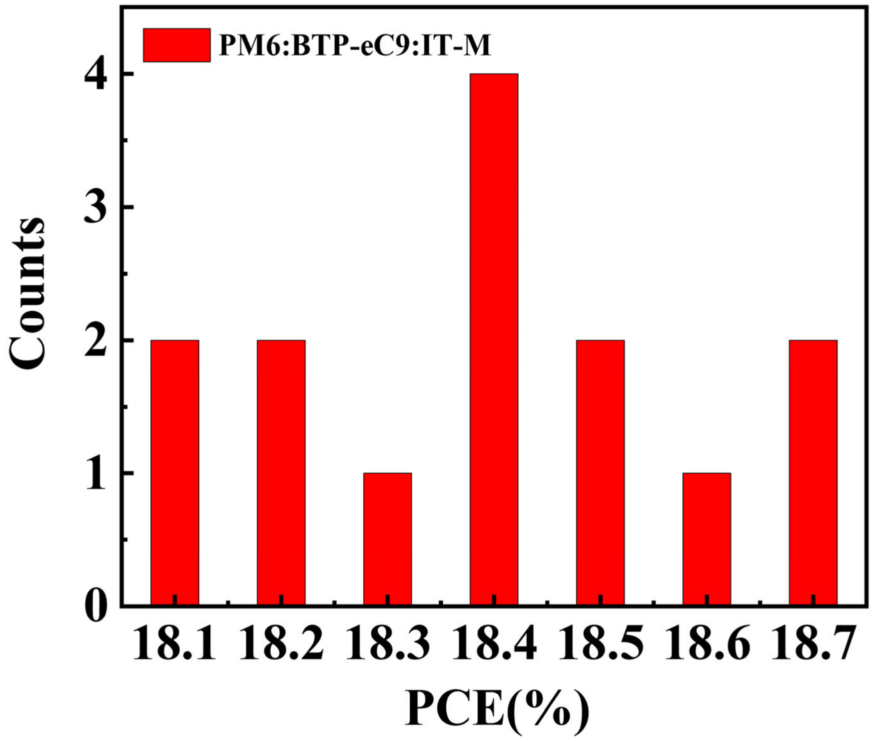

Figure S2. The statistical histograms of PCE distribution for the optimized TOSCs with 10 wt% IT-M in acceptors.

Table S1. Key parameters of the binary and ternary OSCs.

IT-M content	J_{sat} [mA cm^{-2}]	J_{ph}^{*} [mA cm^{-2}]	$J_{ph}^{\&}$ [mA cm^{-2}]	J_{ph}^{*}/J_{sat} [%]	$J_{ph}^{\&}/J_{sat}$ [%]	$J_{ph}^{*}/J_{ph}^{\&}$
0%	26.837	25.98	23.73	96.8	88.4	1.095
10%	27.404	26.95	24.97	98.3	91.1	1.079
100%	16.769	15.21	11.98	90.7	71.4	1.269

J_{sat}: The J_{ph} under condition of V_{eff}=4 V.

J_{ph}^{*}: The J_{ph} under short circuit conditions.

$J_{ph}^{\&}$: The J_{ph} under maximum power output conditions.

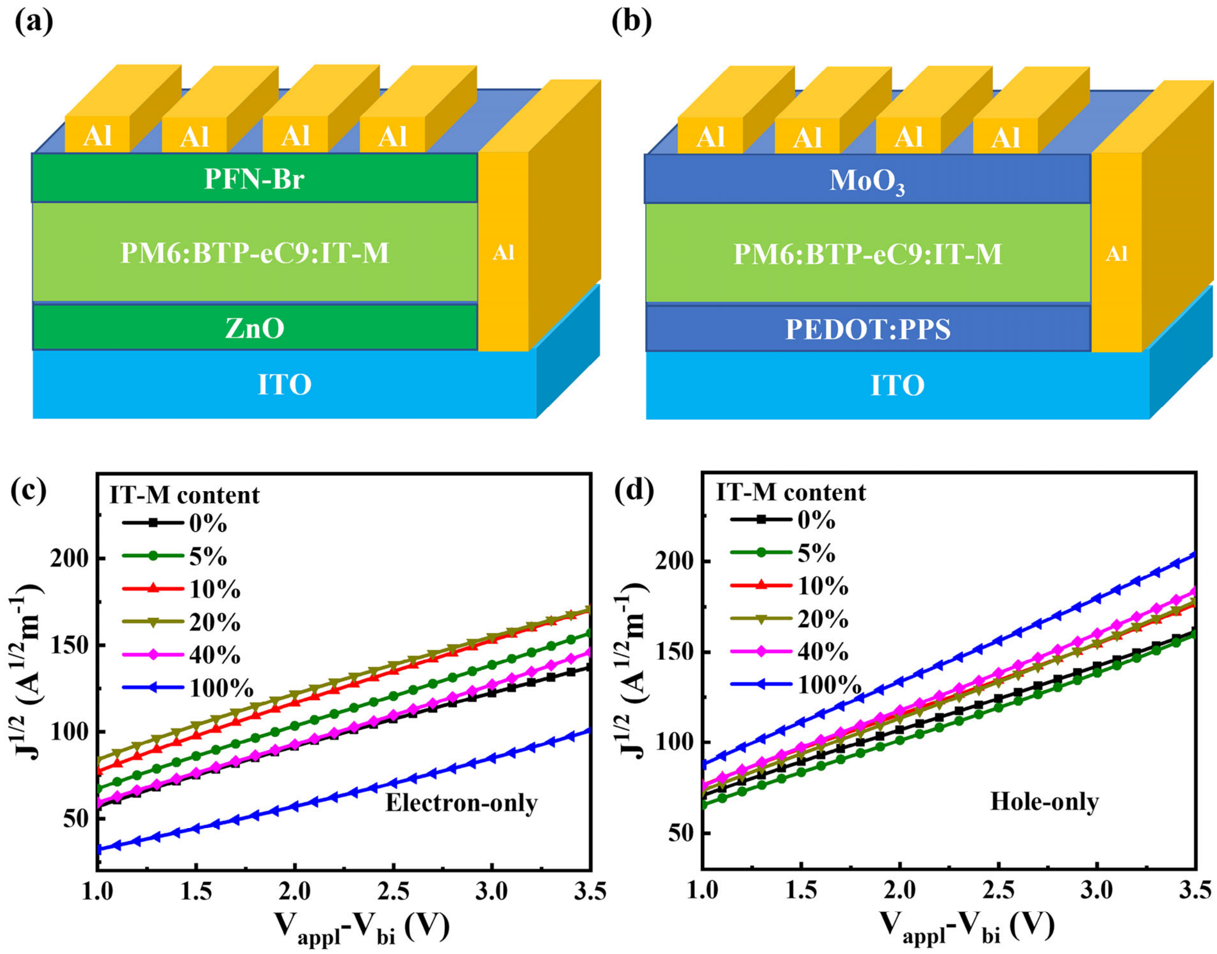

Figure S3. (a-b) schematic diagram of the hole-only, electron-only device structure. (c-d) $J^{1/2}$ -V plots of electron-only and hole-only devices

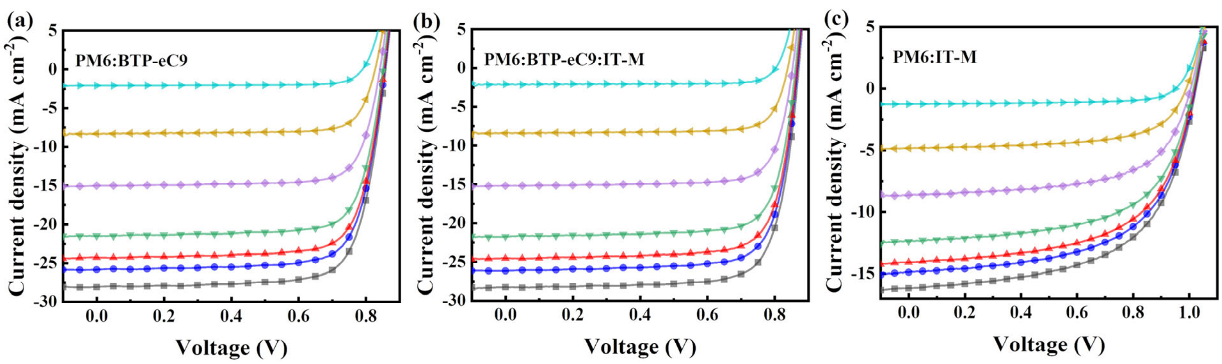

Figure S4. (a-c) The *J-V* curves of the binary and optimized ternary OSCs under different light illumination intensity, obtained from standard AM 1.5G (100 mW cm^{-2}) illumination using a set of neutral optical filters.

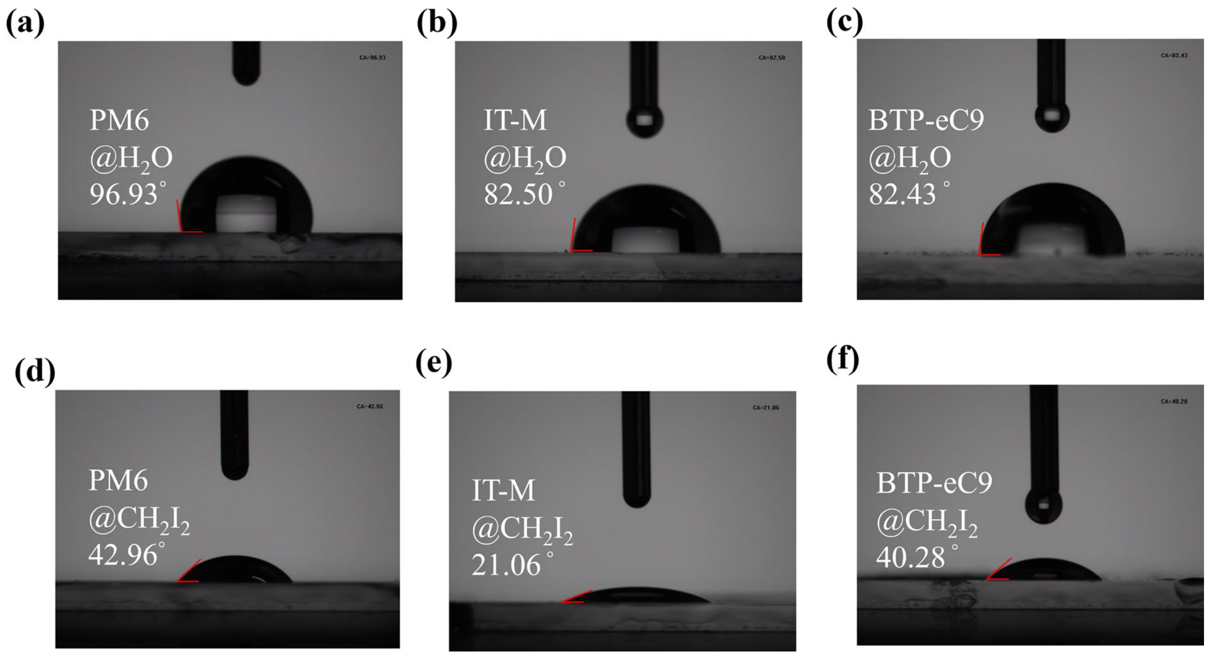

Figure S6. Contact angle images of neat PM6, IT-M, and BTP-eC9 films with H_2O (a-c) and CH_2I_2 (d-f) on top.

Table S3. Contact angle, surface tension and interfacial tension (γ) of individual materials.

Materials	H_2O (°)	CH_2I_2 (°)	Surface (mN/m)	γ^d (mN/m)	γ^p (mN/m)	$\gamma_{X:BTP\text{-}eC9}$ (mN/m)	$\gamma_{X:IT\text{-}M}$ (mN/m)
PM6	96.93	42.96	32.3	31.73	0.63	3.46	2.06
BTP-ec9	82.43	40.28	34.1	29.09	5.02	----	1.33
IT-M	82.50	21.06	40.1	36.89	3.20	1.33	----

Table S4. Comparison of the V_{OC} of recently reported PM6:BTP-eC9-based ternary OSCs and this work

Third component	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)	reference
PBB-TSD	0.850	26.86	79.48	18.14	[1]
ITIC-Th	0.87	28.0	77.0	18.7	[2]
G6-BO	0.85	27.6	77.67	18.13	[3]
UV329	0.83	27.81	76.84	17.76	[4]
isoIDTIC	0.866	27.30	80.4	19.0	[5]
BTP-S9	0.861	27.50	79.34	18.8	[6]
MOIT-M	0.87	27.4	77.3	18.5	[7]
PBB1-F	0.859	27.44	78.51	18.51	[8]
PM6-Si30	0.870	26.90	78.40	18.27	[9]
BN-T	0.859	26.84	80.2	18.49	[10]
ThPy4	0.849	27.08	80.2	18.43	[11]
BTP-S2	0.878	26.78	79.44	18.66	[12]
PTO2	0.90	27.09	73.28	18.01	[13]
ZY-4Cl	0.863	27.40	79.0	18.69	[14]
ADA	0.859	27.58	77.34	18.32	[15]
PB2F	0.860	26.6	79.9	18.3	[16]
PM7-Si	0.864	26.35	77.6	17.7	[17]
BTP-F	0.858	26.99	79.7	18.45	[18]
BPR-SCl	0.856	27.13	77.6	18.02	[19]
L8-BO-F	0.853	27.35	80.0	18.66	[20]
TB-S1-O	0.857	27.40	77.2	18.14	[21]
PCN3	0.858	26.90	78.20	18.10	[22]
BTP-ICBCF3	0.853	27.4	77.8	18.2	[23]
D18-Cl	0.842	25.99	77.95	17.06	[24]
LA23	0.858	28.03	79.50	19.12	[25]
LA21	0.863	27.79	78.00	18.71	[25]
LA22	0.842	27.51	77.98	18.06	[25]
L8-BO	0.87	28.57	77.92	19.33	[26]
BTP-S16	0.863	27.73	80.64	19.31	[27]
BTP-S17	0.873	27.59	79.55	19.19	[27]

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