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Supplementary Information

From Binary to Quaternary: High-tolerance of Multi-acceptors Enables Efficient Polymer Solar Cells

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Experimental methods

Materials: PTB7-Th, ITIC, IT-M, IT-4F were synthesized by our laboratory. IEICO-4F, $PC_{71}BM$ and $PC_{61}BM$ were all purchased from the 1-material company.

PSCs Fabrication and characterization: Firstly, use the non-dust cloth with ethyl alcohol to wipe the ITO, and then following an ultrasonic cleaning with solvent including detergent, deionized water, isopropanol consequently. Secondly, after dried in an oven, these substrates need to further clean in UV-Ozone for 15min. Thirdly, spin-coating the layer of ZnO on the surface of ITO at 3000rpm /20s is done. While the binary, ternary, quaternary active layer is prepared in advance as D/A(total)=1:1.5 ratios in chlorobenzene (CB) at 10mg/ml. The additives 1,8-diiodooctane (DIO) for PTB7-Th:$PC_{61}BM$, PTB7-Th:$PC_{71}BM$ binary blend is 3% (v/v). Binay and quaternary blends based PTB7-Th:NFAs (IEICO-4F, ITIC, IT-M, IT-4F) were all added into 0.5% (v/v) DIO. A speed of spinning cast is suggested 1800rpm/30s for quaternary (PTB7-Th:IEICO-4F:$PC_{71}BM$:$PC_{61}BM$) blend and 1500rpm/45s for other PTB7-Th:NFAs:$PC_{71}BM$:$PC_{61}BM$ blend. After that, evaporation of electric layers would finish as the inverted structure ITO/ZnO/PTB7-Th:Acceptors/MoO_3(10nm)/Ag(100nm) through a 0.045cm^2 mask. And thermal evaporation in a vacuum chamber requires a pressure of nerarly 3×10^{-6} Pa. All the operation was processed in the nitrogen glove box.

Morpholgy characterization: Grazing incident wide-angle X-ray scattering (GIWAXS) measurements were performed at the 8ID-E beamline at the Advanced Photon Source (APS), Argonne National Laboratory using x-rays with a wavelength of λ = 1.1385 Å and a beam size of 200 μm (h) and 20 μm (v). A 2-D PILATUS 1M-F detector was used to capture the scattering patterns and was situated at 208.7 mm from samples. Transmission electron microscope (TEM) image of the blend film was conducted by JEOL-JEM 2100F microscope. The film morphology was conducted by atomic force microscopy (AFM, Veeco Metrology Group/Digital Instruments) with tapping mode. Thin film thickness were obtained by surface profilemeter (Tencor, Alpha-500).

Photovoltaic performance characterization: A Keithley 2400 source-measurement unit under AM 1.5 G spectrum from a solar simulator (Enlitech.Inc) calibrated by a silicon reference cell (Hamamatsu S1133 color, with KG-5 visible fiith) is used for testing Steady-state current-voltage (*J-V*) curves of devices. The the relationship of J_{sc} to the light intensity were measured by steady-state current-voltage measurement, the light intensity was modulated by neutral density filters (NDF) with different values of optical density (OD). The external quantum efficiency (EQE) was measured by a solar cells–photodetector responsibility measurement system (Enlitech. Inc). The mobility of electron was tested by fitting the current-bias characteristics in dark utilizing a field-independent space charge limited current (SCLC) model according to the Mott-Gurney rule of $J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{L^3}$. The device structures for hole-only and electron-only device are respectively followed as ITO/PEDOT:PSS/PTB7-Th:Acceptors/MoO_3/Ag and ITO/ZnO//PTB7-Th:Acceptors/Ca/Al.

Table S1. The best performance parameters of PSCs based on PTB7-Th:IEICO-4F with tunning ratios of $PC_{61}BM$ and $PC_{71}BM$ in ternary and quarternary devices under 100 mW cm^{-2} AM 1.5 G irradiation.

Composition	*Voc* (V)	*Jsc* (mA cm^{-2})	FF (%)	PCE (%)	Rs (Ohm cm^2)
Q1: PTB7-Th:IEICO-4F:$PC_{71}BM$: $PC_{61}BM$ (1:1.1:0.1:0.3)	0.74	22.96	70.30	12.02	4.05
Q2: PTB7-Th:IEICO-4F:$PC_{71}BM$: $PC_{61}BM$ (1:1.1:0.2:0.2)	0.74	24.37	69.30	12.52	3.92
Q3: PTB7-Th:IEICO-4F:$PC_{71}BM$: $PC_{61}BM$ (1:1.1:0.3:0.1)	0.73	23.77	68.46	11.94	4.18
T1: PTB7-Th:IEICO-4F:$PC_{71}BM$ (1:1.3:0.2)	0.75	23.17	65.03	11.32	4.57
T2: PTB7-Th:IEICO-4F:$PC_{61}BM$ (1:1.3:0.2)	0.74	22.38	67.01	11.13	4.22
T3: PTB7-Th:IEICO-4F:$PC_{71}BM$ (1:1.1:0.4)	0.73	22.35	65.54	10.69	5.11
T4: PTB7-Th:IEICO-4F:$PC_{61}BM$ (1:1.1:0.4)	0.75	19.81	68.35	10.22	4.81

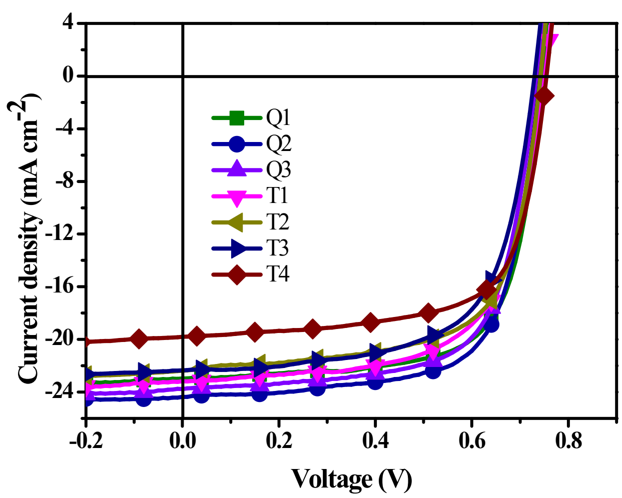

Figure S1. The J-V of PSCs based on PTB7-Th:IEICO-4F with tunning ratios of $PC_{61}BM$ and $PC_{71}BM$ in ternary and quarternary devices under 100 mW cm^{-2} AM 1.5 G irradiation.

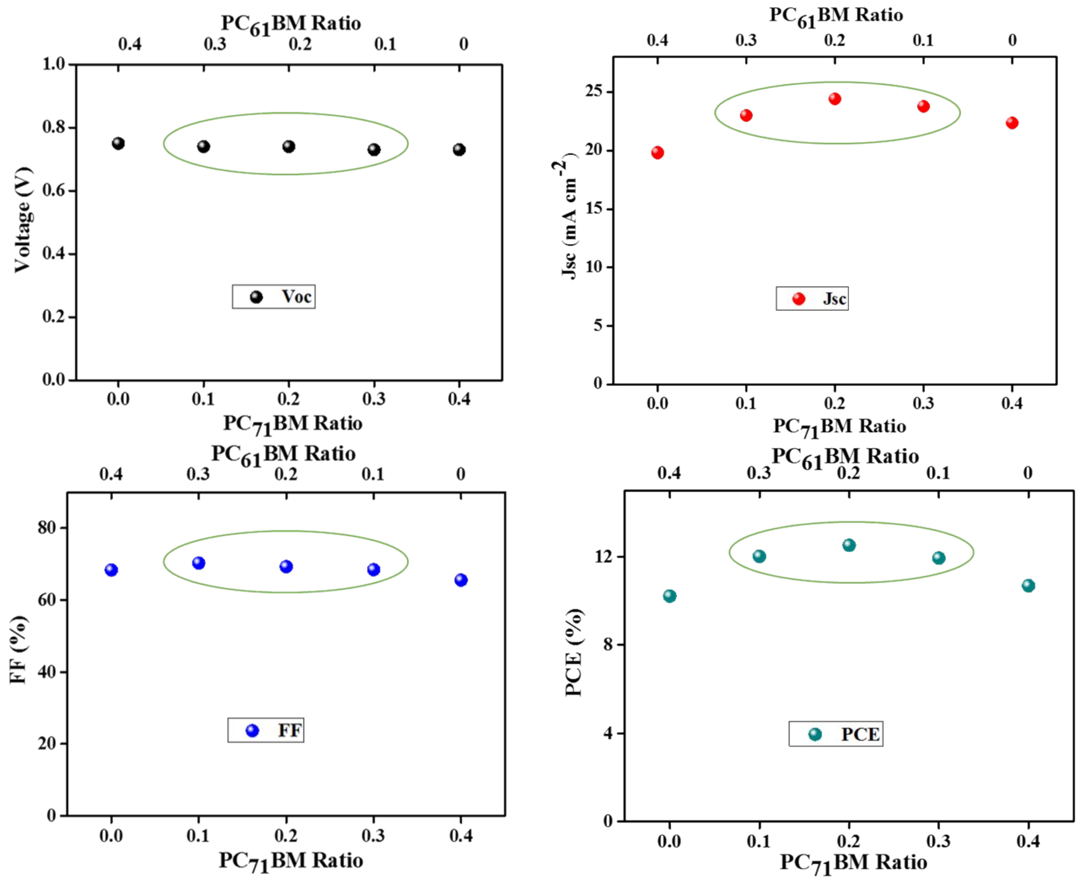

Figure S2. The snapshots to demonstrate high-tolerance ratios PSCs of $PC_{61}BM$ and $PC_{71}BM$ in PTB7-Th:IEICO-4F based ternary and quaternary devices under 100 mW cm^{-2} AM 1.5 G irradiation.

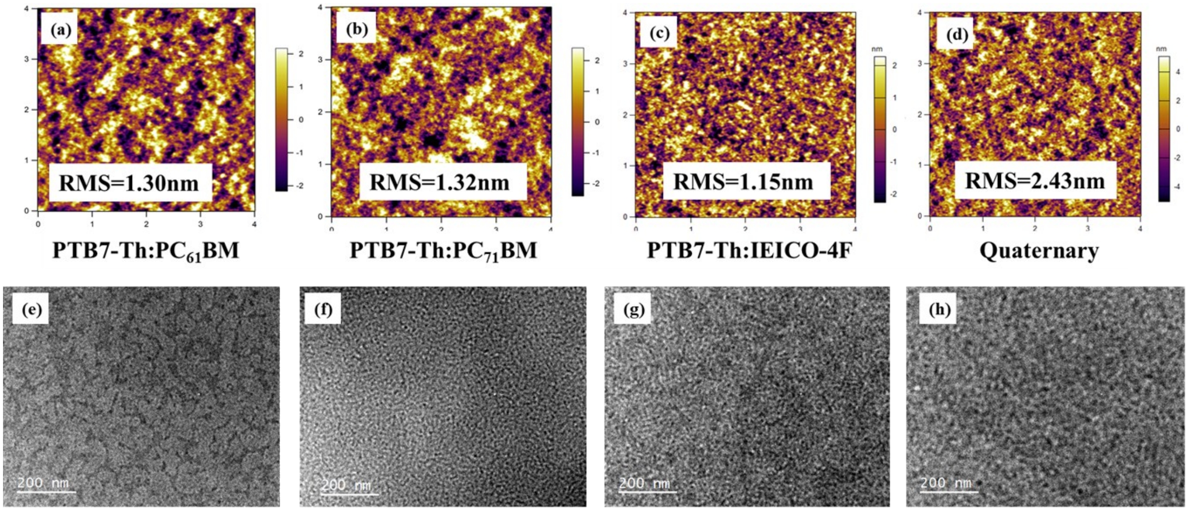

Figure S3. AFM images (a) PTB7-Th:$PC_{61}BM$, (b) PTB7-Th:$PC_{71}BM$, (c) PTB7-Th:IEICO-4F) and (d) quaternary, and TEM image (e) PTB7-Th:$PC_{61}BM$, (f) PTB7-Th:$PC_{71}BM$, (g) PTB7-Th:IEICO-4F and (h) quaternary of blend films under optimal condition.

Table S2. The data of carrier mobility based on hole-only (μ_h) and electron-only (μ_e) devices of binary (PTB7-Th:$PC_{61}BM$, PTB7-Th:$PC_{71}BM$,PTB7-Th:IEICO-4F) and quaternary in dark and with the μ_h/μ_e.

Composition	μ_h (cm^2 V^{-1} S^{-1})	μ_e (cm^2 V^{-1} S^{-1})	μ_h/μ_e	thickness
PTB7-Th:$PC_{61}BM$	4.0×10^{-4}	4.4×10^{-4}	0.91	120nm
PTB7-Th:$PC_{71}BM$	4.3×10^{-4}	4.6×10^{-4}	0.93	120nm
PTB7-Th:IEICO-4F	3.1×10^{-4}	3.7×10^{-4}	0.84	120nm
Quaternary	**9.3×10^{-4}**	**1.0×10^{-3}**	**0.93**	**150nm**

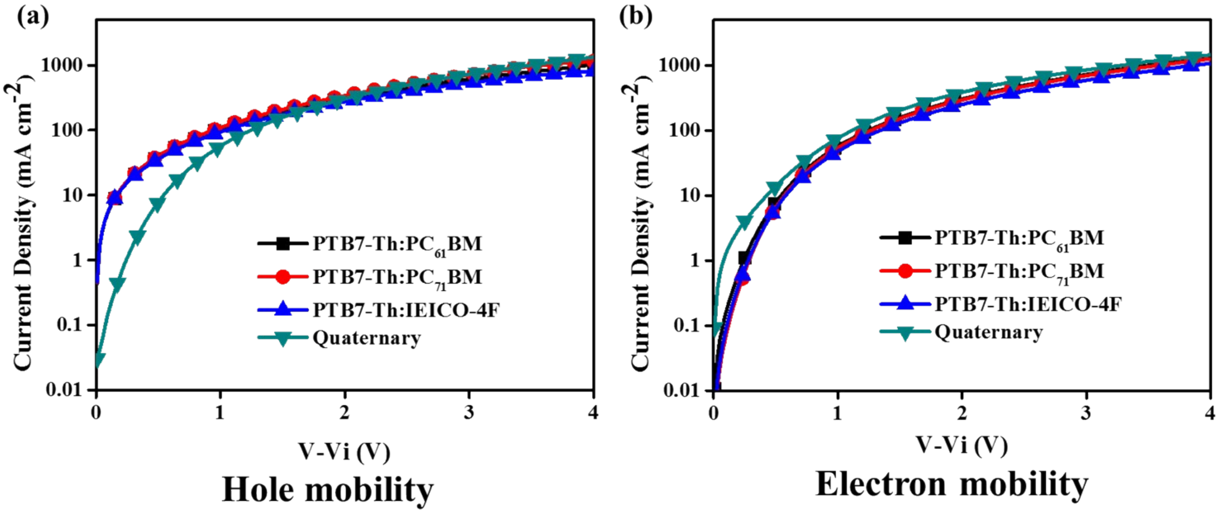

Figure S4. J-V curves of (a) hole-only and (b) electron-only devices based on binary (PTB7-Th:$PC_{61}BM$, PTB7-Th:$PC_{71}BM$,PTB7-Th:IEICO-4F) and quaternary in dark.

Table S3. The calculated time of charge extraction (t_s) from TPC and the lifetime of carriers (τ_R) from TPV simulations of binary (PTB7-Th:$PC_{61}BM$, PTB7-Th:$PC_{71}BM$,PTB7-Th:IEICO-4F) and quaternary in steady and transient test.

Composition	TPV τ_R (μs)	TPC t_s (μs)
PTB7-Th:$PC_{61}BM$	0.65	0.22
PTB7-Th:$PC_{71}BM$	0.70	0.23
PTB7-Th:IEICO-4F	0.96	0.34
Quaternary	**1.21**	**0.26**

Table S4. The champion performance parameters of different binary and corresponding quaternary PSCs with best ratios of $PC_{61}BM$ and $PC_{71}BM$ under 100 mW cm^{-2} AM 1.5 G irradiation.

Composition	*Voc* (V)	*Jsc* (mA cm^{-2})	FF (%)	PCE (%)	*Jcal*[a]
PTB7-Th:ITIC	0.79	14.30	61.07	6.83	13.85
PTB7-Th:ITIC:0.2$PC_{71}BM$:0.2$PC_{61}BM$	0.79	15.51	59.68	7.31	15.32
PTB7-Th:IT-M	0.83	15.40	54.23	6.91	14.98
PTB7-Th:IT-M:0.2$PC_{71}BM$:0.2$PC_{61}BM$	0.82	16.02	63.25	8.32	15.46
PTB7-Th:IT-4F	0.68	16.10	63.56	6.98	15.40
PTB7-Th:IT-4F:0.2$PC_{71}BM$:0.2$PC_{61}BM$	0.67	18.59	71.27	8.82	18.10

[a] The calculated *Jsc* values from EQE curves;

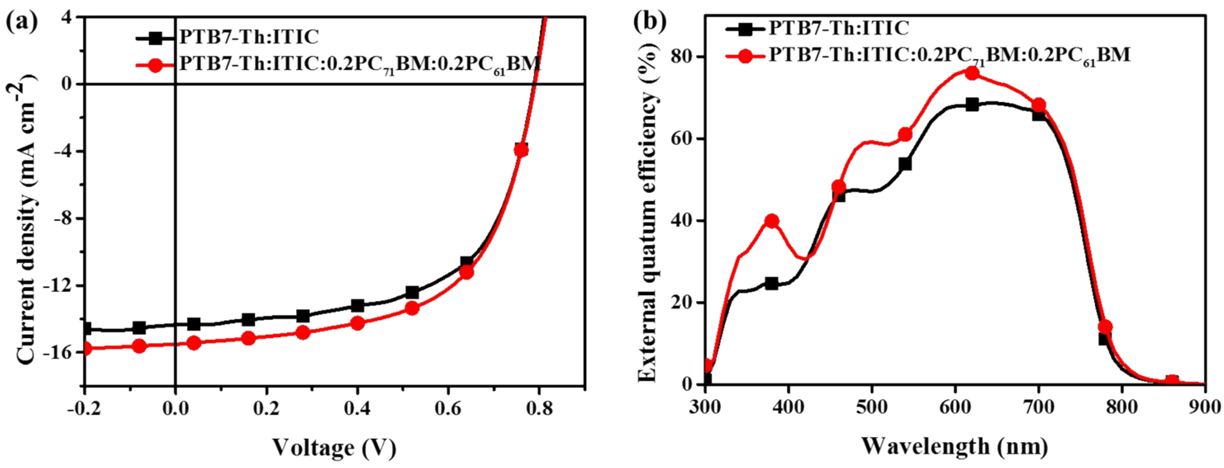

Figure S5. The (a) J-V and (b) EQE curves of PSC based on binary (PTB7-Th:ITIC) and quaternary (PTB7-Th:ITIC:0.2$PC_{71}BM$:0.2$PC_{61}BM$) devices under 100 mW cm^{-2} AM 1.5 G irradiation.

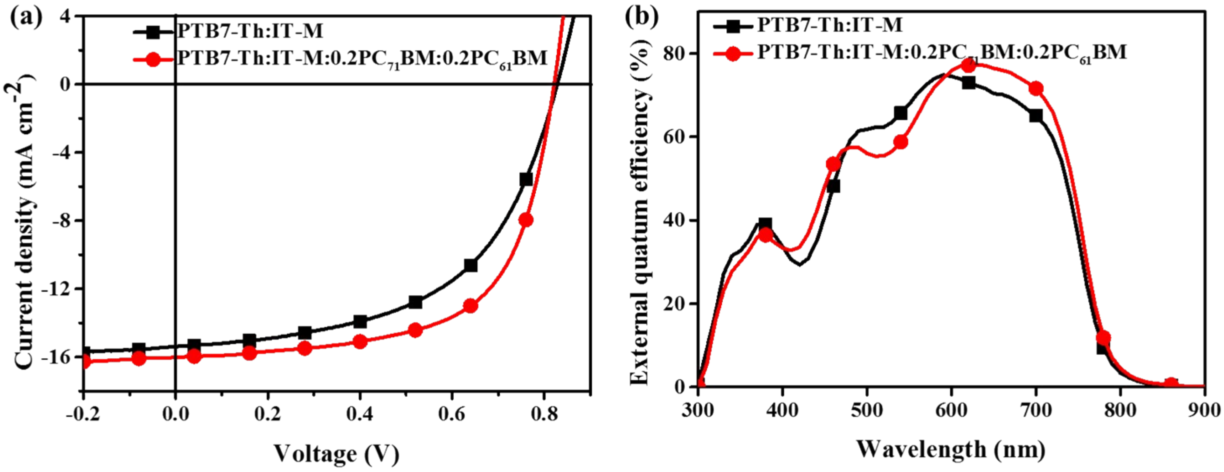

Figure S6. The (a) J-V and (b) EQE of PSC based on binary (PTB7-Th:IT-M) and quaternary (PTB7-Th:IT-M:0.2PC$_{71}$BM:0.2PC$_{61}$BM) devices under 100 mW cm^{-2} AM 1.5 G irradiation.

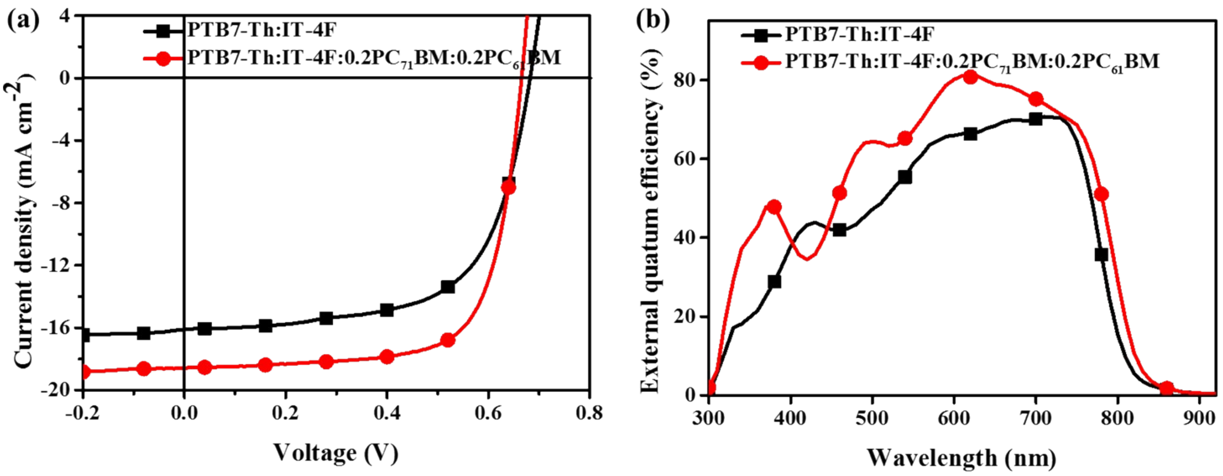

Figure S7. The (a) J-V and (b) EQE curves of PSC based on binary (PTB7-Th:IT-4F) and quaternary (PTB7-Th:IT-4F:0.2PC$_{71}$BM:0.2PC$_{61}$BM) devices under 100 mW cm^{-2} AM 1.5 G irradiation.

Table S5. The summary of amount of increase referring recent ternary and even multi-components systems

Binary host blend	PCE[a] (%)	Additive components	PCE[b] (%)	Amount of increase
PTB7-Th:IEICO-4F	10.00	J52[1]	10.90	0.09
PBDB-T:IEICO-4F	10.25	PTB7-Th[2]	11.62	0.13
J52:IT-M	9.40	IEICO[3]	11.10	0.18
PTB7-Th:$PC_{71}BM$	9.03	BTR[4]	10.16	0.13
PTB7-Th:3TT-FIC	12.21	$PC_{71}BM$[5]	13.54	0.11
PTB7-Th:COi8FIC	10.48	$PC_{71}BM$[6]	14.08	0.34
PBT1-C:IT-2F	11.04	$PC_{71}BM$[7]	12.19	0.10
PTB7-Th:P(NDI2HD-T2)	6.32	$PC_{71}BM$[8]	7.33	0.16
PTB7-Th:$PC_{71}BM$	9.28	ICBA[9]	10.50	0.13
PBDTTT-E-T:IEICO	8.33	Bis-$PC_{71}BM$[10]	10.21	0.23
PBDB-T:IT-M[11]	11.48	Bis-$PC_{71}BM$[12]	12.10	0.05
PBDB-T:IT-M[11]	11.48	Bis-$PC_{71}BM$:$PC_{71}BM$[13]	13.05	0.14
PBDB-T:ITIC[14]	11.21	$PC_{61}BM$:$IC_{61}BA$[15]	12.76	0.14
PBDB-T:IT-M[11]	11.48	Bis-$PC_{71}BM$:$IC_{61}BA$[16]	13.31	0.16
PTB7-Th:IEICO-4F	**9.67**	**$PC_{71}BM$:$PC_{61}BM$**	**12.52**	**0.30**

[a] The PCE of binary systems, [b]The PCE of multi-components systems.

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