

**Tandem organic solar cells with 18.67% efficiency via the careful subcell design and selection**

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Content

1. Materials and Synthesis
2. Measurements and Instruments
3. Fabrication and Measurements
4. NMR Spectra
5. Reference

## 1. Materials and Synthesis

All other materials were purchased and used as received. Tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone before use, and 1,2-dichloroethane was dried with calcium hydride. All reactions and manipulations were carried out under argon atmosphere with the use of standard Schlenk techniques. All starting materials were purchased from commercial suppliers and used without further purification unless indicated otherwise. Polymer donor PM6, D18 was purchased from Solarmer Material (Beijing) Inc. CH1007, CPTCN-Br were synthesized following the literature methods [1,2]. FDTCHO was synthesized according to our previous report method[3].

### *Synthesis of Compound F-ThBr.*

Under the protection of argon, FDTCHO (100 mg, 0.08 mmol) and CPTCN-Br (223.3 mg, 0.8 mmol) was dissolved in dry chloroform (30 mL), followed by the addition of pyridine (0.5 mL). After stirring at room temperature for 12 h, the mixture was poured into water and then extracted with  $\text{CHCl}_3$  (30 mL  $\times$  2), the organic layer was dried over anhydrous  $\text{MgSO}_4$  for 3 h. After removal of solvent, the crude product was purified by flash chromatography on silica gel, and then recrystallized from  $\text{CHCl}_3$  and methanol to give F-ThBr as a dark blue solid (106.6 mg, 83%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.73 (s, 1H), 8.00 (s, 1H), 7.67 (d,  $J = 2.1$  Hz, 4H), 7.58 (d,  $J = 2.4$  Hz, 2H), 2.08 (dq,  $J = 23.0, 9.9, 7.3$  Hz, 8H), 2.00 – 1.88 (m, 4H), 1.23 – 0.62 (m, 94H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  179.81, 179.71, 160.83, 160.75, 156.36, 155.98, 155.93, 152.11, 150.90, 148.10, 142.20, 142.11, 139.16, 139.09, 138.40, 137.82, 136.57, 136.50, 128.17, 128.15, 126.87, 125.07, 121.78, 116.66, 115.13, 114.63, 114.18, 113.80, 113.65, 113.56, 68.84, 40.38, 39.12, 37.88, 32.95, 31.70, 31.15, 30.44, 29.91, 29.18, 28.67, 27.94, 24.41, 23.81, 22.55, 21.31, 14.64, 13.40. MS (MALDI-TOF): calcd for  $\text{C}_{93}\text{H}_{112}\text{Br}_2\text{N}_4\text{O}_2\text{S}_4$  [ $\text{M}^+$ ], 1605.60; found: 1605.68.

## 2. Measurements and Instruments

The  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra were taken on a Bruker AV400 Spectrometer. UV-vis spectra were obtained with a Cary 5000 Spectrophotometers. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry were performed on a Bruker Autoflex III instrument. Varian 7.0T FTMS was used to achieve the HR-MS data. Cyclic voltammogram (CV) was performed with a LK2010 Microcomputer based Electrochemical Analyzer at a scan rate of 100 mV/s. The current density-voltage (J-V) curves of photovoltaic devices were obtained by a Keithley 2400 source-measure unit. The photocurrent was measured under simulated illumination of 100 mW  $\text{cm}^{-2}$  with AM1.5G irradiation using a SAN-EI XES-70S1 solar simulator, calibrated with a standard Si solar cell. The external quantum efficiency (EQE) spectrum was measured using a QE-R Solar Cell Spectral Response Measurement System (Enli Technology Co., Ltd., Taiwan). Atomic force microscopy (AFM) images were performed using in tapping mode on a Bruker MultiMode 8 atomic force microscope. The GIWAXS (grazing incidence wide angle X-ray scattering) samples were prepared on ZnO-coated

Si substrates using the same preparation conditions as for devices. The optical simulation model was preformed based on the TM formalism model. Electroluminescence (EL) and electroluminescence quantum efficiency ( $EQE_{EL}$ ) measurements were performed by an integrated system (REPS, Enli Technology Co., Ltd.).  $EQE_{EL}$  measurements were carried out from 1 to 4 V. Fourier-transform photocurrent spectroscopy external quantum efficiency (FTPS-EQE) was measured by an integrated system (PECT-600, Enli Technology Co., Ltd.), where the photocurrent was amplified and modulated by a lock-in instrument. The refractive index ( $n$ ) and extinction coefficient ( $k$ ) spectra of each layer in the devices were measured using a J.A. WOOLAM Co. V-VASE ellipsometer (VB-400 Control Module).

### 3. Device Fabrication and Measurements

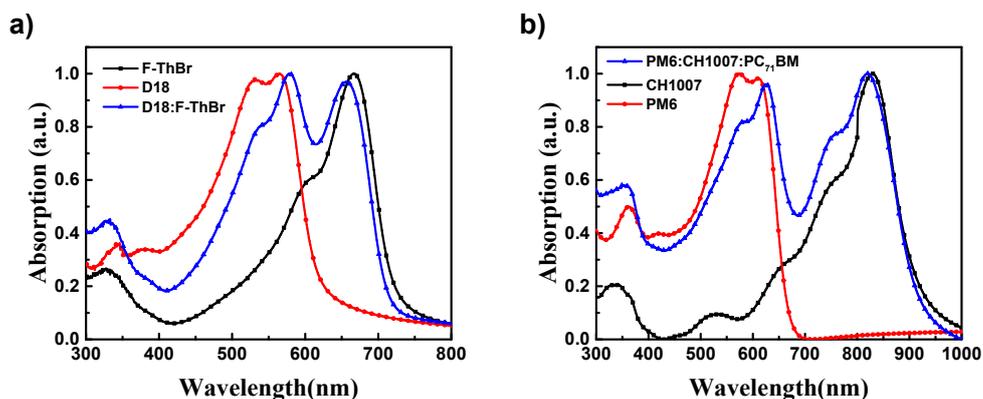
#### *Single junction OSC Fabrication.*

The photovoltaic devices were fabricated with a structure of indium tin oxide (ITO)/ZnO/PFN-Br or P4VP/ active layer /MoOx/Ag. The ITO-coated glass substrates were cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 minutes each time and subsequently dried by a nitrogen flow. A 30 nm thick layer of ZnO precursor solution was spin-coated (3000 rpm) onto the ITO surface. After baked at 200 °C for 60 min, the substrates were transferred into an argon-filled glove box. A thin film of PFN-Br or P4VP was spin-coated on ZnO. Subsequently, the active layer was spincoated from its chloroform solution. The blend of PM6:CH1007:PC<sub>71</sub>BM (13mg/mL in total, 1:1.05:0.15, w:w) was dissolved in the mixture of chloroform and chlornaphthalene (1:0.005, v:v). The solution was spin-coated with 1800 rpm for 30s followed by annealing at 90°C for 5 min. The blend of D18:F-ThBr (10mg/mL in total, 1:1.5, w:w) was dissolved in chloroform and spin-coated with 2000rpm followed by dual solvents vapor annealing. Then MoOx (~2 nm) and Ag (~150 nm) was successively evaporated onto the active layer through a shadow mask to define the active area of the devices (~0.04 cm<sup>2</sup>) in a vacuum chamber (<2x10<sup>-4</sup> Pa).

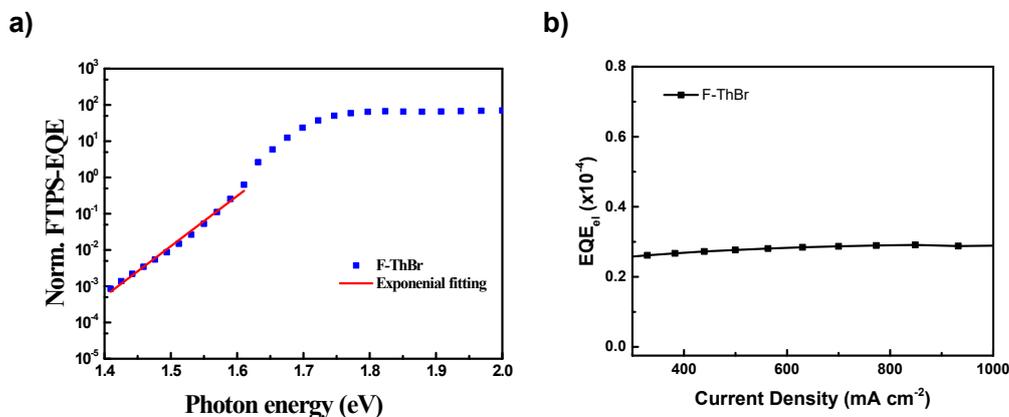
#### *Tandem Cell Device Fabrication.*

The photovoltaic devices were fabricated with a structure of indium tin oxide (ITO)/ZnO/PFN-Br/D18:F-ThBr/M-PEDOT/ZnO(NPs)/P4VP/PM6:CH1007:PC<sub>71</sub>B M/MoOx/Ag. The ITO-coated glass substrates were cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 minutes each time and subsequently dried by a nitrogen flow. A 30 nm thick layer of ZnO precursor solution was spin-coated (3000 rpm) onto the ITO surface. After baked at 200 °C for 60 min, the substrates were transferred into an argon-filled glove box. A thin film of PFN-Br was spin-coated on ZnO. The solution of D18:F-ThBr (D:A ratio of 1:2, 5mg/mL in CF) was spincoated with different thickness, followed by CB SVA and THF SVA. Subsequently, the M-PEDOT (Clevios P VP Al 4083 diluted with equal volume of isopropyl alcohol and 0.3 wt% of Polyoxyethylene tridecyl ether) (~40 nm) was spin coated on top of the active layer of the front subcell, followed by annealing at 120 °C for 5 min, and then ZnO nanoparticles layer (~15 nm) was spin

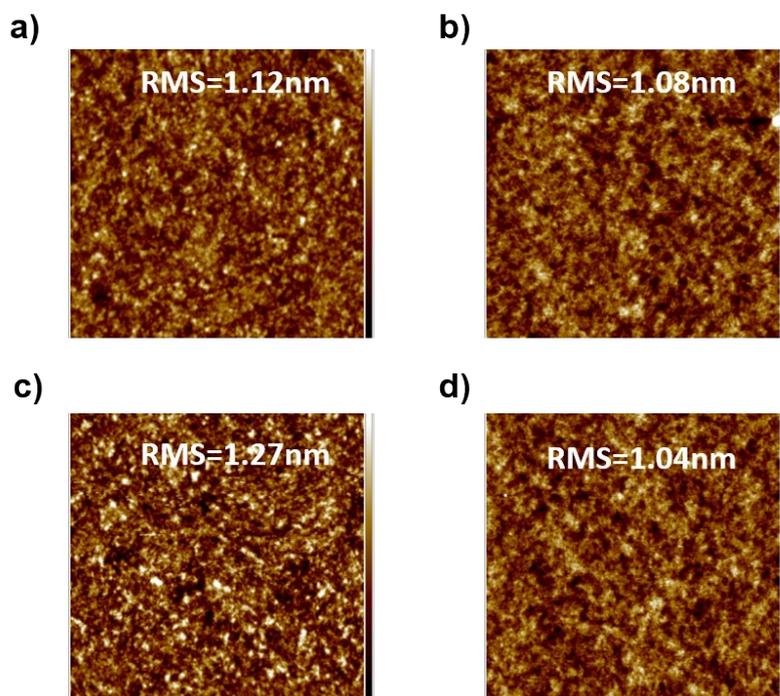
coated and annealed at 120 °C for 5 min. A thin film of P4VP ( $\approx 10$  nm) was spin-coated on ZnO nanoparticles layer. Then the solution of PM6:CH1007:PC<sub>71</sub>BM (1:1.05:0.15, CF:CN=100:0.5, v:v) was spincoated with different thickness, followed by annealing at 90°C for 5 min. A MoOx ( $\sim 2$  nm) and Ag ( $\sim 150$  nm) was successively evaporated onto the active layer through a shadow mask to define the active area of the devices ( $\sim 0.04$  cm<sup>2</sup>) in a vacuum chamber ( $< 2 \times 10^{-4}$  Pa).



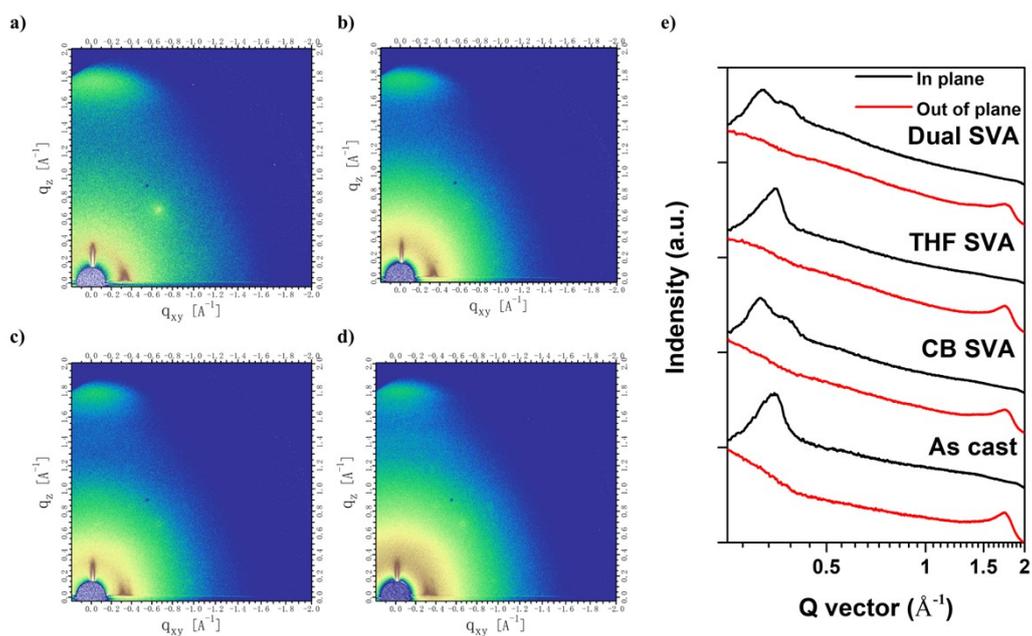
**Fig. S1** a) The absorptions of F-ThBr, D18 and blend film. b) The absorptions of PM6, CH1007 and their blend film.



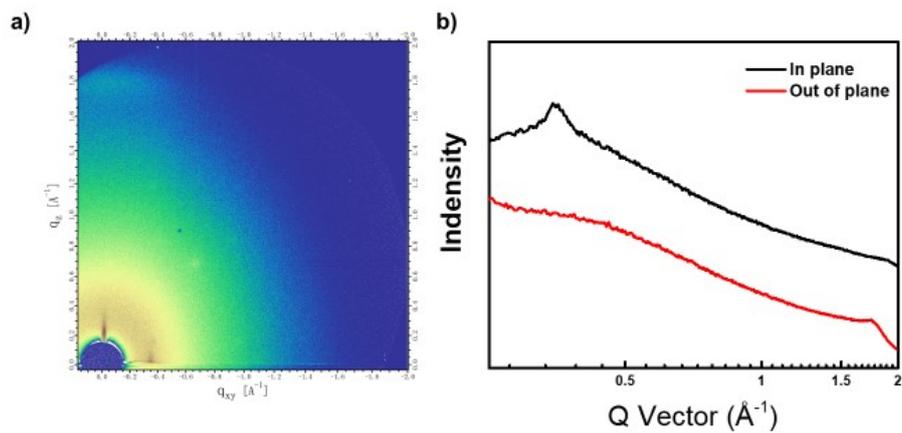
**Fig. S2** a) FTSP-EQE of D18:F-ThBr device. b) EQE<sub>cl</sub> of D18:F-ThBr device.



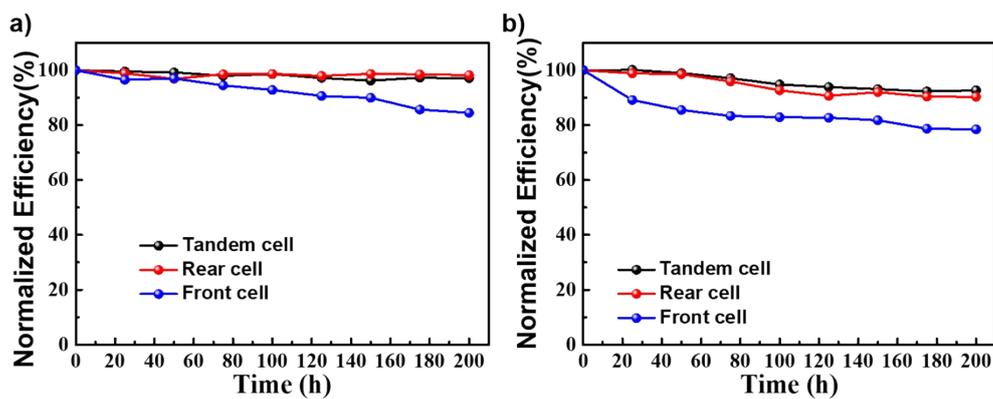
**Fig. S3** AFM image of D18:F-ThBr blend film treat with a) THF SVA. b) dual- SVA. c) CB SVA. and d) as cast.



**Fig. S4** GIWAXS pattern for a) As cast blend film. b) Blend film treat with THF SVA. c) Blend film treat with CB SVA. d) Blend film treat with dual- SVA. e) in-plane and out-of-plane line cuts of the corresponding GIWAXS patterns.



**Fig. S5** a) GIWAXS pattern for F-ThBr neat film. b) In-plane and out-of-plane line cuts of the corresponding GIWAXS patterns.



**Fig. S6** a) PCE versus storage time with device stored in Ar protected glove box without encapsulation. b) PCE versus storage time with device stored in Ar protected glove box without encapsulation under 80°C.

**Table S1.** Photovoltaic performance of the solar cells based on D18:F-ThBr blend films with different SVA solvents under illumination of AM 1.5 G, 100 mW cm<sup>-2</sup>.

Solvent	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE (%) <sup>a)</sup>
As cast	1.095	15.55	64.90	11.05
	(1.094±0.003)	(15.33±0.48)	(64.84±1.36)	(10.79±0.32)
CB	1.086	16.97	68.40	12.61
	(1.086±0.001)	(16.81±0.27)	(68.41±0.60)	(12.46±0.12)
THF	1.091	16.35	70.36	12.55
	(1.087±0.002)	(16.35±0.21)	(69.54±0.63)	(12.36±0.21)
CB+THF	1.089	16.68	71.69	13.03
	(1.085±0.002)	(16.56±0.36)	(70.01±0.91)	(12.88±0.12)

<sup>a)</sup> Statistical and optimal results are listed outside of parentheses and in parentheses, respectively, and the average parameters were calculated from 10 independent cells.

**Table 2.** E<sub>loss</sub> parameters of the device based on D18:F-ThBr.

V <sub>oc</sub> (V)	E <sub>g</sub> <sup>a</sup> (eV)	E <sub>loss</sub> (V)	V <sub>oc</sub> <sup>SQ</sup> <sup>b</sup> (V)	ΔE <sub>1</sub> (eV) <sup>c</sup>	V <sub>oc</sub> <sup>rad</sup> <sup>c</sup> (V)	ΔE <sub>2</sub> (eV)	ΔE <sub>3</sub> (cal.V)	ΔE <sub>3</sub> (exp. V)
1.089	1.782	0.693	1.498	0.284	1.375	0.123	0.286	0.270

<sup>a</sup>E<sub>g</sub> was estimated via the crossing points between normalized absorption and PL spectra of films. <sup>b</sup>V<sub>oc</sub><sup>SQ</sup> is the maximum Voc from the SQ limit. <sup>c</sup>V<sub>oc</sub><sup>rad</sup> is the Voc when there is only radiative recombination and are calculated from EL and sEQE measurements. ΔE<sub>3</sub> (ΔV<sub>nr</sub>) is determined by two approaches: 1) calculated by V<sub>oc</sub><sup>rad</sup> - V<sub>oc</sub> and 2) obtained from the equation ΔV<sub>nr</sub> = (kT/q)ln (1/EQE<sub>EL</sub>) by measuring the device EQE<sub>EL</sub>.

**Table S3.** Photovoltaic performance of the rear cells with different ETL under illumination of AM 1.5 G, 100 mW cm<sup>-2</sup>.

ETL	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	FF(%)	PCE (%) <sup>a)</sup>
ZnO	0.825 (0.820±0.003)	25.33 (25.80±0.29)	69.58 (69.27±1.09)	14.54 (14.63±0.21)
ZnO/ PFN-Br	0.829 (0.827±0.002)	26.19 (25.90±0.40)	71.47 (70.61±0.51)	15.52 (15.46±0.26)
ZnO/ P4VP	0.832 (0.835±0.003)	27.01 (26.50±0.40)	73.69 (71.98±1.21)	16.58 (15.95±0.39)

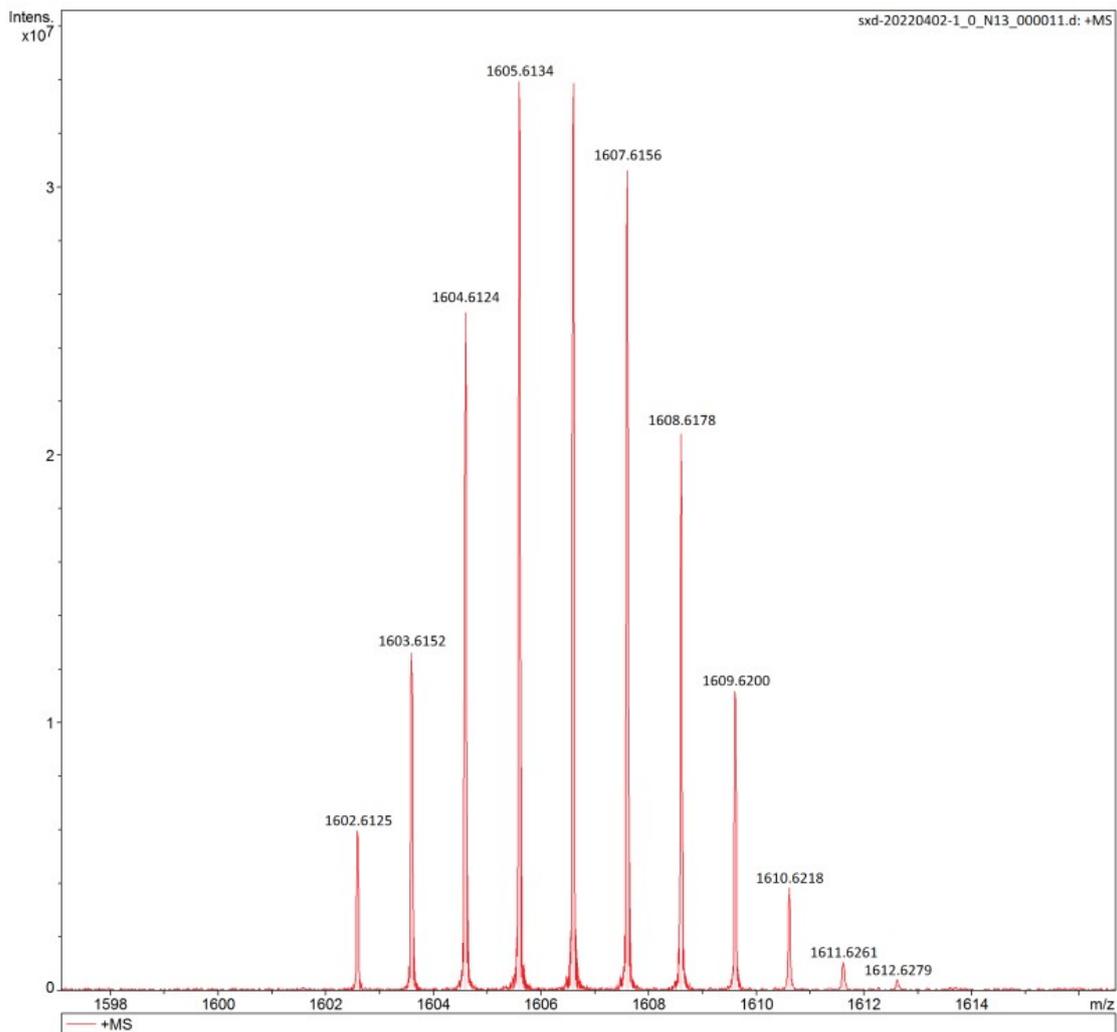
<sup>a)</sup> Statistical and optimal results are listed outside of parentheses and in parentheses, respectively, and the average parameters were calculated from 10 independent cells.

**Table S4.** Photovoltaic performance of the tandem cells with different ICL under illumination of AM 1.5 G, 100 mW cm<sup>-2</sup>.

ICL	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE (%) <sup>a)</sup>
M-PEDOT: ZnO (NPs)	1.884 (1.873±0.007)	12.63 (12.55±0.34)	69.73 (68.82±0.96)	16.59 (16.18±0.42)
M-PEDOT: ZnO (NPs): P4VP	1.882 (1.880±0.007)	12.92 (12.75±0.34)	72.54 (70.05±1.03)	17.67 (17.29±0.41)

<sup>a)</sup> Statistical and optimal results are listed outside of parentheses and in parentheses, respectively, and the average parameters were calculated from 10 independent cells.





**Figure. S9** High resolution mass spectra of *F-ThBr*.

## 5. References

1. F. Lin, K. Jiang, W. Kaminsky, Z. Zhu, A. K. Y. Jen, *J. Am. Chem. Soc.*, **2020**, 142, 15246.
2. Z. Luo, T. Liu, Y. Xiao, T. Yang, Z. Chen, G. Zhang, C. Zhong, R. Ma, Y. Chen, Y. Zou, X. Lu, H. Yan, C. Yang, *Nano Energy*, **2019**, 66, 104146.
3. N. Qiu, H. Zhang, X. Wan, C. Li, X. Ke, H. Feng, B. Kan, H. Zhang, Q. Zhang, Y. Lu, Y. Chen, *Adv. Mater.*, **2017**, 29, 1604964.