

## Electronic Supplementary Information

### **Chemical Engineering of Methylammonium Lead Iodide / Bromide Perovskites: Tuning of Opto-electronic Properties and Photovoltaic Performance**

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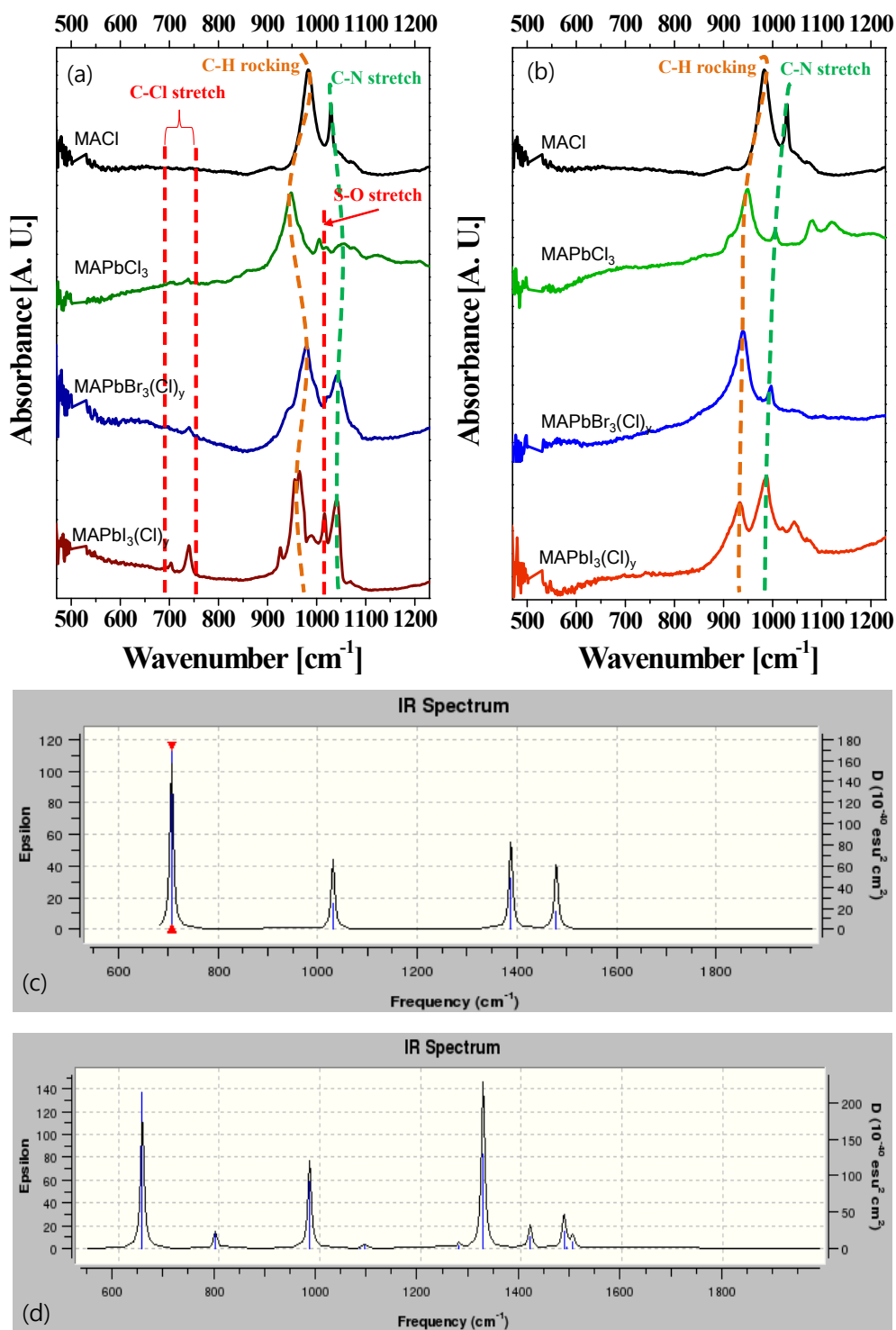


Figure S1. ATR FT-IR full spectra summarized (a) before annealing the OIHPs and (b) after annealing the OIHPs. Theoretical IR spectrum of (c)  $\text{CH}_3\text{Cl}$  with a C-Cl vibration at 707  $\text{cm}^{-1}$  and (d)  $\text{C}_2\text{H}_5\text{Cl}$  with a C-Cl vibration at 647  $\text{cm}^{-1}$  calculated on a B3LYP/6-311(d,p) level.

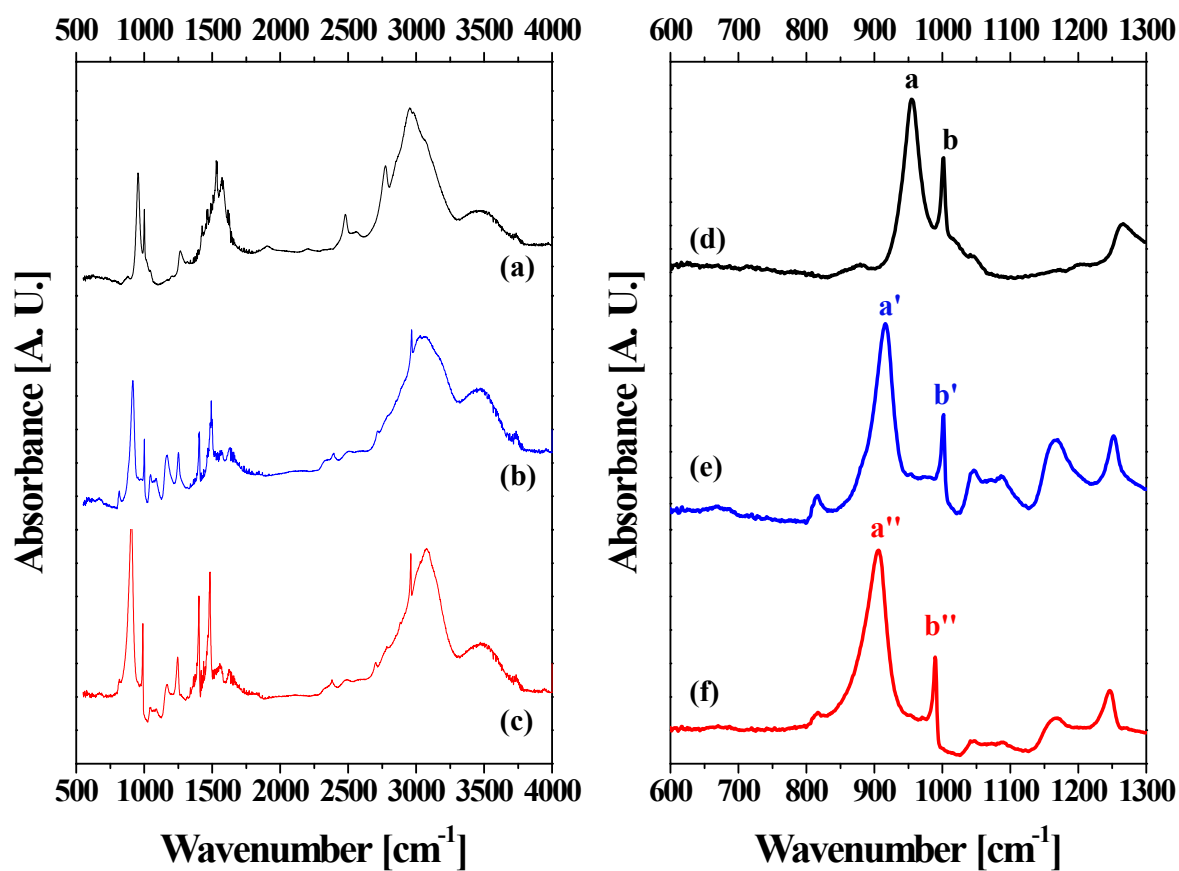


Figure S2. ATR FT-IR full spectra for (a) MACl, (b) MABr and (c) MAI display at left panel appeared the two vibration modes such as N-C stretch (*a*, *a'* and *a''*) and NH<sub>3</sub> rocking (*b*, *b'* and *b''*) modes.

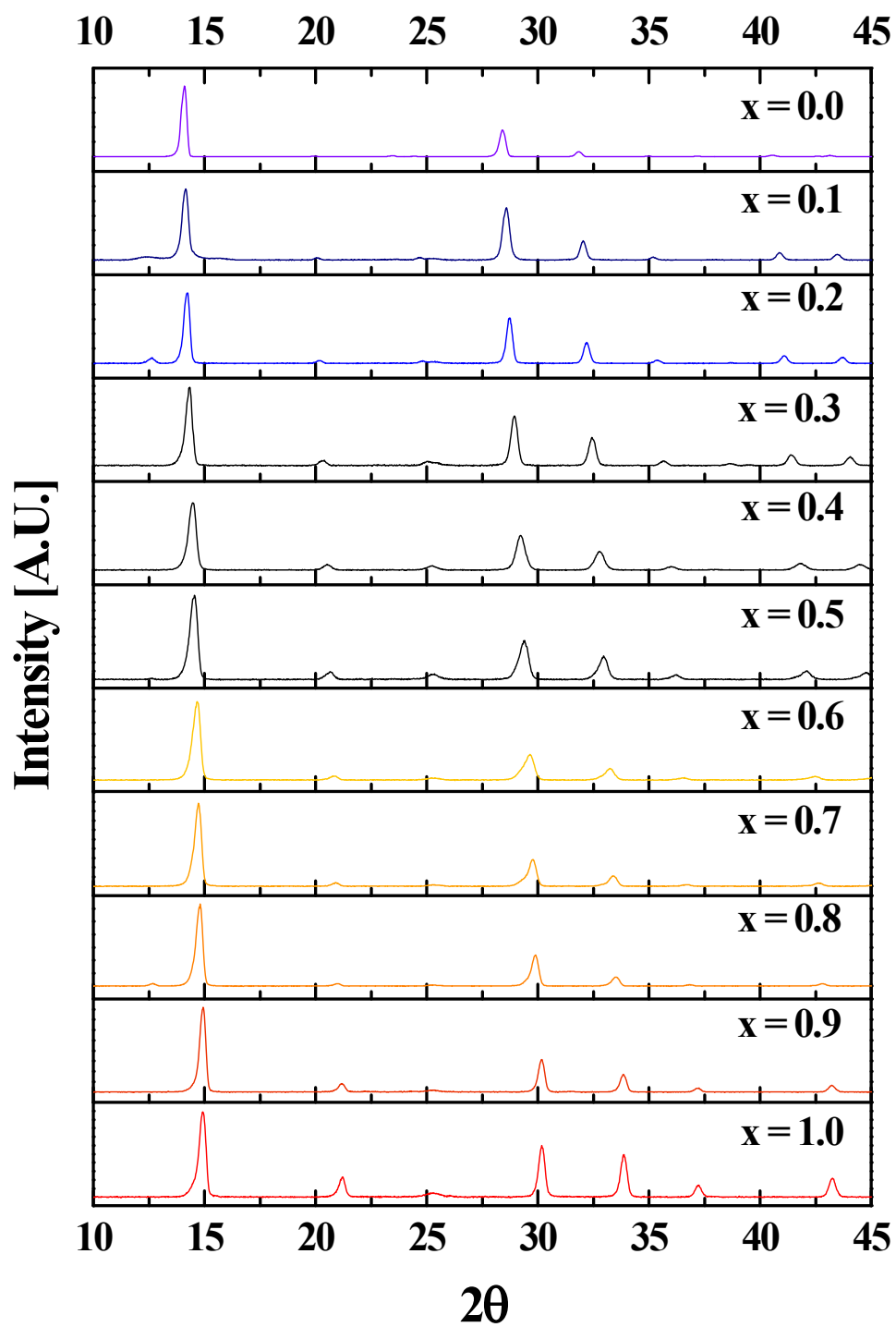


Figure S3. XRD patterns for  $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3\text{Cl}_3$  perovskite. ( $x$  ; 0.0 ~1.0).



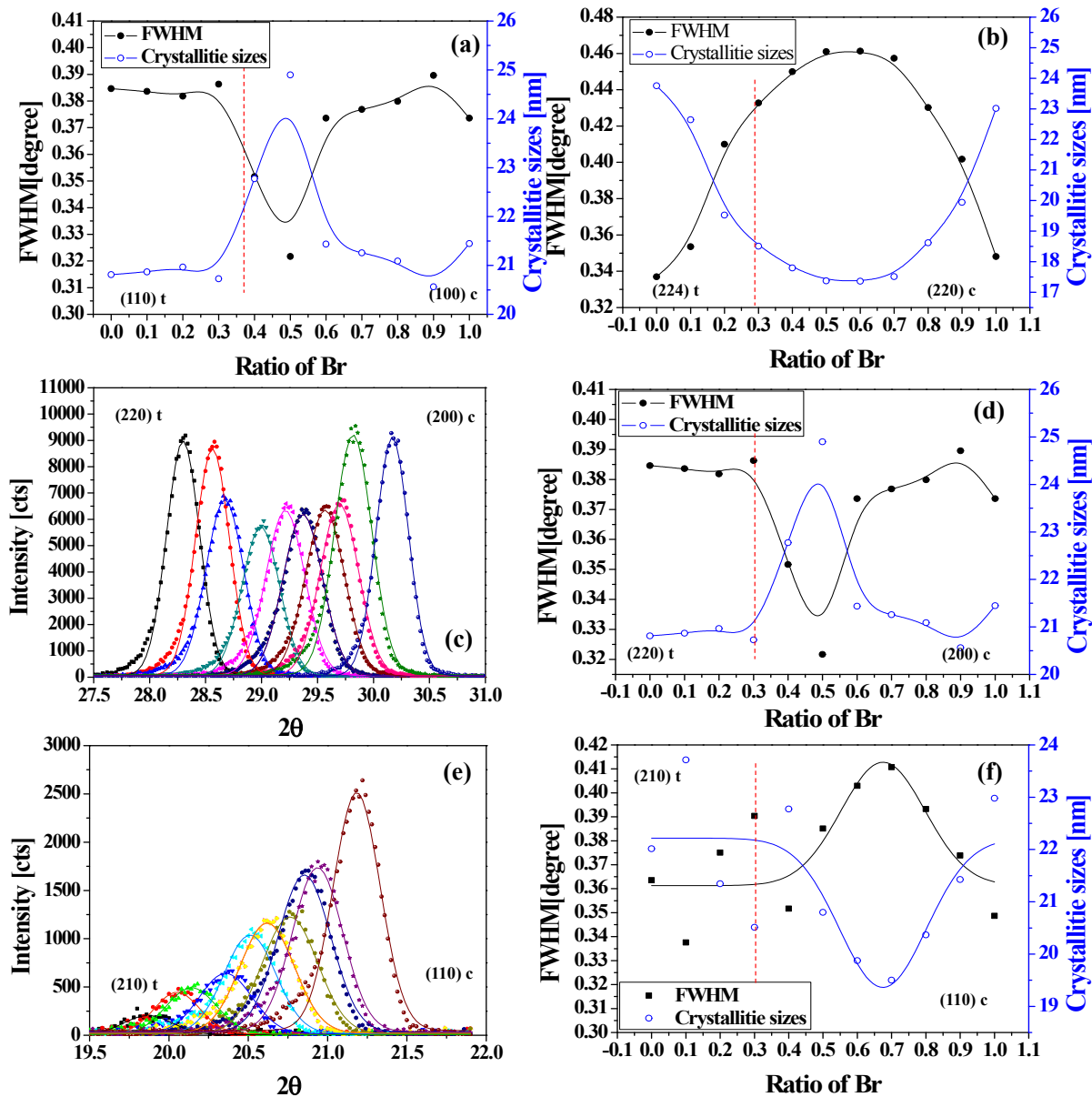


Figure S4. The parameters of crystalline sizes and FWHM ; (a) (110)t to (100)c of orientation transition, (b) (224)t to (220)c of orientation transition, (c) crystalline phase transition of (220)t and (200)c with (d) calculated parameters, (e) crystalline phase transition of (220)t and (200)c with (f) calculated parameters

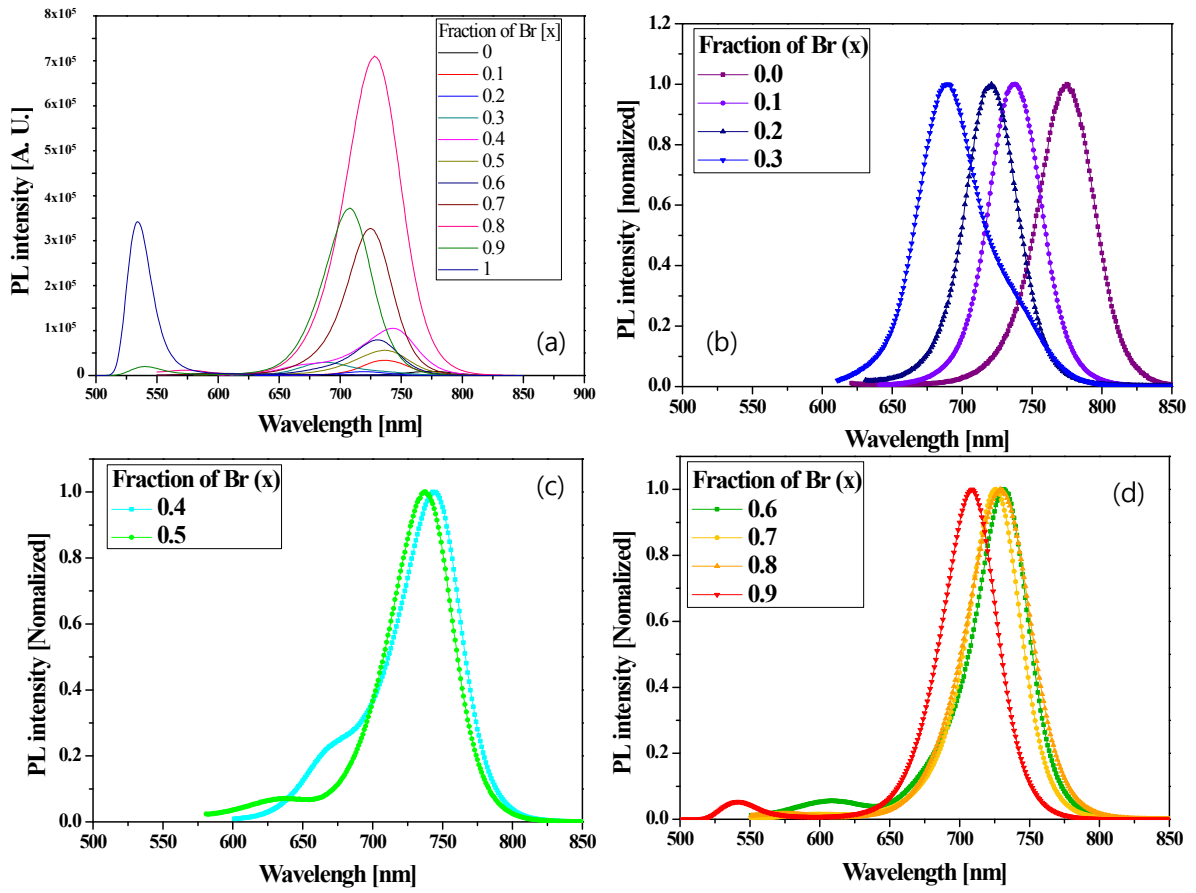


Figure S5. PL spectra for different  $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3\text{Cl}_y$  perovskite films. (x ; 0.0 ~1.0). (a) Raw data. (b-d) Normalized spectra for different fractions of Br.

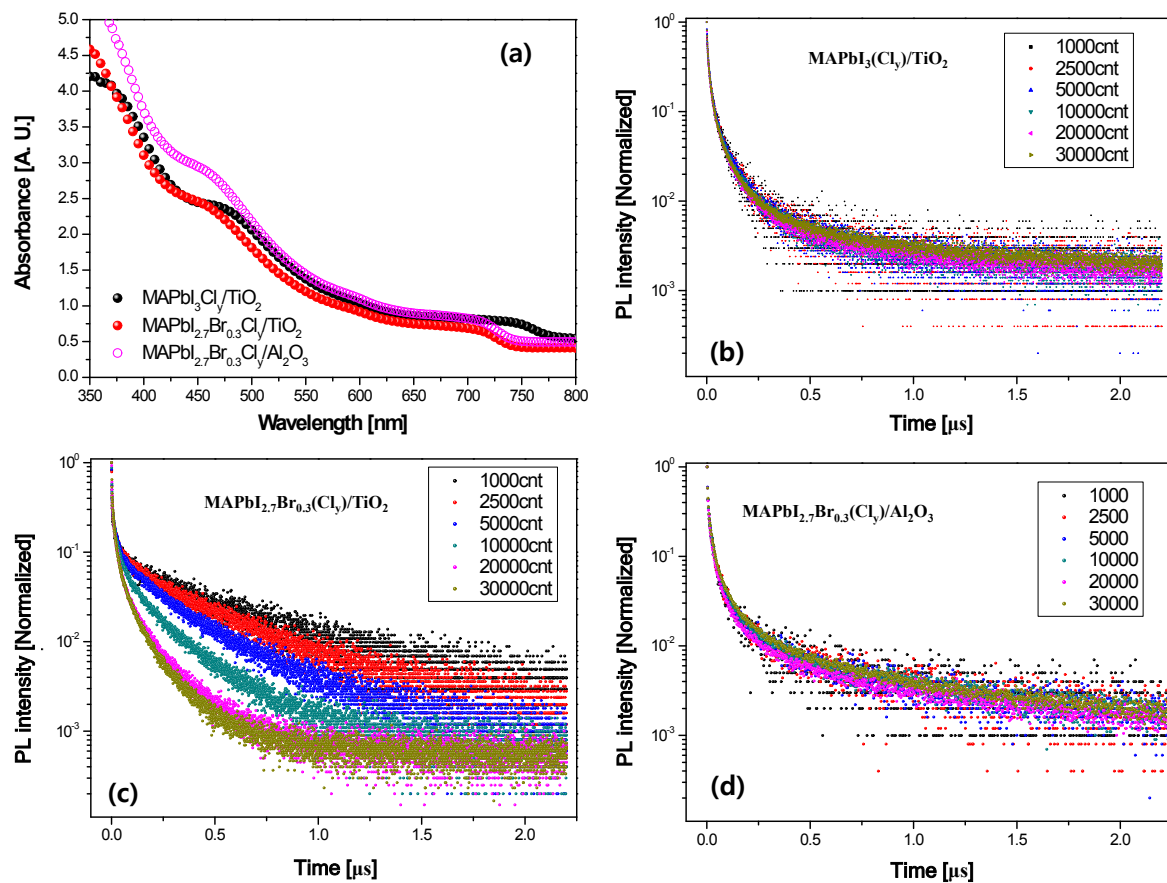


Figure S6. UV-vis spectra and single photon counting results for different  $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3\text{Cl}_y$  perovskite. ( $x$  ; 0.0 ~1.0)

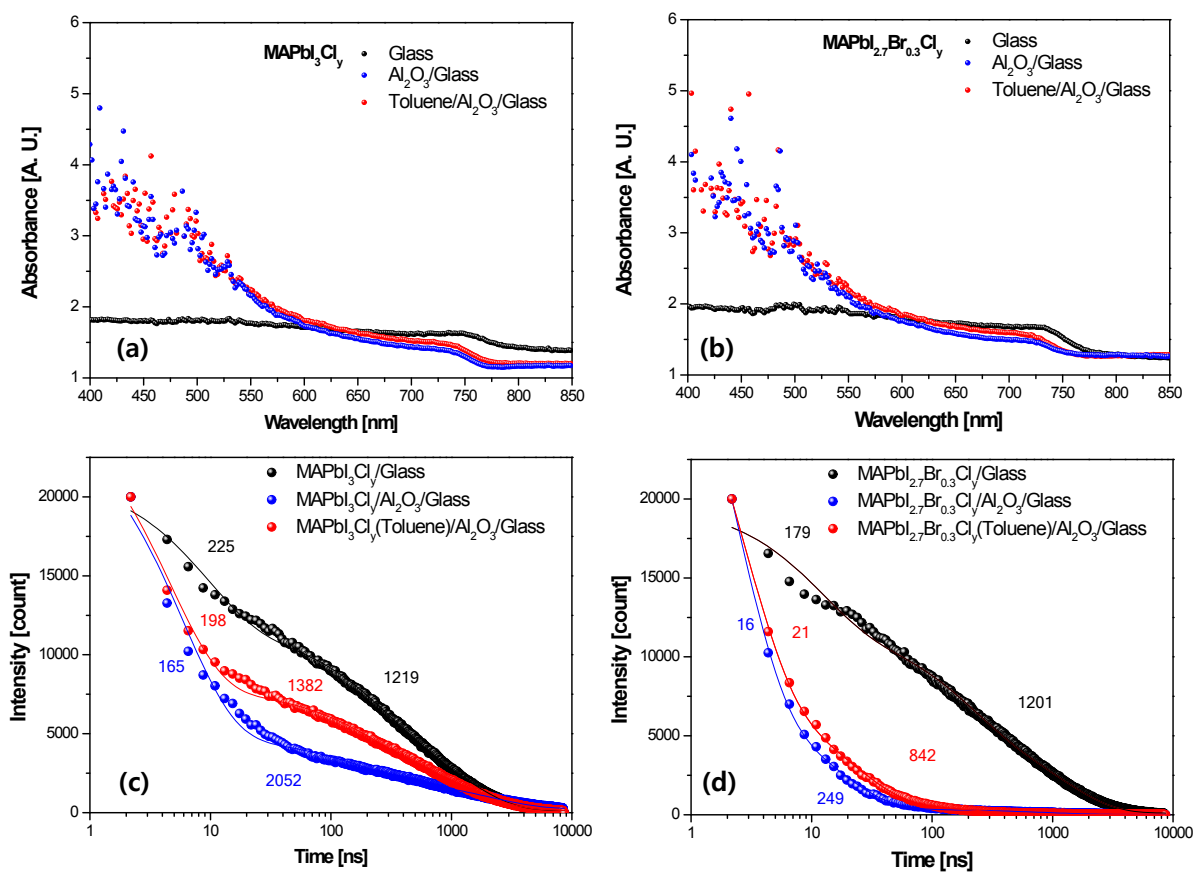


Figure S7. UV-vis spectra and single photon counting results for different  $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3\text{Cl}_y$  perovskite. ( $x$  ; 0.0 and 0.1) (with and without scaffold layers, toluene addition effect)

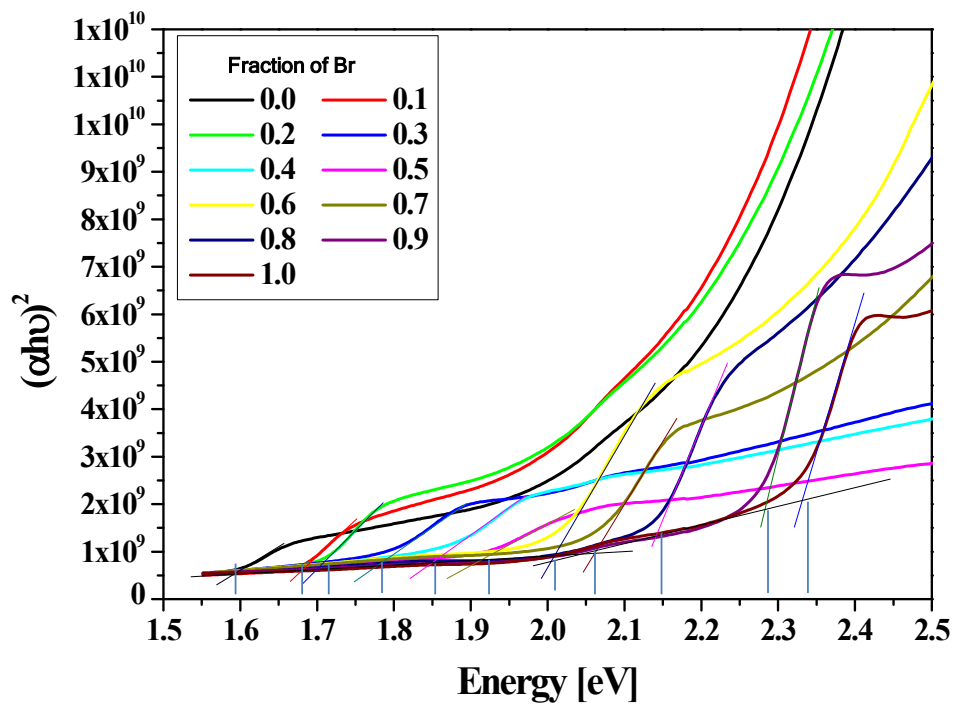


Figure S8. Tauc plots for optical band gap determination for  $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3\text{Cl}_y$ . ( $x = 0.0 \sim 1.0$ ) thin films.

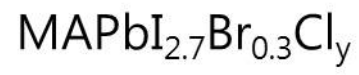
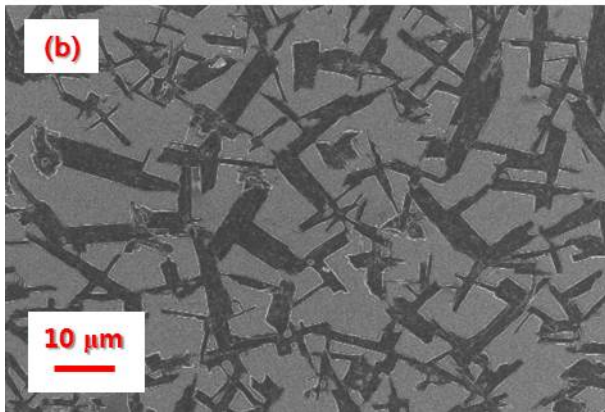
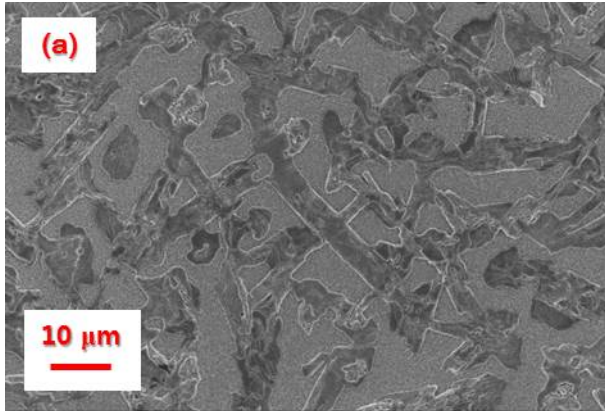


Figure S9. Surface SEM images onto  $\text{Al}_2\text{O}_3$  scaffold layer



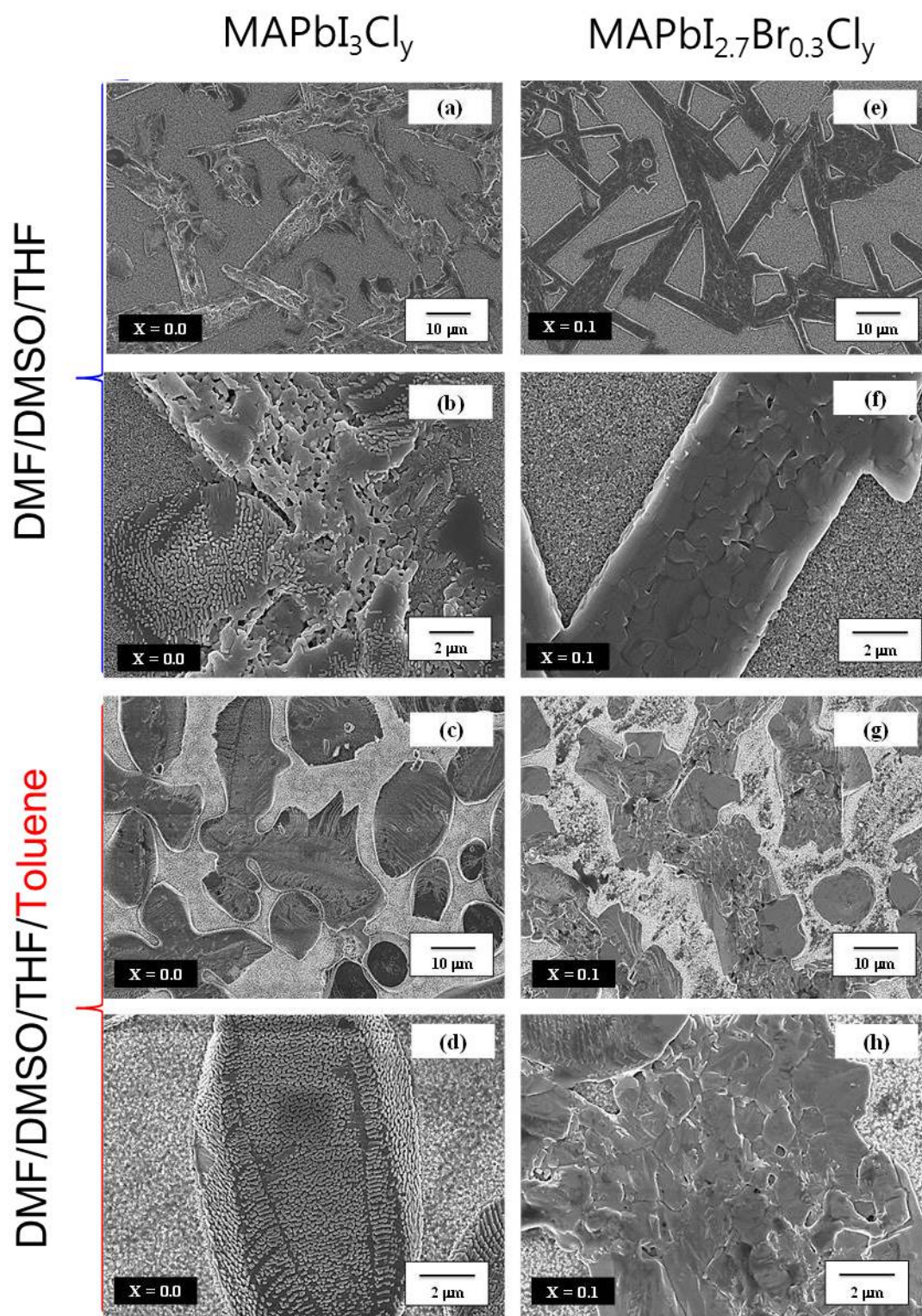


Figure S10. Surface SEM images on an effect of Toluene addition. (TiO<sub>2</sub> scaffold layer)

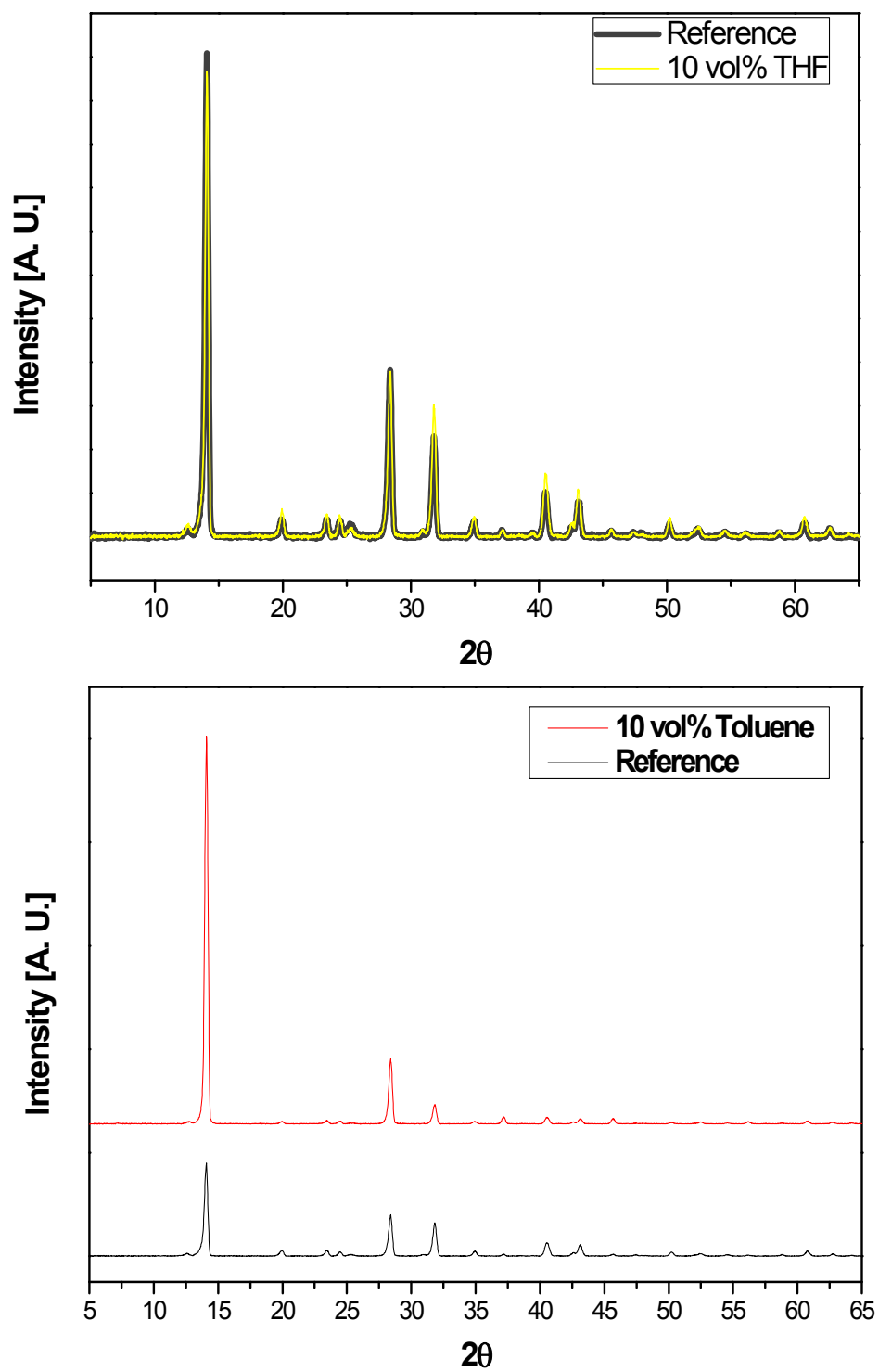


Figure S11. (Top) XRD patterns for 10vol% THF solvent as additive within a mixed solvent of DMSO and DMF (30 : 70, v/v), (Bottom) The effect of toluene as an additive within  $\text{MAPbI}_3\text{Cl}_y$  precursors



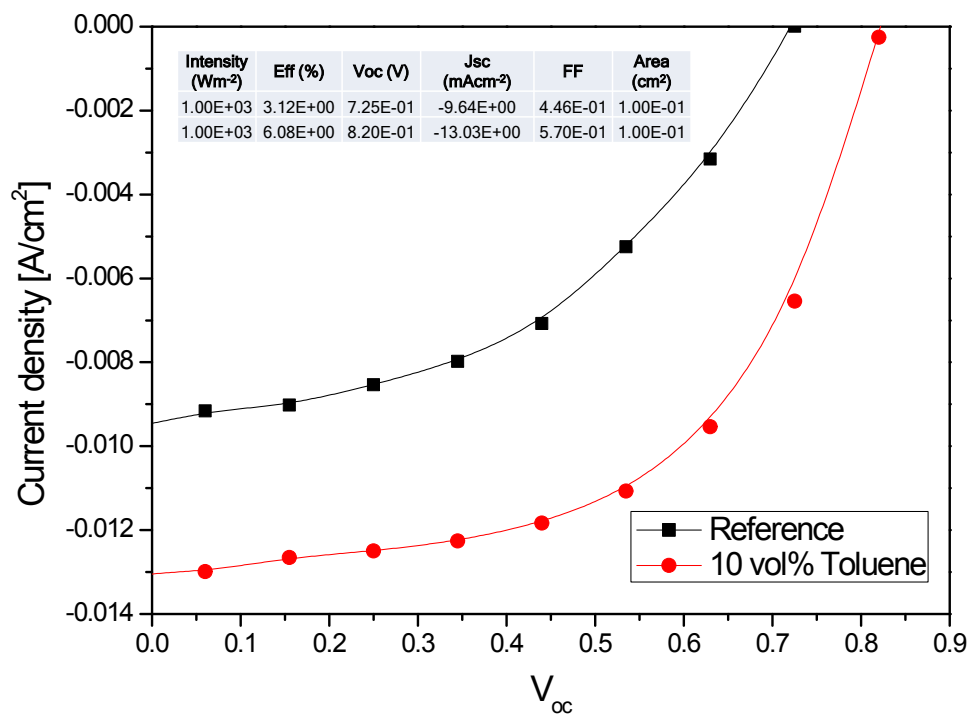


Figure S12. J-V curves of OIHPs solar cells display for 10 vol% Toluene effect as an additive in DMSO and DMF (30 : 70, v/v)

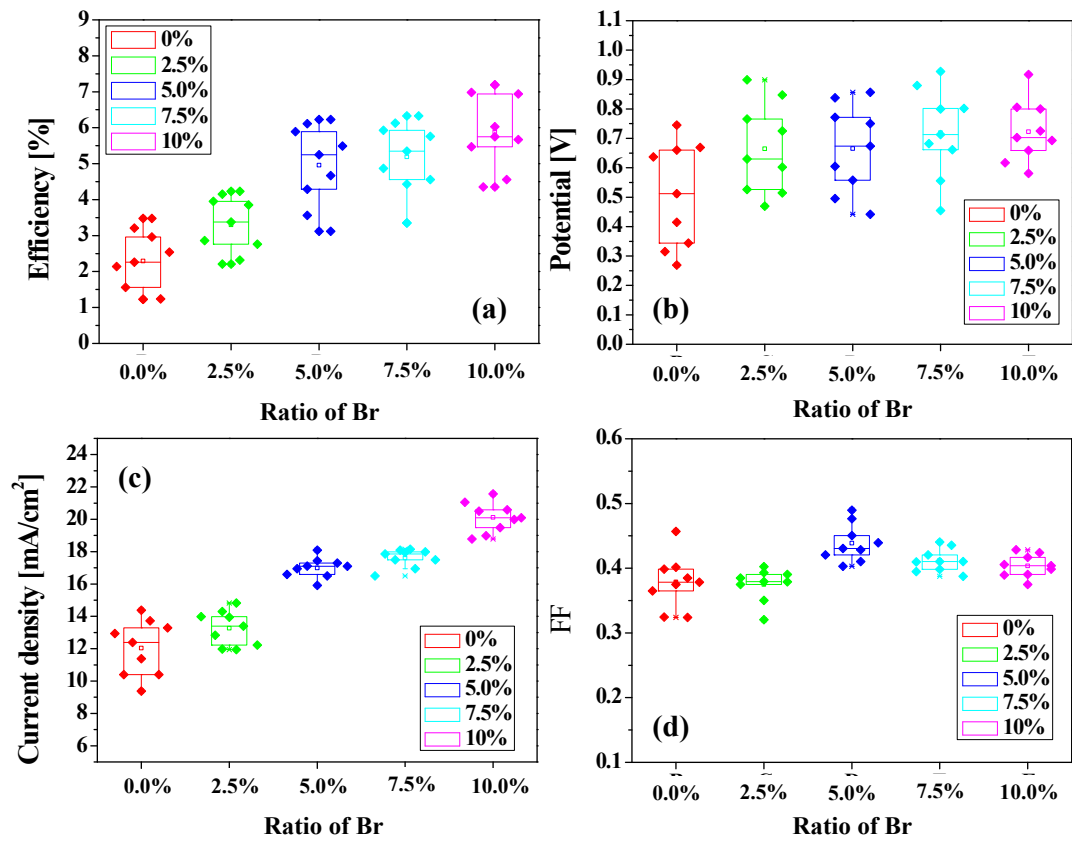


Figure S13. The parameters of OIHP solar cell performances with increment Br ratio from 0% to 10%. It is extracted from one batch with each Br substitution ratio. (TiO<sub>2</sub> scaffold layer)

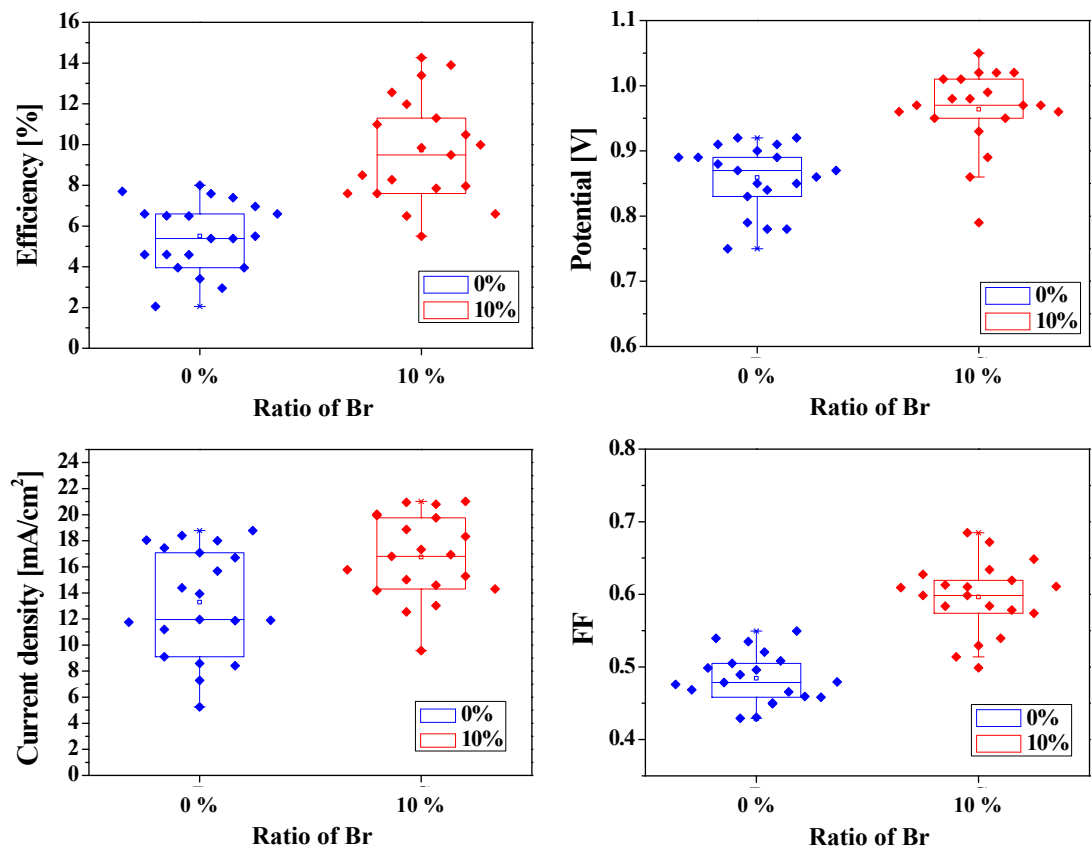


Figure S14. The parameters of OIHP solar cell performances with increment Br ratio from 0% and 10%. It is extracted from data from 20 devices from different batches. ( $\text{Al}_2\text{O}_3$  scaffold layer)

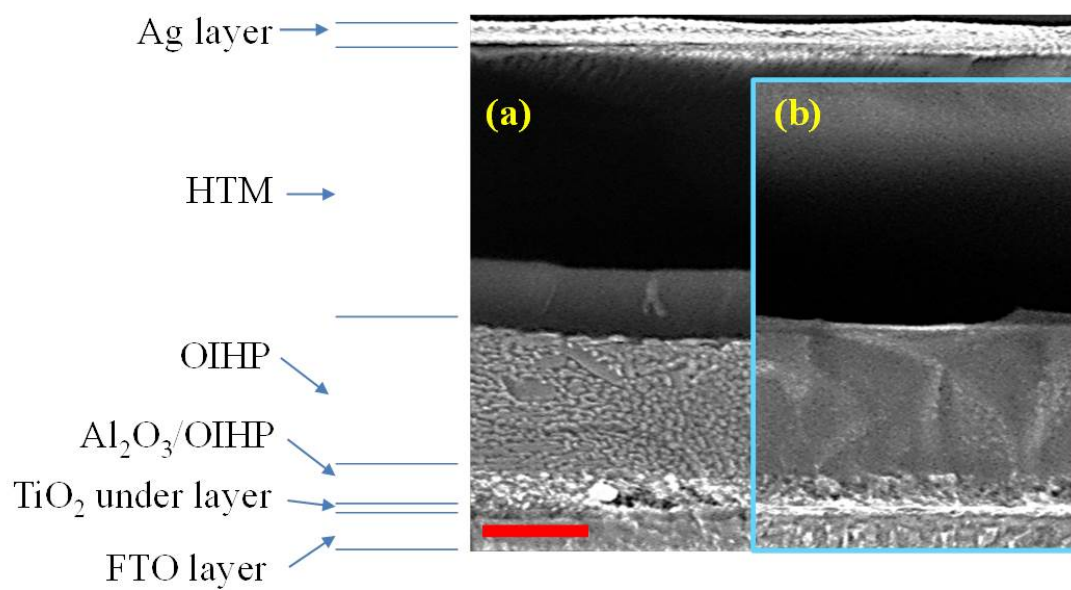


Figure S15. Cross-sectional SEM images on (a) MAPbI<sub>3</sub>(Cl)<sub>y</sub> and (b) MAPbI<sub>2.7</sub>Br<sub>0.3</sub>(Cl)<sub>y</sub>. The red scale bar is assigned to 250 nm.

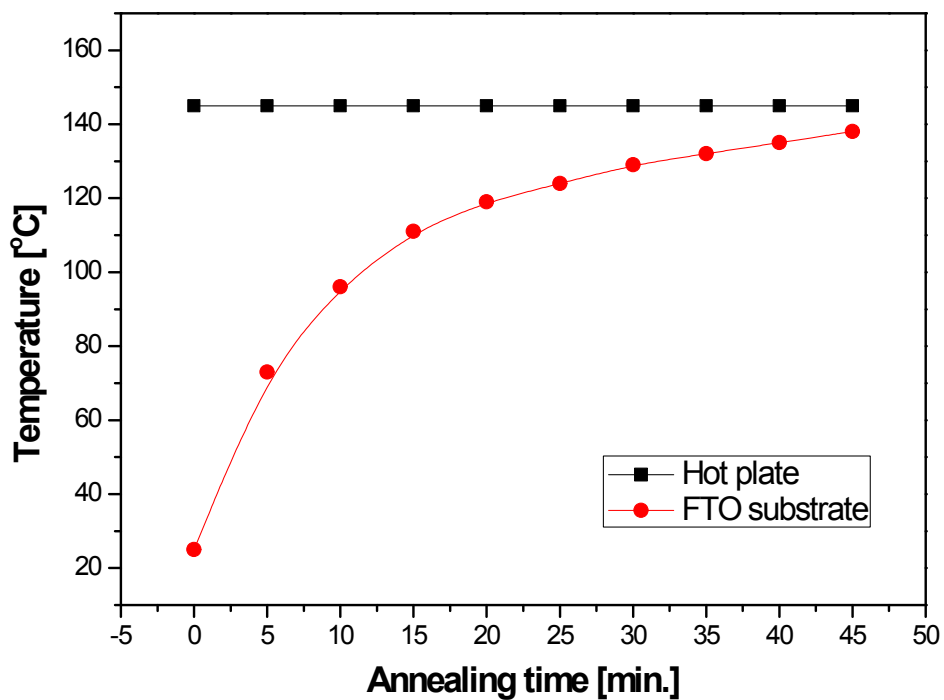


Figure S16. Surface temperature of hot plate and FTO glass substrate during annealing process for OIHPs.

Table S1. Summary of the solar cell parameters from JV curves shown in Figure 8(a and c)

Ratio of Br	Eff (%)	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF	Area (cm <sup>2</sup> )
0.0 %	3.6	0.68	13.7	0.39	0.2
2.5 %	4.4	0.77	14.8	0.39	0.2
5.0 %	6.5	0.78	17.4	0.48	0.2
7.5 %	6.6	0.79	18.2	0.46	0.2
10.0 %	7.8	0.82	21.6	0.44	0.2
0.0 % (Al <sub>2</sub> O <sub>3</sub> ) Forward	8.0	0.90	17.1	0.52	0.1
0.0 % (Al <sub>2</sub> O <sub>3</sub> ) Backward	5.6	0.84	16.0	0.41	0.1
10.0 % (Al <sub>2</sub> O <sub>3</sub> ) Forward	14.2	1.02	20.8	0.67	0.1
10.0 % (Al <sub>2</sub> O <sub>3</sub> ) Backward	12.8	1.01	20.4	0.62	0.1