Supporting Information

Efficient bandgap widening of co-evaporated $MAPbI_3$ perovskite

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Experimental Section

Perovskite Absorber

$MAPbI_3$ with excess PbI_2 was deposited using the co-evaporation deposition method [2], employing PbI_2 powder (TCI) and MAI powder (Lumtec). The PbI_2 source was fit at 260 °C and the MAI source was set at 100 °C with a total deposition time of 180 mins inside a vacuum chamber with a base starting chamber pressure of $8*10^{-6}$ Torr. Upon deposition, the $MAPbI_3$ film was subsequently annealed at 100 °C for 30 mins. QCM deposition rate was not given due to instability of the QCM reading due to MAI background pressure.

$MAPb(Br_xI_{1-x})_3$ was prepared using as-deposited $MAPbI_3$ as a template. The 750 nm $MAPbI_3$ is chosen since it results in the highest PCE [27]. The MABr (Greatcell) is dissolved in anhydrous isopropanol (IPA) with concentrations ranging from 5 - 15 mg/mL. The as-deposited $MAPbI_3$ was then subjected to MABr/IPA treatment with a different conversion time of 1 min and 5 mins respectively, follows by spin coating at 5000 rpm for 30 s to remove unreacted MABr/IPA and consequently being annealed at 100 °C for 30 mins.

Perovskite solar cell fabrication

Fluorine-doped tin oxide (FTO) glass substrates were cleaned using decon soap, water, and ethanol. Low-temperature bilayer p-SnO_2/PCBM is used as an electron transport layer, following previous procedures [2]. The Spiro-OMeTAD (70 mg/mL in chlorobenzene) (Lumtec) was prepared with addition of 28.5 μL 4-tert-butylpyridine (Sigma Aldrich) and 17.5 μL bis(trifluoromethane)sulfonamide lithium salt (Sigma Aldrich) solution (520 mg/mL in ACN). The Spiro-OMeTAD is deposited by spin-coating at 5000 rpm for 30 s. The PTAA solution is prepared by dissolving PTAA (EM Index) with concentration of 10 mg/mL inside toluene. 4 μL 4-tert-butylpyridine (Sigma Aldrich) and 6 μL bis(trifluoromethane)sulfonamide lithium salt (Sigma Aldrich) solution (170 mg/mL in ACN). The PTAA spin coating condition is at 5000 rpm for 30 s. A 100 nm gold electrode was deposited as back contact using thermal evaporation.

Textured silicon substrates

Polished wafers (Topsil) are textured in alkaline (KOH) solution to obtain randomly distributed pyramids. To accommodate the evaporated perovskite films, the size of the pyramids is controlled with different KOH concentrations, targeting pyramid sizes in the range of 5-7 μm. The wafers have been then cleaned with a standard RCA process as reported elsewhere.

Characterization

Morphological characterization was recorded using a Field Emission Scanning Electron Microscope (FESEM, JEOL JSM-7600F, 5 kV, and 10 mA). The absorbance was recorded using UV-Vis-NIR Spectrophotometer (UV3600, Shimadzu). The steady photoluminescence spectra were measured by Spectro-fluorophotometer (Shimadzu, RF-5301PC). The current density-voltage (J-V) curves were measured using Newport Oriel Sol3ATM solar simulator with a 450-Watt Xenon lamp which is calibrated using a standard silicon solar cell. The active area of 0.086 cm^2 was determined by a metal shadow mask. The incident photon-to-current conversion efficiency (IPCE) was measured by using a PVE300 (Bentham), with a dual xenon/quartz halogen light source in DC mode Newport Oriel. The XRD patterns of the thin films were recorded using X-ray diffraction (XRD; Bruker D8 Advance XRD). The XPS was conducted using Kratos AXIS Supra.

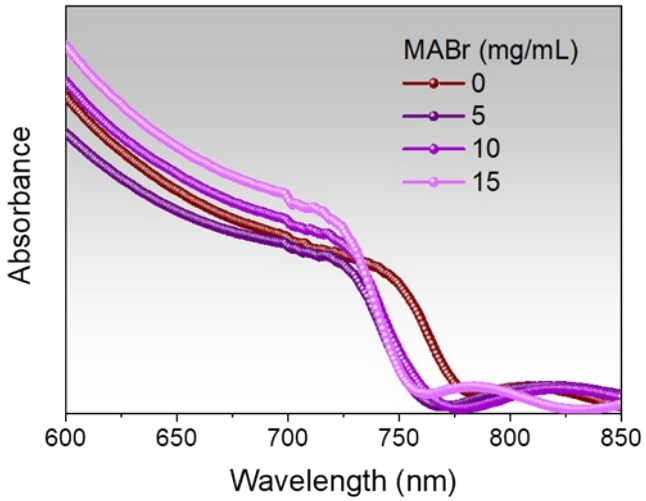

Fig. S1. The absorbance of $MAPbI_3$ and $MAPbI_3$+MABr treated with various MABr concentrations

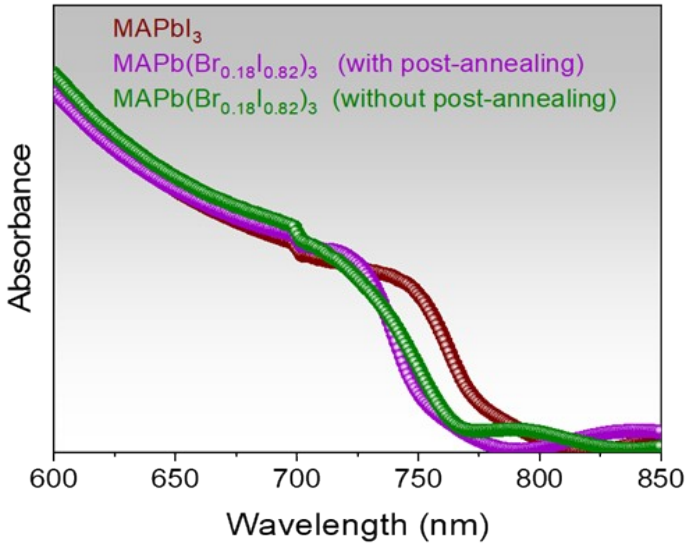

Fig S2. The absorbance of $MAPbI_3$ and $MAPb(Br_{0.18}I_{0.82})_3$ with (purple) and without post-annealing (green) at 100 °C for 30 mins

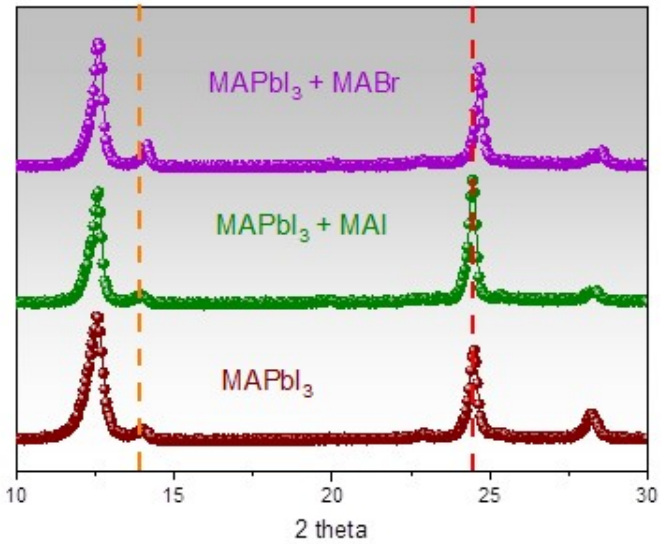

Fig. S3. XRD patterns of $MAPbI_3$ (brown), $MAPbI_3$ +MAI (green), and $MAPbI_3$ +MABr (purple) treated for 1 minute. The <110> perovskite peak (orange line) and <202> perovskite peak (red line) for $MAPbI_3$

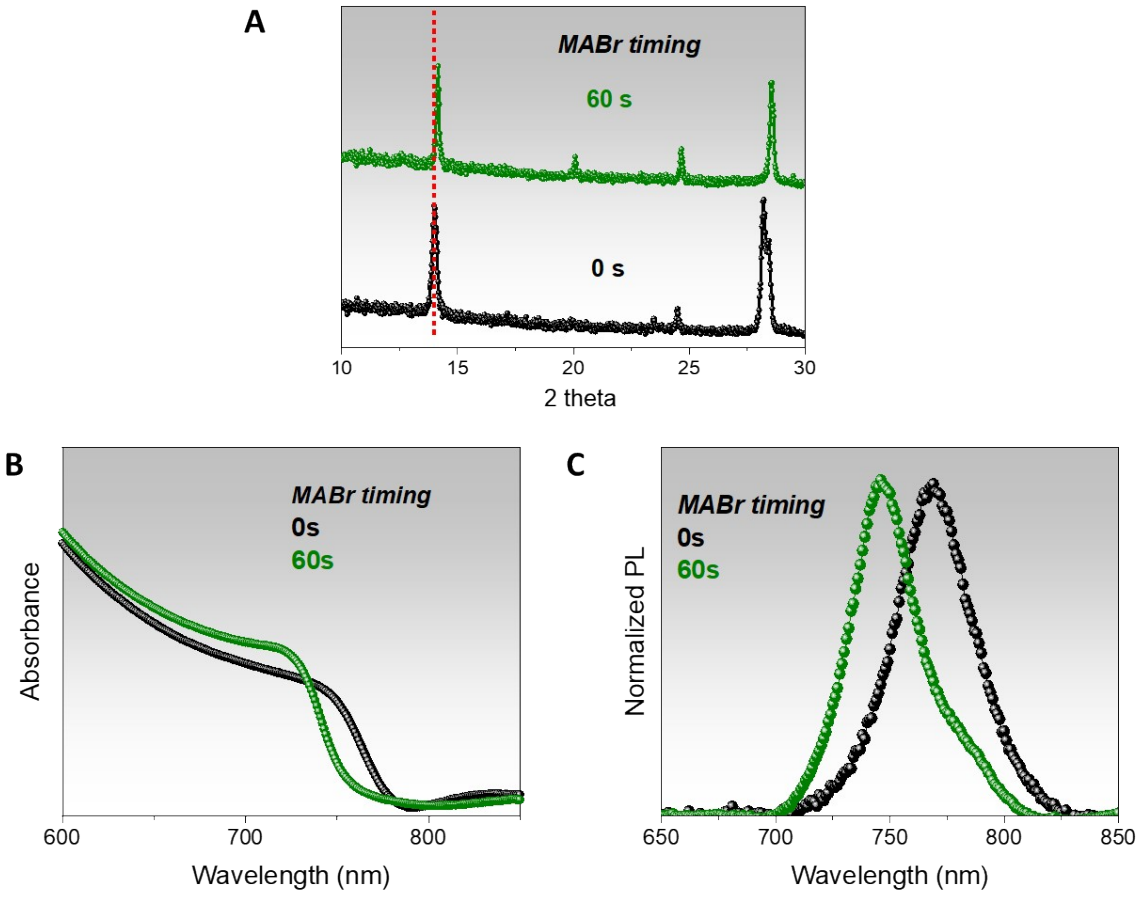

Fig. S4. MABr treatment on stoichiometric grown co-evaporated $MAPbI_3$. (A) XRD patterns. The red dotted line shows the <110> perovskite growth orientation. (B) Absorbance, and (C)

Normalized steady-state photoluminescence, of $MAPbI_3$ (black) and $MAPbI_3$ treated with MABr for 60 s (green).

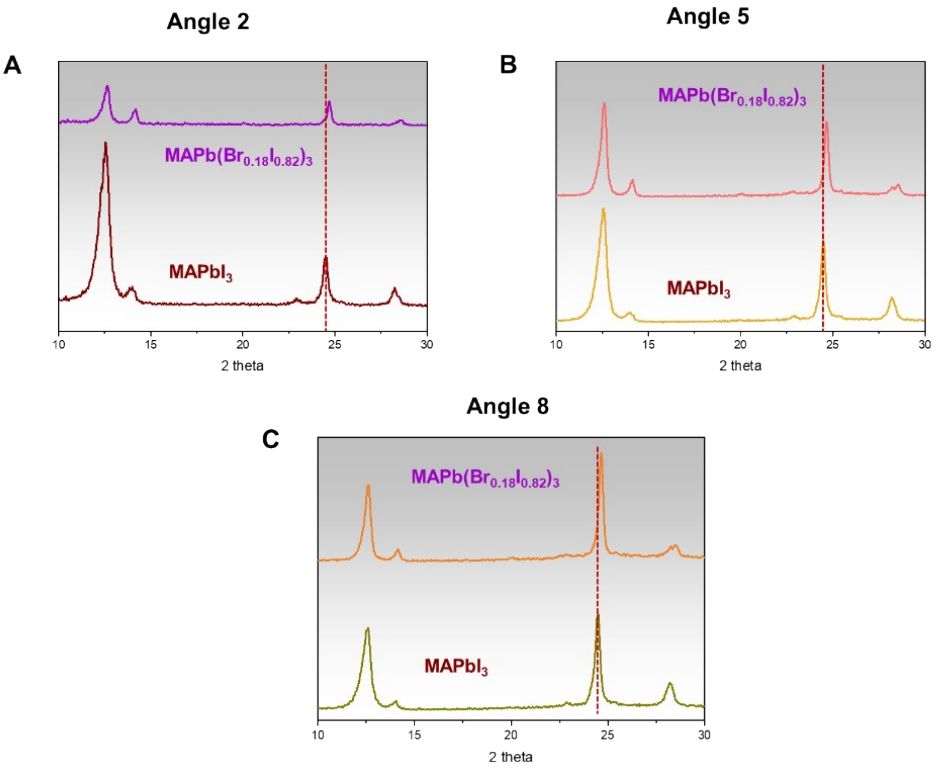

Fig. S5. The non-normalized XRD spectra were taken at (A) 2°, (B) 5°, and (C) 8° XRD angle for both $MAPbI_3$ and $MAPb(Br_{0.18}I_{0.82})_3$ films. The dotted lines represent <202> perovskite orientation for $MAPbI_3$ composition.

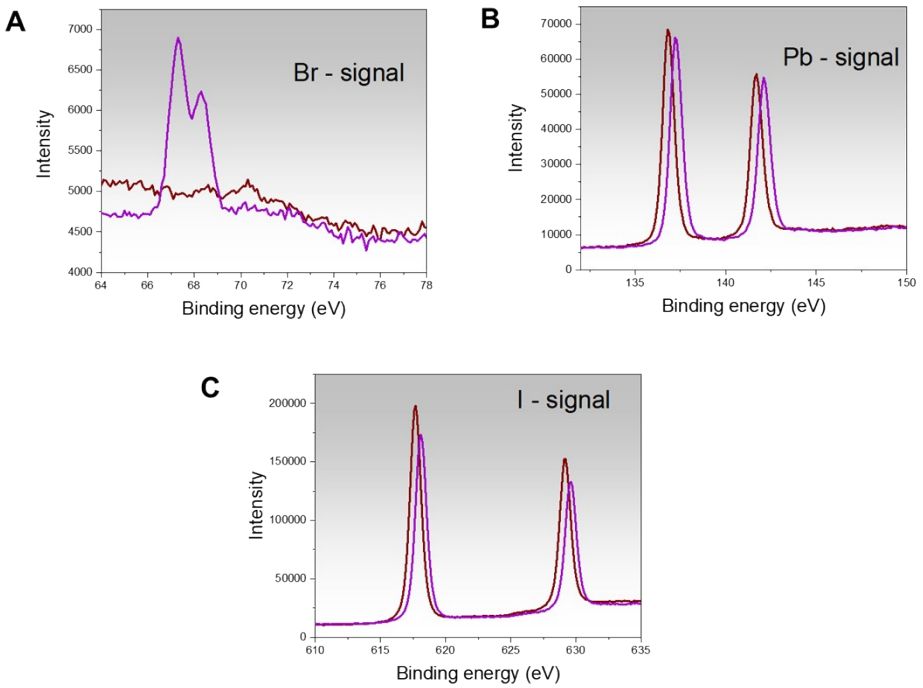

Fig. S6. XPS of $MAPbI_3$ (brown) and $MAPb(Br_{0.18}I_{0.82})_3$ (purple) films (A) Br, (B) Pb, and (C)

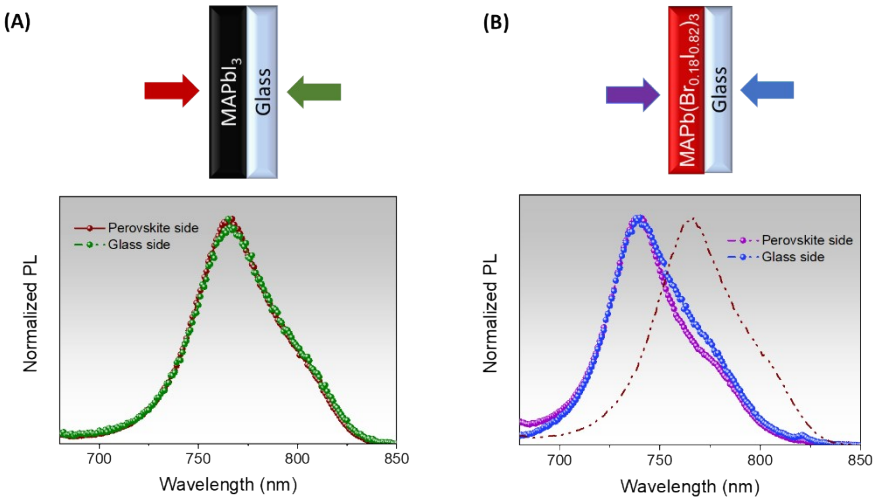

Fig. S7. Schematic of steady-state photoluminescence taken from both perovskite and glass side for (A) $MAPbI_3$ and (B) $MAPb(Br_{0.18}I_{0.82})_3$ films, the dotted brown line refer to steady-state photoluminescence of $MAPbI_3$.

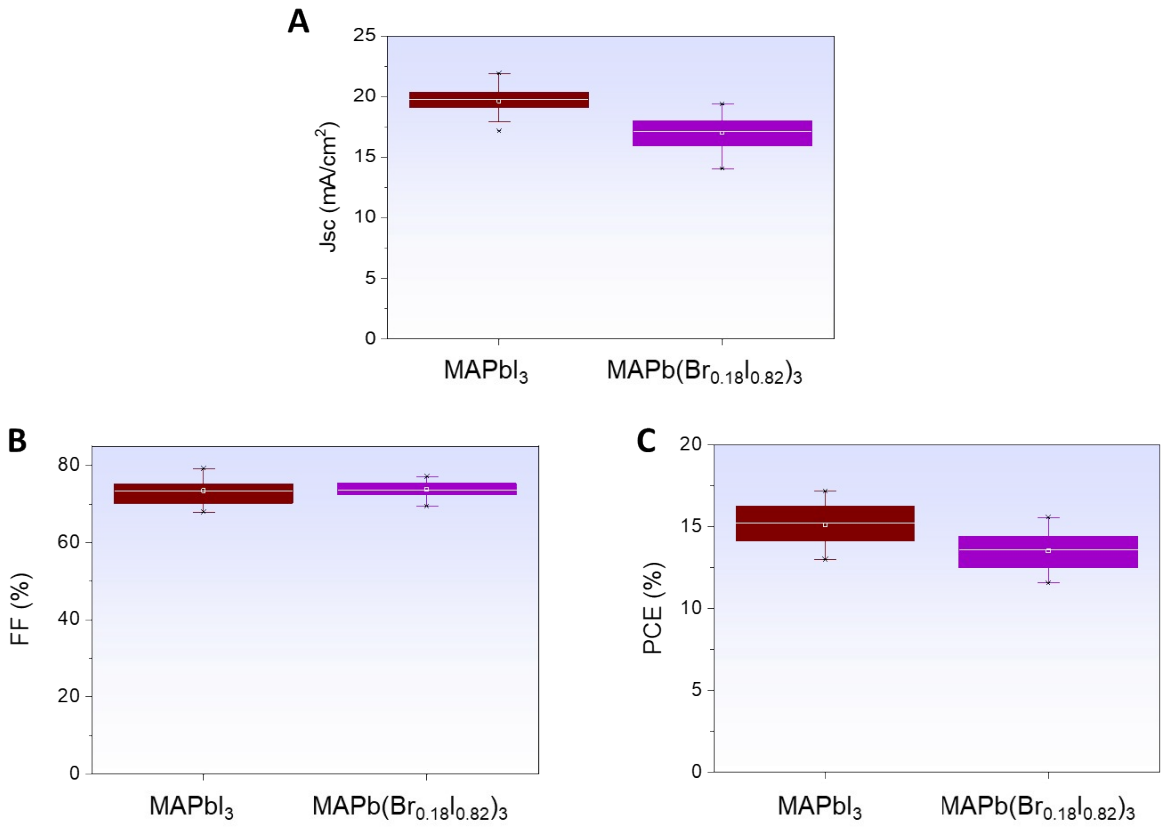

Fig. S8. Photovoltaic parameters of n-i-p PSCs based on Spiro-OMeTAD as HTM (A) J_{sc}, (B) FF, and (C) PCE for $MAPbI_3$ (brown) and $MAPb(Br_{0.18}I_{0.82})_3$ (purple).

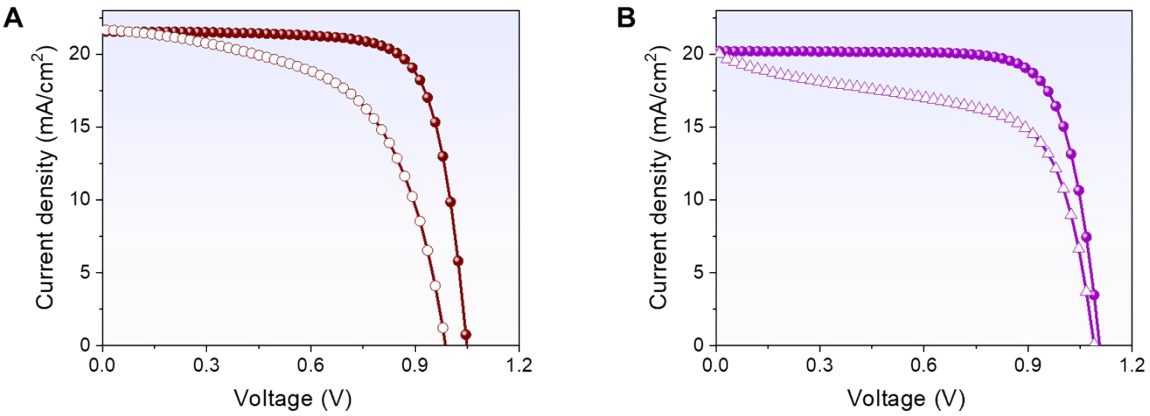

Fig. S9 J-V curves of Spiro-OMeTAD HTL based PSCs using (A) $MAPbI_3$ and (B) $MAPb(Br_{0.18}I_{0.82})_3$ perovskite compositions taken from reverse (solid) and forward (hollow) scan direction.

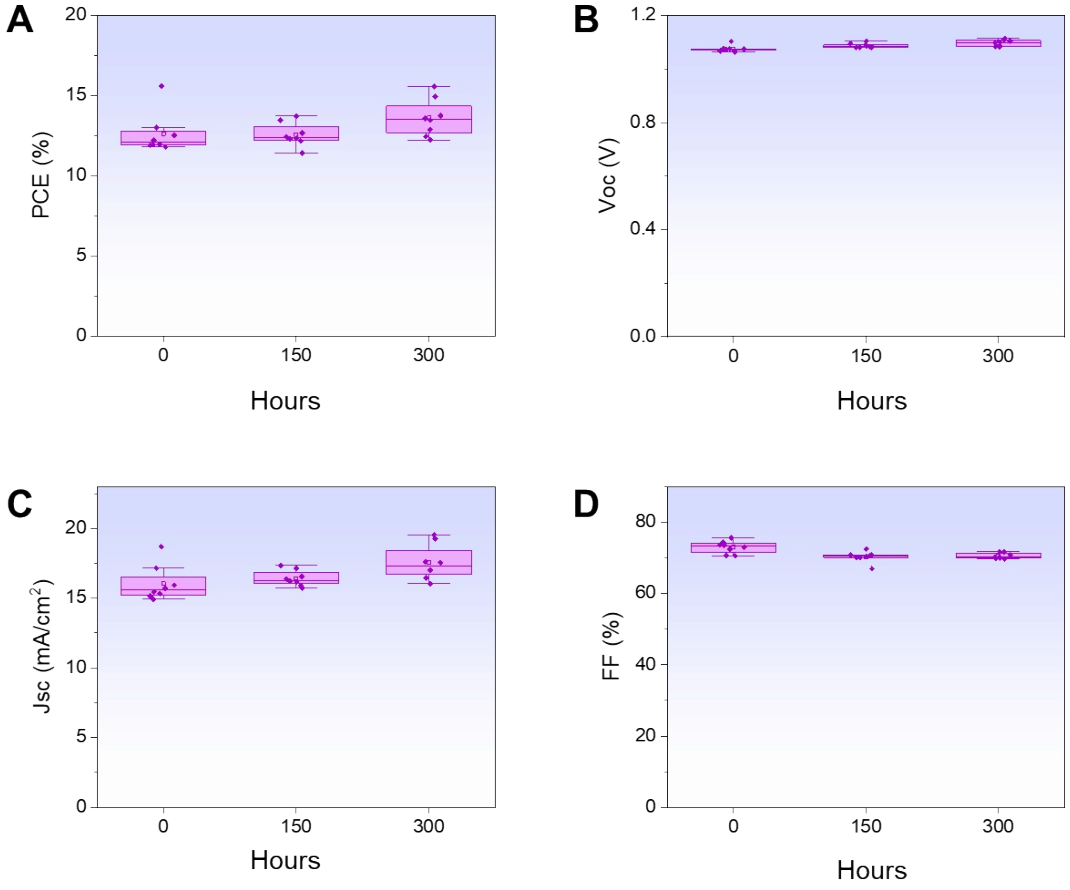

Fig. S10. Shelf stability of $MAPb(Br_{0.18}I_{0.82})_3$ PSCs with Spiro-OMeTAD as HTM. Photovoltaic parameters (A) PCE, (B) Voc, (C) Jsc, and (D) FF of PSCs based on

$MAPb(Br_{0.18}I_{0.82})_3$ when stored at room temperature and in a controlled environment with 30% RH for 300 hours.

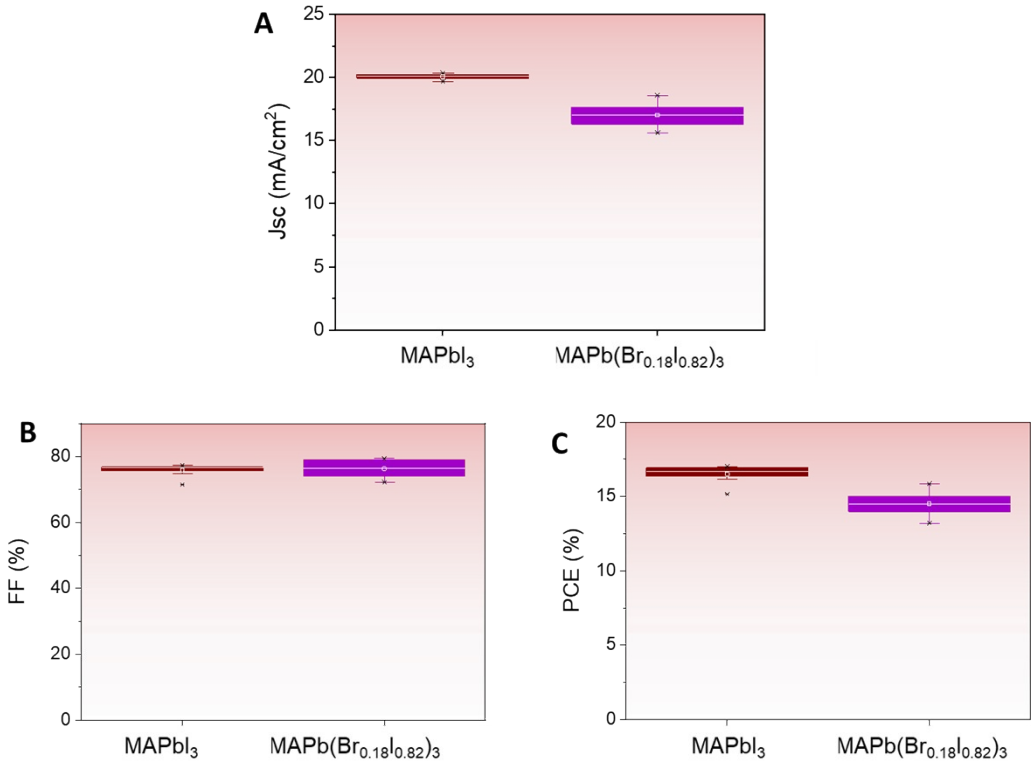

Fig. S11. Photovoltaic parameters of n-i-p PSCs based on PTAA as HTM (A) J_{sc}, (B) FF, and (C) PCE for $MAPbI_3$ (brown) and $MAPb(Br_{0.18}I_{0.82})_3$ (purple).

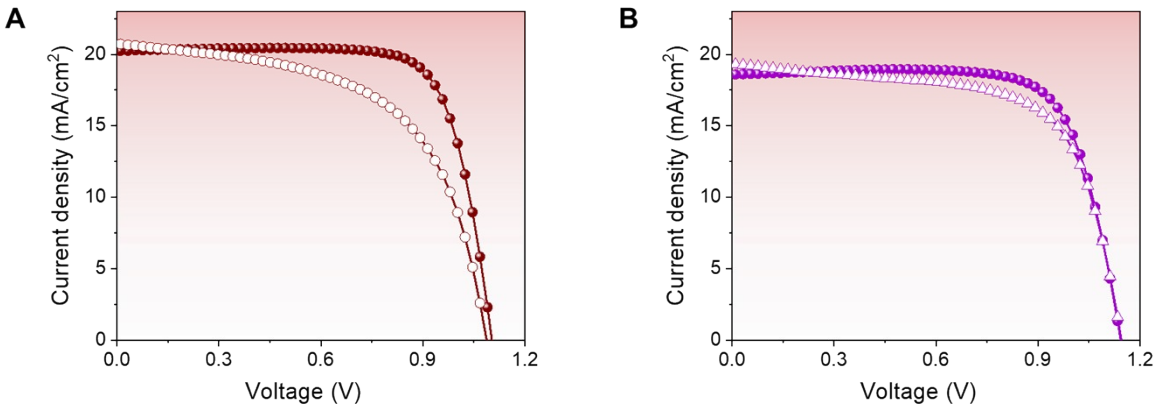

Fig. S12. J-V curves of PTAA HTL based PSCs using (A) $MAPbI_3$ and (B) $MAPb(Br_{0.18}I_{0.82})_3$ perovskite compositions taken from reverse (solid) and forward (hollow) scan direction.

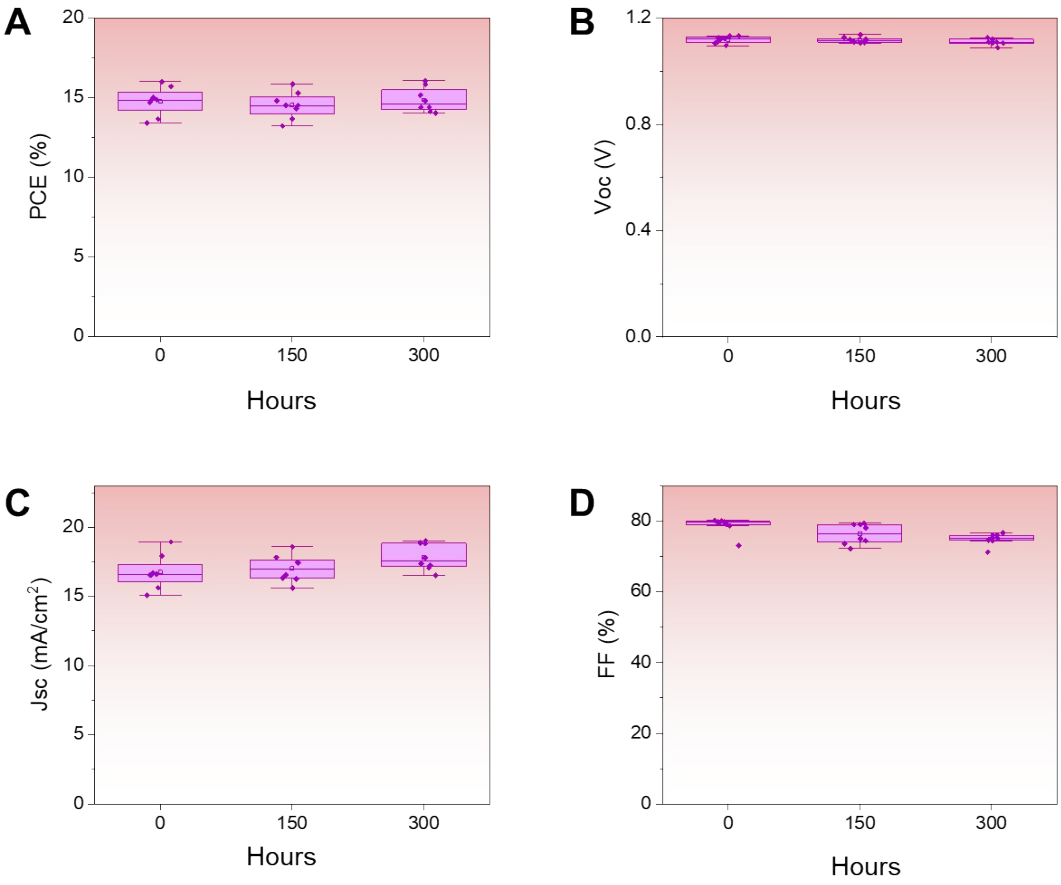

Fig. S13. Shelf stability of $MAPb(Br_{0.18}I_{0.82})_3$ PSCs with PTAA as HTM. Photovoltaic parameters (A) PCE, (B) Voc, (C) Jsc, and (D) FF when stored at room temperature and in a controlled environment with 30% RH for 300 hours.

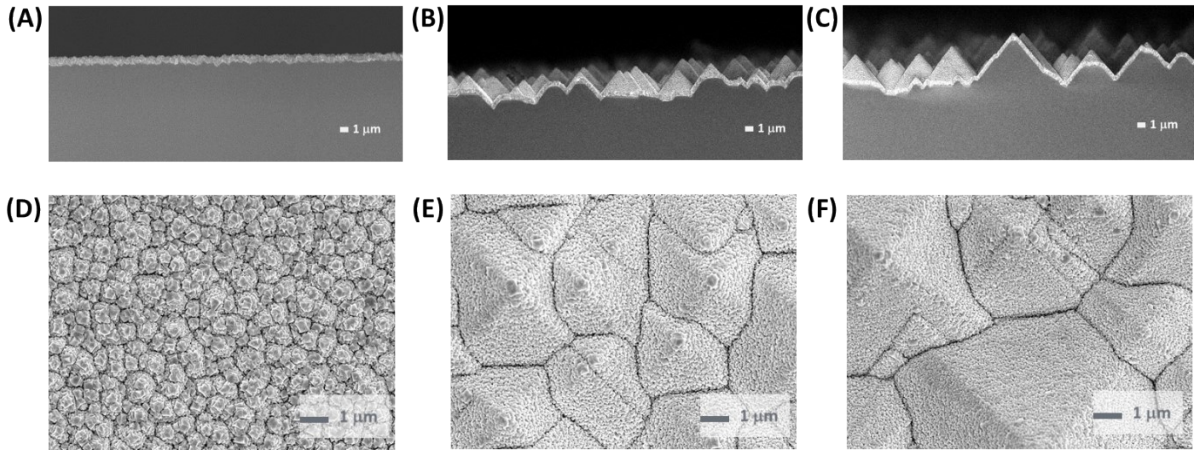

Fig. S14. Cross-section and top view FESEM images of $MAPbI_3$ deposited on Silicon wafers with three different pyramidal heights (A,D) 1-3 µm , (B,E) 3-5 µm , and (C,F) 5-7 µm of bottom silicon substrates taken at low magnification (scale bar of 1 µm)

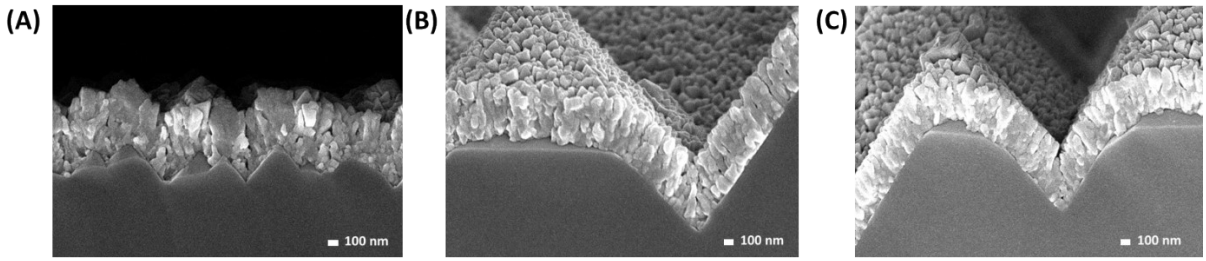

Fig. S15. Cross-section FESEM images of $MAPbI_3$ deposited on Silicon wafers with three different pyramidal heights (A,D) 1-3 µm , (B,E) 3-5 µm , and (C,F) 5-7 µm of bottom silicon substrates taken at high magnification (scale bar of 100 nm)

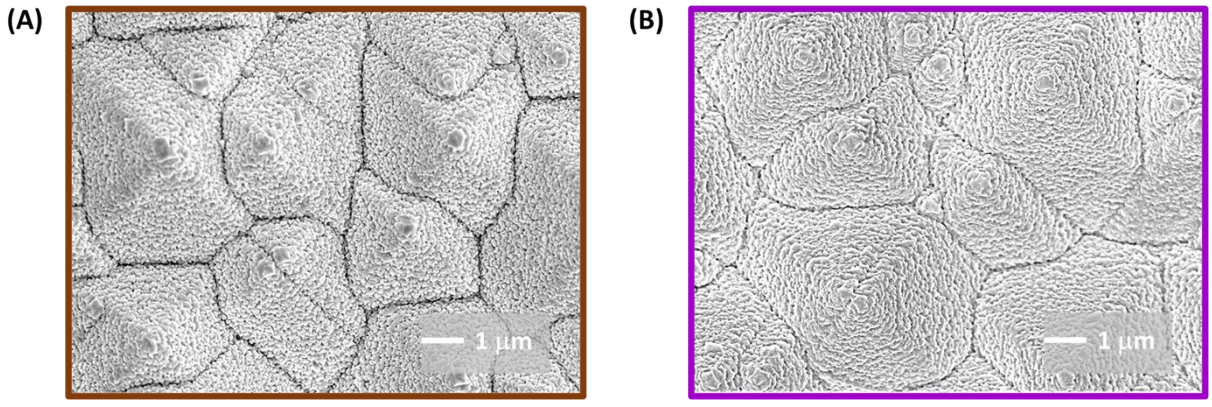

Fig. S16. Top view FESEM of (A) $MAPbI_3$ (brown) and (B) $MAPb(Br_{0.18}I_{0.82})_3$ (purple) deposited on a 3-5 µm textured silicon surface taken at low magnification (scale bar of 1 µm)

Table S1. The penetration depth of X-ray into $MAPbI_3$ film. The penetration depth is calculated according to the formula, $Z = \frac{sin\alpha}{\mu}$, where α is the incident angle, μ is the attenuation coefficient (1181.5 cm^{-1} for $MAPbI_3$).

Incident angle (°)	Penetration depth (nm)
2	290±15
5	740±15
8	1200±15

Table S2. Surface binding energies (BE) and the atomic concentrations of both $MAPbI_3$ and $MAPb(Br_{0.18}I_{0.82})_3$ were measured using XPS.

$MAPbI_3$

	BE [eV]	Atomic conc. [%]
I 3d	617.70	38.25
C 1s	284.60	46.74
Pb 4f	136.80	14.21
Br 3d	70.30	0.80

$MAPb(Br_{0.18}I_{0.82})_3$

	BE [eV]	Atomic conc. [%]
I 3d	618.10	32.37
C 1s	284.00	50.16
Pb 4f	137.20	13.52
Br 3d	67.30	3.95

Table S3. Photovoltaic parameters of PSCs based on Spiro-OMeTAD and PTAA HTLs for both $MAPbI_3$ and $MAPb(Br_{0.18}I_{0.82})_3$ taken from reverse scan directions. The data have been averaged over 20 PSCs in each configuration.

HTL/Perovskite	Voc (V)	Jsc (mA/cm^2)	FF (%)	PCE (%)
Spiro/$MAPbI_3$	1.05 ± 0.02	20 ± 1	74 ± 3	16 ± 1.0
Spiro/$MAPb(Br_{0.18}I_{0.82})_3$	1.08 ± 0.01	17 ± 1.5	74 ± 2	14 ± 1.5
PTAA/$MAPbI_3$	1.08 ± 0.01	20.1 ± 0.2	76 ± 2	16.5 ± 0.6
PTAA/$MAPb(Br_{0.18}I_{0.82})_3$	1.12 ± 0.01	17. ± 1.0	77 ± 3	14.5 ± 0.8