

Supporting Information

Iodine-rich mixed composition perovskites optimised for tin(IV) oxide transport layers: The influence of halide ion ratio, annealing time, and ambient air aging on solar cell performance

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1. Materials

Methylammonium iodide (MAI, 99.0%), methylammonium bromide (MABr, 98.0%), formamidinium iodide (FAI, 98.0%), formamidinium bromide (FABr, 98.0%), lead(II) bromide (PbBr_2 , 98.0%), and trifluoroacetic acid (TFA, 99.0%) were purchased from Tokyo Chemical Industry Co., Ltd. (TCI). Cesium(I) iodide (CsI, 95%) and lithium(I) bis(trifluoromethanesulfonyl)imide (LiTFSI) were purchased from Wako Pure Chemical Industries, Ltd. Co(III) (4-*tert*-butylpyridyl-2-1H-pyrazole)₃·3bis(trifluoromethanesulfonyl)imide (FK 209, Co(III)TFSI, 98%) was purchased from Sigma-Aldrich Co., Ltd. 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamino)-9,9'-spirobifluorene (spiro-OMeTAD) was purchased from Merck Co., Ltd. These materials were used as received. Acetone (99%), ethanol (EtOH, super dehydrated), dimethylsulfoxide (DMSO, super dehydrated), dimethylformamide (DMF, super dehydrated) were purchased from Wako Pure Chemical Industries, Ltd. Toluene (super dehydrated) was purchased from Kanto Chemical Co., Inc. 4-*tert*-butylpyridine (TBP, 96%) was purchased from Sigma-Aldrich Co., Ltd. All of these solvents were degassed by Ar gas bubbling for 1 h and further dried over molecular sieves in a N_2 -filled glove box ($\text{O}_2 < 1$ ppm) before use. Glass-ITO substrates (10 $\Omega/\text{sq.}$) and quartz glass substrates were purchased from Geomatec Co., Ltd. and Asahi Glass Co., Ltd., respectively.

2. Equipment

Thermogravimetric analysis (TGA) was performed on TGA-50 (Shimadzu Co.) and TG-8120 (Rigaku Co.) instruments. Single crystal X-ray structure analysis was performed on a Bruker Single Crystal CCD X-ray Diffractometer SMART APEX II with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) and graphite monochromator (Bruker Co.). ^1H NMR spectra were recorded with JEOL JNM ECA400 (400 MHz). Chemical shifts are reported in δ ppm using residual protons in the deuterated solvents. Inductively coupled plasma mass spectrometry (ICP-MS) was conducted at NANO SCIENCE Co. Energy dispersive X-ray spectroscopy (EDX) observation was conducted at Toray Research Center Inc. Photo-electron spectroscopy in air (PESA) measurement was performed on an AC-3 (RIKEN KEIKI Co., Ltd). UV-Vis-NIR absorption measurement was performed with a UV-3600Plus spectrometer (Shimadzu Co.). Scanning electron microscope (SEM) images were recorded on a

SU8010 (Hitachi High-Technologies Co.) equipped with EDAX (AMETEK Inc.). Transmission electron microscope (TEM) images were recorded on a JEM-F200 (JEOL Ltd.). For aging, devices were stored in a cabinet with middle humidity (TDC-157-DD, TOLIHAN Co.).

The $J-V$ curves and IPCE spectra of perovskite solar cells were measured in air with OTENTO-SUNIII and OTENTO-SUN-P1G instruments (Bunkoukeiki, Co. Ltd.), respectively. The scans were performed in both forward and reverse directions, with 50 mV voltage step and 1 s dwell time. IPCE spectra were recorded on a Bunkoukeiki SMO-250III system. The light intensity of the illumination source was calibrated against standard BS520 and SiPD S1337-1010BQ silicon photodiodes for the $J-V$ and IPCE measurements, respectively. During the $J-V$ and IPCE measurement, a shadow mask was used giving an active area of 0.1 cm². Impedance spectroscopy data was obtained in air with a 4192A LF impedance analyzer (Hewlett-Packard Company), at zero volts applied bias, 30 mV oscillator voltage, 10-10,000 Hz frequency scan, with the measurement devices under AM1.5G simulated solar radiation with a 0.04 cm⁻² shadow mask.

3. Preparation of FAPbI₃·2DMF and Derivatives

FAPbI₃·2DMF

FAI (344 mg, 2.0 mmol) and PbI₂ (922 mg, 2.0 mmol) were dissolved in DMF (2.0 mL) at 70 °C for 10 min. The resulting clear yellow solution was filtered with a membrane filter to remove an insoluble component. 200 μL of the solution was transferred to a glass tube. A small quantity of DMF was added to the top of this layer, then toluene (1.0 mL) was slowly layered over the solution. After standing at room temperature for two days, colorless needle-like FAPbI₃·2DMF crystals were collected by filtration (105 mg, 0.13 mmol, 65% yield).

FAPbI₃·DMF

FAI (18.7 g, 109 mmol) and PbI₂ (49.8 g, 108 mmol) were dissolved in DMF (120 mL). The resulting clear yellow solution was filtered with a membrane filter to remove an insoluble component. 40 mL of DMF was added to the top of this layer, then toluene (550 mL) was slowly layered over the solution. After standing at room temperature for four days, colorless needle-like FAPbI₃·2DMF crystals were collected by filtration (53.9 g, 76.3 mmol, 70% yield). The ratio of FA⁺:DMF was confirmed ¹H NMR analysis (Figure S4).

FAPbI₃

After drying of FAPbI₃·DMF complex (18.2 g, 25.8 mmol) under vacuum at 50 °C for two days, yellow crystalline solids of FAPbI₃ were obtained (16.3 g, 25.7 mmol, 99% yield). The absence of DMF was confirmed by ¹H NMR analysis (Figure S6).

4. Single Crystal X-Ray Structure Analysis of FAPbI₃·2DMF

The crystallographic data has been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication number CCDC-1881162 (FAPbI₃·2DMF). Data files can be obtained free of charge from the CCDC *via* www.ccdc.cam.ac.uk/data_request/cif.

Intensity data were collected at 100 K. A total of 7146 reflections were measured with a maximum 2θ angle of 51.0°, of which 3465 were independent reflections ($R_{\text{int}} = 0.0225$). The

structure was solved by direct methods (SHELXS-97¹) and refined by the full-matrix least-squares on F^2 (SHELXL-97¹). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_7H_{19}I_3N_4O_2Pb$; FW = 779.15, crystal size $0.46 \times 0.12 \times 0.10$ mm³, Triclinic, $P-1$, $a = 7.8936(9)$ Å, $b = 10.5075(12)$ Å, $c = 12.6927(15)$ Å, $\alpha = 75.8214(12)^\circ$, $\beta = 74.9250(12)^\circ$, $\gamma = 68.9286(12)^\circ$, $V = 935.06(19)$ Å³, $Z = 2$, $D_c = 2.767$ g cm⁻³. The refinement converged to $R_1 = 0.0199$, $wR_2 = 0.0503$ ($I > 2$ s(I)), GOF = 1.056.

5. Thin Film Fabrication

Preparation of the SnO₂ layer

Glass-ITO substrates (10 Ω/sq.) were etched with zinc powder and HCl (6 M in de-ionized water). The patterned substrates (25 mm × 25 mm) were then treated with ultrasonic cleaning for 10 min cycles for, in order: a 1 wt% neutral aqueous detergent solution, acetone, and 2-propanol. This was followed by UV-ozone treatment for 15 min. The SnO₂ layer was prepared by spin-coating a colloidal dispersion (15% in H₂O, 3.0 mL) diluted with deionized water (3.0 mL) on the glass-ITO substrates (slope 3 s, 2000 rpm 30 s, slope 3 s) followed by annealing at 150 °C for 30 min. After cooling to room temperature, organic residues on the substrates were removed with 15 min UV-ozone treatment.

All the subsequent procedures described in this section were conducted in an inert gas filled glove box.

Fabrication of Cs_{0.05}FA_{0.80}MA_{0.15}PbI_{2.75}Br_{0.25} layer (for PES and UV-Vis-NIR measurement)

The precursor solution was prepared from CsI (83 mg, 0.32 mmol), MABr (102 mg, 0.91 mmol), PbBr₂ (116 mg, 0.32 mmol), PbI₂ (422 mg, 0.92 mmol), and FAPbI₃·DMF (3464 mg, 4.91 mmol) dissolved in a mixture of DMF (3.2 mL) and DMSO (1.1 mL). After stirring at 40 °C for 30 min, the solution was filtered with a 0.45 μm PTFE filter. 200 μL of the solution was placed on a ITO substrate (for PES) or on a quartz plate (for UV-Vis-NIR), and spread by spin-coating (slope 1 s, 1000 rpm 10 s, slope 5 s, 6000 rpm 20 s, slope 1 s) to make a thin film. A 300 μL of

chlorobenzene was dripped over the rotating substrate at 3 s before the end of the spinning at 6000 rpm. The films were then annealed on a hot plate at 150 °C for 10 min.

Fabrication of $Cs_{0.05}FA_{0.80}MA_{0.15}PbI_{2.75}Br_{0.25}$ layer (for SEM observation)

The precursor solution was prepared from CsI (44 mg, 0.17 mmol), MABr (54 mg, 0.48 mmol), $PbBr_2$ (68 mg, 0.18 mmol), PbI_2 (225 mg, 0.49 mmol), and $FAPbI_3 \cdot DMF$ (1659 mg, 2.35 mmol) dissolved in DMF (2.4 mL) and DMSO (0.72 mL). After stirring at 40 °C for 30 min, the solution was filtered with a 0.45 μm PTFE filter. 200 μL of the solution was placed on a SnO_2 substrate and spread by spin-coating (slope 1 s, 1000 rpm 10 s, slope 5 s, 3000 rpm 20 s, slope 1 s) to make a thin film. At 3 s before the end of the spinning at 3000 rpm, 300 μL of chlorobenzene was dripped over the rotating substrate. The film was annealed on a hot plate at 150 °C for 0, 10 s, 1 min, 5 min, 10 min, 30 min, or 120 min.

6. Solar Cell Fabrication

All the procedures described in this section were conducted in a glove box filled with inert gas.

Fabrication of $Cs_{0.05}FA_{0.79}MA_{0.16}PbI_{2.44}Br_{0.56}$ layer (from FAI: influence of FA source)

The precursor solution was prepared from CsI (37 mg, 0.14 mmol), MABr (49 mg, 0.44 mmol), FAI (342 mg, 2.0 mmol), $PbBr_2$ (199 mg, 0.54 mmol), and PbI_2 (1.01 g, 2.2 mmol) dissolved in DMF (1.60 mL) and DMSO (0.48 mL). After stirring at 40 °C for 30 min, the solution was filtered with a 0.45 μm PTFE filter. 200 μL of the solution was placed on the SnO_2 substrate and spread by spin-coating (slope 1 s, 1000 rpm 10 s, slope 5 s, 6000 rpm 20 s, slope 1 s) to make a thin film. 300 μL of chlorobenzene was dripped over the rotating substrate at 3 s before the end of spinning at 6000 rpm. The film was annealed on a hot plate at 150 °C for 10 min.

Fabrication of $Cs_{0.05}FA_{0.79}MA_{0.16}PbI_{2.44}Br_{0.56}$ layer (from $FAPbI_3 \cdot DMF$: influence of FA source)

The precursor solution was prepared from CsI (37 mg, 0.14 mmol), MABr (49 mg, 0.44 mmol), $PbBr_2$ (199 mg, 0.54 mmol), PbI_2 (16 mg, 0.03 mmol), and $FAPbI_3 \cdot DMF$ (1.52 g, 2.15 mmol) dissolved in DMF (1.43 mL) and DMSO (0.48 mL). After stirring at 40 °C for 30 min, the

solution was filtered with a 0.45 μm PTFE filter. 200 μL of the solution was placed on the SnO_2 substrate and spread by spin-coating (slope 1 s, 1000 rpm 10 s, slope 5 s, 6000 rpm 20 s, slope 1 s) to make a thin film. 300 μL of chlorobenzene was dripped over the rotating substrate at 3 s before the end of spinning at 6000 rpm. The film was annealed on a hot plate at 150 $^\circ\text{C}$ for 10 min.

Fabrication of $\text{Cs}_{0.05}\text{FA}_{0.78}\text{MA}_{0.12}\text{PbI}_{2.49}\text{Br}_{0.51}$ layer ($I:\text{Br} = 5:1$)

The precursor solution was prepared from CsI (55 mg, 0.21 mmol), MABr (67 mg, 0.60 mmol), FAI (516 mg, 3.0 mmol), PbBr_2 (297 mg, 0.81 mmol), and PbI_2 (1521 mg, 3.0 mmol) dissolved in DMF (2.4 mL) and DMSO (0.6 mL). After stirring at 40 $^\circ\text{C}$ for 30 min, the solution was filtered with a 0.45 μm PTFE filter. 200 μL of the solution was placed on the SnO_2 substrate and spread by spin-coating (slope 1 s, 1000 rpm 10 s, slope 5 s, 6000 rpm 20 s, slope 1 s) to make a thin film. 300 μL of chlorobenzene was dripped over the rotating substrate at 3 s before the end of spinning at 6000 rpm. The film was annealed on a hot plate at 150 $^\circ\text{C}$ for 10 min.

Fabrication of $\text{Cs}_{0.06}\text{FA}_{0.84}\text{MA}_{0.10}\text{PbI}_{2.59}\text{Br}_{0.41}$ layer ($I:\text{Br} = 6:1$)

The precursor solution was prepared from CsI (55 mg, 0.21 mmol), MABr (44 mg, 0.39 mmol), PbBr_2 (228 mg, 0.62 mmol), PbI_2 (128 mg, 0.28 mmol), and $\text{FAPbI}_3\cdot\text{DMF}$ (2255 mg, 3.19 mmol) dissolved in DMF (2.125 mL) and DMSO (0.72 mL). After stirring at 40 $^\circ\text{C}$ for 30 min, the solution was filtered with a 0.45 μm PTFE filter. 200 μL of the solution was placed on the SnO_2 substrate and spread by spin-coating (slope 1 s, 1000 rpm 10 s, slope 5 s, 6000 rpm 20 s, slope 1 s) to make a thin film. 300 μL of chlorobenzene was dripped over the rotating substrate 3 s before the end of spinning at 6000 rpm. The film was annealed on a hot plate at 150 $^\circ\text{C}$ for 10 min.

Fabrication of $\text{Cs}_{0.05}\text{FA}_{0.80}\text{MA}_{0.15}\text{PbI}_{2.75}\text{Br}_{0.25}$ layer ($I:\text{Br} = 11:1$, Reference)

The precursor solution was prepared from CsI (55 mg, 0.21 mmol), MABr (68 mg, 0.61 mmol), PbBr_2 (77 mg, 0.21 mmol), PbI_2 (281 mg, 0.61 mmol), and $\text{FAPbI}_3\cdot\text{DMF}$ (2309 mg, 3.27 mmol) dissolved in DMF (2.147 mL) and DMSO (0.72 mL). After stirring at 40 $^\circ\text{C}$ for 30 min, the solution was filtered with a 0.45 μm PTFE filter. 200 μL of the solution was placed on the SnO_2 substrate and spread by spin-coating (slope 1 s, 1000 rpm 10 s, slope 5 s, 6000 rpm 20 s, slope 1 s)

to make a thin film. 300 μ L of chlorobenzene was dripped over the rotating substrate at 3 s before the end of spinning at 6000 rpm. The film was annealed on a hot plate at 150 $^{\circ}$ C for 10 min.

Fabrication of $Cs_{0.05}FA_{0.80}MA_{0.15}PbI_{2.75}Br_{0.25}$ layer (Annealing Experiments)

The precursor solution was prepared from CsI (55 mg, 0.21 mmol), MABr (68 mg, 0.61 mmol), PbBr₂ (77 mg, 0.21 mmol), PbI₂ (281 mg, 0.61 mmol), and FAPbI₃·DMF (2309 mg, 3.27 mmol) dissolved in DMF (2.147 mL) and DMSO (0.72 mL). After stirring at 40 $^{\circ}$ C for 30 min, the solution was filtered with a 0.45 μ m PTFE filter. 200 μ L of the solution was placed on the SnO₂ substrate and spread by spin-coating (slope 1 s, 1000 rpm 10 s, slope 5 s, 6000 rpm 20 s, slope 1 s) to make a thin film. At 3 s before the end of spinning at 6000 rpm, 300 μ L of chlorobenzene was dripped over the rotating substrate. The resulting brown film was annealed on a hot plate at 150 $^{\circ}$ C for 1 min, 5 min, 10 min, or 30 min.

Fabrication of $Cs_{0.05}FA_{0.80}MA_{0.15}PbI_{2.75}Br_{0.25}$ (from FAPbI₃·DMF: influence of FAPbI₃ source)

The precursor solution was prepared from CsI (22 mg, 0.085 mmol), MABr (27 mg, 0.24 mmol), PbBr₂ (31 mg, 0.084 mmol), PbI₂ (113 mg, 0.25 mmol), and FAPbI₃·DMF (0.93 g, 1.31 mmol) dissolved in DMF (1.10 mL) and DMSO (0.36 mL). After stirring at 40 $^{\circ}$ C for 30 min, the solution was filtered with a 0.45 μ m PTFE filter. 200 μ L of the solution was placed on the SnO₂ substrate and spread by spin-coating (slope 1 s, 1000 rpm 10 s, slope 5 s, 3000 rpm 20 s, slope 1 s) to make a thin film. 300 μ L of chlorobenzene was dripped over the rotating substrate at 3 s before the end of spinning at 3000 rpm. The film was annealed on a hot plate at 150 $^{\circ}$ C for 10 min.

Fabrication of $Cs_{0.05}FA_{0.80}MA_{0.15}PbI_{2.75}Br_{0.25}$ (from FAPbI₃: influence of FAPbI₃ source)

The precursor solution was prepared from CsI (22 mg, 0.085 mmol), MABr (27 mg, 0.24 mmol), PbBr₂ (31 mg, 0.084 mmol), PbI₂ (113 mg, 0.25 mmol), and FAPbI₃ (0.83 g, 1.31 mmol) dissolved in DMF (1.20 mL) and DMSO (0.36 mL). After stirring at 40 $^{\circ}$ C for 30 min, the solution was filtered with a 0.45 μ m PTFE filter. 200 μ L of the solution was placed on the SnO₂ substrate and spread by spin-coating (slope 1 s, 1000 rpm 10 s, slope 5 s, 3000 rpm 20 s, slope 1 s) to make a

thin film. 300 μ L of chlorobenzene was dripped over the rotating substrate at 3 s before the end of spinning at 3000 rpm. The film was annealed on a hot plate at 150 $^{\circ}$ C for 10 min.

Deposition of the spiro-OMeTAD layer and the Au electrodes

Spiro-OMeTAD (73.5 mg, 0.060 mmol), Co(III)TFSI complex (FK 209, 13.5 mg, 0.0090 mmol), TBP (27.0 μ L, 0.20 mmol), and LiTFSI (8.6 mg, 0.030 mmol) were dissolved in chlorobenzene (1.0 mL). After stirring at 70 $^{\circ}$ C for 30 min, the suspension was filtered with a 0.45 μ m PTFE filter. 100 μ L of the solution was spread over on the perovskite layer by spin-coating (slope 5 s, 4000 rpm, 30 s, slope 5 s), followed by annealing at 70 $^{\circ}$ C for 30 min. The devices were transferred under inert atmosphere to a vacuum chamber where 80 nm gold electrodes were thermally evaporated on the spiro-OMeTAD layer through a shadow mask.

7. Neutron Activation Analysis (NAA)

Preparation of perovskite powder ($Cs_{0.05}FA_{0.80}MA_{0.15}PbI_{2.75}Br_{0.25}$)

The precursor solution was prepared from CsI (133 mg, 0.51 mmol), MABr (163 mg, 1.46 mmol), PbBr₂ (184 mg, 0.50 mmol), PbI₂ (675 mg, 1.46 mmol), and FAPbI₃·DMF (5551 mg, 7.86 mmol) dissolved in DMF (6.59 mL) and DMSO (2.16 mL). After stirring at 40 $^{\circ}$ C for 30 min, the solution was filtered with a 0.45 μ m PTFE filter. 200 μ L of the solution was placed on a quartz plate and spread by spin-coating (slope 1 s, 1000 rpm 10 s, slope 5 s, 3000 rpm 20 s, slope 1 s) to make a thin film. At 3 s before the end of spinning at 3000 rpm, 300 μ L of chlorobenzene was dripped over the rotating substrate. The resulting film was annealed on a hot plate at 150 $^{\circ}$ C for 10 min. After cooling to room temperature, the sample of 15.3 mg of perovskite powder was scraped off from 35 substrates with a spatula. The sample was placed in doubly sealed clean polyethylene bags.

Reference sample preparation

50 mg of KI, KBr, CsI and CsBr were weighed and placed in doubly sealed clean polyethylene bags.

Neutron irradiation and gamma-ray spectrometry

The sample of the perovskite powder, together with the four chemical reagents for the reference samples, were irradiated for 10 sec with a thermal neutron flux of $3.3 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ at Kyoto University Reactor (KUR) in Institute for Integrated Radiation and Nuclear Science, Kyoto University (KURNS). After irradiation, outer bags of all the samples were exchanged by new (non-irradiated) plastic bags and they were subjected to gamma-ray counting. Gamma rays emitted from irradiated samples were measured using germanium semiconductor detectors at KURNS.

Measurements were repeated with different cooling intervals. Iodine in the perovskite powder and references were determined with measurement time of 100–400 sec just after irradiation. After a day cooling, Br in the perovskite powder and references were determined with measurement time of 3000–15000 sec and 200–400 sec, respectively. After three weeks cooling, Cs in the perovskite powder and references were determined with measurement time of 70000–100000 sec and 300–800 sec, respectively. In relative method of NAA, test samples and reference samples for quantification are usually measured at the same position in gamma-ray counting for simplifying the data reduction procedure and reducing analytical uncertainty. In gamma-ray measurements for Br and I, those samples were placed at 26 cm apart from the Ge detector surface to keep the counting loss smaller than 10% while for Cs the counting position was as close as possible to the detector surface.

Data reduction

Nuclear data related to this study are summarized in Table S3. An (n, γ) reaction was used in NAA for all elements. The elemental contents were determined by a relative method. Iodine was determined by using the reagents, KI and CsI and two sets of results were consistent. Bromine was determined by KBr and CsBr and two sets of results were consistent. Cesium was determined by CsI and CsBr and two sets of results were also consistent. Table S4 showed result of NAA.

Customer: **Kyoto University**
Date: 24-Nov-15

P.O.# **EJM-67214H**
Job # **JOFSR559**

Customer ID: **Pb**
FAPbI3 2DMF

Sample ID: **S151120037**

[Rev: 2015-11-24 12:14:30]

Element	Concentration [ppm wt]	Element	Concentration [ppm wt]
Li	< 0.5	In	< 0.5
Be	< 0.5	Sn	< 0.5
B	< 0.5	Sb	< 0.5
Na	5	Te	< 0.5
Mg	< 0.5	Cs	< 0.5
Al	< 0.5	Ba	< 0.5
Si	< 5	La	< 0.5
P	< 5	Ce	< 0.5
K	< 5	Pr	< 0.5
Ca	< 5	Nd	< 0.5
Sc	< 0.5	Sm	< 0.5
Ti	< 0.5	Eu	< 0.5
V	< 0.5	Gd	< 0.5
Cr	< 0.5	Tb	< 0.5
Mn	< 0.5	Dy	< 0.5
Fe	< 5	Ho	< 0.5
Co	< 0.5	Er	< 0.5
Ni	< 0.5	Tm	< 0.5
Cu	3.9	Yb	< 0.5
Zn	3.7	Lu	< 0.5
Ga	< 0.5	Hf	< 0.5
Ge	< 0.5	Ta	< 0.5
As	< 0.5	W	< 0.5
Se	< 0.5	Re	< 0.5
Rb	< 0.5	Os	< 0.5
Sr	< 0.5	Ir	< 0.5
Y	< 0.5	Pt	< 0.5
Zr	< 0.5	Au	< 0.5
Nb	< 0.5	Hg	< 0.5
Mo	< 0.5	Tl	< 0.5
Ru	< 0.5	Pb	< 0.5
Rh	2.7	Bi	< 0.5
Pd	< 0.5	Th	< 0.5
Ag	< 0.5	U	< 0.5
Cd	< 0.5		



Testing Cert. #2797.03

Concentration measurements of major elements done by ICP have an uncertainty typically in the range from 3 to 5% (at the 95% confidence level).
The uncertainty in the concentrations of trace elements might be significantly higher.
This shall not be reproduced except in full without written approval of the laboratory.

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Reviewed by _____

p.ferguson (Analyst)

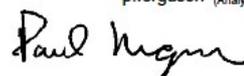


Figure S1. Inductively coupled plasma-mass spectrometry (ICP-MS) elemental analysis of FAPbI₃·2DMF.

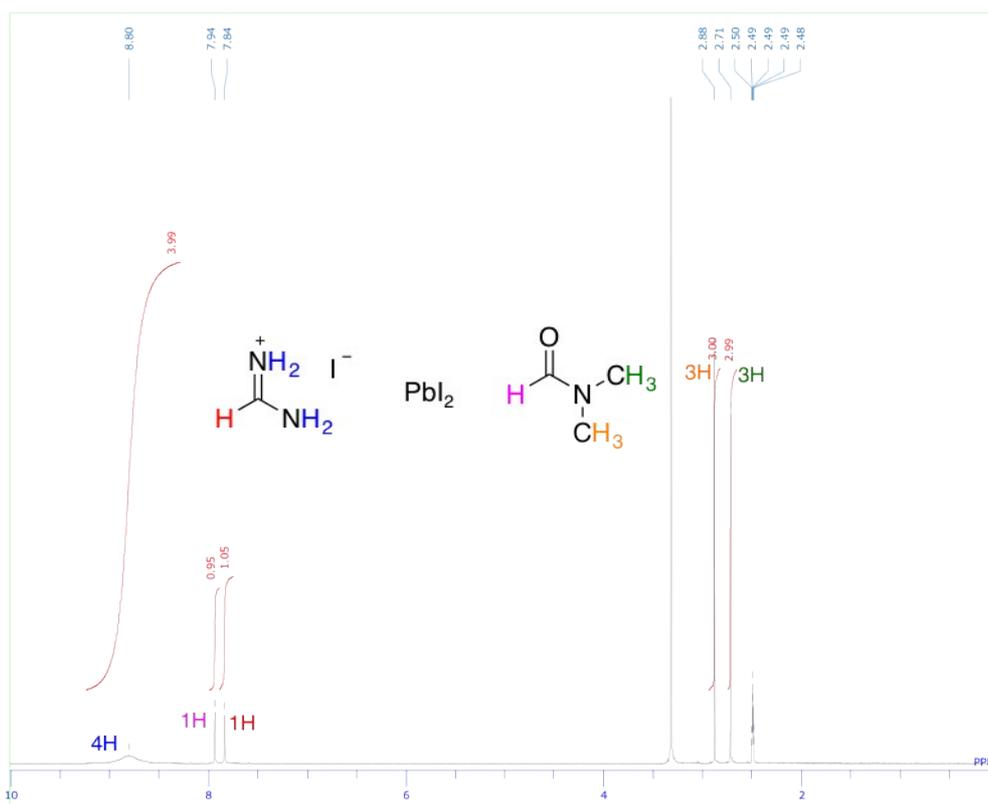


Figure S2. ^1H NMR of $\text{FAPbI}_3 \cdot \text{DMF}$ complex in $\text{DMSO-}d_6$.

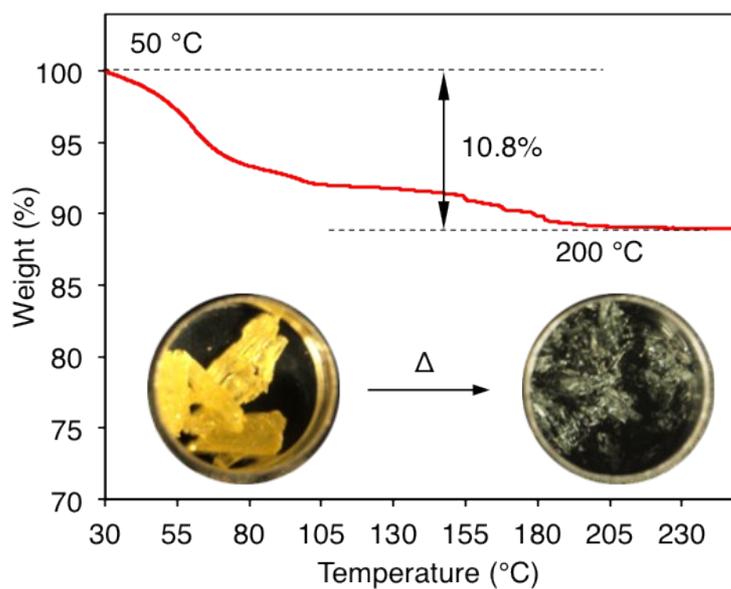


Figure S3. TG curve and photographs of the $\text{FAPbI}_3 \cdot \text{DMF}$ complex.

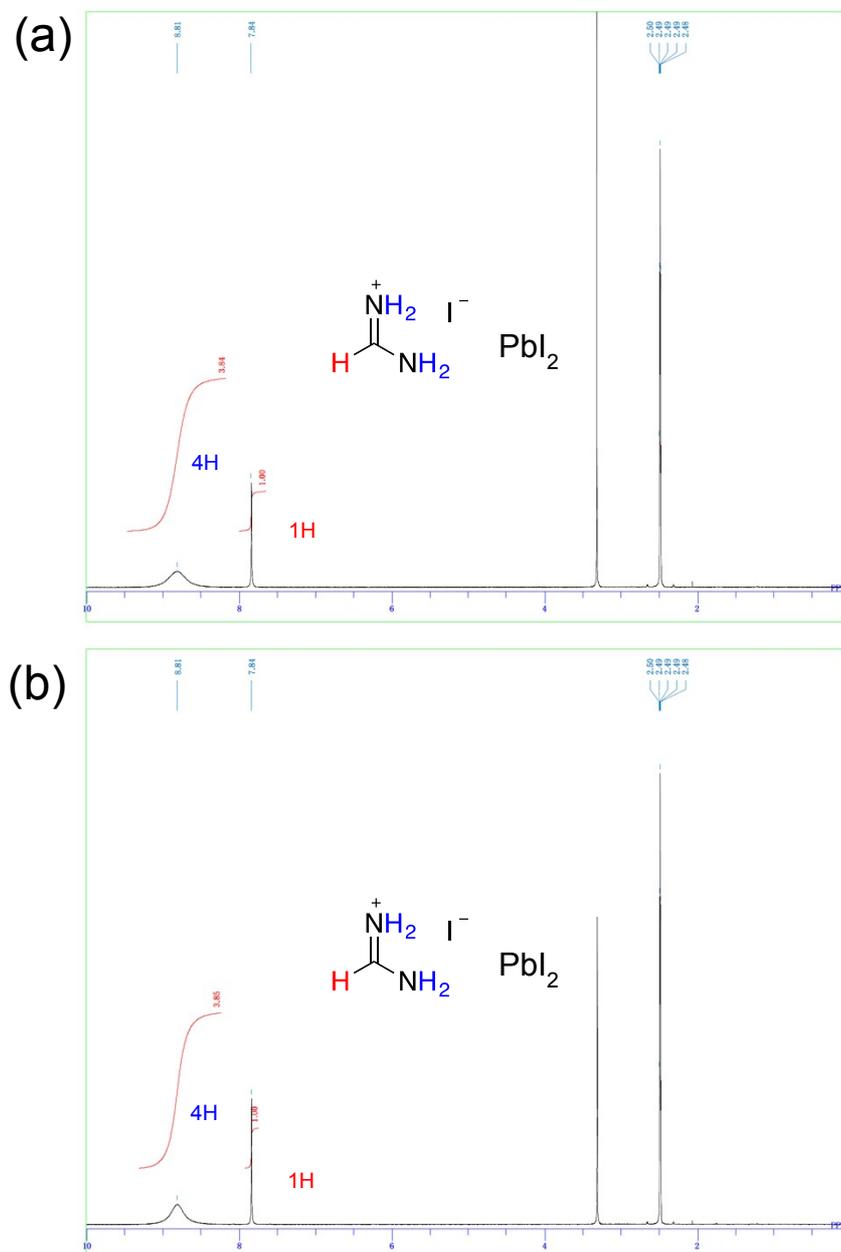


Figure S4. ^1H NMR FAPbI_3 in $\text{DMSO-}d_6$ (a) freshly prepared and (b) after 13 months stored under inert atmosphere.

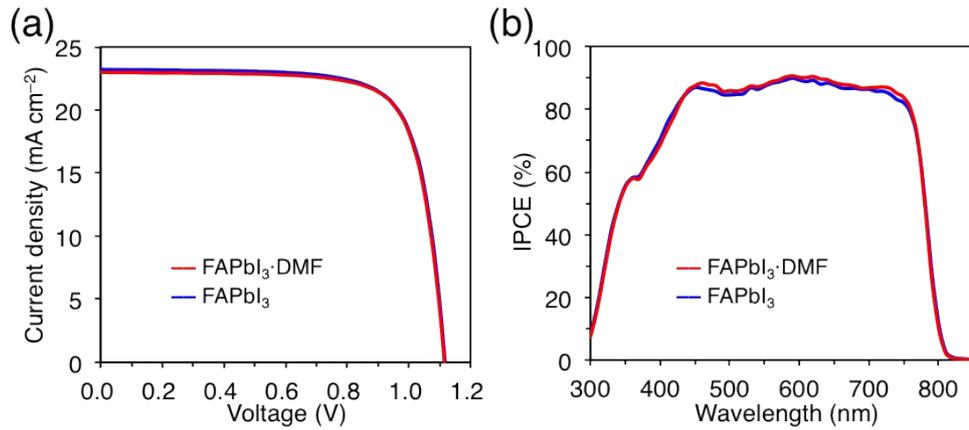


Figure S5. (a) The J - V curves and (b) IPCE spectra of $\text{Cs}_{0.05}\text{FA}_{0.80}\text{MA}_{0.15}\text{PbI}_{2.75}\text{Br}_{0.25}$ -based (I/Br ratio 11:1) perovskite solar cells fabricated with two different FAPbI_3 sources: $\text{FAPbI}_3\cdot\text{DMF}$ (red line) and FAPbI_3 (blue line). The integrated J_{SC} estimated from IPCE was 22.0 and 22.2 mA cm^{-2} for the $\text{FAPbI}_3\cdot\text{DMF}$ and FAPbI_3 , respectively.

Table S1. Photovoltaic parameters of the $\text{Cs}_{0.05}\text{FA}_{0.80}\text{MA}_{0.15}\text{PbI}_{2.75}\text{Br}_{0.25}$ -based (I/Br ratio 11:1) perovskite solar cells with different FAPbI_3 sources

FAPbI_3 source	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	PCE (%)	R_s ($\Omega \text{ cm}^2$)	R_{sh} ($\Omega \text{ cm}^2$)
$\text{FAPbI}_3\cdot\text{DMF}$	23.2	1.11	0.75	19.4	5.6	5162
FAPbI_3	23.0	1.11	0.75	19.4	5.9	8943

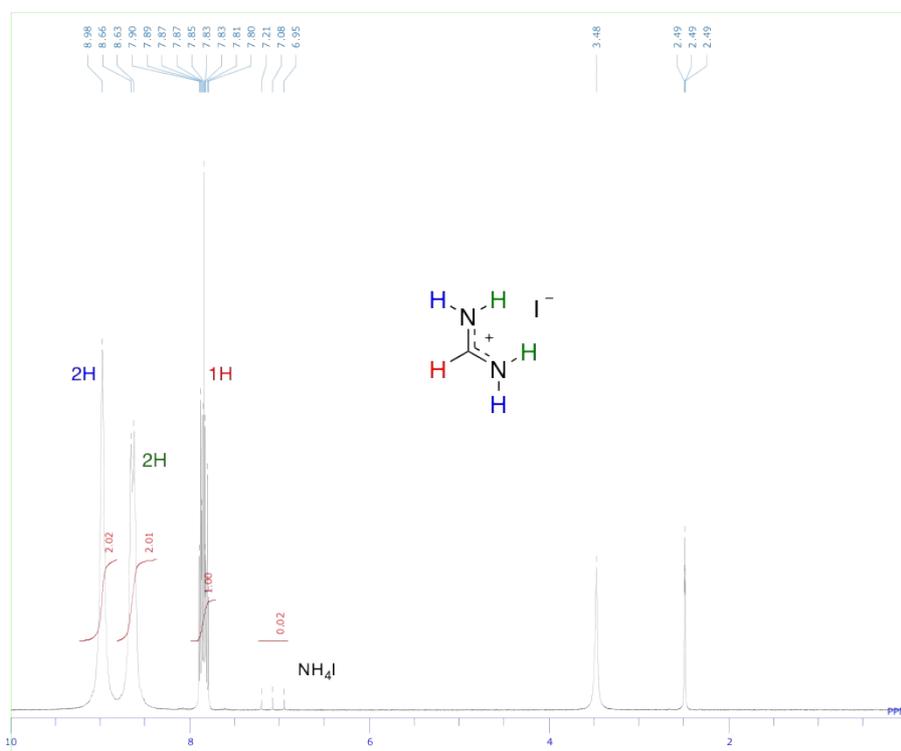


Figure S6. ^1H NMR of FAI (98.0%, stored in inert gas for 17 month) in $\text{DMSO-}d_6$ with 0.1% TFA.

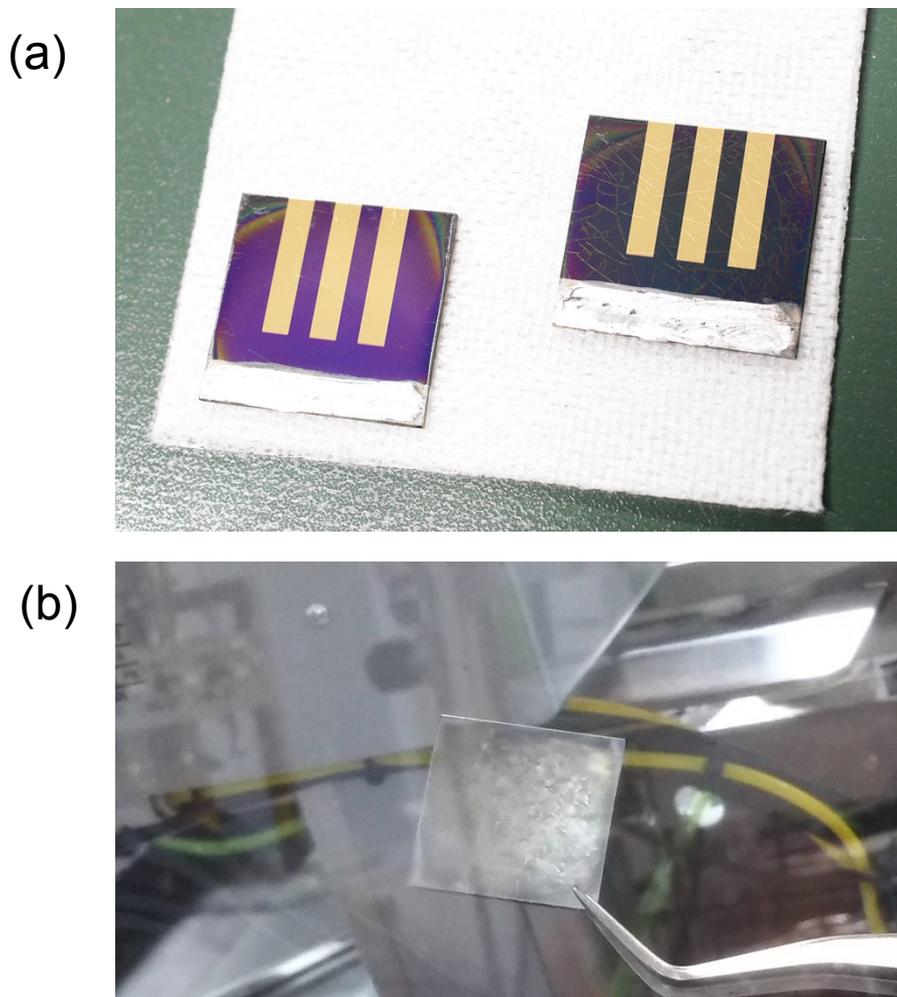


Figure S7. (a) Comparison photographs of the solar cell devices fabricated with $\text{Cs}_{0.05}\text{FA}_{0.80}\text{MA}_{0.15}\text{PbI}_{2.75}\text{Br}_{0.25}$ (I/Br ratio 11:1) (left) and all-iodine $\text{Cs}_{0.05}\text{FA}_{0.80}\text{MA}_{0.15}\text{PbI}_3$ (I/Br ratio 1:0) mixed composition perovskites (right). (b) Photo of the annealed $\text{Cs}_{0.05}\text{FA}_{0.80}\text{MA}_{0.15}\text{PbI}_3$ perovskite film before the hole transport and top electrode layers were added.

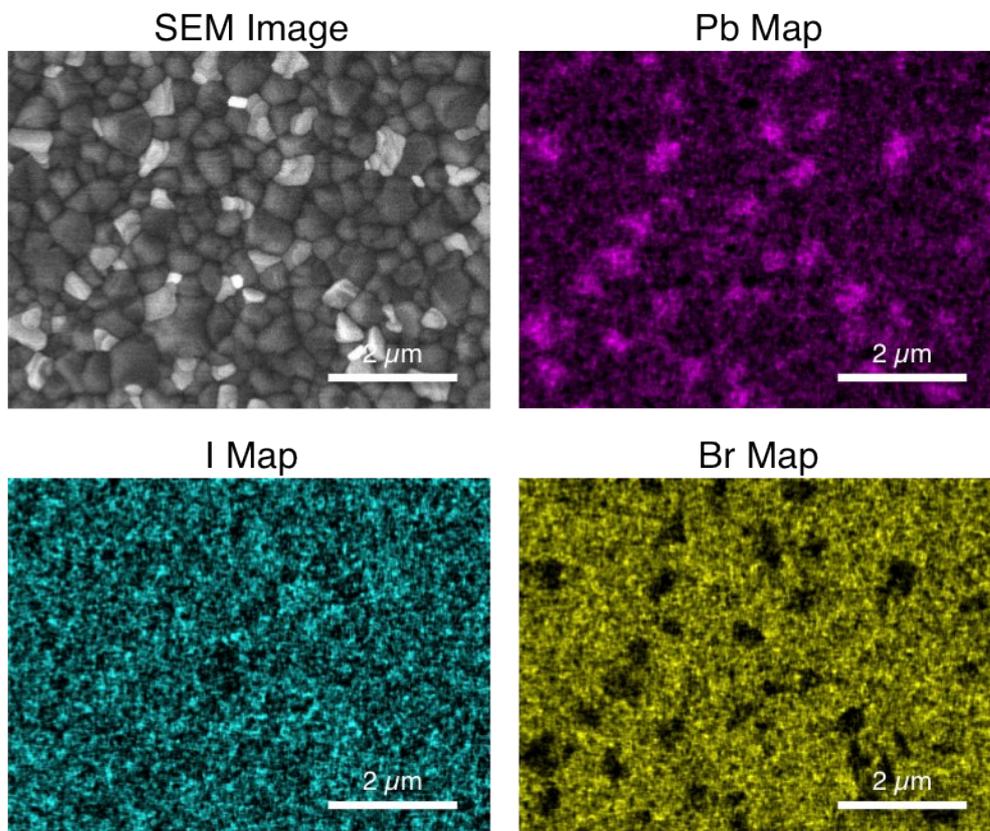


Figure S8. The top-view SEM image of the $\text{Cs}_{0.05}\text{FA}_{0.80}\text{MA}_{0.15}\text{PbI}_{2.75}\text{Br}_{0.25}$ (I/Br ratio 11:1) perovskite film annealed at 150 °C for 30 min, and the corresponding EDX mapping for Pb, I, and Br.

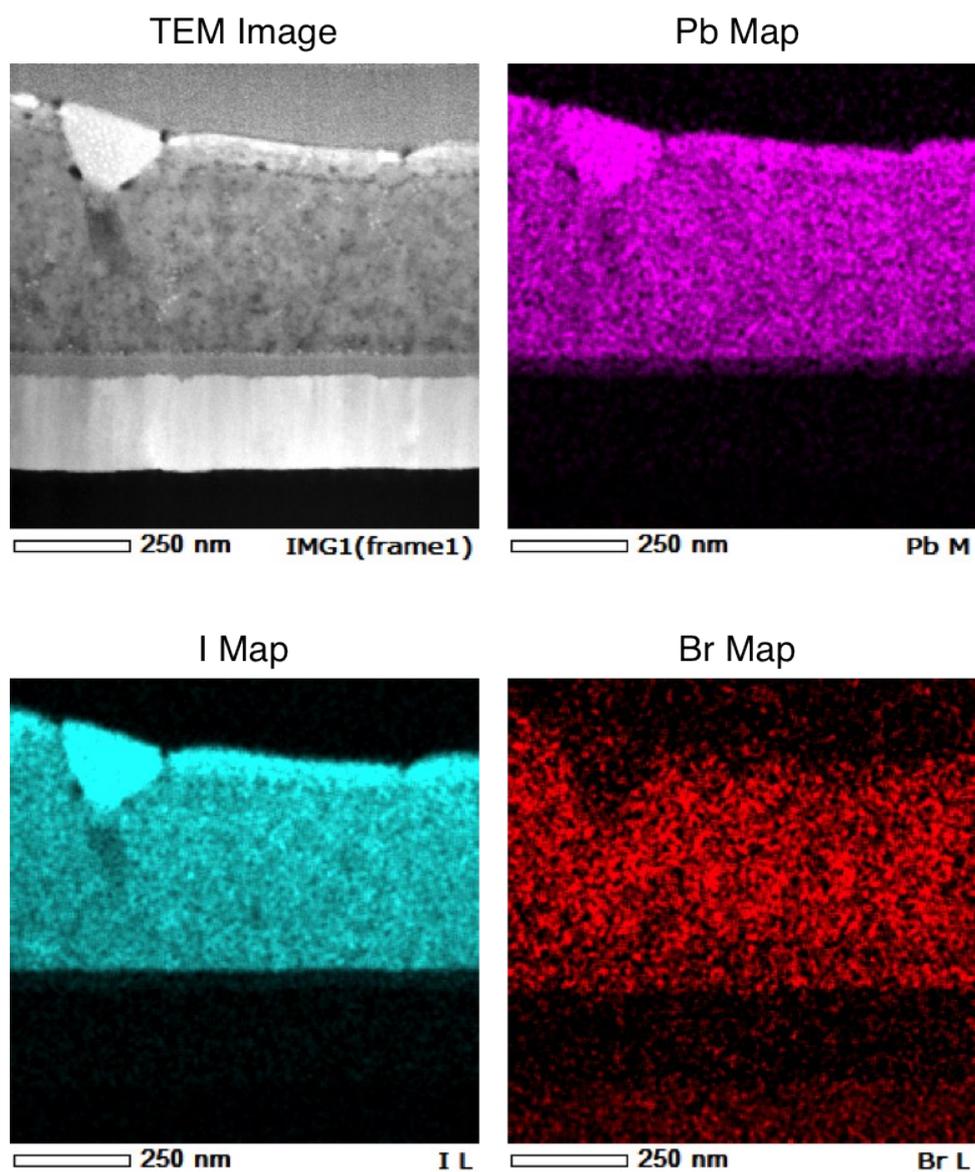
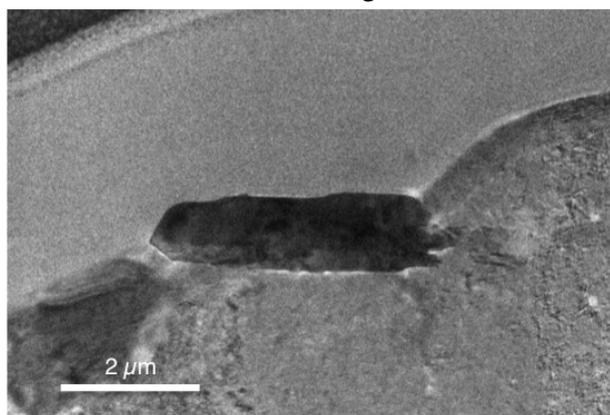
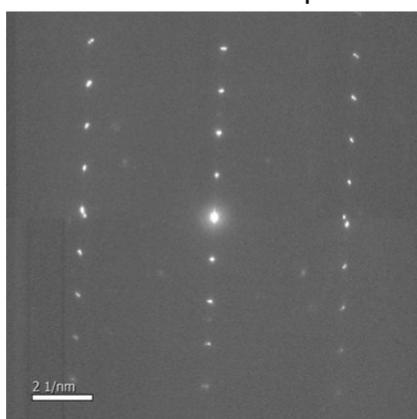


Figure S9. The cross-sectional TEM image of the $\text{Cs}_{0.05}\text{FA}_{0.80}\text{MA}_{0.15}\text{PbI}_{2.75}\text{Br}_{0.25}$ (I/Br ratio 11:1) perovskite film annealed at 150 °C for 10 min, and the corresponding EDX mapping for Pb, I, and Br.

TEM Image



Electron diffraction pattern



Simulation pattern
(PbI_2 , $P6_3mc$)

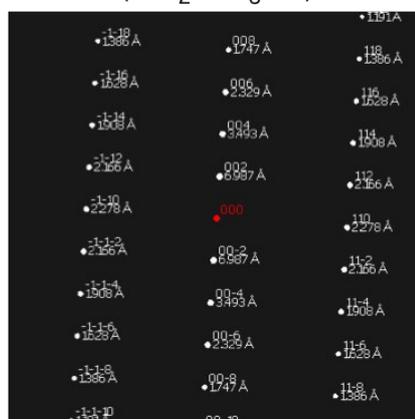


Figure S10. A TEM image of the $\text{Cs}_{0.05}\text{FA}_{0.80}\text{MA}_{0.15}\text{PbI}_{2.75}\text{Br}_{0.25}$ (I/Br ratio 11:1) perovskite film and the selected-area electron diffraction pattern indicating a PbI_2 (Hexagonal, $P6_3mc$).

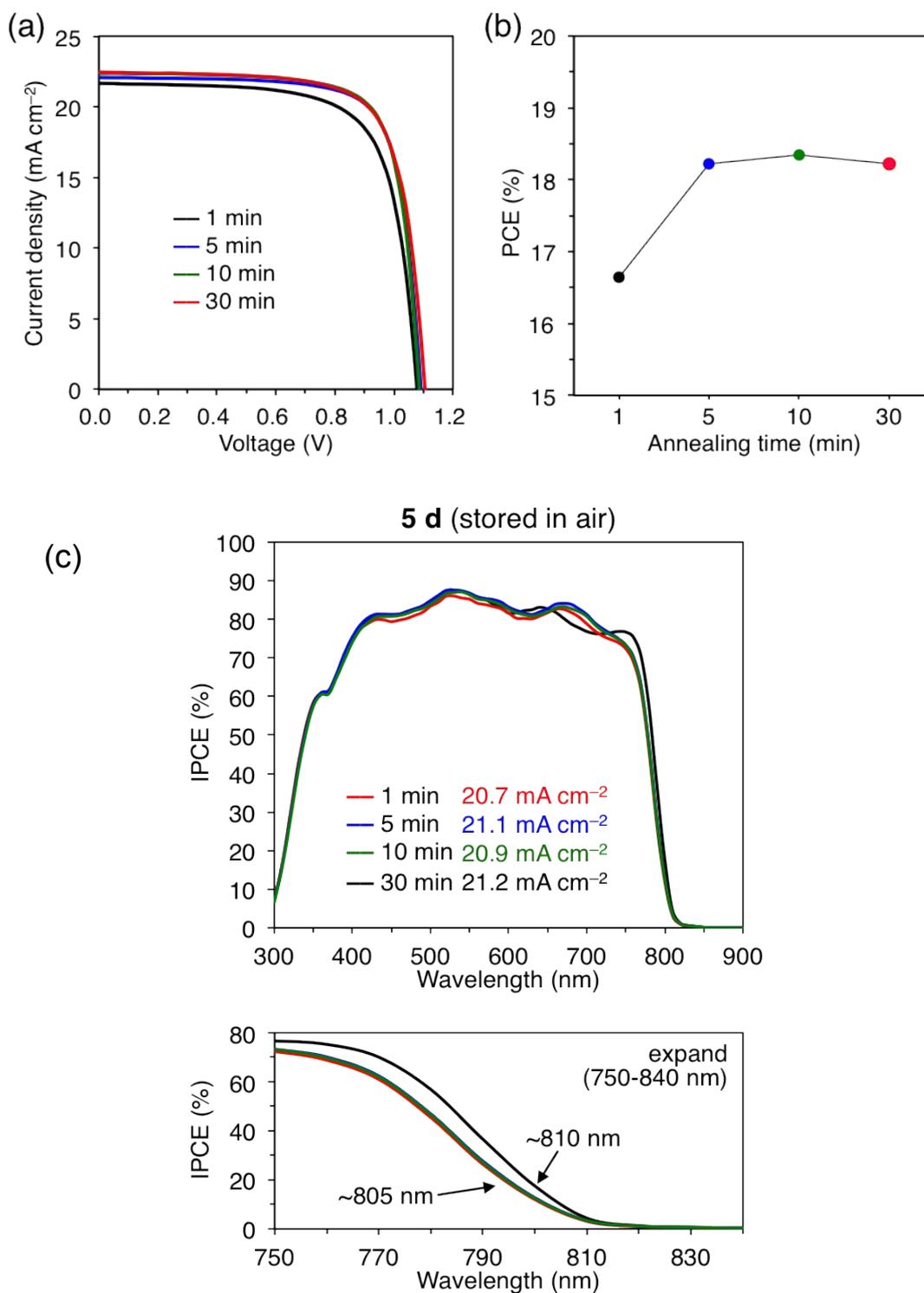


Figure S11. (a) $J-V$ curves (b) PCE plots, and (c) IPCE spectra of the solar cells for different annealing times of the $\text{Cs}_{0.05}\text{FA}_{0.80}\text{MA}_{0.15}\text{PbI}_{2.75}\text{Br}_{0.25}$ (I/Br ratio 11:1) perovskite layer: 1 min (black), 5 min (blue), 10 min (green), and 30 min (red).

Table S2. Photovoltaic parameters of $\text{Cs}_{0.05}\text{FA}_{0.80}\text{MA}_{0.15}\text{PbI}_{2.75}\text{Br}_{0.25}$ (I/Br ratio 11:1) perovskite solar cells annealed for different times

Annealing time	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	PCE (%)	R_s ($\Omega \text{ cm}^2$)	R_{sh} ($\Omega \text{ cm}^2$)
1 min	21.7	1.07	0.72	16.6	4.8	2198
5 min	22.1	1.09	0.76	18.2	5.4	4785
10 min	22.6	1.07	0.76	18.4	4.5	3183
30 min	22.4	1.10	0.74	18.2	5.2	2711

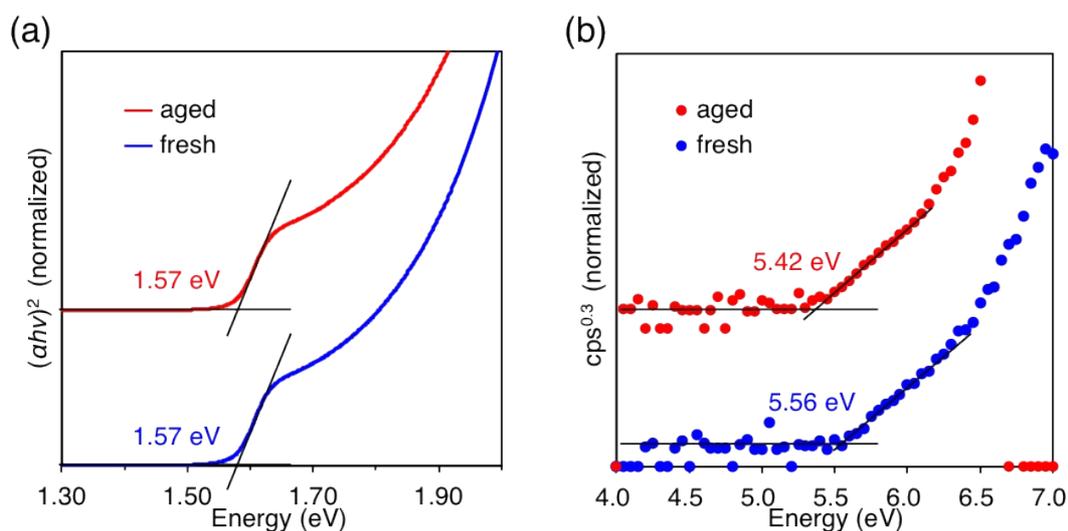


Figure S12. (a) Tauc plot and (b) PES spectra of the $\text{Cs}_{0.05}\text{FA}_{0.80}\text{MA}_{0.15}\text{PbI}_{2.75}\text{Br}_{0.25}$ (I/Br ratio 11:1) perovskite film before (blue) and after aging (red).

Table S3. Nuclear data of radioactive nuclides

Element	Target nuclides	Isotopic abundance (%)	Cross section ^a (barn)	Produced nuclide ^b	Half life	γ -ray energy ^c (keV)
Br	⁸¹ Br	49.31	2.64	⁸² Br	35.34 h	776, 554
I	¹²⁷ I	100	6.2	¹²⁸ I	25.0 m	443
Cs	¹³³ Cs	100	30	¹³⁴ Cs	2.0652 y	605, 796

^aNeutron capture cross-section for thermal neutrons.

^bProduced by neutron capture reaction.

^cUsed in gamma-ray spectrometry for quantification of elements.

Table S4. Neutron activation analysis of Cs_{0.05}FA_{0.80}MA_{0.15}PbI_{2.75}Br_{0.25} (I/Br ratio 11:1) perovskite

films

Perovskite powder (mg)	Br (mg)	I (mg)	Cs (mg)
15.3	0.680 ± 0.007	6.59 ± 0.19	0.133 ± 0.003

References

1. G. M. Sheldrick, SHELX-97, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, **1997**.