

Electronic Supplementary Information
for
Formamidine and cesium-based quasi-two-dimensional perovskites as
photovoltaic absorbers

Ryuki Hamaguchi^a, Masahiro Yoshizawa-Fujita^a, Tsutomu Miyasaka^b, Hideyuki
Kunugita^a, Kazuhiro Ema^a, Yuko Takeoka^{*a}, and Masahiro Rikukawa^a

^a Faculty of Science and Engineering, Sophia University, 7-1 Kioi-cho, Chiyoda-ku,
Tokyo 102-8554, Japan

^b Graduate School of Engineering, Toin University of Yokohama, 1614 Kurogane-cho,
Aoba-ku, Yokohama 225-8503, Japan

1. Materials

Titanium diisopropoxide bis(acetylacetonate), cesium iodide and chlorobenzene were purchased from Sigma-Aldrich. Transparent titania paste (TS/P) for use in the photovoltaic solar cells (PSCs) was purchased from SOLARONIX. Hellmanex was purchased from Hellma Analytics. Formamidinium hydroiodide (FAI), lead iodide, and 4-*tert*-butylpyridine were purchased from the Tokyo Chemical Industry Co., Ltd. Au was purchased from the Kojundo Chemical Laboratory Co., Ltd. All other chemicals were obtained from Wako Pure Chemical Industries, Ltd. Methylamine hydroiodide (MAI) and hexylamine hydroiodide (HAI) were synthesized by neutralizing methylamine or hexylamine, respectively, with stoichiometric quantities of hydroiodic acid.

2. Synthesis of quasi-two-dimensional (q-2D) perovskite compounds

HAI, PbI₂ and MAI or FAI were dissolved in dimethylformamide (DMF) to obtain the precursor solutions for the preparation of HAMAPbI and HAFAPbI, respectively. HAI, PbI₂ and CsI were dissolved in a mixed solvent of DMF and dimethylsulfoxide (DMSO) to make the precursor solution for HACsPbI. The concentrations of these solutions were 40 wt.% (for PSC fabrication and stability tests) and 10 wt.% (for other measurements). The solutions were heated at 70 °C with magnetic stirring for 30 min. Perovskite films were prepared by spin-coating of the above solutions at 3000 rpm for 30 s on glass substrates pre-heated to 70 °C. During this process, red quasi-2D perovskite films were found to appear on the substrates within several seconds as the result of stoichiometric reactions between the constituent compounds. For comparison purposes, HAPbI and MAPbI₃ films were also fabricated, using a similar method. Details of the reaction solutions are presented in Table S1. Each operation was conducted outside the glove box.

Elemental analysis data for HAFAPbI: Calc. C10.2, H 2.40, N 3.61, I 57.23%, Exp. C 10.4, H 2.16, N 3.50, I 57.22%.

Elemental analysis data for HACsPbI: Calc. C8.79, H 1.97, N 1.71, I 54.17%, Exp. C 9.00, H 1.68, N 1.73, I 54.23%.

Table S1. Compositions of perovskite precursor solutions

	HAI	B site cation iodide	PbI ₂	DMF	DMSO
	/ mg (10 ⁻⁴ mol)	/ mg (10 ⁻⁴ mol)	/ mg (10 ⁻⁴ mol)	/ μL	/ μL
HAMAPbI	93.4 (4.08)	MAI: 32.4 (2.04)	189 (4.10)	500	-
HAFAPbI	92.3 (4.03)	FAI: 35.3 (2.05)	187 (4.06)	500	-
HACsPbI	90.0 (3.93)	CsI: 50.5 (1.94)	180 (3.90)	250	250

3. Device fabrication

Fluorine doped tin oxide (FTO)-coated glass substrates (20 cm × 15 cm × 1.1 mm, Peccell Technologies Inc.) were cleaned by sequential sonication in a 2% Hellmanex aqueous solution, 2-propanol, and acetone for 30 min each. A compact TiO₂ layer was subsequently deposited on each substrate via spray pyrolysis at 300 °C from a precursor solution of titanium diisopropoxide bis(acetylacetonate) in ethanol (1.1 wt.%). Each substrate was then annealed at 450 °C for 30 min by a box furnace (KBF314N, Koyo Thermo Systems Co., Ltd.) and left to cool to room temperature.

The substrates were cleaned for 10 min with a UV ozone cleaner (UV253, Filgen), after which a mesoporous TiO₂ layer was deposited by spin-coating a 75 wt.% ethanol solution of TiO₂ paste at 500 rpm for 10 s, followed by 3000 rpm for 30 s. The TiO₂ solution was applied during the initial period of slower rotation. After spin-coating, the obtained films

were annealed at 500 °C for 40 min by a box furnace. Perovskite layers were prepared by the same method employed for the synthesis of the quasi-2D perovskite compounds. After the preparation of the perovskite layer, a hole transport layer containing 2,2',7,7'-tetrakis(*N,N'*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) was deposited. The precursor solution for this step was made by combining spiro-OMeTAD and 4-*tert*-butylpyridine dissolved in chlorobenzene with a 0.592 mM acetonitrile solution of lithium bis(trifluoro methanesulfonyl) imide (Li-TFSI). Details of the reaction solution are provided in Table S2. This spiro-OMeTAD solution was spin-coated at 3000 rpm for 30 s on the perovskite layer, followed by overnight aging. Finally, Au was vapor-deposited over top as a cathode. Each operation was conducted outside the glove box.

Table S2. Composition of the spiro-OMeTAD precursor solution

Spiro-OMeTAD	Chlorobenzene	4- <i>tert</i> -Butylpyridine	Li-TFSI solution ¹⁾
/ mg (mol)	/ μ L	/ μ L (mol)	/ μ L
18 (1.5×10^{-5})	200	1.8 (1.23×10^{-5})	10.3

¹⁾ 0.592 mM acetonitrile solution

4. Characterization

The photovoltaic properties of each device were assessed after applying a black mask (aperture area: 0.09 cm²), using a Keithley 2400 source meter, under 1 sun illumination provided with a Peccell Technologies PEC-L01 solar simulator (AM 1.5 G, 100 mW cm⁻²) under ambient conditions. A reference crystalline Si cell (BS-520, calibrated and certified by Bunkou Keiki) was employed to calibrate the incident light intensity. Photocurrent density-voltage (*I-V*) curves were acquired at a scan speed and dwell time

of 0.125 V s^{-1} and 0.05 s , respectively. The absorption spectra of the films were obtained with a UV-vis-NIR spectrophotometer (UV-3100PC, SHIMAZU). X-ray diffraction (XRD) patterns were obtained with an X-ray diffractometer (SmartLab, Rigaku), in conjunction with a Ni-filtered copper $K\alpha$ target and operating at 45 kV and 200 mA . Thermogravimetric and differential thermal analysis (TG-DTA) was performed using a TG-DTA 7200 (SII nanotechnology). Scanning electron microscopy (SEM) images were obtained with an SU8000 instrument (HITACHI).

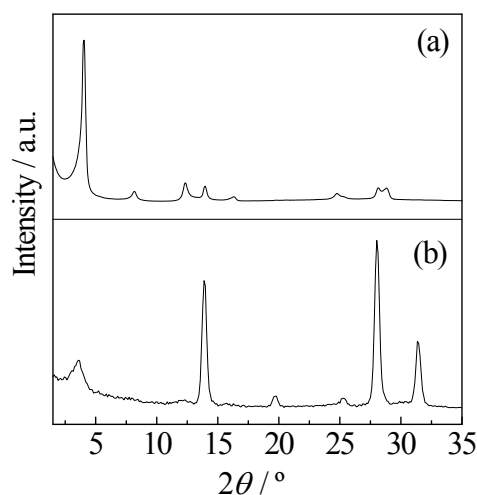


Figure S1. (a) Out-of-plane and (b) in-plane XRD patterns obtained from a HAFAPbI film spin-coated on a mesoporous TiO_2 layer.

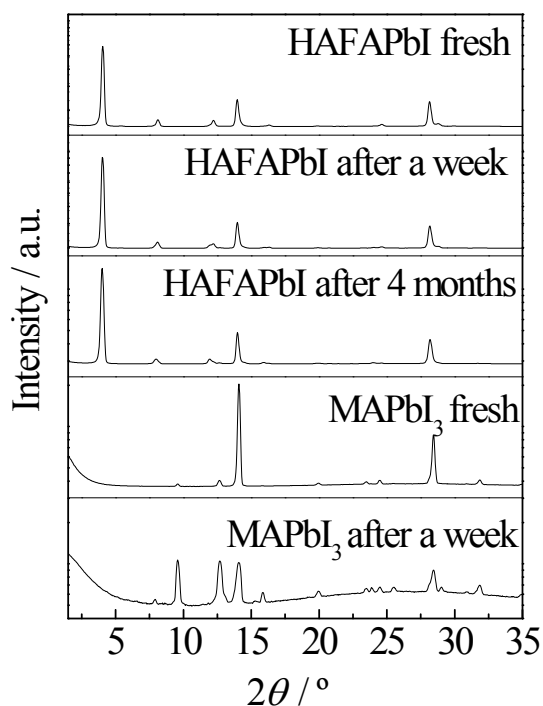


Figure S2. XRD patterns obtained from HAFAPbI and MAPbI₃ before and after storage under ambient conditions (25 °C, 40–50% RH) without encapsulation.

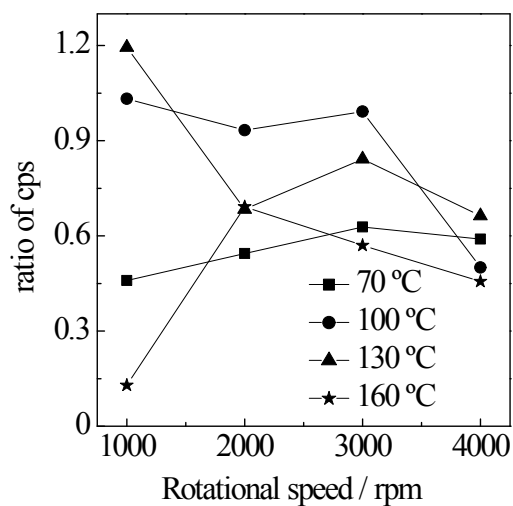


Figure S3. Rotational speed and casting temperature dependencies of the ratio of the X-ray diffraction peak intensities at 3.8° and 14° for HAFAPbI films.

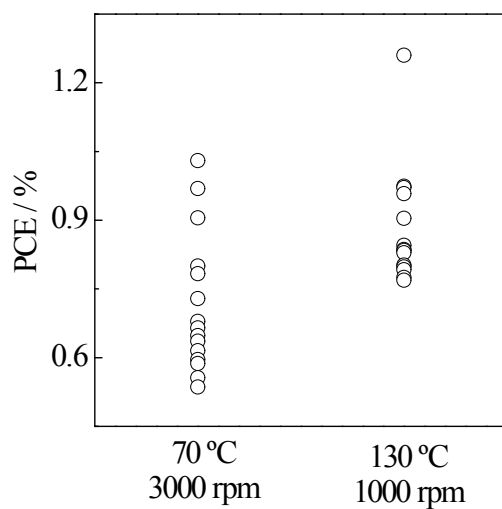


Figure S4. PCE data for HAFAPbI-based PSCs made using different fabrication conditions.

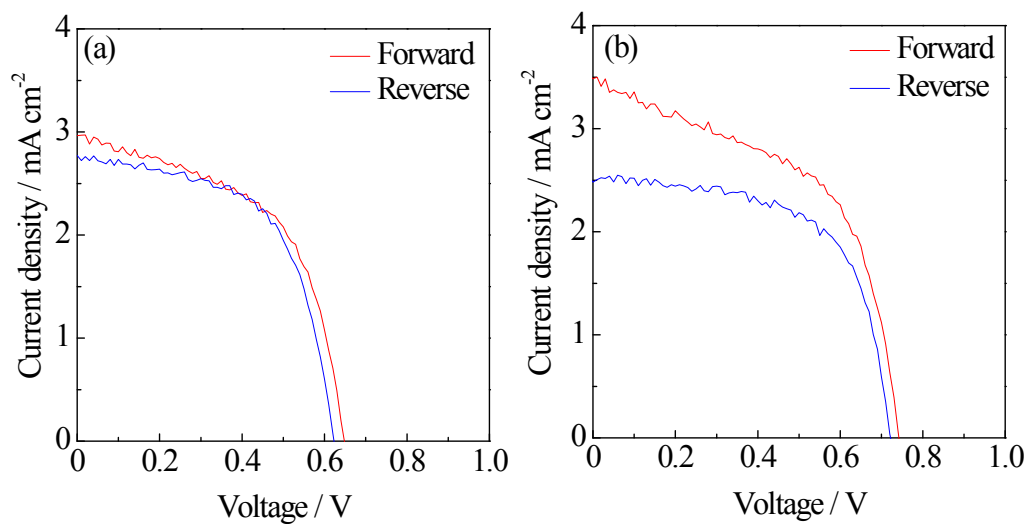


Figure S5. Hysteresis of HAFAPbI-based PSCs fabricated at (a) 70 °C, 3000 rpm and at (b) 130 °C, 1000 rpm.

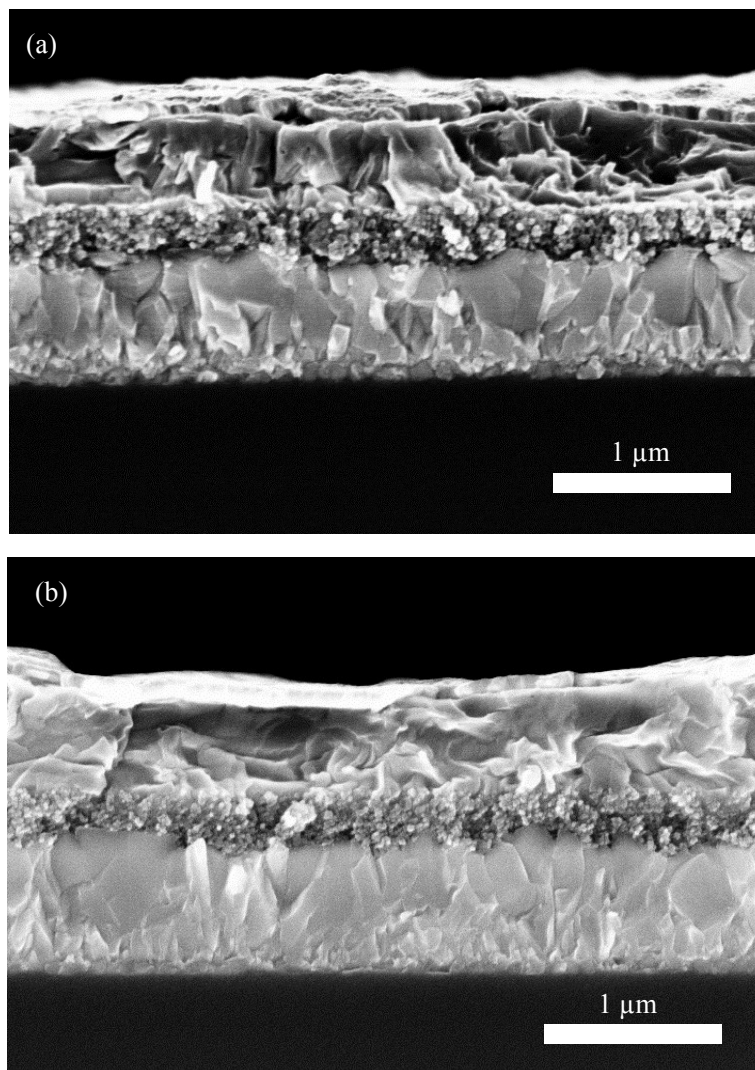


Figure S6. Cross-sectional SEM images of HAFAPbI-based PSCs fabricated at (a) 70 °C, 3000 rpm (perovskite layer = 180 ~ 250 nm, mesoporous TiO₂ layer = 250 ~ 280 nm) and at (b) 130 °C, 1000 rpm (perovskite layer = 150 ~ 220 nm, mesoporous TiO₂ layer = 250 ~ 300 nm).