

Supporting Information

Enhanced Photovoltaic Performance of FASnI₃-Based Perovskite Solar Cells with Hydrazinium Chloride Coadditive

Md. Emrul Kayesh,^{1, 2} Towhid H. Chowdhury,¹ Kiyoto Matsuishi,^{3*} Ryuji Kaneko,^{1, 4} Said Kazaoui,⁵ Jae-Joon Lee,⁶ Takeshi Noda,¹ Ashraful Islam^{1*}

M. E. Kayesh, Dr. T H. Chowdhury, R. Kaneko, Dr. T. Noda, Dr. A. Islam

¹Photovoltaic Materials Group, Center for Green Research on Energy and Environmental Materials, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, 305-0047, Japan

M. E. Kayesh

²Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

Dr. K. Matsuishi

³Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

R. Kaneko

⁴College of Science and Technology, Nihon University, 1-8-14 Kanda Surugadai, Chiyoda-ku, Tokyo, 101-8308, Japan

Dr. S. Kazaoui

⁵Research Center for Photovoltaics (RCPV), National Institute of Advanced Industrial Science and Technology (AIST), Ibaraki 305-8565, Japan

Dr. J.J. Lee

⁶Department of Energy & Materials Engineering & Research Center for Photoenergy Harvesting and Conversion Technology, Dongguk University, Seoul 04620, Republic of Korea

*Corresponding Author: islam.ashraful@nims.go.jp. *E-mail: kiyoto@bk.tsukuba.ac.jp

Experimental Section

Materials: We have used all the chemicals as received without any further purification, including- SnI₂ (99.99%, Sigma–Aldrich), FAI (> 98%, Tokyo Chemical Industry Co., Japan), SnF₂ (>99%, Sigma-Aldrich), N₂H₅Cl (97%, Sigma-Aldrich), Poly (3,4-ethylenedioxythiophene)-poly (styrenesulfonate) (PEDOT:PSS) (Clevious P VP Al 4083), PCBM (Phenyl-C61-butyric acid methyl ester) (99.5%, Lumtec Co., Taiwan). Bathocuproine (BCP) and super dehydrated solvents of dimethyl sulfoxide (DMSO), chlorobenzene, methanol and ethanol, were purchased from Wako Co., Japan.

Perovskite film fabrication: The precursor solution for FASnI₃ perovskite film was prepared by mixing equimolar ratio of (1 mmol) SnI₂ and FAI with 10 mol% SnF₂ in 1ml of DMSO solvent. For the co-additive engineered FASnI₃ films, varying amount of N₂H₅Cl (0 mol%, 2.5 mol%, 5.0 mol% and 10 mol% in respect to the content of FASnI₃) was added into the solution of SnI₂ and FAI in DMSO. The perovskite film was deposited by spin-coating 70μL of precursor solution at 5000 rpm for 45 s. During spin-coating, 80 μL chlorobenzene was dripped on the substrate after 17 seconds. The spin-coated films were then annealed at 100 °C for 30 min.

Solar cell fabrication: PSCs were fabricated on the patterned indium tin oxide (ITO) coated glass substrates. The substrates were ultrasonically cleaned with detergent, de-ionized water, acetone, and ethanol respectively for 15 min each. The cleaned substrates were treated with ultraviolet (UV)/ozone radiation for 30 min. The hole transport layer (HTL) was deposited on top of the ITO substrate by spin-coating 70μL of PEDOT:PSS solution at 4000 rpm for 30 s. The PEDOT:PSS films were then annealed at 150 °C for 15 min and cooled down to room temperature. After cooling

at room temperature, the substrates were transferred to glove box and the FASnI₃ perovskite films were deposited. An electron transporting layer PCBM (20 mg ml⁻¹ in chlorobenzene) and BCP (saturated solution in isopropanol) were deposited by spin-coating at 1000 rpm for 30 s and 6000 rpm for 30 s respectively. Finally, a 90 nm thick silver layer was vacuum deposited through a shadow mask with an active area of 0.09 cm². The PSCs were sealed, by a cavity glass using UV curable glue on top of the front active area of ITO.

Characterization: The optical absorption spectra were measured by a Shimadzu UV/Vis 3600 spectrophotometer. The morphology of the films and structure of devices were observed by scanning electron microscope (JSM-6500F field-emission under an acceleration voltage of 5 kV). The XRD was measured by a Rigaku RINT-2500 powder X-ray diffractometer using Cu K α radiation. X-ray photoelectron spectroscopy (XPS) was performed on the film deposited on glass substrate by using PHI Quantera SXM (ULVAC- PHI). XPS measurement was carried out at ultrahigh vacuum as high as 5x10⁻¹¹ mbar. X-ray from monochromatic Al K α source ($h\nu = 1486.7$ eV) was used to excite the samples and electrons were detected at 45° take off angle. Multi pack software was used for curve fitting. Steady state photoluminescence (PL) and time resolve photoluminescence (TRPL) were measured by a Hamamatsu C12132 fluorescence lifetime spectrometer using a 1.5 ns pulsed laser (frequency 15 kHz), at an excitation wavelength of $\lambda = 532$ nm, and an excitation power of 0.1 mW. For PL and TRPL measurement, the relevant films were deposited on glass substrates and encapsulated in glovebox but were measured in ambient conditions.

The current-voltage (J - V) curves were measured using a solar simulator with standard air mass 1.5 sunlight (100mWcm⁻², WXS-155S-10: Wacom Denso Co., Japan) under ambient conditions. The J - V curves were measured in forward (-0.1V to 0.5V) or reverse (0.5V to -0.1V) scans by using

the Keithley 2400 as a digital source meter. The step voltage was fixed at 10mV and the delay time was set at 50 ms. *J-V* curves for all devices were measured by masking the cells with a metal mask 0.09 cm² in area. A monochromatic incident light (1×10^{16} photons/cm²) in direct current mode (CEP-2000BX, Bunkoukeiki Co., LTD) was used to measure monochromatic incident photon-to-current conversion efficiency (IPCE) spectra. The stability (shelf-life) of the fabricated PSCs were measured in ambient environment and stored in N₂ filled glove box after measurement.

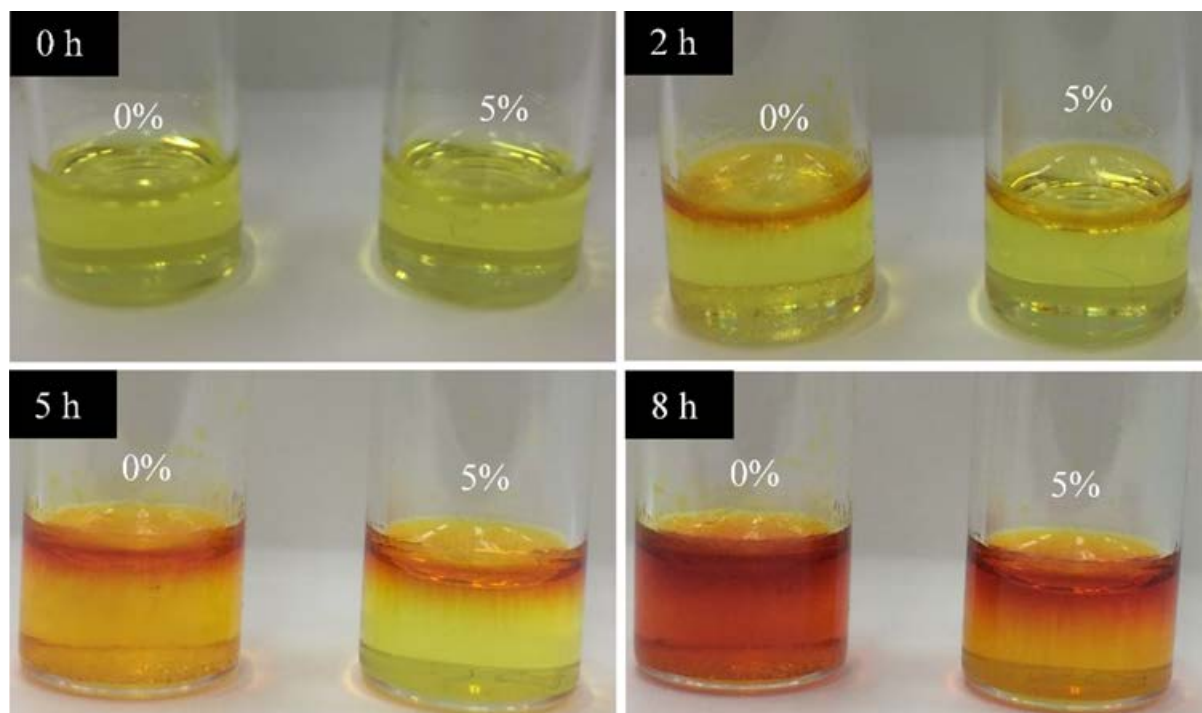


Figure S1. Photographic images of FASnI₃ precursor solution (1 mmol SnI₂, 1 mmol FAI and 0.1 mmol SnF₂) and SnF₂+5 mol% N₂H₅Cl exposed in air for different period of time.

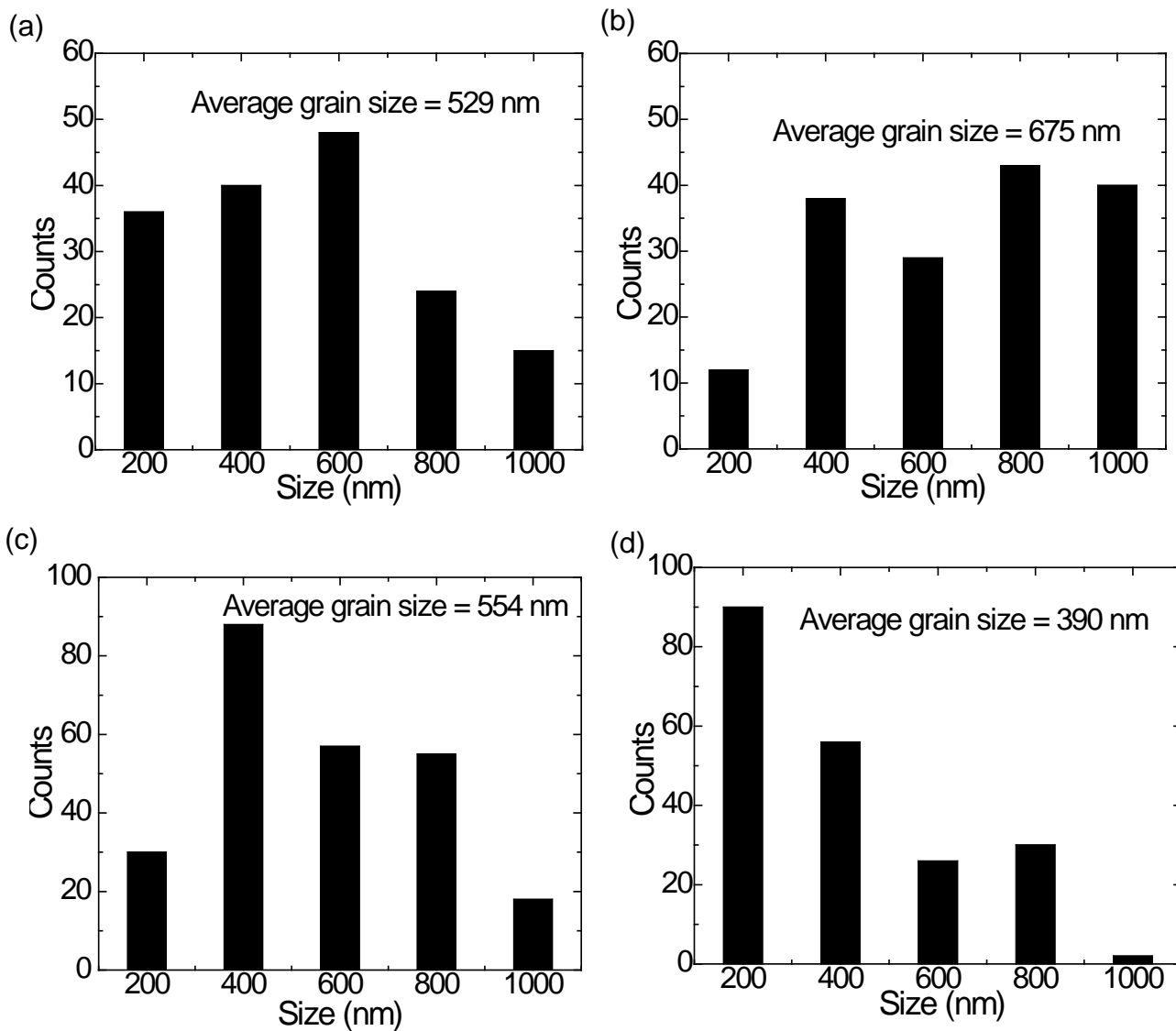


Figure S2. Grain size distributions determined from SEM images in figure 1a, b, c and d for perovskite films with only SnF₂, SnF₂+2.5 mol% N₂H₅Cl, SnF₂+5 mol% N₂H₅Cl and SnF₂+10 mol% N₂H₅Cl respectively.

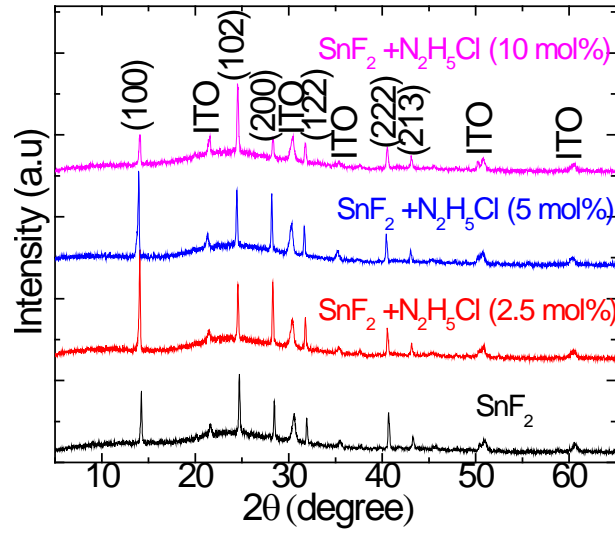


Figure S3. XRD patterns of FASnI₃ films at various concentrations of N₂H₅Cl deposited on ITO coated glass substrate.

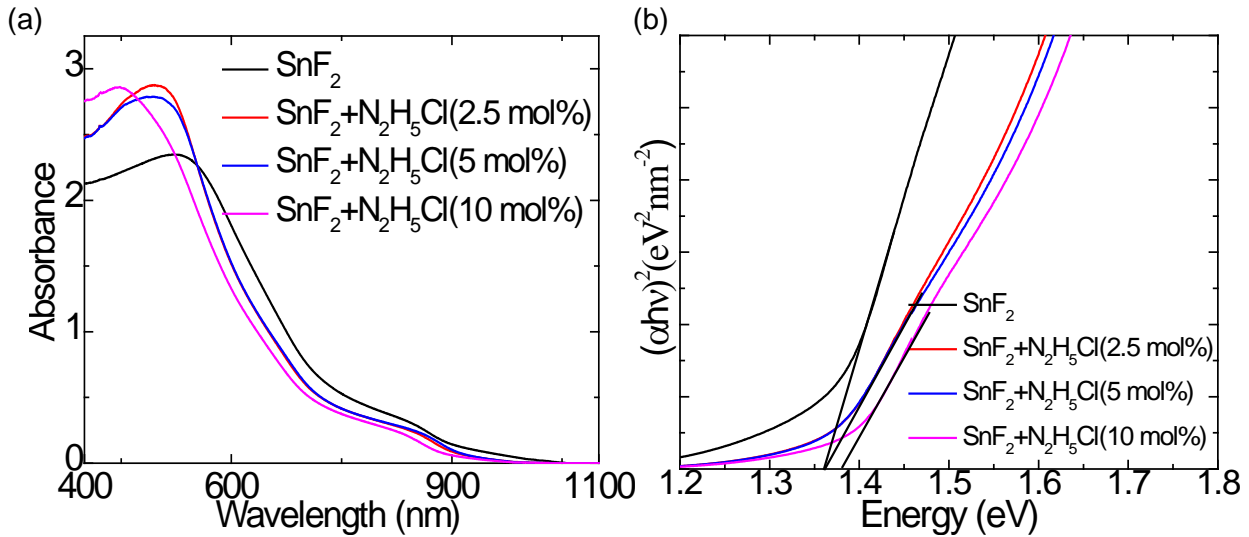


Figure S4. (a) UV-Vis spectra (b) Tauc plot of FASnI₃ films with only SnF₂ and with SnF₂ + various concentration of N₂H₅Cl.

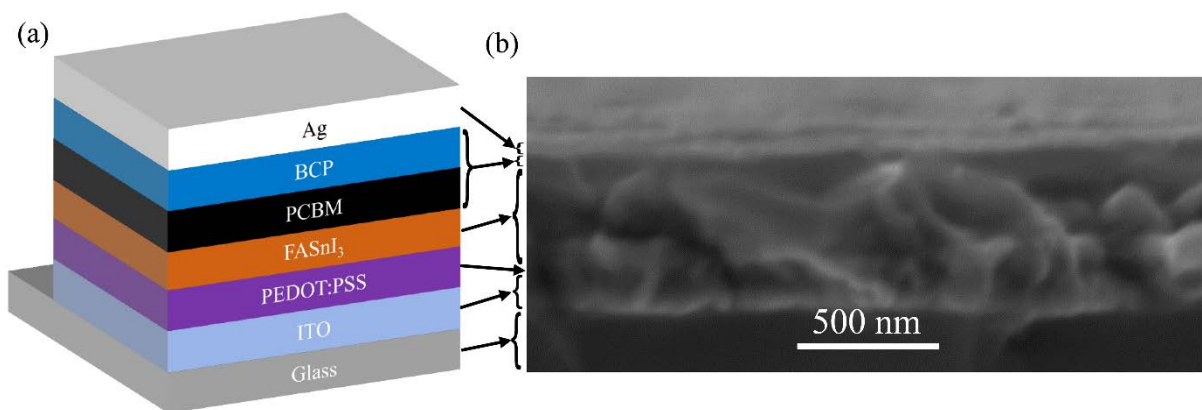


Figure S5. (a) Schematic illustration of the device structure, and (b) cross-sectional scanning electron microscope image of complete FASnI₃ based PSC.

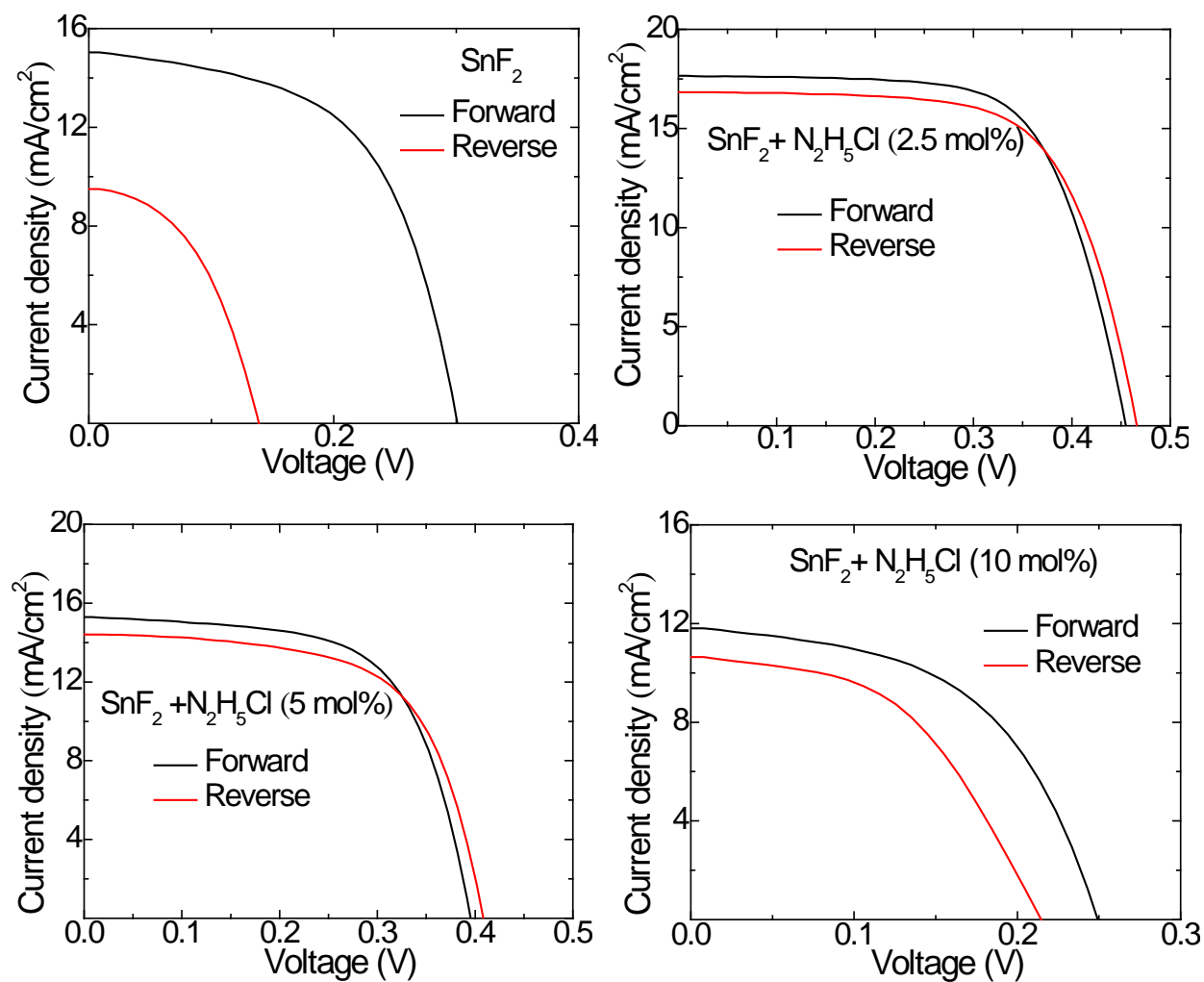


Figure S6. Current density-voltage (J - V) curves of SnF₂ and SnF₂ + various concentration of N₂H₅Cl based PSCs measured under forward and reverse voltage scan.

Table S1. The full width at half maxima (FWHM) of different peaks at different angles

Sample	FWHM at		
	14.1 ⁰	24.5 ⁰	28.4 ⁰
FASnI ₃ (SnF ₂)	0.145	0.121	0.118
FASnI ₃ (SnF ₂ +2.5 mol% N ₂ H ₅ Cl)	0.110	0.125	0.093
FASnI ₃ (SnF ₂ +5 mol% N ₂ H ₅ Cl)	0.124	0.121	0.116
FASnI ₃ (SnF ₂ +10 mol% N ₂ H ₅ Cl)	0.196	0.163	0.174

Table S2. The fitting results of XPS spectra for the SnF₂ added FASnI₃ films.

FASnI ₃ (10 mol% SnF ₂)	Sn 3d _{5/2}		Sn 3d _{3/2}	
	Sn ²⁺	Sn ⁴⁺	Sn ²⁺	Sn ⁴⁺
Energy position (eV)	486.54	487.47	494.95	495.88
FWHM	1.20	1.57	1.20	1.54
% Gauss	80	80	80	80
Area	103185	57483	69134	38514
Area ratio	1	0.56	1	0.56
Atomic %	13.1	7.3	13.1	7.3

Table S3. The fitting results of XPS spectra for the SnF₂+ N₂H₅Cl added FASnI₃ films.

FASnI ₃ (10 mol% SnF ₂ + 2.5 mol% N ₂ H ₅ Cl)	Sn 3d _{5/2}		Sn 3d _{3/2}	
	Sn ²⁺	Sn ⁴⁺	Sn ²⁺	Sn ⁴⁺
Energy position (eV)	486.56	487.47	494.97	495.86
FWHM	1.20	1.33	1.20	1.33
% Gauss	80	80	80	80
Area	103357	35525	69249	23802
Area ratio	1	0.34	1	0.34
Atomic %	14.3	4.9	14.3	4.9

Table S4. Photovoltaic parameters of PSCs as a function of $\text{N}_2\text{H}_5\text{Cl}$ concentration in the precursor solution under forward and reverse bias condition.

$\text{N}_2\text{H}_5\text{Cl}$ concentration in mol %	Scan direction	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
0	Forward	15.069	0.297	0.559	2.5
	Reverse	9.54	0.139	0.458	0.61
2.5	Forward	17.63	0.455	0.673	5.40
	Reverse	16.822	0.466	0.669	5.24
5	Forward	15.317	0.395	0.632	3.83
	Reverse	14.43	0.408	0.629	3.71
10	Forward	10.53	0.351	0.497	1.84
	Reverse	8.902	0.365	0.564	1.83