Electronic Supplementary Information

Synergistic Improvements in Stability and Performance of Lead Iodide Perovskite Solar Cells Incorporating Salt Additives

Karunakara Moorthy Boopathi[a,b,c], Ramesh Mohan[c], Tzu-Yen Huang[c,d], Widhya Budiawan[a,b,c], Ming-Yi Lin[c], Chih-Hao Lee[a], Kuo-Chuan Ho[d], Chih-Wei Chu[c,*]

[a]*Department of Engineering and Systems Science, National Tsing Hua University, Hsinchu 30013, Taiwan*
[b]*Nano Science and Technology Program, Taiwan International Graduate Program, Academia Sinica and National Tsing Hua University*
[c]*Research Center for Applied Science, Academia Sinica, Taipei 115, Taiwan*
[d]*Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan.*

Experimental section

Methylammonium iodide (MAI) preparation

Aqueous HI (57 wt.% in water), methylamine (CH_3NH_2, 40 wt.% in aqueous solution), PbI_2 (99.998%), dimethyl sulfoxide (DMSO), and diethyl ether were purchased from Alfa Aesar and used without further purification. MAI (CH_3NH_3I) was synthesized by reacting aqueous HI (15 mL) with CH_3NH_2 (13.5 mL) at 0 °C for 2 h in three-neck flask under a N_2 atmosphere with constant stirring. A white precipitate (CH_3NH_3I) formed during rotary evaporation of the solvent. The precipitated white powder was collected, washed three times with diethyl ether, and then dried under vacuum at 60 °C overnight. This dried powder was stored in a glove box.

Device fabrication and characterization

Indium tin oxide (ITO)–coated glass substrates (<10 Ω sq^{-1}, RiTdisplay) were cleaned through sonication, once in detergent (20 min) and then twice in deionized (DI) water (20 min each), and dried under N_2 gas. The substrates were treated with ultraviolet (UV)/ozone for 15 min to clean the surfaces and also to improve the surface adhesion. PEDOT:PSS was spin-coated (4000 rpm, 60 s) onto the ITO surfaces, followed by annealing (130 °C, 30 min).

The substrates were transferred to a glove box for deposition of the perovskite active layer through the two-step spin-coating method. PbI_2 (40 wt.%) and a salt (various wt.%) were dissolved in DMSO; MAI was dissolved in 2-propanol at 3 wt.%. Both solutions were kept on a hot plate at 70 °C overnight. A hot PbI_2/salt mixture was spin-coated onto PEDOT:PSS and annealed directly (70 °C, 30 min). The hot MAI solution was then spin-coated onto the PbI_2 film; the structure was kept on the hot plate at 100 °C for 120 min to form a crystalline perovskite film. A solution (20 mg/mL) of [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) in chlorobenzene (CB) and was spin-coated (6000 rpm, 60 s) onto the perovskite layer, followed by annealing (100 °C, 30 min). The device was completed through sequential thermal evaporation of C_{60} (30 nm), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP, 7 nm), and an aluminum electrode (100 nm) through a shadow mask under vacuum (pressure: 1×10^{-6} torr). The active area of each device was 10 mm^2.

XRD patterns were recorded at room temperature using a Bruker D8 X-ray diffractometer (2θ range: 10–60°; step size: 0.008°) equipped with a diffracted beam monochromator set for Cu $K\alpha$ radiation (λ = 1.54056 Å). SEM images were recorded using an FEI Noval 200 scanning electron microscope (15 kV). Glass substrates spin-coated with PEDOT:PSS were used for XRD measurements; ITO substrates spin-coated with PEDOT:PSS were used for recording SEM images. PL emission spectra of the samples were recorded using an optically excited Q-switched Nd:YAG laser (266 nm, 3–5 ns pulse, 10 Hz) focused at a beam diameter of approximately 0.5 mm. Absorption spectra of the films were measured using a Jacobs V-670 UV–Vis spectrophotometer. XPS was performed using a PHI 5000 Versa Probe apparatus equipped with an Al $K\alpha$ X-ray source (1486.6 eV). All measurements were performed at room temperature. EQE spectra were obtained under short-circuit conditions.

Devices were encapsulated before they were removed for EQE measurement. The light source was a 75-W Xe lamp (Enlitech, QE-R3011); the light output from the monochromator was focused on the photovoltaic cell being tested (DC mode). The devices were illuminated inside a glove box by a Xe lamp as a solar simulator (Thermal Oriel 1000 W), which provided a simulated AM 1.5 spectrum (100 mW cm^{-2}). The light intensity was calibrated using a mono-silicon photodiode with a KG-5 color filter (Hamamatsu).

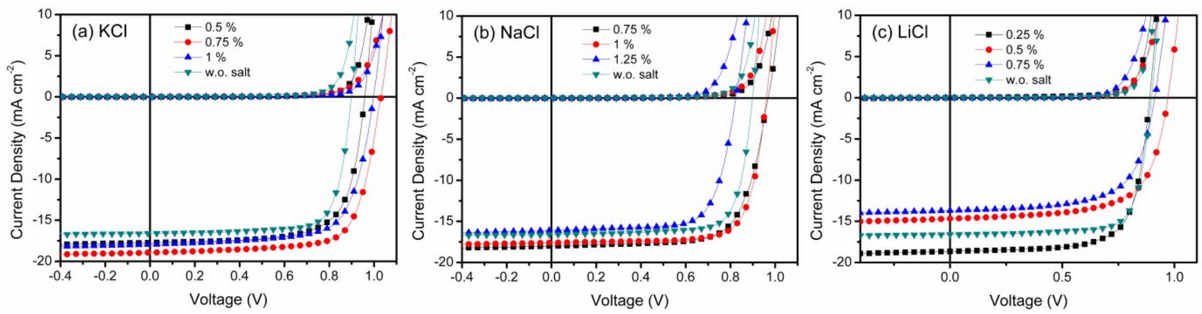

Figure S1 Photo and dark currents of devices incorporating perovskite films prepared at various salt concentrations: (a) KCl from 0.5 to 1 wt.%, (b) NaCl from 0.75 to 1.25 wt.%, and (c) LiCl from 0.25 to 0.75 wt.%

Table S1 Photovoltaic performance parameters of devices incorporating perovskite films prepared in the presence of various concentrations of salt additives

Salt	**Wt.%**	**V_{oc} (V)**	**J_{sc} (mA cm^{-2})**	**FF (%)**	**PCE (%)**
KCl	0.5	0.96	17.73	70.80	12.05^{a} (11.38)^{b}
	0.75	**1.04**	**19.42**	**74.67**	**15.08**^{a} (14.12)^{b}
	1.0	1.00	17.94	70.90	12.72^{a} (12.07)^{b}
NaCl	0.75	0.97	17.98	70.98	12.38^{a} (11.55)^{b}
	1.0	**0.96**	**17.59**	**75.62**	**12.77**^{a} (12.14)^{b}
	1.25	0.83	16.10	71.39	9.54^{a} (8.83)^{b}
LiCl	**0.25**	**0.91**	**15.97**	**68.67**	**9.98**^{a} (9.35)^{b}
	0.5	0.96	14.68	67.12	9.46^{a} (8.53)^{b}
	0.75	0.91	13.69	66.06	8.23^{a} (7.05)^{b}
Without salt	–	0.90	16.60	76.31	11.40^{a} (10.86)^{b}

[a] Best device performance. [b] Average performance of 10 devices.

Table S2 Reported photovoltaic performance parameters of devices incorporating perovskite films prepared in the presence of additives

Additive	**V_{oc} (V)**	**J_{sc} (mA cm^{-2})**	**FF (%)**	**PCE (%)**	**Reference**
NH_4Cl	0.88	14.08	80.11	9.93	S1
HCl	1.06	21.77	64.0	14.8	S2
DIO	0.92	17.5	73.0	11.8	S3
CN	0.854	16.7	63.4	8.97	S4
PVP	0.848	17.54	58.8	8.74	S5
PEG	0.94	19.53	70.35	12.90	S6
KCl	1.04	19.42	74.67	15.08	**Current study**
NaCl	0.96	17.59	75.62	12.77	
LiCl	0.91	15.97	68.67	9.98	

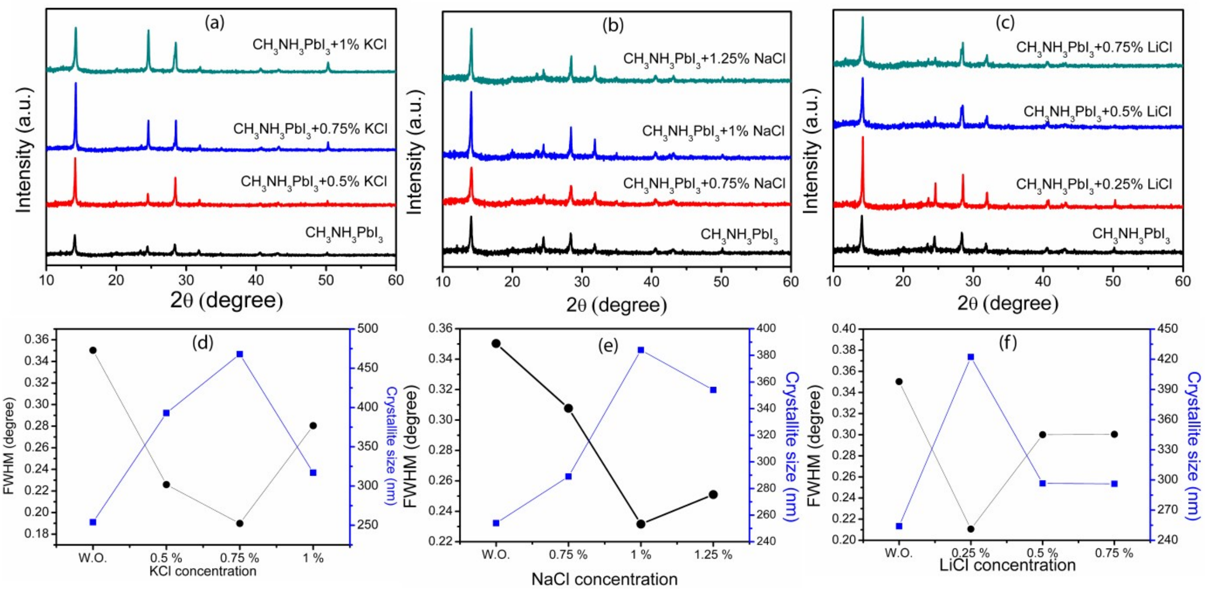

Figure S2 (a–c) XRD patterns and (d–f) crystallite sizes of perovskite thin films prepared in the presence of alkali metal salts at various concentrations: (a, d) KCl from 0.5 to 1 wt.%, (b, e) NaCl from 0.75 to 1.25 wt.%, and (c, f) LiCl from 0.25 to 0.75 wt.%.

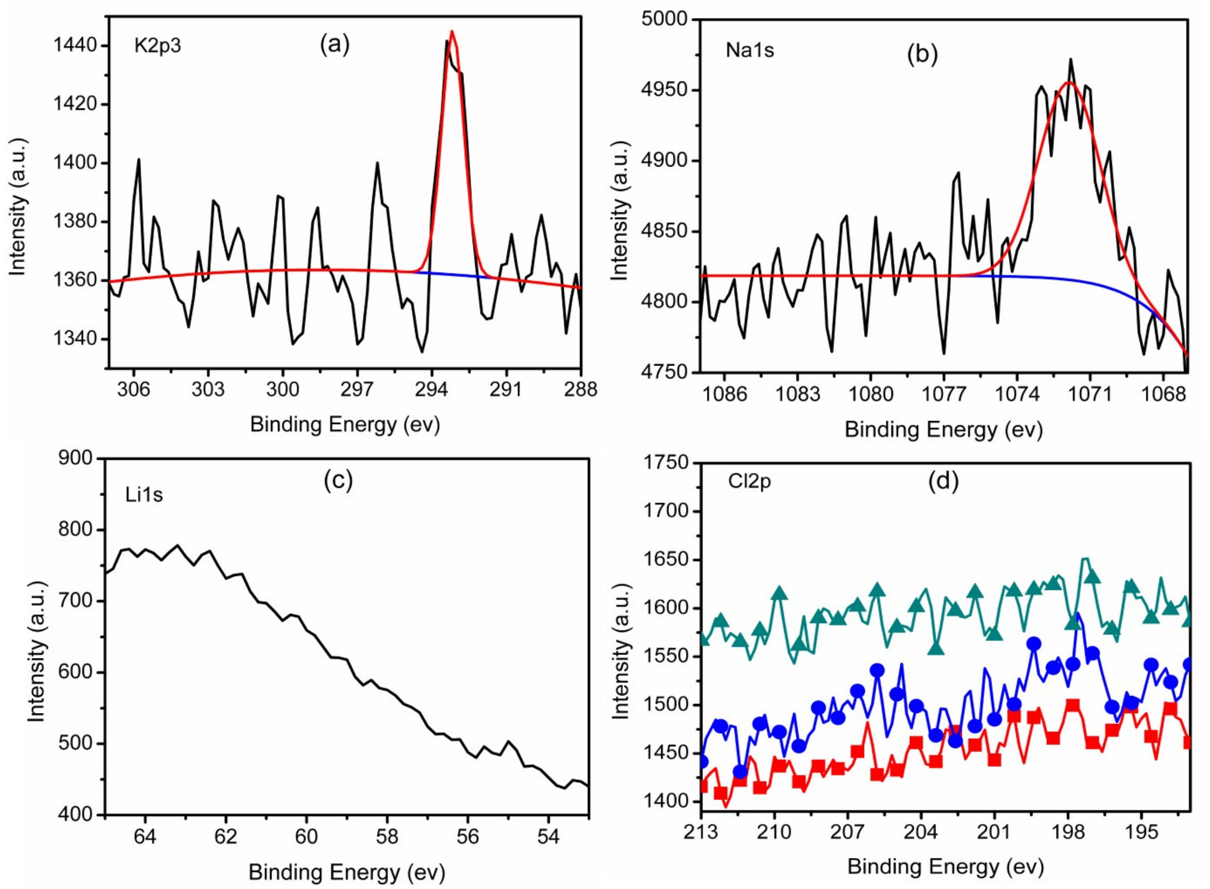

Figure S3 XPS spectra of (a) K 2p3, (b) Na 1s, and (c) Li 1s binding energies for KCl-, NaCl-, and LiCl-added perovskite thin films, respectively, and (d) Cl 2p peaks for KCl (square)-, NaCl (circle)-, LiCl (triangle)-added perovskite films.

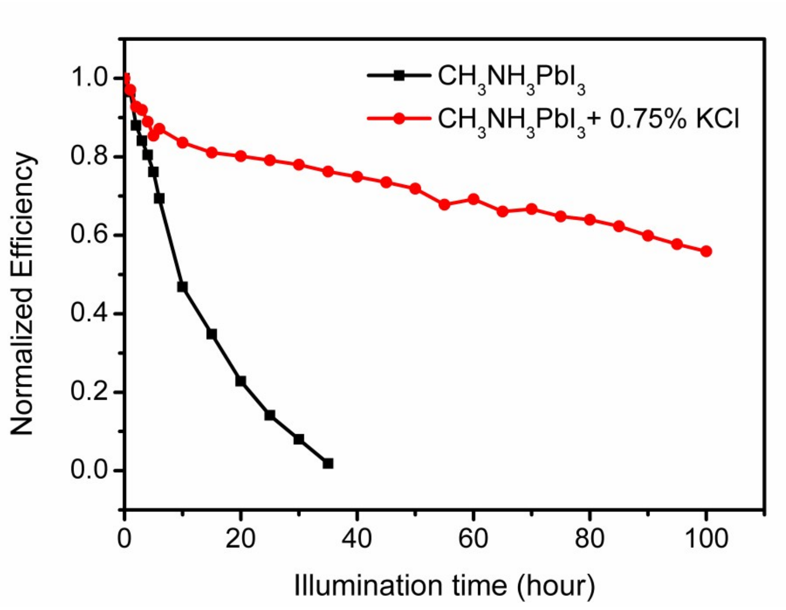

Figure S4 Comparison of perovskite device stability with and without salt additives under continuous illumination (1 sun).

References

S1. C. Zuo, L. Ding, Nanoscale, 2014, **6**, 9935.

S2. L. Yang, J. Wang, W.W.-F. Leung, ACS Appl. Mater. Interfaces, 2015, **7** (27), 14614.

S3. P.-W. Liang, C.-Y. Liao, C.-C. Chueh, F. Zuo, S.T. Williams, X.-K. Xin, J. Lin, A.K.Y. Jen, Adv. Mater., 2014, **26**, 3748.

S4. X. Song, W. Wang, P. Sun, W. Ma, Z.-K. Chen, Appl. Phys. Lett., 2015, **106**, 033901.

S5. Y. Ding, X. Yao, X. Zhang, C. Wei, Y. Zhao, J. Power Sources, 2014, **272**, 351.

S6. C.-Y. Chang, C.-Y. Chu, Y.-C. Huang, C.-W. Huang, S.-Y. Chang, C.-A. Chen, C.-Y. Chao, W.-F. Su, ACS Appl. Mater. Interfaces, 2015, **7**, 4955.