Supporting Information

How Additives for Tin Halide Perovskites Influence the Sn⁴⁺ Concentration

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Materials:

Tin (II) iodide (SnI₂, 99.99% metals basis, Alfa Aesar), tin (II) fluoride (SnF₂, 99.99%, Acros Organics), tin (IV) iodide (SnI₄, 99.99%, Alfa Aesar), tin (II) chloride (SnCl₂, 98%, Fluka), tin (IV) chloride (SnCl₄, 99.99% trace metals basis, Beantown chemical) formamidinium iodide (FAI, Greatcell solar), methylammonium chloride (MACl, Greatcell solar), silver nitrate (AgNO₃, 99.9% metals basis, Alfa Aesar), tetrabutylammonium hexafluorophosphate (TBAPF₆, TCI), anhydrous N,N-dimethylformamide (DMF, 99.98%, DriSolv[®]), anhydrous dimethyl sulfoxide (DMSO, 99.9%, Sigma-Aldrich), anhydrous chlorobenzene (CB, 99.8%, Acros Organics), anhydrous dichloromethane (DCM, 99.8%, Acros Organics), indium tin oxide (ITO) glass (12 Ω/\Box), 1,2-dihydroxybenzene (Cat, TCI), 1,4-dihydroxybenzene (HQ, TCI), pyrogallol (PG, TCI), dopamine hydrochloride (DHCl, TCI), 3,5-di-tert-butylcatechol (DTBC, Thermoscientific), benzylhydrazine monohydrochloride (BHzHCl, TCI), benzoic acid (BA, Matrix Scientific), 3,4dihydroxybenzoic acid (DHBA, 97%, Alfa Aesar), dihydrocaffeic acid (DHCA, 98%, Alfa Aesar), caffeic acid (CA, TCI), 4-fluorobenzohydrazide (4-FBH, 97%, Alfa Aesar), hydroquinonesulfonic acid potassium salt (KHQSA, Aldrich), hydrazine dihydrochloride (HzHCl, Aldrich), 1,4dihydroxynapthalene (DHNT, TCI), 1,4-naphthaquinone (NQ, TCI), 2,5-dihydroxy-1,4benzoquinone (DHBQ, 98%, Alfa Aesar), 1,8-dihydroxyanthraquinone (1,8-DHAQ, Acros Organics), 2,6-dihydroxyanthraquinone (2,6-DHAQ, TCI). All chemicals were used as received without further purification. All solvents were degassed before use.

Perovskite Film Processing:

Non-patterned ITO glass was cleaned through sequential sonication with a sodium dodecylsulfate solution, distilled water, acetone, and 2-propanol for 15 minutes each, followed by 15 min UV-ozone cleaning. Immediately following UV-ozone cleaning the substrates were taken into a glovebox. To prepare 1.0 mL of 1.0 M FASnI₃ solution, SnI₂ (0.3725 g, 1.0 mmol), FAI (0.1719 g, 1.0 mmol), and 10% SnF₂ (0.0157 g, 0.1 mmol) were measured in a vial, and then 800 μ L of DMF and 200 μ L of DMSO (4:1) were added to it. The mixture was heated at 70 °C for 30 min to dissolve the solids. Before deposition, the mixture was filtered through a 0.2 μ m PTFE filter and cooled down to room temperature. Then the precursor solution was spun-cast at 6000 rpm for 30 s while 120 μ L of CB anti-solvent was added after 12 s of spinning. The resulting film was then annealed at 100 °C for 10 min. For FASnI₃ films with additives, 2.5 mol% of additives were added to the perovskite precursor solution before coating the thin film. Film processing was carried out under continuous purging of the N₂-filled glovebox to maintain O₂ and H₂O levels of less than 0.1 ppm.

Cyclic Voltammetry:

Glassy carbon, Pt wire, and a non-aqueous Ag/AgNO₃ (Ag/Ag+, 1.0 M in DMF:DMSO, 4:1) were used as working electrode, counter electrode and reference electrode, respectively. TBAPF₆ was dried at 100 °C under vacuum overnight prior to use. TBAPF₆ was used as the supporting electrolyte at 0.1 M in DMF:DMSO. All analyte concentrations were kept at 0.01 M. A 0.02 V/sec scan rate was used for all CVs. Solution preparation and CV measurements were carried out in the N₂-filled glovebox (O₂ and H₂O level were <0.1 ppm). Working electrode was polished with alumina and DI water slurry before each measurement. Anhydrous and degassed solvents were used to avoid H₂O and O₂ presence during CV measurements. For the CV of FASnI₃ film, perovskite film was made on non-patterned ITO glass according to the description before. Anhydrous and degassed DCM solvent was used for this measurement. The redox potential (E_{1/2}) of analytes was calculated by taking the average of cathodic (Ep,c) and anodic (Ep,a) peak potential *i.e.*, E_{1/2}= (Ep,c + Ep,a)/2.

¹¹⁹Sn and ¹H NMR:

The NMR solutions (0.5 M of SnI₄, SnI₂, SnCl₂, SnCl₄, MACl, DHCl, BHzHCl, DHCA, HzHCl, 4-FBH, BA, KHQSA, DHNT, HQ, NQ; or 0.1 M of 1,8-DHAQ and 2,6-DHAQ) were prepared in anhydrous and degassed DMSO- d_6 solvent. Additives and SnI₄ were mixed in a 1:1 stoichiometry. Tin (II) chloride solutions were filtered with 0.2 µm PTFE filters to remove precipitates.

¹H and ¹¹⁹Sn NMR studies were carried out using a Bruker Advance NEO (400MHz) spectrometer equipped with a 5mm broadband SmartProbe. All experiments were run at 298K. Chemical shifts in the ¹¹⁹Sn NMR studies were referenced to an external standard Sn(CH₃)₄ ($\delta = 0.00$ ppm) and the ¹H NMR chemical shifts were referenced to the residual solvent protons. ¹¹⁹Sn was detected via the broadband channel using a 3.33 µs 30° excitation pulse, and inverse gated ¹H decoupling during the 0.655 s signal acquisition, with 4 s relaxation delays between transients. A spectral width of 500k Hz encompassing -3000 ppm to 1000 ppm was collected. Spectra were processed with 120 Hz line broadening and represent averaging of 512 to 6144 scans. ¹H spectra were obtained using a 30° excitation pulse, digitization over 3.99 seconds and 4 s relaxation delay between transients. Spectra were processed with 0.3 Hz line broadening and represent averages of 512 and 1024 scans.

Absorbance:

UV-vis absorbance spectra were collected using an Ocean Optics QE Pro high-performance spectrometer with 700 ms integration time and 5 μ m slit width. The final concentration of analytes was kept at 1.0 mM and the solutions were prepared by mixing SnI₄ and additives in a 1:1 mole ratio in DMF:DMSO (4:1).

Photoluminescence:

PL spectra of thin films were collected using a 550 nm laser (Thorlabs, CPS532) and an Ocean Optics QE pro high-performance spectrometer with 1100 ms integration time and 200 μ m slit width.

X-Ray Diffraction:

Thin films for XRD measurements were prepared on non-pattered ITO glass as mentioned before. The XRD patterns were recorded with a Bruker-AXS D8 DISCOVER diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å) operating at 40 kV and 40 mA.

X-ray Photoelectron (XPS) and Ultraviolet Photoelectron (UPS) Spectroscopy:

All films were prepared on non-pattered ITO glass as mentioned before. XPS and UPS measurements were carried out in a PHI 5600 UHV system with a base pressure $< 4 \times 10^{-10}$. XPS were carried out using an Al K α source (1486.6 eV) with a pass energy of 23.5 eV. UPS were obtained with 10.2 eV photons for excitation (Excitech H Lyman- α lamp). The pass energy used for UPS was 5.85 eV and all samples were biased at -5 V. All the samples were measured within 24 h after sample preparation and the samples were kept entirely under nitrogen (<0.1 ppm O₂ and H₂O). Our UHV system is directly connected to one of our gloveboxes, thereby completely eliminating air exposure.



Figure S1. CV of SnI₂, SnF₂ (multiplied by a factor of 5), SnI₄, SnI₂ + 10% SnF₂, and SnI₂ + FAI + 10% SnF₂ in DMF with 0.1 M TBAPF₆ as the supporting electrolyte.



Figure S2. CV of FASnI₃ thin film in DCM with 0.1 M TBAPF₆ as the supporting electrolyte.



Figure S3. UV-vis absorbance spectra of FASnI₃ films with 1.0 mol% of varying additives.



Figure S4. Photoluminescence intensity of FASnI₃ films with A) 0.5; B) 1.0; and C) 2.5 mol% of varying additives, respectively.



Figure S5. XRD patterns of FASnI₃ films with 2.5 mol% of varying additives.

Table S1. Sn^{4+} to Sn^2	+ ratio in 2.5 mol%	6 additive treated	l FASnI3 films.
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Additive	Sn ⁴⁺ :Sn ²⁺ ratio
None (control)	0.07
BHzHCl	0.04
DHC1	0.05
DHCA	0.04
DHBA	0.06
BA	0.06
DHNT	0.03
HzHC1	0.05
4-FBH	0.06
HQ	0.08
KHQSA*	0.03
DHBQ	0.07
NQ	0.08
2,6-DHAQ	0.05
1,8-DHAQ	0.07

*There is significant uncertainty in the KHQSA Sn⁴⁺:Sn²⁺ ratio due to the presence of an additional Sn species at the surface, which we attribute to a KHQSA:Sn complex.



Figure S6. XPS spectra of the Sn 3d region for FASnI₃ films with fits to the Sn²⁺ and Sn⁴⁺ peaks for the films made with 2.5 mol% of varying additives. *There is significant uncertainty in the KHQSA Sn⁴⁺:Sn²⁺ ratio due to the presence of an additional Sn species at the surface, which we attribute to a KHQSA:Sn complex.



Figure S7. UPS spectra of FASnI₃ film with 2.5 mol% varying additives; A) the secondary electron cut-off regions; B) the valence band onset regions.

Table S2. Work Function vs. Id	onization energy (IE)) of 2.5 mol% ad	dditive treated FASnI3 films.
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Additive	Work Function (eV)	IE (eV)
None (control)	4.85	5.09
BHzHC1	4.50	5.24
DHC1	4.62	5.41
DHCA	4.57	5.13
DHNT	4.17	4.91
HzHC1	4.83	5.36
DHBA	4.86	5.39
BA	4.90	5.29
4-FBH	4.87	5.36
HQ	4.97	5.26
KHQSA	4.73	5.15
DHBQ	4.88	5.27
NQ	4.77	5.10
2,6-DHAQ	4.82	5.23
1,8-DHAQ	4.72	4.78



Figure S8. CV of (A, B) SnI_4 , $SnI_4 + FAI$, $SnI_2 + SnI_4 + FAI$, and $SnI_2 + SnI_4 + FAI + additive$ (1:1:1:1 mole ratio); and (C) $SnCl_4$ in DMF:DMSO (4:1) with 0.1 M TBAPF₆ as the supporting electrolyte.



Figure S9. Absorbance spectra of solutions of SnI₄ with varying reducing additives (1:1 mol ratio) in DMF:DMSO (4:1). The spectra were recorded 10 min after addition of the additives into SnI₄ solution in N₂-filled glovebox.



Figure S10. ¹¹⁹Sn NMR of the reference Sn compounds (SnI₂, SnI₄, SnCl₂, SnCl₄) (top) and SnI₄ + additive (1:1 mole ratio) in DMSO-*d*₆.



Figure S11. Absorbance spectra supporting that halide exchange occurs between SnI₄ and A) MACl and between SnI₄ and B) SnCl₂ with varying mole ratios. C) ¹¹⁹Sn-NMR of SnI₄ and MACl in DMSO- d_6 with varying mole ratios.



Figure S12. Comparison of ¹H NMR spectra of BHzHCl ligand alone (blue) and coordinating SnI₄ (red) in DMSO-*d*₆, at $\delta = 2.50$ ppm.



Figure S13. Comparison of ¹H NMR spectra of HzHCl ligand alone (blue) and coordinating SnI₄ (red) in DMSO-*d*₆, at δ = 2.50 ppm.



Figure S14. Comparison of ¹H NMR spectra of DHCl ligand alone (blue) and coordinating SnI₄ (red) in DMSO-*d*₆, at δ = 2.50 ppm.



Figure S15. Comparison of ¹H NMR spectra of DHCA ligand alone (blue) and coordinating SnI₄ (red) in DMSO-*d*₆, at δ = 2.50 ppm.



Figure S16. Comparison of ¹H NMR spectra of NQ (yellow), SnI₂:DHNT at a 1:1 mole ratio (purple), SnI₂:DHNT at a 1:1 mole ratio after 30 minutes of air exposure (green), DHNT after 30 minutes of air exposure (red), and DHNT with no air exposure (blue). NQ is included to show that DHNT does not oxidize to form NQ upon air exposure. All spectra are in DMSO-*d*₆, at δ = 2.50 ppm.



Figure S17. Comparison of ¹H NMR spectra of DHBA ligand alone (blue) and coordinating SnI₄ (red) in DMSO-*d*₆, at δ = 2.50 ppm.



Figure S18. Comparison of ¹H NMR spectra of MACl ligand alone (blue) and coordinating SnI₄ (red) in DMSO-*d*₆, at $\delta = 2.50$ ppm.