Supporting Information

Hydrazine dihydrochloride as a new additive to promote performance of tin-based mixed organic cation perovskite solar cells

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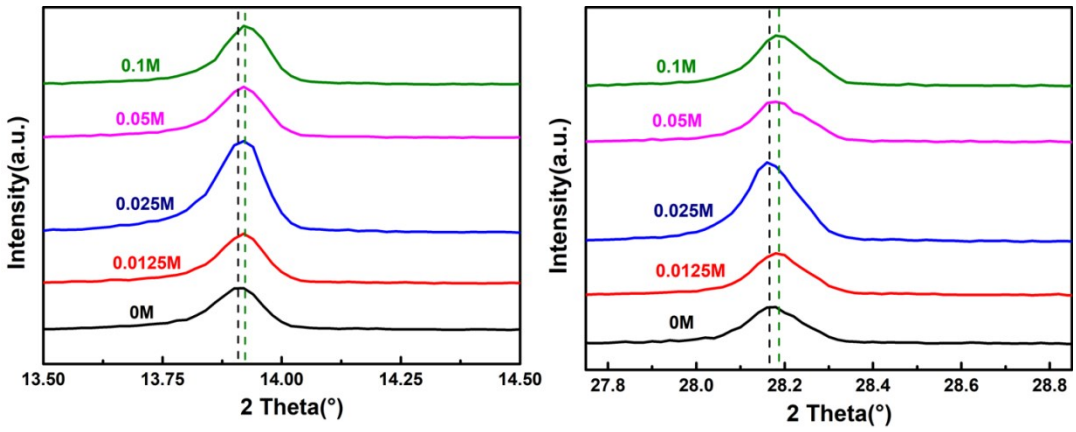


Figure S1. The enlarged XRD pattern of various concentrations of HD in the 13.5~14.5°and 27.75~28.85° regions.

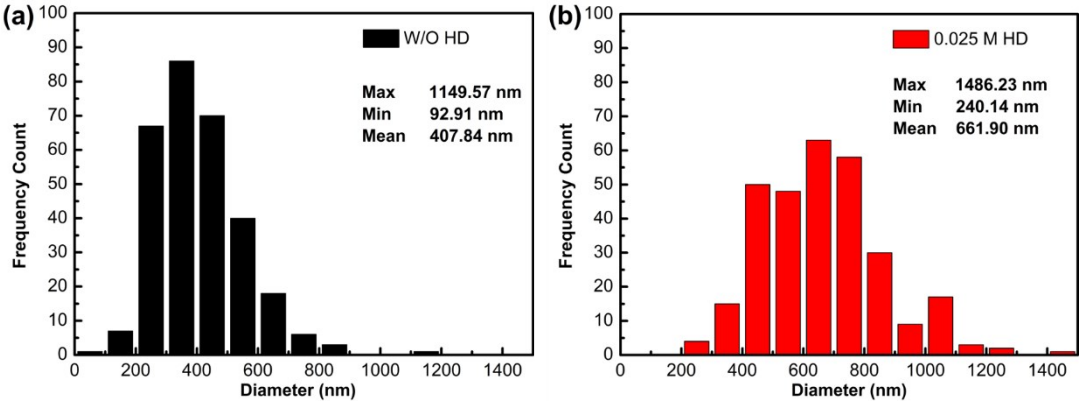


Figure S2. The grain size distributions of the (a) $FA_{0.75}MA_{0.25}SnI_3$ and (b) 0.025 M HD $FA_{0.75}MA_{0.25}SnI_3$ film.

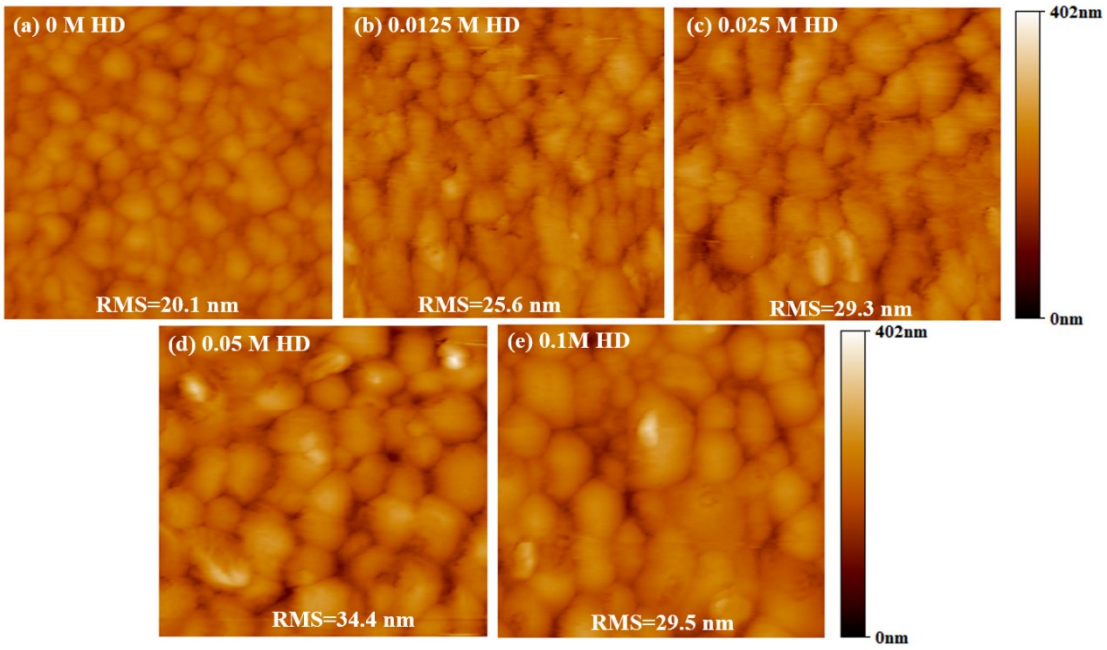
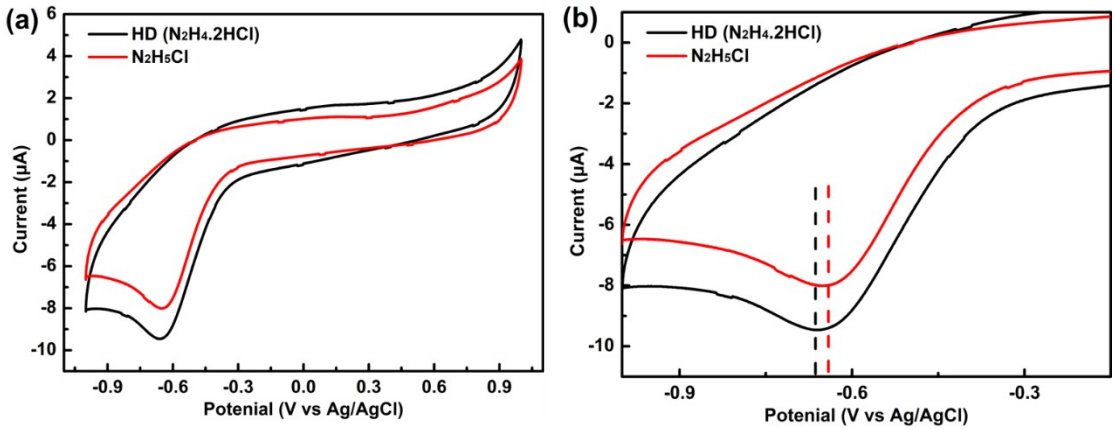


Figure S3. Atomic force microscope images of (a) the control $FA_{0.75}MA_{0.25}SnI_3$ without HD and the $FA_{0.75}MA_{0.25}SnI_3$ perovskite films with (b) 0.0125M HD, (c) 0.025M HD, (d) 0.05M HD, (e) 0.1M HD.



FigureS4. The CV curves of HD and N_2H_5Cl.

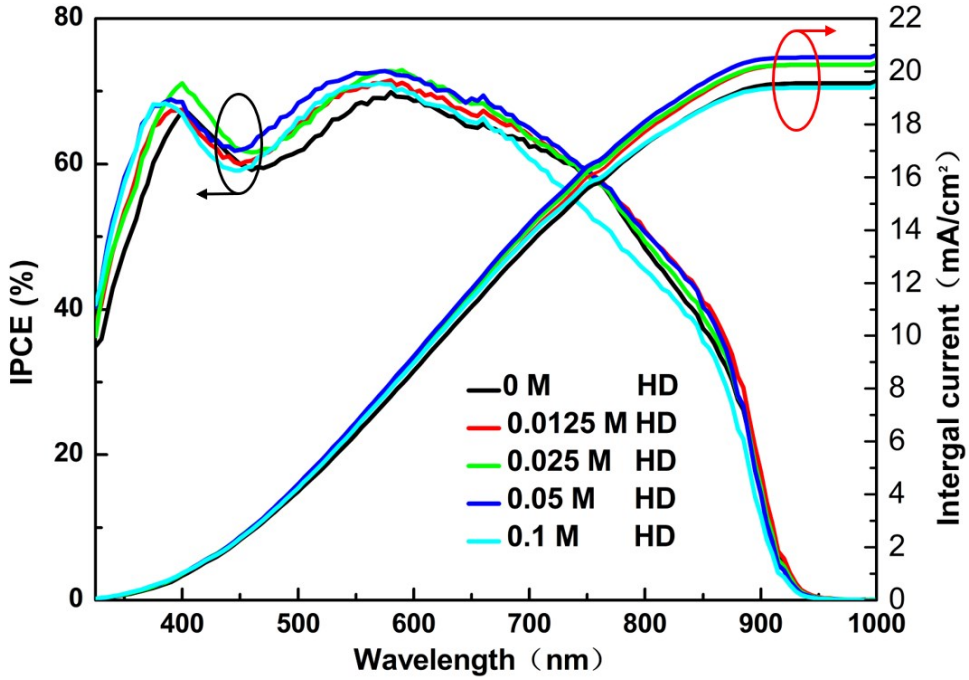


Figure S5. IPCE of the control $FA_{0.75}MA_{0.25}SnI_3$ without HD and the $FA_{0.75}MA_{0.25}SnI_3$ perovskite films with 0.0125, 0.025, 0.05 and 0.1 M HD, respectively.

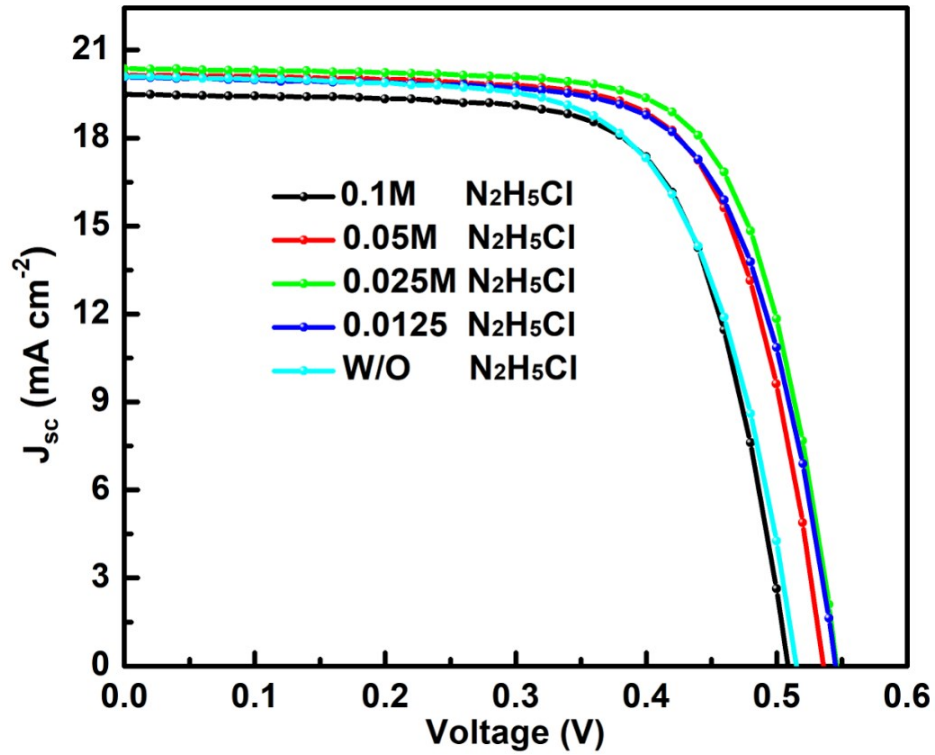


Figure S6. The J-V curves of the devices with different contents of N_2H_5Cl.

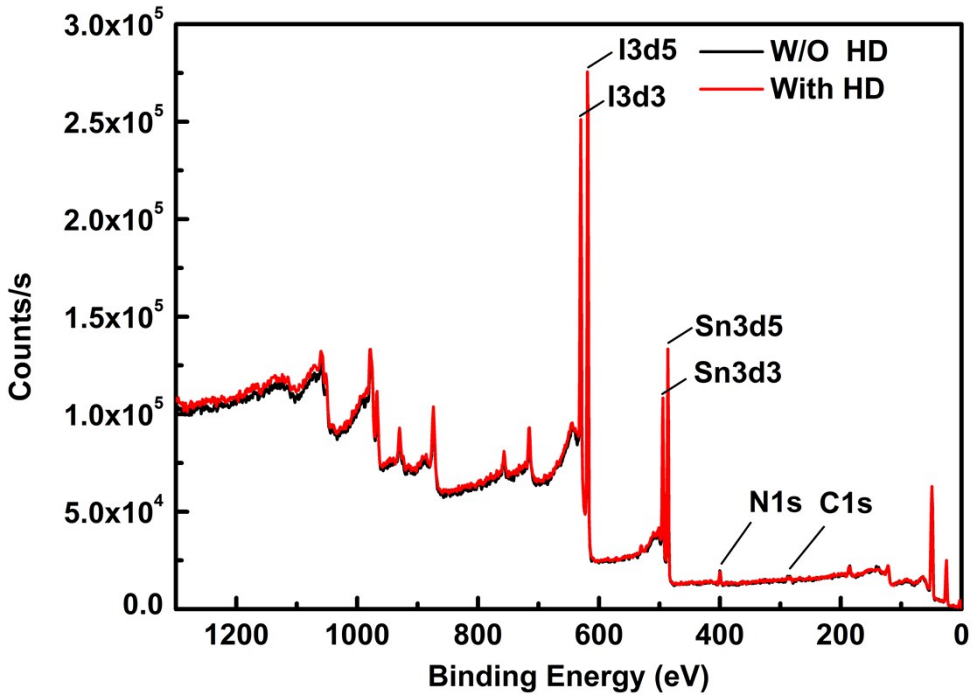
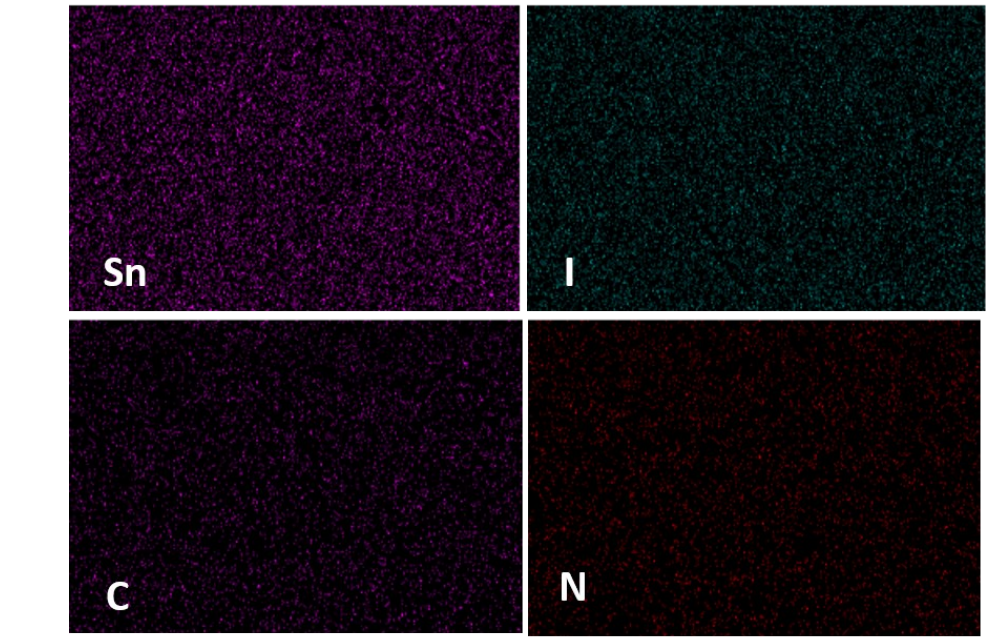
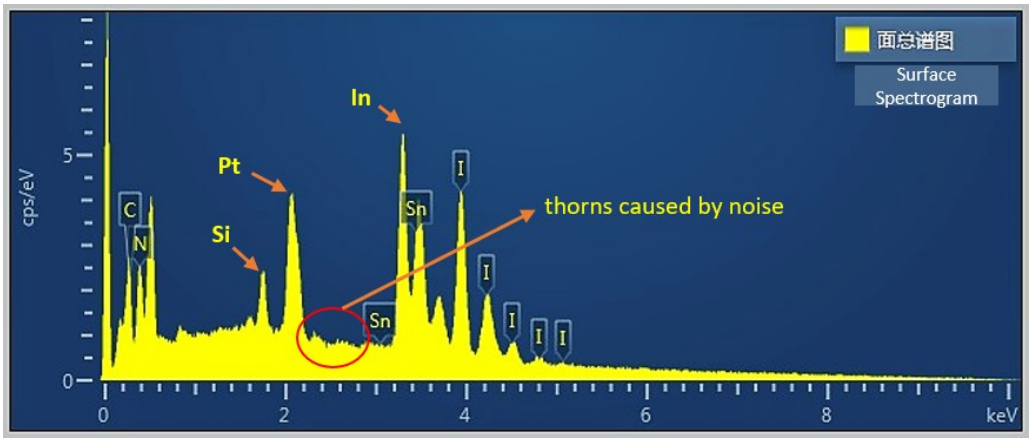


Figure S7. The X-ray photo-electron spectra of $FA_{0.75}MA_{0.25}SnI_3$ and $FA_{0.75}MA_{0.25}SnI_3$ with 0.025 M HD.





Notes: The whole spectrum of elemental analysis. (1) Si and In are the result of a small amount of ITO and glass powder sputtering on the perovskite surface during sample preparation, Pt is the result of spraying on the film surface during element analysis rather than the characteristic peak of chlorine.

Figure S8. The energy-dispersive X-ray spectroscopy (EDS) mapping and the whole spectrum of elemental analysis for the perovskite film with 0.025 M HD.

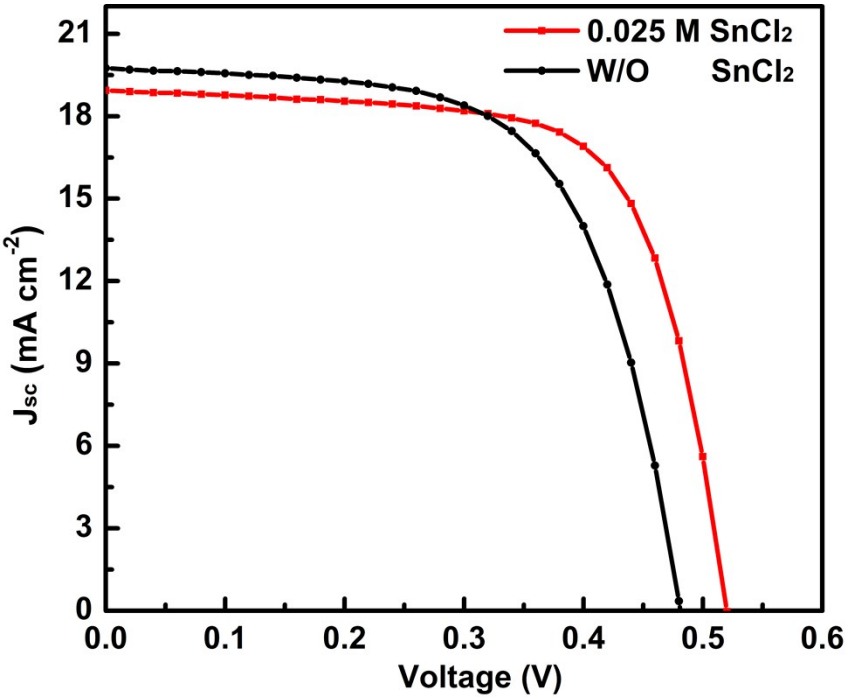


Figure S9. The J-V curve of the device fabricated from $FA_{0.75}MA_{0.25}SnI_3$ perovskite precursor with 0.025 M $SnCl_2$ additive.

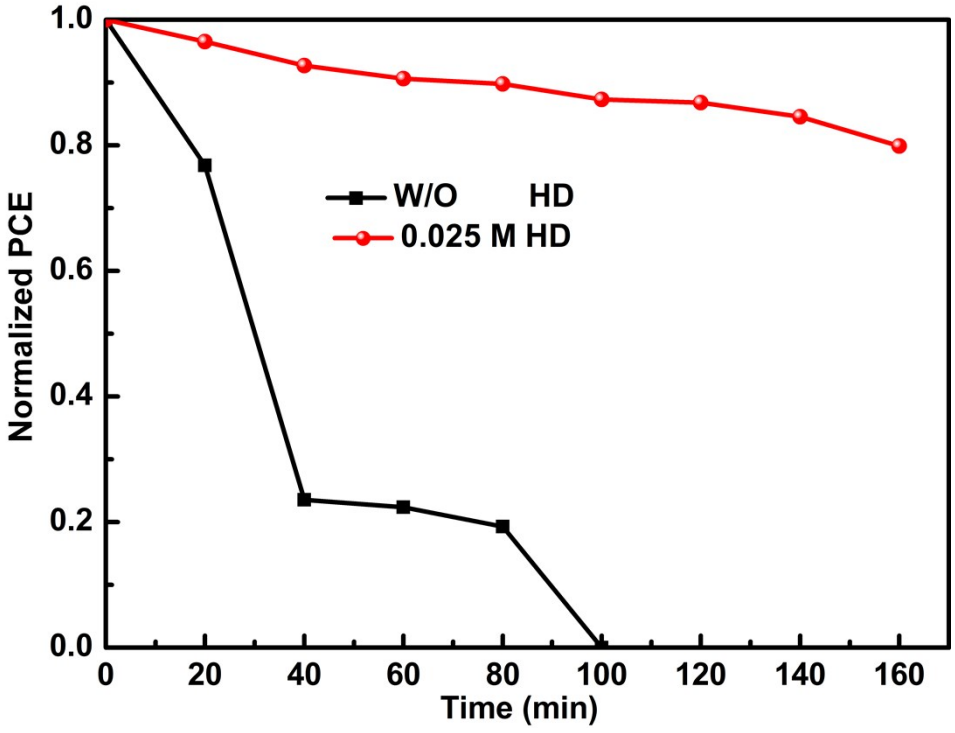


Figure S10. The thermal stability of devices without and with 0.025 M HD additive which were placed on an 85℃ hotplate.

Equation S1. The reaction equations of tin (II) in different acid-base environments [1]

Spontaneous reduction of tin in alkaline medium：

$HSnO_2^-+H_2O+2e^-=Sn+3OH^-$ $E^\theta=-0.909$ V (1)

$[Sn(OH)_6]_2^-+2e^-=HSnO_2^-+H_2O+3OH^-$ $E^\theta=-0.93$ V (2)

$HSnO_2^-+H_2O=Sn+[Sn(OH)_6]_2^-$ $E^\theta=0.021$ V (3)

Spontaneous reduction of tin in acidic medium：

$Sn^{2+}+2e^-=Sn$ $E^\theta=-0.13$ V (4)

$Sn^{4+}+2e^-=Sn^{2+}$ $E^\theta=0.151$ V (5)

$Sn^{4+}+Sn=2Sn^{2+}$ $E^\theta=0.281$ V (6)

Table S1a. The pH of $FA_{0.75}MA_{0.25}SnI_3$ perovskite precursors with various amounts of HD.

Concentration (mol/L)	0	0.0125	0.025	0.05	0.1
pH	5.8	5.5	5.1	4.9	4.4

Table S1b. The pH of $FA_{0.75}MA_{0.25}SnI_3$ perovskite precursors with various amount of N_2H_5Cl.

Concentration (mol/L)	0	0.0125	0.025	0.05	0.1
pH	5.8	5.7	5.5	5.4	4.8

Table S2. The fitting results of XPS spectra for the control $FA_{0.75}MA_{0.25}SnI_3$ and the optimal $FA_{0.75}MA_{0.25}SnI_3$ films.

W/O HD	Sn $3d_{5/2}$		Sn $3d_{3/2}$	
	Sn^{2+}	Sn^{4+}	Sn^{2+}	Sn^{4+}
Position(eV)	485.196	485.97	493.796	494.57
FWHM	1.112	1.31	1.112	1.31
Area	39464.66	18851.27	31685.63	14138.45
0.025M HD	Sn $3d_{5/2}$		Sn $3d_{3/2}$	
	Sn^{2+}	Sn^{4+}	Sn^{2+}	Sn^{4+}
Position(eV)	485.683	486.58	494.093	495.18
FWHM	1.047	1.672	1.047	1.672
Area	39464.66	18851.27	31685.63	14138.45

Table S3. Photovoltaic parameters of devices with different concentrations of N_2H_5Cl as additives.

Concentration (mol/L)	V_{oc} (V)	J_{sc} (mA·cm^{-2})	FF (%)	PCE (%)
0	0.556	18.92	64.64	6.80
0.0125	0.542	19.42	67.48	7.11
0.025	0.569	20.42	70.93	8.24
0.05	0.536	19.59	71.04	7.45
0.1	0.509	19.09	69.75	6.77

Table S4. Perovskite film thickness corresponding to different concentrations of HD as additive.

Concentration (mol/L)	0	0.0125	0.025	0.05	0.1
Thickness (nm)	197.11	197.63	196.16	194.43	195.25

Table S5. The photovoltage parameter comparison of devices with and without 0.025M $SnCl_2$ additive.

Additive	V_{oc} (V)	J_{sc} (mA·cm^{-2})	FF (%)	PCE (%)
W/O $SnCl_2$	0.520	18.98	68.62	6.77
0.025 M $SnCl_2$	0.481	19.72	63.17	5.99

Reference

1. X. Meng, T. Wu, X. Liu, X. He, T. Noda, Y. Wang, H. Segawa and L. Han, *The Journal of Physical Chemistry Letters*, 2020, **11**, 2965-2971.