

## Supporting Information

### *Enhanced $\alpha$ -Phase Stability of Formamidinium Lead Iodide with Addition of 5-Ammonium Valeric Acid Chloride*

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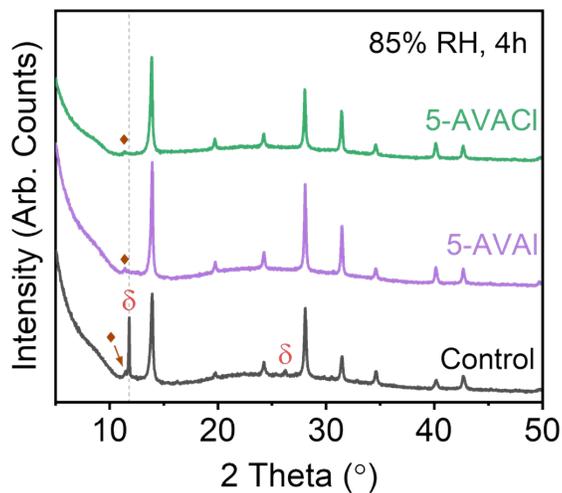
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**Table S1.** FWHM of XRD (100) peaks and intensity of XRD (100) and (111) peaks for FAPbI<sub>3</sub> films without and with additives.

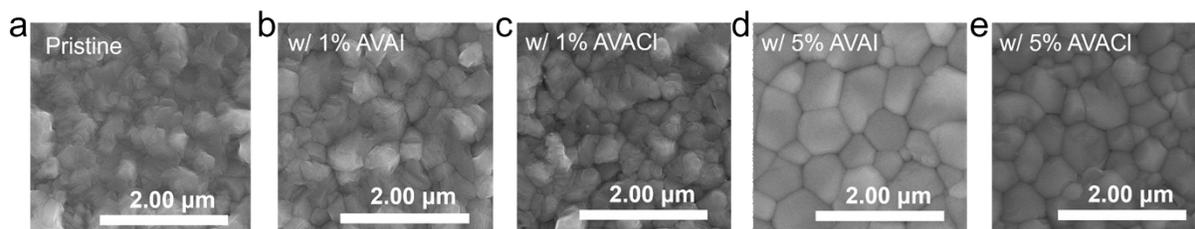
Additive	(100) FWHM	(100) Intensity	(111) Intensity	(111)/(100)
None	0.248 ± 0.007	3631.33 ± 284.82	451.67 ± 52.78	0.124 ± 0.005
1% 5-AVAI	0.241 ± 0.002	3452.33 ± 567.95	493.00 ± 71.84	0.144 ± 0.021
2% 5-AVAI	0.153 ± 0.005	10220.00 ± 806.29	948.33 ± 29.57	0.093 ± 0.005
3% 5-AVAI	0.135 ± 0.002	12866.50 ± 348.60	1150.50 ± 122.33	0.089 ± 0.007
5% 5-AVAI	0.126 ± 0.004	19081.67 ± 1472.22	1254.00 ± 235.37	0.066 ± 0.012
1% 5-AVACl	0.235 ± 0.005	3779.00 ± 122.43	556.33 ± 47.52	0.147 ± 0.010
2% 5-AVACl	0.181 ± 0.016	7324.33 ± 319.25	1116.67 ± 51.05	0.153 ± 0.012
3% 5-AVACl	0.154 ± 0.004	8390.67 ± 269.34	1380.67 ± 67.34	0.164 ± 0.003
5% 5-AVACl	0.143 ± 0.002	8086.33 ± 424.46	1248.33 ± 66.12	0.154 ± 0.009



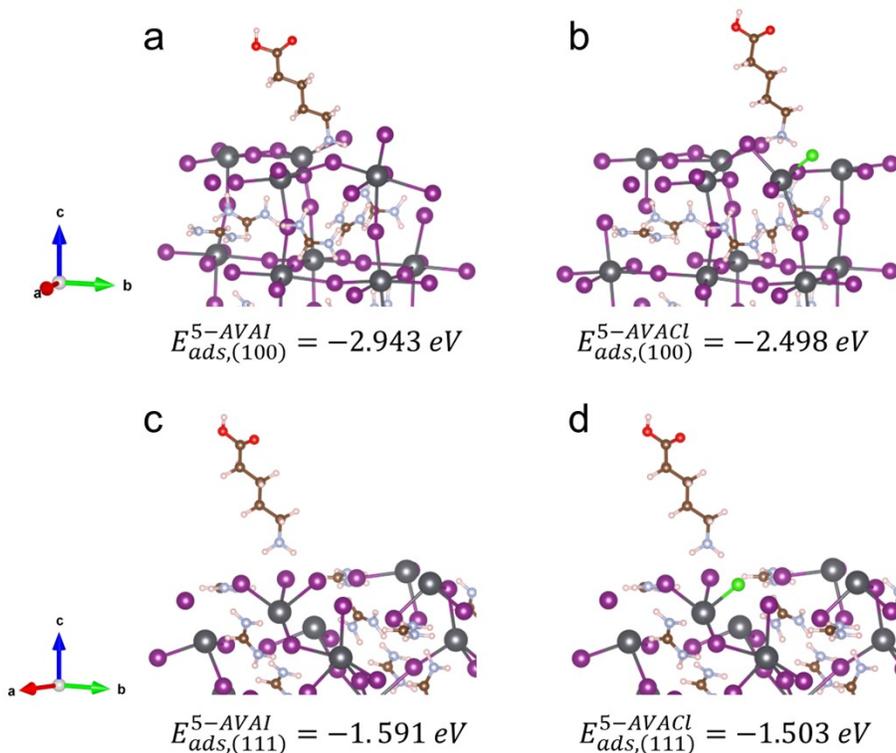
**Figure S1.** XRD patterns of the pristine FAPbI<sub>3</sub> film and the films prepared with 1 mol% of 5-AVAI and 5-AVACl after 4 h of aging under 85% RH and room temperature.

**Table S2.** Integrated FAPbI<sub>3</sub> (100) peak areas of fresh and aged samples for FAPbI<sub>3</sub> thin films with and without additives (at a concentration of 1 mol%).

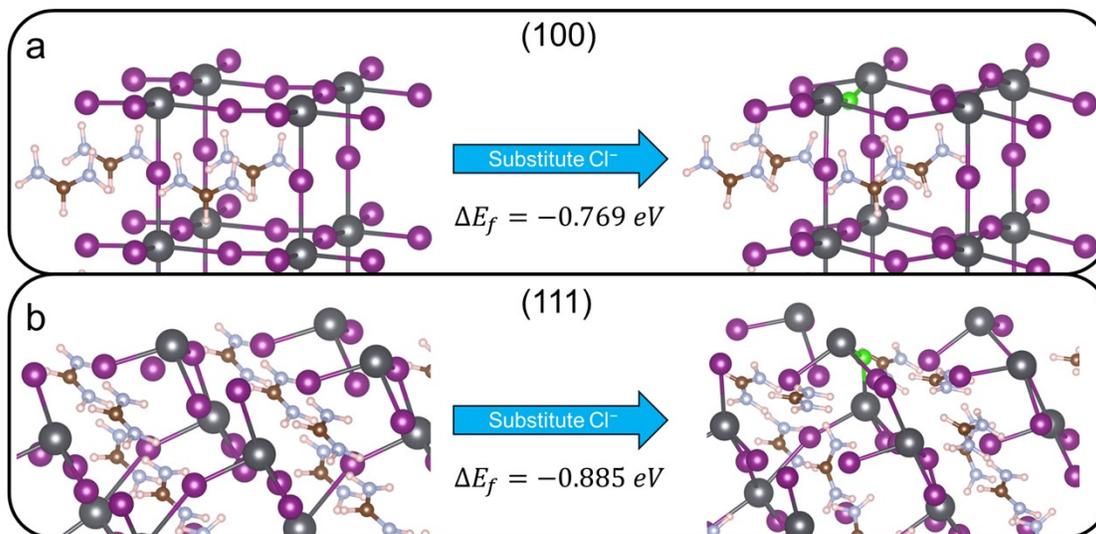
	Fresh	Aged	Ratio of aged/fresh
None	2105.28	1527.34	0.7255
5-AVAI	1960.56	1698.79	0.8665
5-AVACl	1856.77	1702.21	0.9168



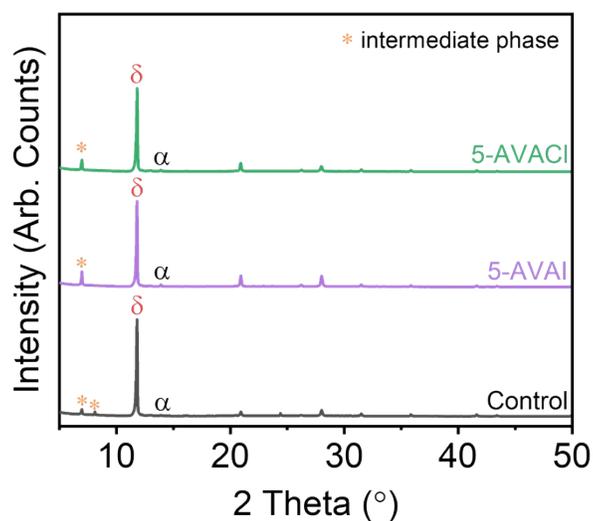
**Figure S2.** SEM micrographs of (a) pristine FAPbI<sub>3</sub> and additive-treated FAPbI<sub>3</sub> films with (b,c) 1 and (d,e) 5 mol% 5-AVAI or 5-AVACl.



**Figure S3.** Final adsorption geometries for (a) 5-AVAI and (b) 5-AVACl on the (100) PbI<sub>2</sub> facet of FAPbI<sub>3</sub> (c) 5-AVAI and (d) 5-AVACl on the (111) PbI<sub>3</sub>FA facet of FAPbI<sub>3</sub>.



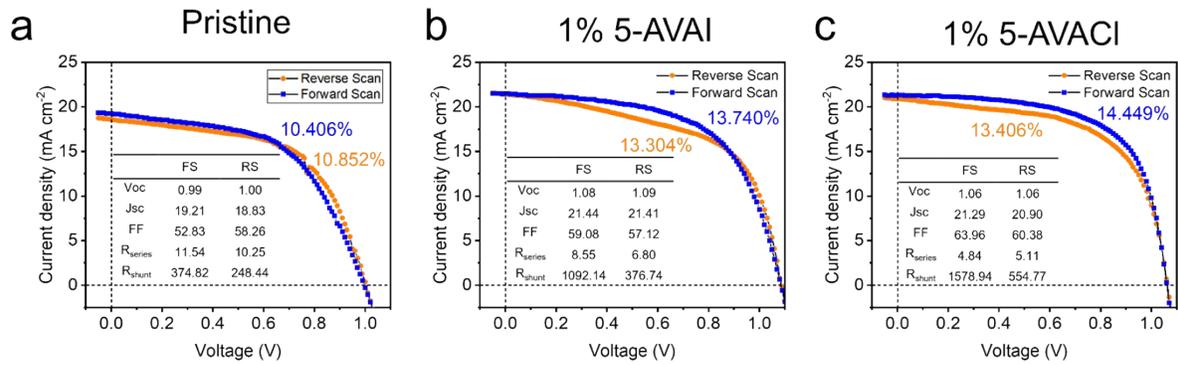
**Figure S4.** Formation energy change upon substitution of surface  $I^-$  with  $Cl^-$  on the (a) (100) and (b) (111) facet of  $FAPbI_3$ .



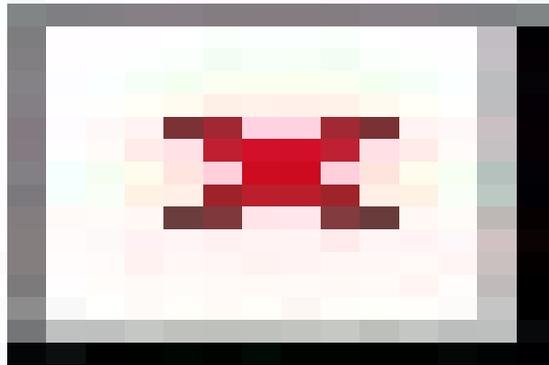
**Figure S5.** XRD patterns of the as-cast  $FAPbI_3$  films without additives and with 1 mol% 5-AVAI or 5-AVACl.

**Table S3.** Time-correlated single-photon counting lifetime measurements for  $FAPbI_3$  thin films with and without additives (at a concentration of 1 mol%).

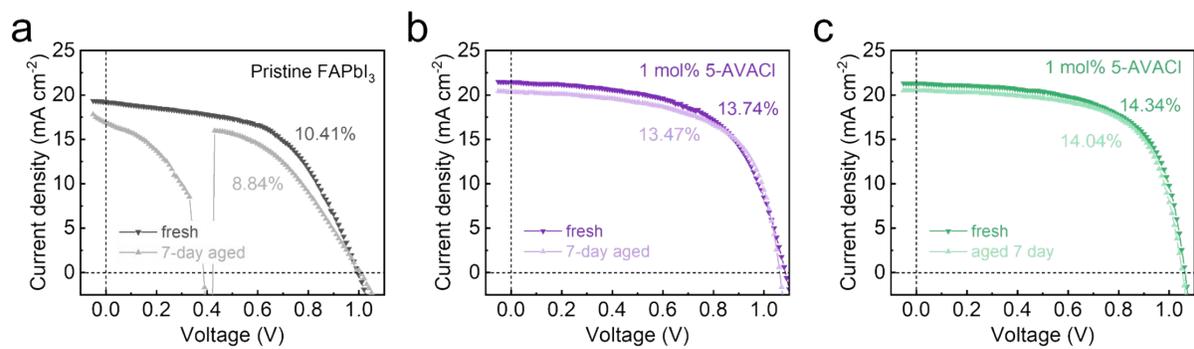
	$A_1$ (%)	$\tau_1$ (ns)	$A_2$ (%)	$\tau_2$ (ns)
None	45.11	33.38	54.89	108.53
5-AVAI	9.23	48.33	90.77	279.05
5-AVACl	3.80	56.29	96.20	347.54



**Figure S6.** Forward and reverse J-V curves for the champion devices of (a) pristine FAPbI<sub>3</sub> and with 1 mol% of (b) 5-AVAI or (c) 5-AVACl.



**Figure S7.** J-V curves for representative devices with 2–5 mol% of (a–c) 5-AVAI and (d–f) 5-AVACl.



**Figure S8.** J-V curves (*forward scans*) of representative FAPbI<sub>3</sub> devices before and after 7 days of aging under ambient environment (15–20% relative humidity) at room temperature. Devices prepared with (a) pristine FAPbI<sub>3</sub> and with 1 mol% of (b) 5-AVAI and (c) 5-AVACl added.