

Electronic Supplementary Information (ESI)

Nonvolatile chlorinated additive adversely influences $\text{CH}_3\text{NH}_3\text{PbI}_3$ based planar solar cells

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Experimental Sections

Materials. All chemicals were purchased from J&K Scientific, Ltd. (China) unless indicated, and used as received.

Sample Preparation. $\text{CH}_3\text{NH}_3\text{I}$ was synthesized by mixing methylamine and HI. The resulting precipitate $\text{CH}_3\text{NH}_3\text{I}$ was washed three times using diethyl ether and dried. PbI_2 was dissolved in DMF, and $\text{CH}_3\text{NH}_3\text{I}$ was then added in stoichiometric ratio. To the mixture was added additional CaCl_2 with different molar ratios. The mixed solutions in DMF (35 wt%) were stirred overnight at 60 °C inside a nitrogen-filled glovebox with oxygen and moisture levels <0.1 ppm. The solution were then filtered and spin-coating at 3000 rpm for 60 s to get perovskite thin films, which were further annealed at 95 °C and changed from yellowish to dark brownish.

Characterization. Optical absorption spectra of film samples were acquired on Agilent 8453 UV-Visible spectrophotometer. X-ray diffraction (XRD) pattern data were collected with a Bruker AX D8 Advance diffractometer with nickel filtered Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$). Scanning Electron Microscopy (SEM) images were acquired on a JEOL JSM-6701F field-

emission SEM at an accelerating voltage of up to 30 kV and coupled with energy-dispersive X-ray (EDX, 20 kV) elemental analysis abilities. Thin films were prepared by spin-coating on (ITO-coated) glass slides using a KW-4A spin-coater (Chemat Technology). XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg K_{α} radiation ($h\nu = 1253.6$ eV) or Al K_{α} radiation ($h\nu = 1486.6$ eV). In general, the X-ray anode was run at 250 W and the high voltage was kept at 14.0 kV with a detection angle at 54° . The pass energy was fixed at 23.5, 46.95 or 93.90 eV to ensure sufficient resolution and sensitivity. The base pressure of the analyzer chamber was about 5×10^{-8} Pa. The sample was directly pressed to a self-supported disk (10×10 mm) and mounted on a sample holder then transferred into the analyzer chamber. The whole spectra (0–1100 eV) and the narrow spectra of all the elements with much high resolution were both recorded by using RBD 147 interface (RBD Enterprises, USA) through the AugerScan 3.21 software. Binding energies were calibrated by using the containment carbon ($C1s = 284.6$ eV).

Device and Measurements. Patterned indium tin oxide (ITO) substrates ($12 \Omega/\square$, Thin Film Devices, Inc.) were cleaned sequentially in an ultrasonic solvent bath of deionized water, acetone, and isopropyl alcohol. After drying with a stream of nitrogen, the substrates were treated in a UV Ozone (UVO) cleaner for 20 min. For the regular cells, a thin layer (~ 30 nm) of PEDOT-PSS (CleviosTM P VP AI 4083, Heraeus) was spin-coated onto the ITO at 3000 rpm for 60 s and then baked in air at 120°C for 20 min. The PEDOT:PSS-coated substrates were immediately transferred to a N_2 -filled glovebox for making the active layer. The ternary mixture solution in DMF (35 wt%) was spin-coated onto PEDOT:PSS-coated substrates at 3000 rpm for 1 min, yielding the active layer of ca. 250 nm thick. Afterwards, a PCBM layer was spin-coated on top of the formed perovskite layer from a 20 mg/mL solution in

dichlorobenzene (DCB). The samples were then loaded into a glovebox-integrated deposition chamber and pumped down to a pressure of $<10^{-5}$ Pa. A sequence of Ca (10 nm) and Al (100 nm) layers were sequentially deposited by thermal evaporation through a shadow mask at a rate of 0.1 Å/s and 1 Å/s, respectively. The active area as defined shadow mask is ~ 0.11 cm². The sample was mounted inside a nitrogen-filled sample holder with a quartz optical window for subsequent measurements. The J - V data was acquired with a Keithley 2400 source-meter unit. The light J - V curves were measured under illumination with a Newport-Oriel (Sol3A Class AAA Solar Simulator, 94043A) AM 1.5G light source operating at an intensity of 100 mW·cm⁻². The light intensity was calibrated by a certified Oriel reference cell (91150V) and verified with a NREL calibrated, filtered silicon diode (Hamamatsu, S1787-04). For the measurement of hysteresis, the JV curves were obtained in the air through forward scan (-1.2 V \rightarrow 1.2 V) with a scan rate of 10 mV/s. External quantum efficiency (EQE) spectra were measured on a commercial EQE set-up (QE-R, Enli Technology Co., Ltd). A calibrated silicon diode with a known spectral response was used as a reference.

Table S1. Best device performance characteristics under both forward and reverse scans.

Devices	Sweep Direction	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
CH ₃ NH ₃ I:PbI ₂ :CaCl ₂ = 1:1:0.5	Forward	3.37	0.95	55.42	1.77
	Reverse	3.76	1.05	78.10	3.08
CH ₃ NH ₃ I:PbI ₂ :CaCl ₂ = 1:1:0.75	Forward	1.27	0.90	55.01	0.63
	Reverse	1.44	1.00	60.20	0.88
CH ₃ NH ₃ I:PbI ₂ :CaCl ₂ = 1:1:1	Forward	0.72	0.75	37.63	0.20
	Reverse	1.17	0.80	48.26	0.45

Table S2. Statistics of device performance characteristics under reverse scan. (10 cells in total)

Devices	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
CH ₃ NH ₃ I:PbI ₂ :CaCl ₂ = 1:1:0.5	3.81 ± 0.05	1.03 ± 0.02	71.60 ± 7.05	2.70 ± 0.38
CH ₃ NH ₃ I:PbI ₂ :CaCl ₂ = 1:1:0.75	1.28 ± 0.16	0.98 ± 0.03	62.10 ± 3.00	0.76 ± 0.12
CH ₃ NH ₃ I:PbI ₂ :CaCl ₂ = 1:1:1	0.98 ± 0.19	0.83 ± 0.03	51.20 ± 4.00	0.37 ± 0.08