

A Correction has been published on 15th June 2020 relating to Fig. S3 of this Supplementary Information document. Please see the accompanying Correction for further details (DOI: 10.1039/D0TA90124E).

Supporting Information for

Triple Cation Additive $\text{NH}_3^+\text{C}_2\text{H}_4\text{NH}_2^+\text{C}_2\text{H}_4\text{NH}_3^+$ - induced Phase-stable Inorganic α - CsPbI_3 Perovskite Films for Use in Solar Cells

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Experimental details

Materials: DETAI₃ was synthesized by reacting DETA (98%+, ACROS ORGANICS) and hydroiodic acid (>45%, Sinopharm Chemical Reagent Co. Ltd) with a molar ratio of 1:3.5 in an ice bath for 2 h with stirring. The excess hydroiodic acid was used to ensure all the DETA turn into DETAI₃. The precipitate was collected by rotary evaporation at 60 °C, washed three times with copious diethyl ether until the supernatant turned to colorless, and then vacuum-dried at 50 °C for 1 h. EDAI₂ and PZI₂ were synthesized following similar procedure. The HPbI₃ was synthesized as previously reported.¹ The CsPbI₃·xDETAI₃ precursor solution was prepared by dissolving 0.5 mmol HPbI₃ and 0.5 mmol of CsI (99%, TCI) in 1 ml of DMF to form a 0.5 M precursor solution mixed with different *x* ratios of 0.5 M DETAI₃ solution. Then the CsPbI₃·xDETAI₃ precursor solution was filtered with a PTFE filter with 0.45 μm pore. The hole transporting material (HTM) was prepared as previous work.² In brief, 15 mg P3HT (poly(3-hexylthiophene-2,5-diyl), Rieke Metals, RMI-001EE, J&K chemical Ltd.) was dissolved in 1 mL chlorobenzene with 54 μL Li-TFSI stock solution (10 mg mL⁻¹ in acetonitrile) and 10.2 μL TBP. All the other chemicals were purchased from Sigma Aldrich and used as received without further purification. Patterned FTO glass (15 ohm sq⁻¹, Pilkington TEC) were cleaned sequentially by ultrasonication in mild detergent,

deionized water, acetone and ethanolamine. The substrates were exposed to UV-ozone for 15 min prior to the spin coating step.

Solar cell fabrication: A dense TiO₂ compact layer (compact-TiO₂) was deposited on the cleaned FTO by spray pyrolysis with an airbrush, using N₂ as carrier gas, at 430 °C for 1 h from a precursor solution of 0.6 ml of titanium diisopropoxide and 0.4 ml of bis (acetylacetonate) in 7 ml of anhydrous isopropanol. The CsPbI₃·xDETAI₃ precursor solutions were then spin-coated onto the prewarmed bl-TiO₂-coated substrate at 3500 rpm for 30 s, followed by annealing at 150 °C for 40 min. After the films were cooled down to room temperature, a layer of HTM was spin-coated at 4600 rpm for 20 s. Finally, a 60-nm-thick Au contact layer was thermally evaporated as back contact. All of the processes were performed in air ambient at a relative humidity <25%.

Characterization: Devices were tested in air ambient. The solar simulators are Newport Oriel Sol3A solar simulators with Xenon lamps. A calibrated Si reference solar cell was used to set the intensity of the lamp to 100 mW cm⁻² AM 1.5 conditions. Current density–voltage (*J–V*) scans were taken from forward bias to reverse bias with a scan rate of 200 mV s⁻¹ (scan parameters: step size = 20 mV, delay time =10 ms). Devices were illuminated for 5 s prior to starting the *J–V* sweep. To minimize possible *J*_{SC} overestimation from current collecting outside the device area, a mask was used, and the equivalent current densities were achieved for the solar

cell. Stabilized power output was measured by holding the device at a constant voltage corresponding to the voltage at the maximum power point of the $J-V$ scan. IPCE spectra were recorded under illumination of monochromatic light from the halogen tungsten lamp using a monochromator (Enlitech, Taiwan) and detected by a computer-controlled lock-in amplifier. XRD patterns were collected by a Rigaku diffractometer (RINT-TTR III) with Cu K_{α} radiation ($k = 1.54056$). UV-Vis absorption spectra were recorded by an ultraviolet-visible-near-infrared spectrometer (SolidSpec-3700/3700DUV, Shimadzu). XPS measurement was taken on a Thermo Scientific K-Alpha XPS instrument with Al K_{α} radiation ($h\nu = 1486.68$ eV). SEM images were collected using a Zeiss SEM (EVO18). Raman spectroscopy was performed by Renishaw inVia Reflex with a laser of 785 nm. Fourier transform infrared spectroscopy (FT-IR, ThermoFisher IS50R, USA) was used to collect the spectral data for various solution in the range of 4000-500 cm^{-1} . PL spectra were performed using a standard 450 W Xenon CW lamp, and the TRPL were recorded on a pulsed nitrogen/dye laser (QM400, Photo Technology International, USA.). The contact angle measurement was performed using OCA15EC with water.

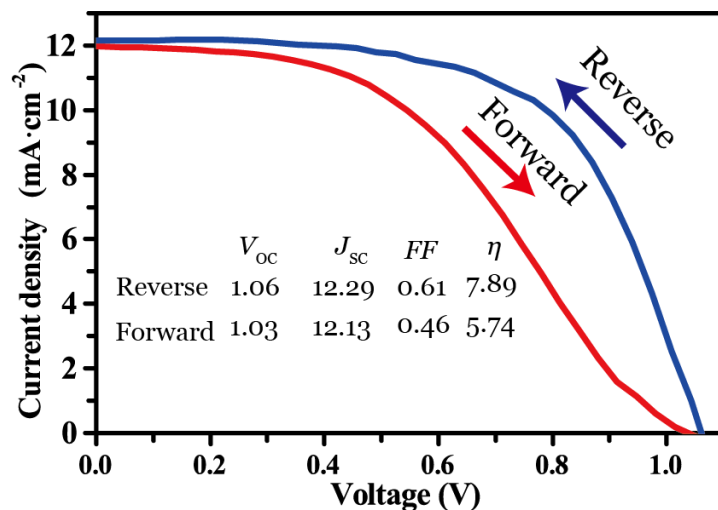


Figure S1. A typical forward and reverse scan J - V curve of the perovskite solar cells based on CsPbI_3 0.05 DETAI_3 samples.

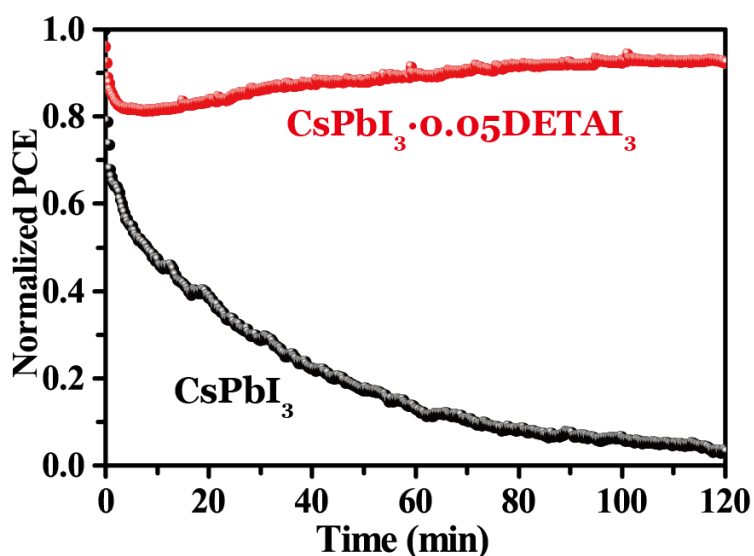


Figure. S2 Operational stability of un-encapsulated $\text{CsPbI}_3 \cdot x\text{DETAI}_3$ ($x=0, 0.05$) PSC at bias voltage of 0.54 V and 0.83 V, respectively, for 120 min. (examined at a maximum-power-point under continuous full-sun illumination at $\sim 30^\circ\text{C}$, 60-70% RH in ambient air)

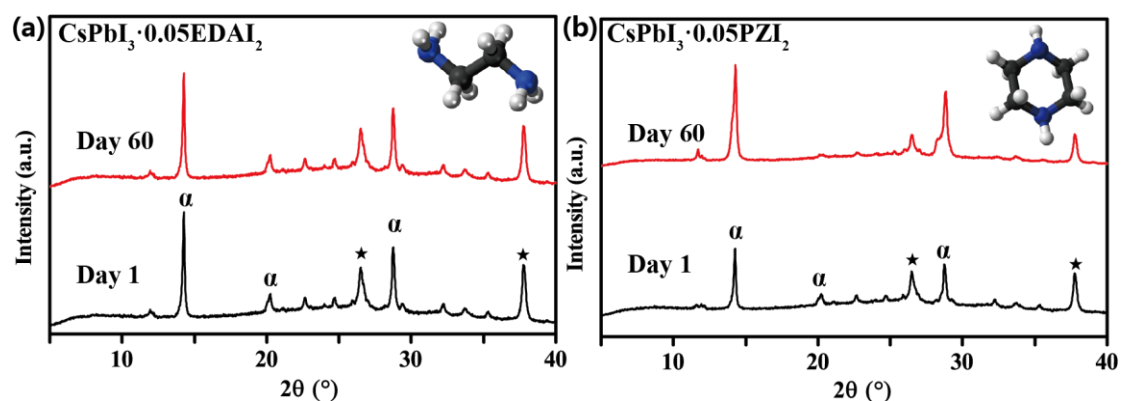


Figure S3. a) XRD patterns of $\text{CsPbI}_3 \cdot 0.05\text{EDAI}_2$ films of day 1 and day 60 stored in a dark dry box, inset image is the structure of ethylenediamine. b) XRD patterns of $\text{CsPbI}_3 \cdot 0.05\text{PZI}_2$ films of day 1 and day 60 stored in a dark dry box, inset image is the structure of pyrazine.

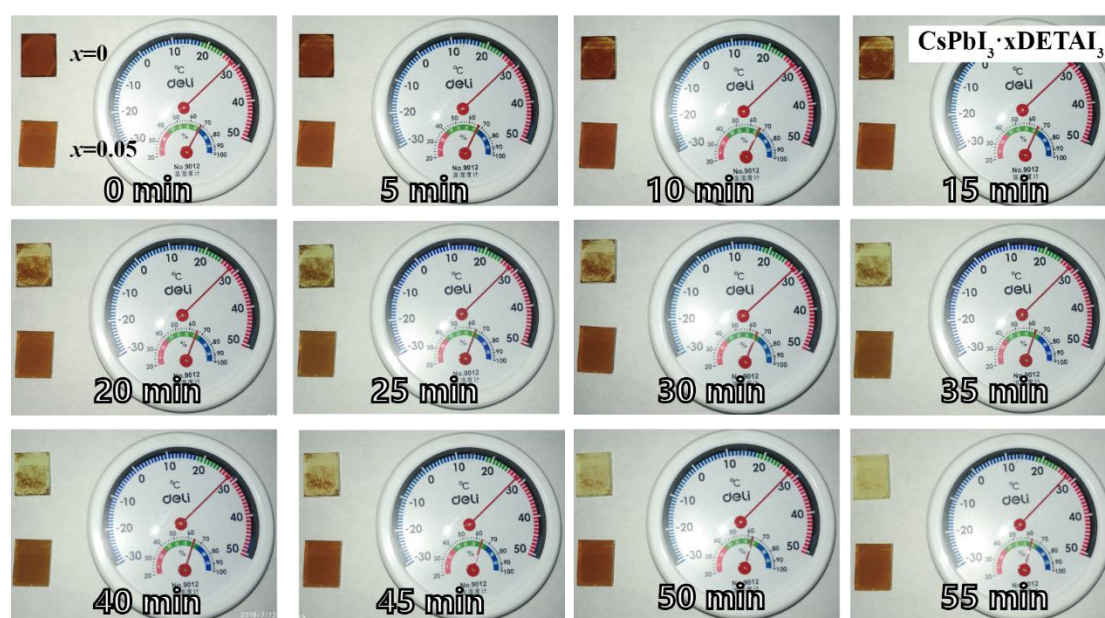


Figure S4. Photographs of $\text{CsPbI}_3 \cdot x\text{DETAI}_3$ ($x=0, 0.05$) in humid environment ($\sim 30^\circ\text{C}$, 60-70% RH)

Note 1

“A dark dry box” we noted in this paper was referred to a dark dry box with 15-20% RH and a temperature of 25-30 °C.

Reference

(1) Wang, F.; Yu, H.; Xu, H.; Zhao, N. HPbI₃: A New Precursor Compound for Highly Efficient Solution - Processed Perovskite Solar Cells. *Adv. Funct. Mater.* **2015**, *25*, 1120-1126.

(2) Zeng, Q.; Zhang, X.; Feng, X.; Lu, S.; Chen, Z.; Yong, X.; Redfern, S. A. T.; Wei, H.; Wang, H.; Shen, H.; Zhang, W.; Zheng, W.; Zhang, H.; Tse, J. S.; Yang, B. Polymer-Passivated Inorganic Cesium Lead Mixed-Halide Perovskites for Stable and Efficient Solar Cells with High Open-Circuit Voltage over 1.3 V. *Adv. Mater.* **2018**, *30*, 1705393.