

Nucleation and Growth Control of $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ for Planar Perovskite Solar Cell

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METHODS

Materials. All chemicals were purchased from Sigma-Aldrich or Alfa Aesar or Lumtec (Luminescence Technology Corp.) and used without further purification. $\text{HC}(\text{NH}_2)_2\text{I}$ were synthesized by reacting 15 g formamidine acetate and 30 ml HI (57 wt% in water) in 100 ml ethanol at 0 °C for 2 hours with stirring. The precipitate was recovered by rotary evaporator at 50 °C for 1 hour. The white crystals were obtained by washing with diethyl ether followed by recrystallization from Ethanol.

Sample fabrication. A dense blocking layer of TiO_2 was deposited by spray pyrolysis (~50 nm) using 20 mM titanium diisopropoxide bis(acetylacetonate) solution at 450 °C on the clean FTO glass (TEC8). To prepare 1.2M $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ solution, the prepared $\text{HC}(\text{NH}_2)_2\text{I}$ is mixed with PbI_2 in Dimethylformamide (DMF) at 1:1 mole ratio at room temperature. The solutions with added HI (57 wt% in water) at specific molar ratio (0 g, 0.05 g, 0.10 g, and 0.20 g of HI solution in 1 ml of $\text{HC}(\text{NH}_2)_2\text{PbI}_3/\text{DMF}$ solution) were spread on the bl- TiO_2/FTO and spun at 6500 rpm for 30 s using gas-assisted method. The films were dried on a hot plate at 160 °C for 20 min. A solution of Spiro-OMeTAD containing 41.6 mg Spiro-OMeTAD, 7.5 μl of a 500 mg ml^{-1} lithium bis (trifluoro-methylsulphonyl)imide in acetonitrile and 16.9 μl 4-tert-butylpyridine in 0.5 ml chlorobenzene was spin-coated on the $\text{HC}(\text{NH}_2)_2\text{PbI}_3/\text{bl-TiO}_2/\text{FTO}$ substrate at 3000 rpm for 30 s. All films on bl- TiO_2 were prepared in nitrogen filled glovebox. A 100 nm gold electrode was deposited by thermal evaporation.

Characterization. X-ray diffraction (XRD) patterns were measured using a PANalytical Xpert Materials Research diffractometer system with a Cu $K\alpha$ radiation source ($\lambda = 0.1541 \text{ nm}$) at 45 kV and 40 mA. Top-view and cross-sectional SEM images were obtained using a field emission

SEM (NanoSEM 230). KPFM measurements were carried out using an AFM (AIST-NT SmartSPM™ 1000) in air, a gold coated Si tip with 6 nm radius of curvature (HYDRA6R-100NG-10, APPNANO) as the probe in a non-contact mode and with an AC voltage of -1 to +1 V. The PL spectrum was measured using a spectrometer detected by a thermoelectric cooled Si-CCD detector, with excitation at 405 nm. Time-resolved PL was measured by Microtime 200 system (Picoquant) with TCSPC technique excited at 470 nm. For electroluminescence measurements, a commercially available 1-mega-pixel Si-CCD camera (Princeton Instruments, Trenton, NJ, USA) was used to detect the luminescence signal. A 750-850 nm bandpass filter was used before the camera lens to exclusively detect the emission from the perovskite active layer. The voltage bias control and current reading was performed by a source measurement unit (Agilent Technologies). The J–V measurements were performed using an IV5 solar cell I–V testing system from PV measurements, Inc. (using a Keithley 2400 source meter) under illumination power of 100 mW cm^{-2} by an AM1.5G solar simulator (Oriel model 94023A) with an 0.159 cm^2 aperture and a scan rate of 1.2 V s^{-1} . All J-V measurements were undertaken at room temperature in ambient condition.

Thermal cycling. The thermal cycling test (IEC61646 standard) consisted of 10 cycles of: 23°C to -40°C over 40 minutes; 10 minutes at -40°C ; -40°C to 85°C over 75 minutes, 10 minutes at 85°C ; 85°C to 23°C over 36 minutes. Humidity was not controlled and was allowed to vary from 5 % to 60 % relative humidity. The test was carried out in an ESPEC SMS-2 environmental chamber. The temperature and humidity data were recorded by the in-built ESPEC thermocouple and humidity sensors, as well as an ONSET HOBO MX1101 humidity and temperature probe close to the sample which is the main temperature and humidity data source.

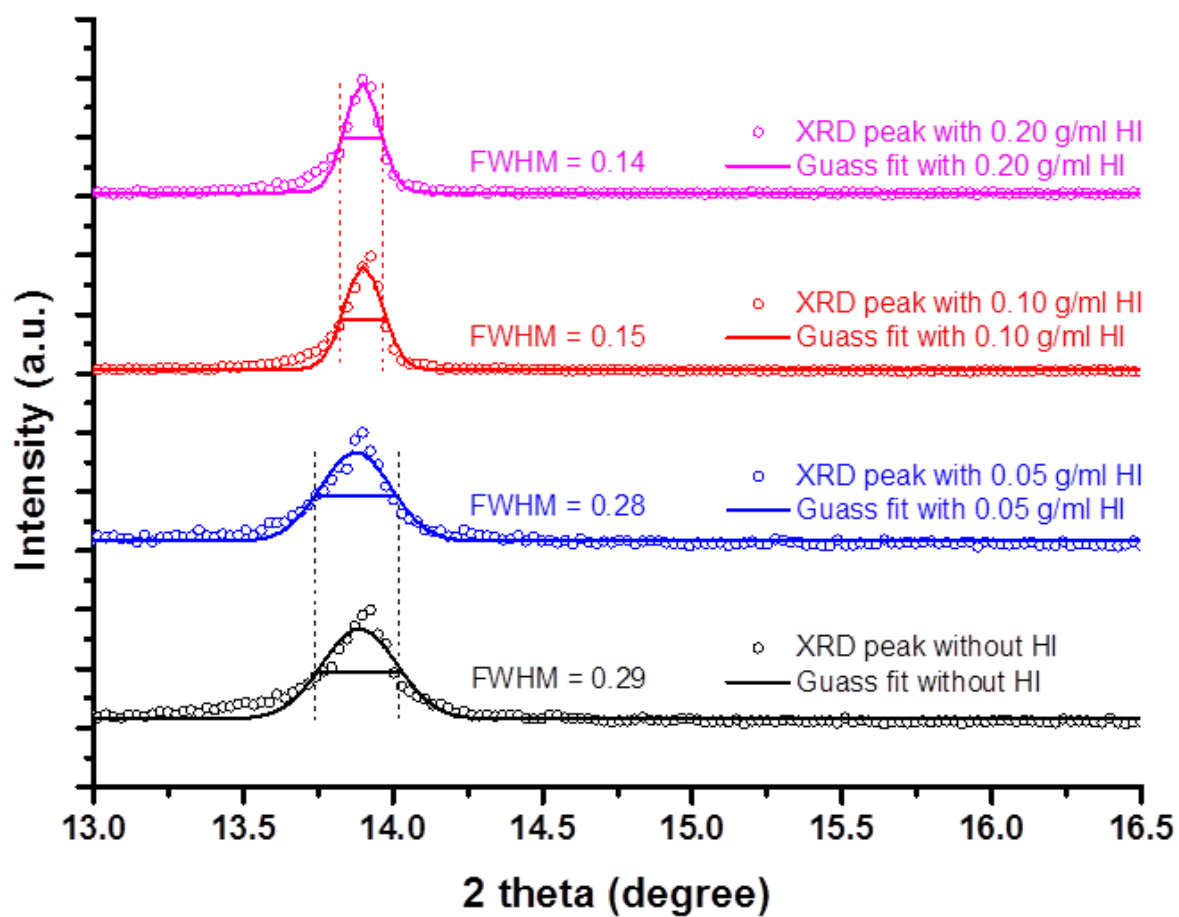


Figure S1. Full width at half maximum (FWHM) of the (110) peak for $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ films formed by various concentration of HI additive in the $\text{HC}(\text{NH}_2)_2\text{PbI}_3/\text{DMF}$ solution.

Kelvin probe force microscopy (KPFM) allows for high lateral resolution measurements of spatial variations of the electrical properties of the devices at the nanometer scale. KPFM is a surface potential detection method that determines the contact potential difference (CPD) during scanning by compensating the electrostatic forces between the probe and the sample. KPFM measurements were performed using a gold coated Si tip with 6 nm a radius of curvature (HYDRA6R-100NG-10, APPNANO) as the probe in a non-contact mode with an AC voltage of -1 to +1 V.

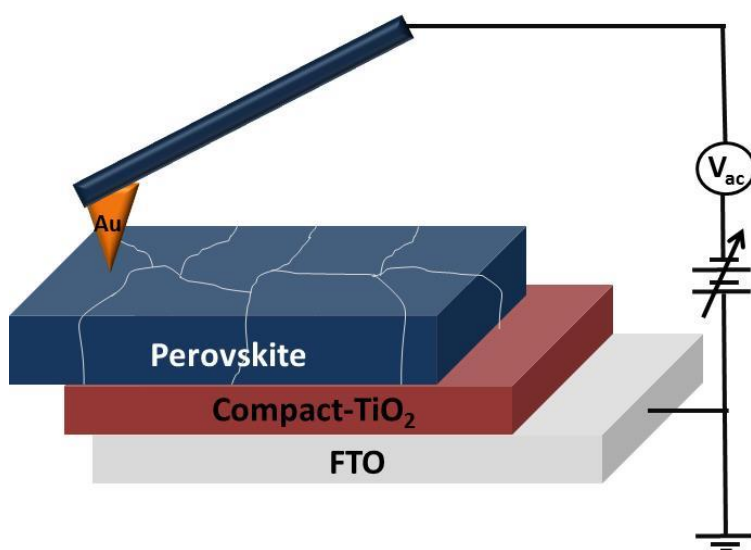


Figure S2. Illustration of the KPFM set up.

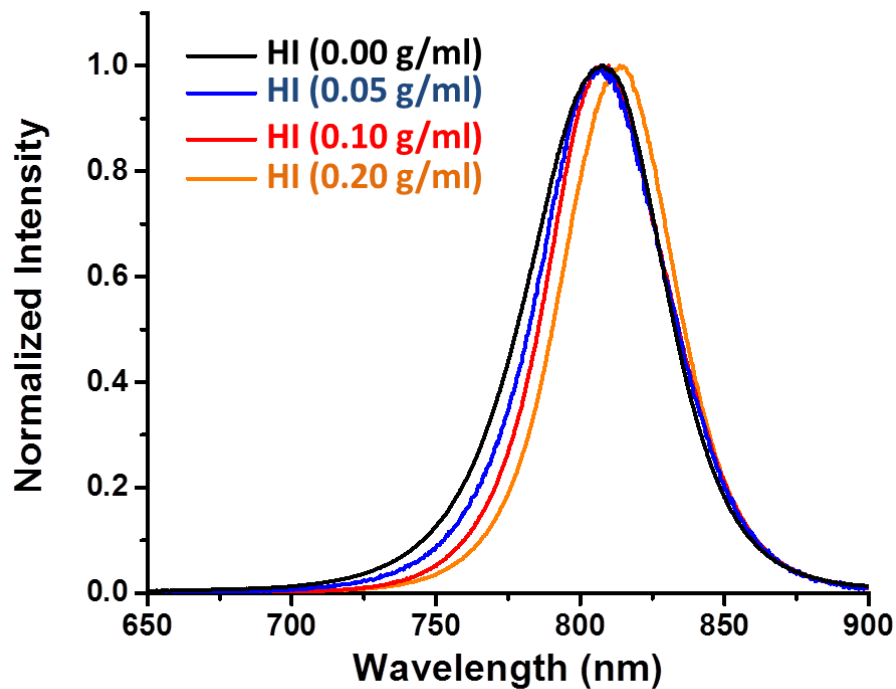


Figure S3. PL spectra of HC(NH₂)₂PbI₃ perovskites excited at 405 nm.

Bi-exponential function $y = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, has been used to extract the time constants for each PL evolution in **Figure 3a** in particular the fast component which is attributed to the extraction of photo-generated carriers (i.e., electrons across the HC(NH₂)₂PbI₃/TiO₂ interface). The results are summarised in the **Table S1**.

Table S1. Time constants extracted from the fitting of PL decay traces in **Figure 3a**.

HI concentration [g ml ⁻¹] ^[a]	0	0.05	0.10	0.20
τ_1 [ns]	8.6	3.5	2.1	2.1

[a] HI contents in 1 ml of HC(NH₂)₂PbI₃/DMF solution

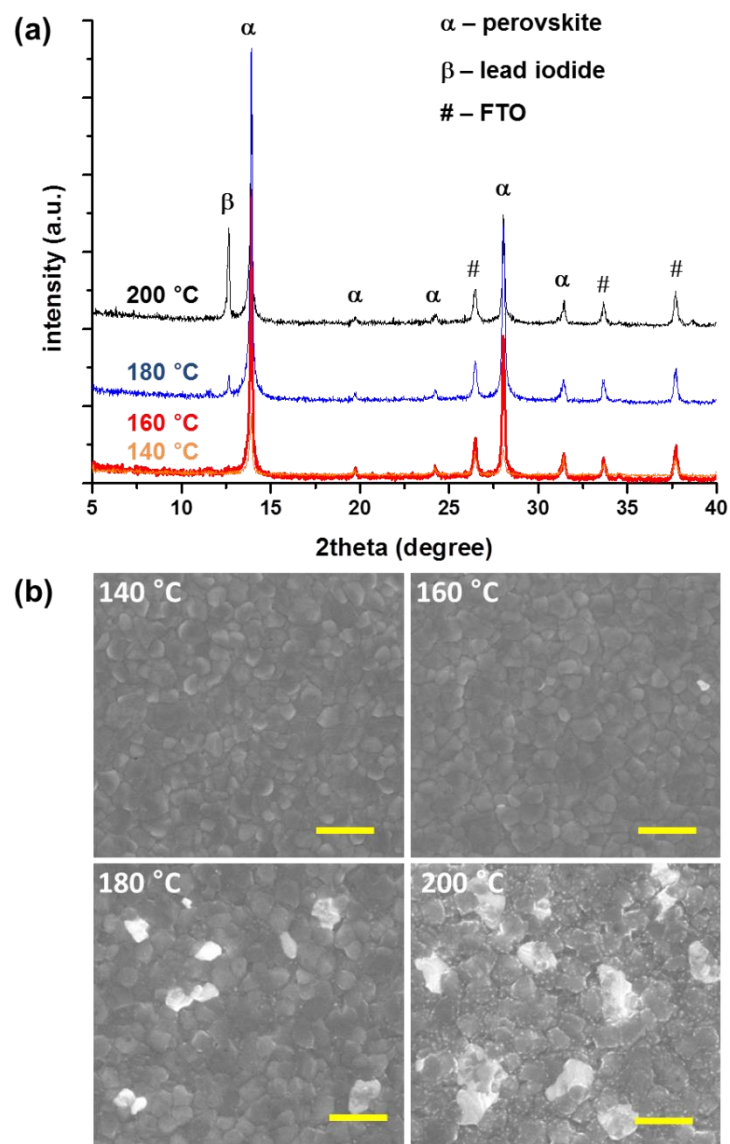


Figure S4. a) XRD patterns and b) top-view SEM images of gas-assisted spin coated $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ films with 0.1 g ml^{-1} HI additive annealed at different temperatures (140, 160, 180, and 200 °C). The yellow scale bar represents 1 μm .

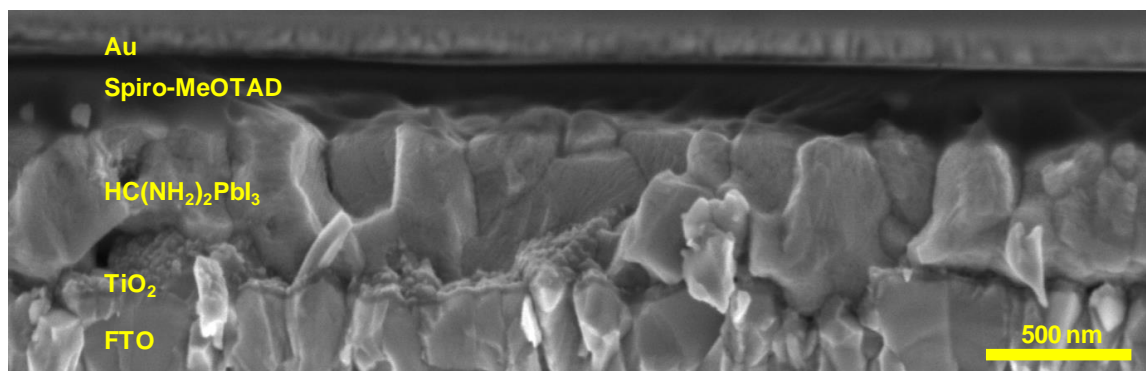


Figure S5. A cross-sectional SEM image of a representative device.

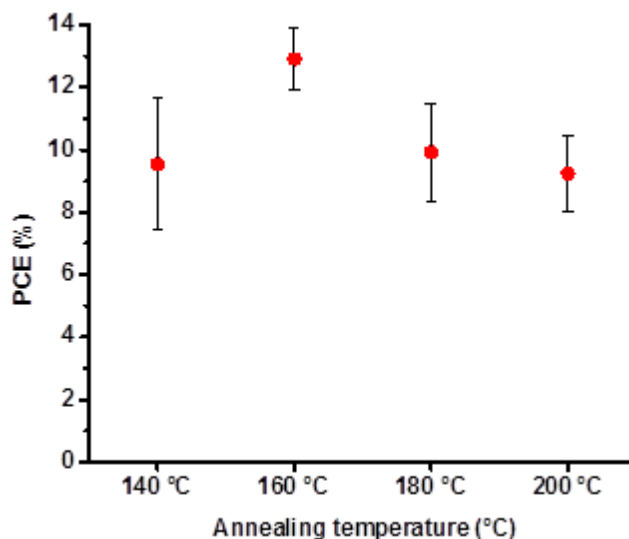


Figure S6. Distributions of energy conversion efficiencies of devices with $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ formed using fixed concentrations of HI additive (0.1 g ml^{-1}) at different annealing temperatures. Error bars are standard deviations of device efficiencies.

Table S2. Average solar cell performance of devices with $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ formed using fixed concentrations of HI additive (0.1 g ml^{-1}) at different annealing temperatures.

Annealing temperature [°C]	Jsc [mA cm ⁻²]	Voc [mV]	FF	Rs [Ω cm]	Rsh [Ω cm]	PCE [%]	Standard deviation of PCE
140	19	911	54	21	3288	10	2.11
160	23	902	63	18	2204	13	0.97
180	22	895	50	56	1813	10	1.56
200	22	881	49	51	2873	9	1.19

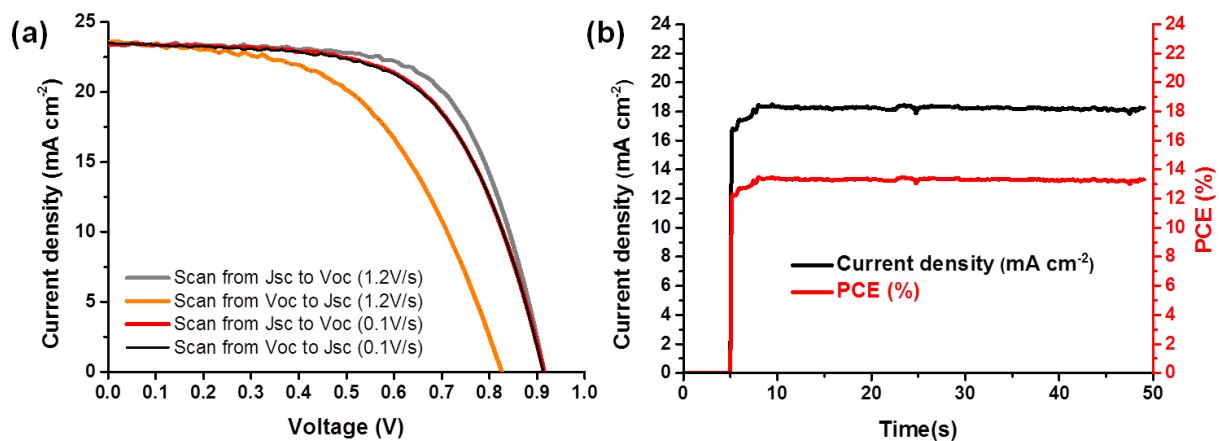


Figure S7. Stabilized J and PCE curves held at maximum power point of a 13 % $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ device.

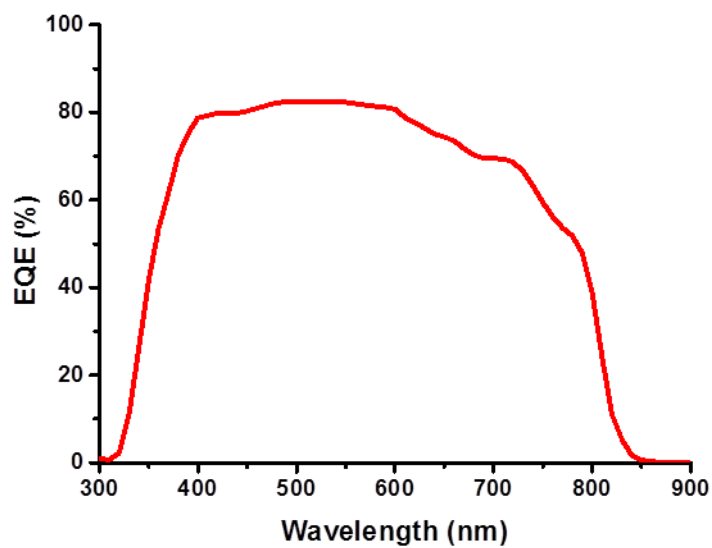


Figure S8. a) J-V curve and b) external quantum efficiency (EQE) of the best performing $\text{HC}(\text{NH}_2)_2\text{PbI}_3$ planar device in this work.

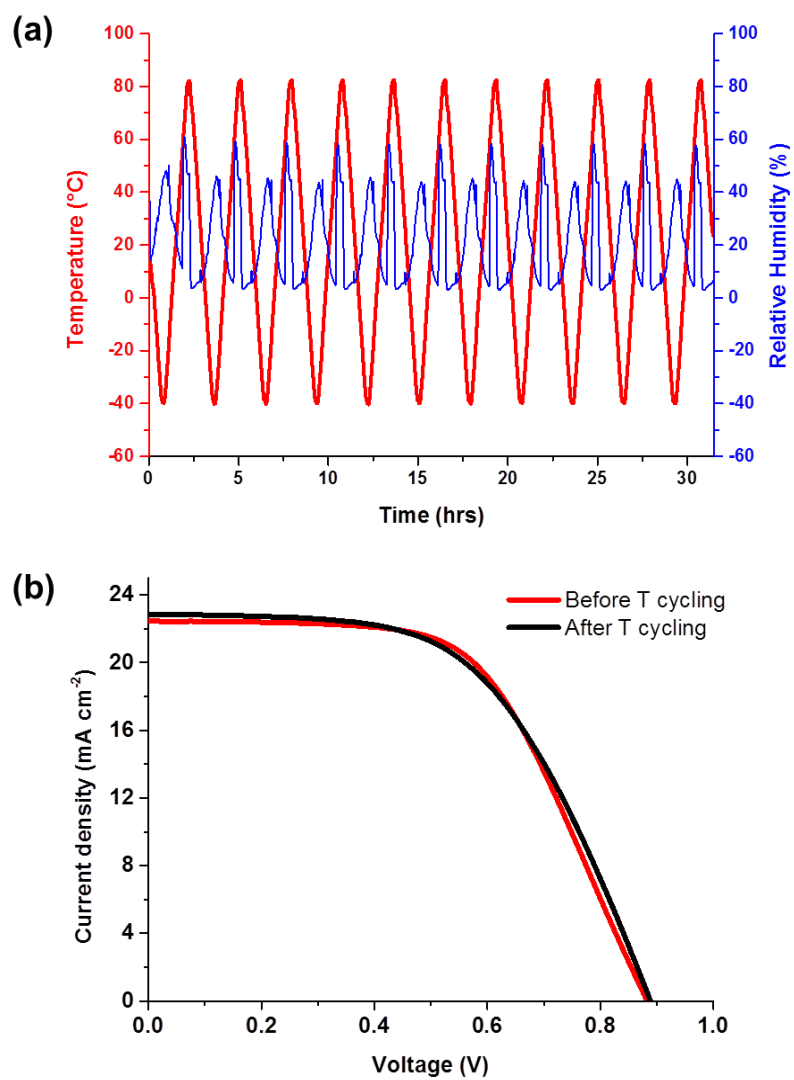


Figure S9. a) Temperature and relative humidity recorded during 10 cycles of thermal cycling.

b) J-V of a 12 % HC(NH₂)₂PbI₃ solar device before and after the thermal cycling test.