

High efficient methylammonium lead triiodide perovskite solar cells: the relevance of non-stoichiometric precursors

Supporting information

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1. Methods

Materials

Chemicals were purchased from Sigma-Aldrich and TCI Europe and used as received without further purification. $\text{CH}_3\text{NH}_3\text{I}$ was prepared similar to a previously published method¹, in brief: $\text{CH}_3\text{NH}_3\text{I}$, was synthesized by reacting 21.6 ml methylamine (40%wt in water, Aldrich) and 30 ml hydroiodic acid (57 wt% in water, Aldrich) in a 250 ml round-bottomed flask at 0 °C for 2 h with stirring. The white precipitate was recovered by evaporation at 50 °C for 1 h. The product, methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$), was dissolved in ethanol, filtered and recrystallized from diethyl ether, and dried at 60 °C in a vacuum oven for 24 h.

Device preparation

Devices were fabricated following a one-step anti-solvent approach as described elsewhere.² The solar cells were prepared on fluorine-doped tin oxide coated glass (NSG10) substrates. After cleaning the substrates by ultrasonic and UV-ozone treatment, a 30 nm thick TiO_2 blocking layer was deposited by spray pyrolysis following a procedure previously reported in the literature.³ The mesoporous TiO_2 layer was spin coated from a solution containing 150mg 30NRD Dyesol paste per 1 ml of EtOH, at 5000rpm, 2000rpm/s, 10s, and annealed at 500°C for 15min. 1.25 M PbI_2 /MAI (1:1) in DMSO was spin coated as described in reference 2, but using chlorobenzene as an antisolvent. Different compositions with 5 – 10 – 15 – 20 % molar excess of PbI_2 were also tested by fixing the MAI concentration in the precursor solution and adjusting the amount of PbI_2 . The perovskite layer was deposited inside a Nitrogen glovebox (MBraun) and annealed at 100 °C during 45 min. After this time, spiroOMETAD was spin-coated at 4000rpm, 20s from a chlorobenzene solution (28.9mg in 400 μl , 60mmol) containing Li-TFSI (7.0 μl from a 520mg/ml stock solution in acetonitrile), TBP (11.5 μl) and Co(II)TFSI (10mol%, 8.8 μl from a 40mg/ml stock solution) as dopants. Finally, a 100 nm gold electrode was evaporated.

Device characterization

The solar cells were measured using a 450 W xenon light source (Oriel) with an irradiance of 100 mW/cm². A Schott K113 Tempax filter (Präzisions Glas & Optik GmbH) was used to reduce the spectral mismatch between AM1.5G and the simulated illumination to ~ 4% between 350-750 nm. Before each measurement, the exact light intensity was determined using a calibrated Si reference diode and JV measurements were obtained by applying an external voltage bias (from forward to reverse and from reverse to forward) while measuring the current response with a source meter (Keithley Model 2400). The cells were covered with a thin mask (0.16 cm²) to reduce scattered light. The compliance was set to 3 mA. All characterization was done outside the glovebox and without any encapsulation of the perovskite cells, under constant exposure to ambient atmosphere.

2. Perovskite film characterization

X-ray diffraction (XRD)

X-ray diffraction spectra of the thin films were recorded on an X'Pert MPD PRO (PANalytical) equipped with a ceramic tube providing Ni-filtered ($\text{CuK}\alpha$, $\lambda = 1.54060 \text{ \AA}$) radiation and a RTMS X'Celerator (PANalytical). The data were collected at room temperature in the 2θ range 10 – 60 °. The automatic divergence slit (10 mm) and beam mask (10 mm) were adjusted to the dimension of the films. A baseline correction was applied to all X-Ray thin film diffractograms to compensate for the broad feature arising from the FTO glass and anatase substrate.

Scanning Electron Microscopy

Film morphology was investigated by using a high-resolution scanning electron microscope (Merlin, Zeiss) equipped with a GEMINI II column and a Schottky Field Emission gun. Images were acquired with an In-Lens Secondary Electron Detector. Film thickness was also investigated using cross-section high-resolution scanning electron microscope.

3. UV-visible spectroscopic measurements: absorption, steady-state PL and time-resolved PL decay.

Absorption spectra were measured on a PerkinElmer UV-Vis spectrophotometer. The source were deuterium and tungsten halogen lamps and the signal was detected by a gridless photomultiplier with Peltier-controlled PbS detector. The UV WinLab software allows to process the data.

PL spectra were recorded by exciting the perovskite films deposited onto mesoporous TiO₂ at 600 nm with a standard 450 W Xenon CW lamp. To avoid any PL enhancement due to inter-system energy transfer from the PbI₂ to the CH₃NH₃PbI₃ present in the film. The signal was recorded by a spectrofluorometer (Fluorolog, FL1065 from Horiba Jobin Yvon Technology) and analyzed by the software FluorEssence.

The time-resolved PL experiments were performed with the same Fluorolog using a pulsed source either at 406 nm (NanoLED 402-LH from Horiba, pulse width <200 ps, 11 pJ/pulse, approx. 1 mm² spot size) or at 460 nm (Ps diode lasers BDS-SM, pulse with < 100 ps, from Photonic Solutions, 0.2 pJ/pulse, approx.. 1 mm² spot size) and the signal was recorded at 770 nm by the Time Correlated Single Photon Counting (TCSPC) technique. The samples were excited from the perovskite side and mesoporous TiO₂ side under ambient conditions. A monoexponential and bi-exponential fitting were used to analyze the background-corrected PL decay signal [kanad and Stranks]. The fitting lifetimes and the relative amplitudes for the as-prepared films are shown in the Table S1.

Excitation from the perovskite capping layer				
PbI ₂ /MAI ratio	τ_1 (ns)	τ_2 (ns)	A1 (%)	A2 (%)
1 : 1	0.70	10.3	48.36	51.64
1.05 : 1	5.4	19.2	25.6	74.4
1.1 : 1	8.9	41.4	16.6	83.3
1.15 : 1	10.7	39.0	15.9	84.1
1.2 : 1	9.0	31.0	22.1	77.9
Excitation from the meso-TiO ₂ layer				
1 : 1	18	-	100	-
1.05 : 1	19	-	100	-
1.1 : 1	13	4,6	77	23
1.15 : 1	11.4	2.7	54	46
1.2 : 1	6.9	2	26	74

Table S1. Decay parameters corresponding to a biexponential fitting of the PL decay curves obtained for the perovskite films, including the lifetime and chi-squared value of the fitting (χ^2).

4. Cross-section SEM pictures for the as-prepared perovskite devices.

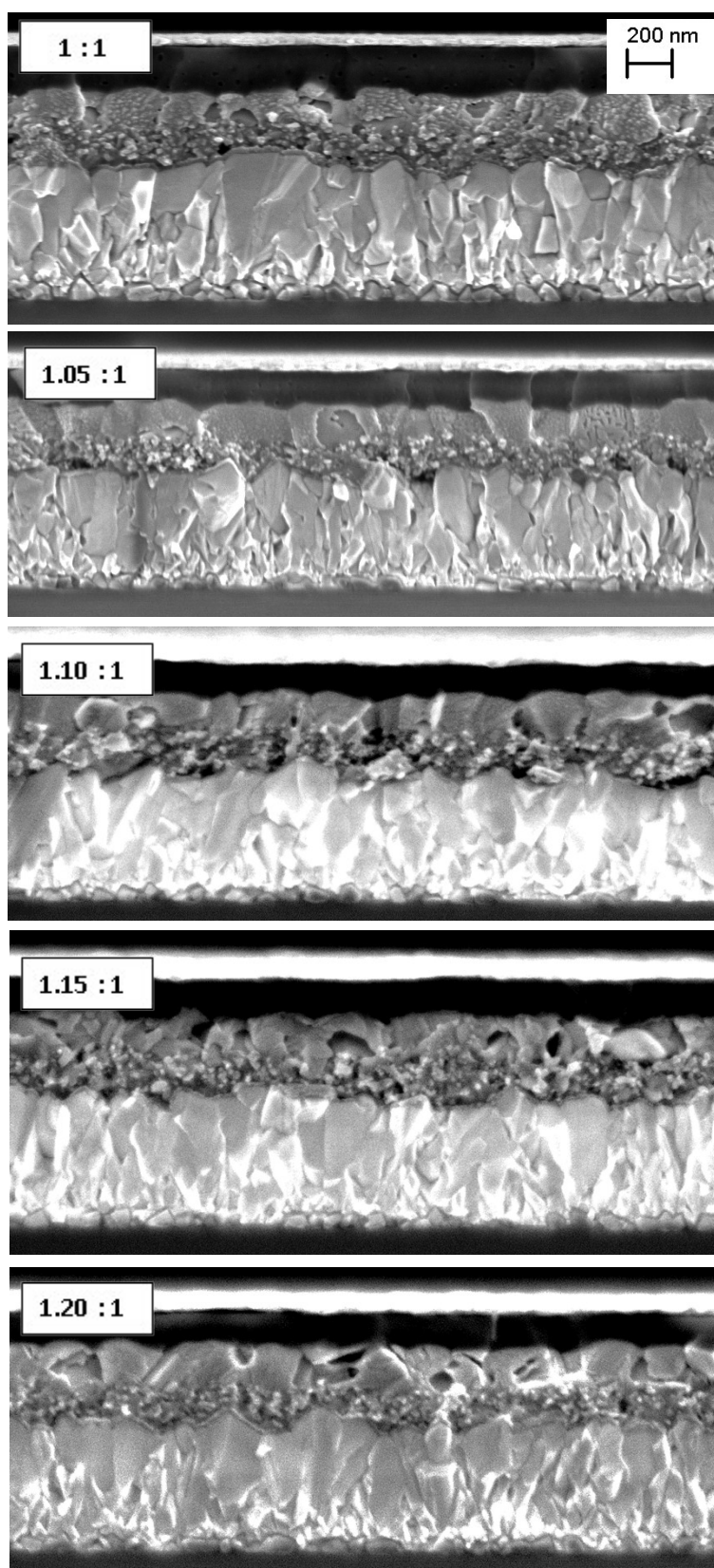


Fig. S1. Cross-section SEM pictures of the perovskite devices prepared with different amount of PbI_2 excess in the active layer. The molar ratio between PbI_2/MAI is indicated in the pictures.

5. Top view of SEM pictures for the as-prepared perovskite devices.

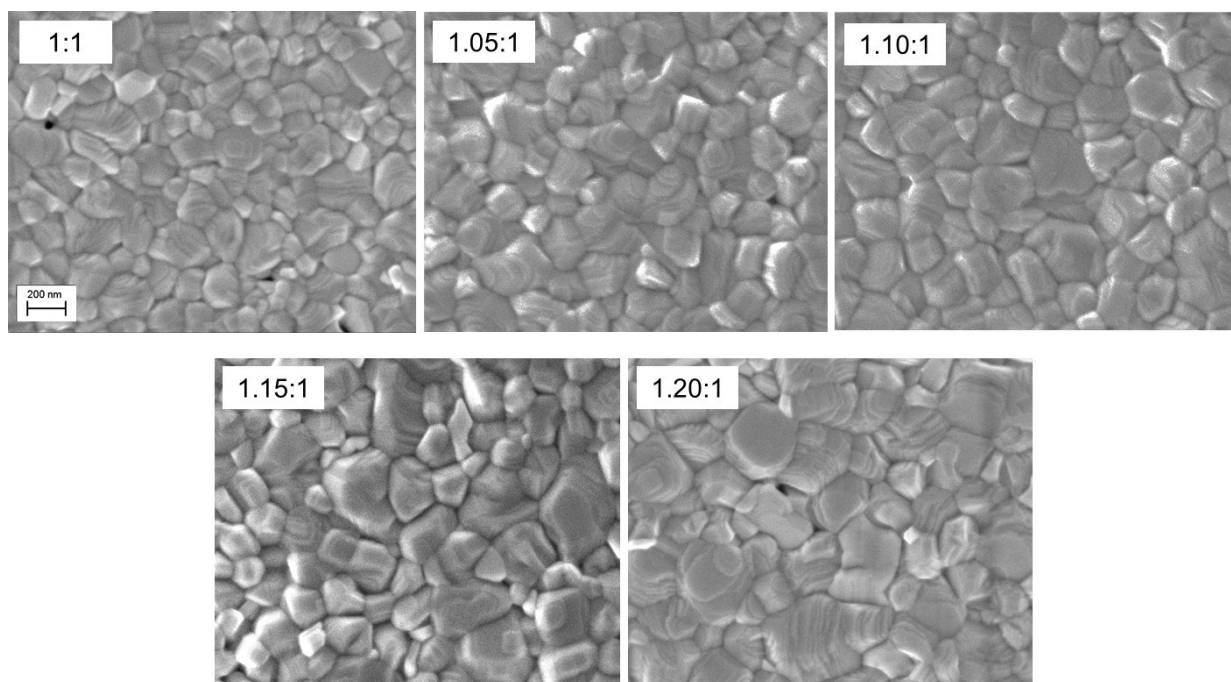


Fig. S2. SEM pictures of the top view of the perovskite films prepared with different amount of PbI_2 excess in the active layer. The molar ratio between PbI_2/MAI is indicated in the pictures.

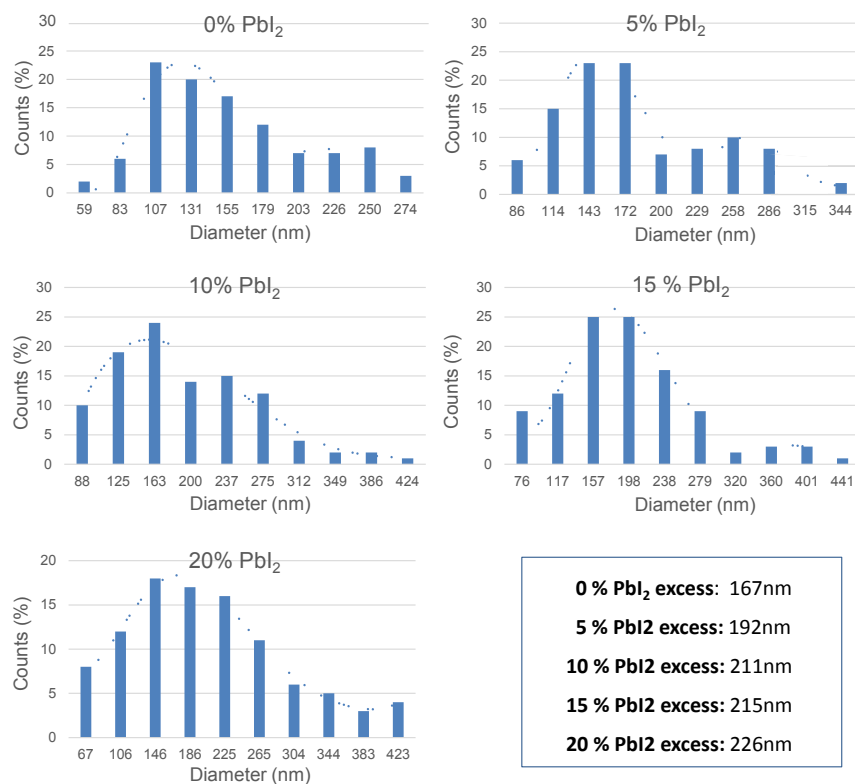


Fig. S3. Grain-size distribution for the perovskite films containing different amount of PbI_2 excess in the precursor solution, calculated from SEM images (analysed surface area: $0.7 \mu\text{m}^2$). The dotted lines are provided as a guideline for eyes. The inset shows the value of the averaged grain-size measured for each composition.

6. Histogram of the main photovoltaic parameters obtained for more than 50 cells

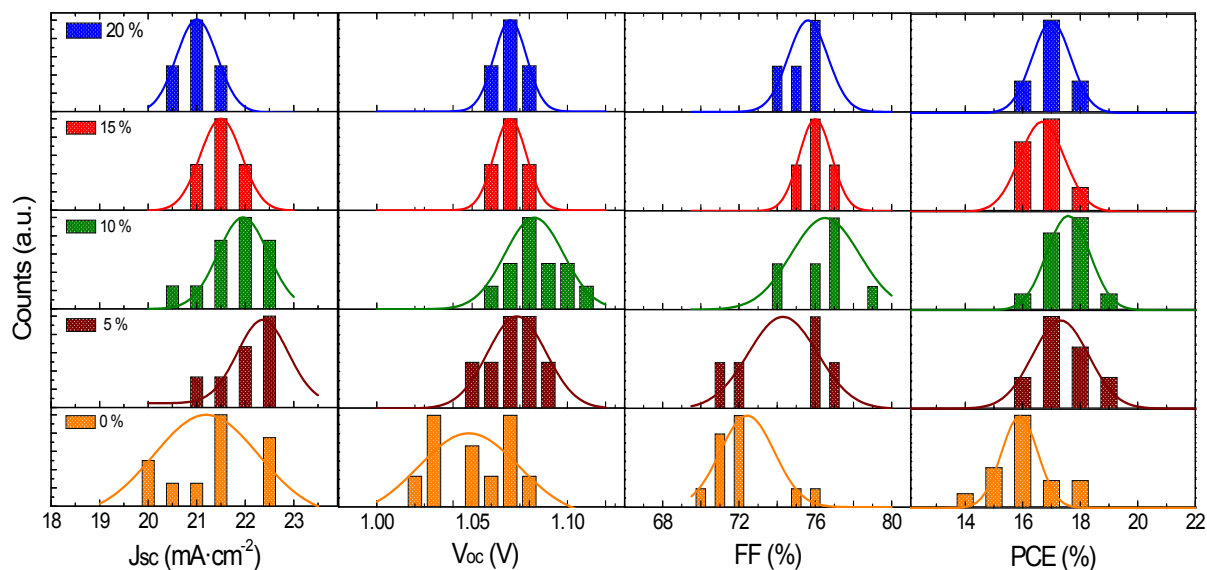


Fig. S4. Histogram of more than 50 devices measured under AM 1.5G illumination in ambient atmosphere. The legend shows the amount of PbI_2 excess present in the samples. The Gaussian fits are provided as a guide to the eye.

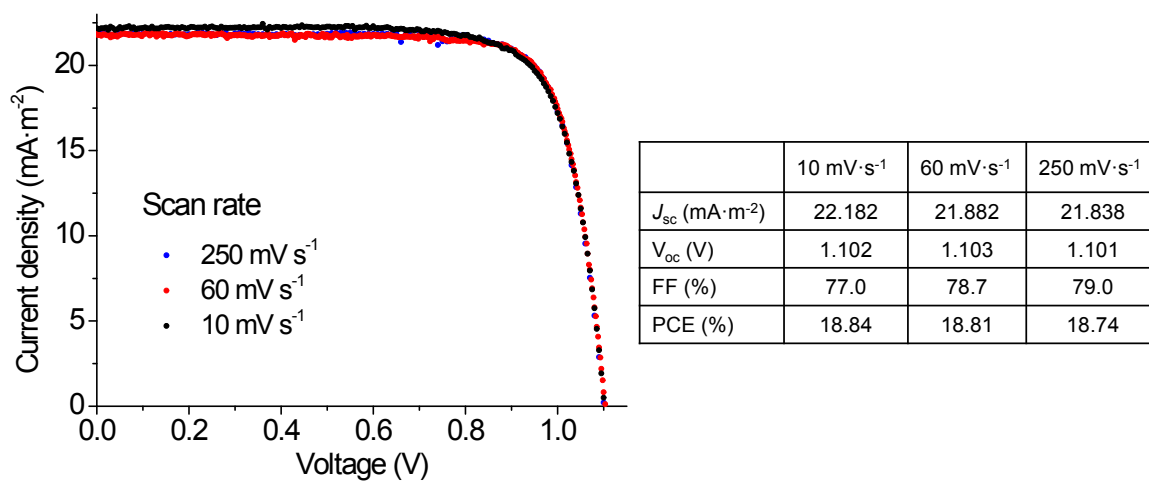


Fig. S5. $J-V$ curve measured for one of the high efficient cells under AM 1.5G illumination in ambient atmosphere. No influence of the scan-rate ($\text{mV}\cdot\text{s}^{-1}$) was observed.

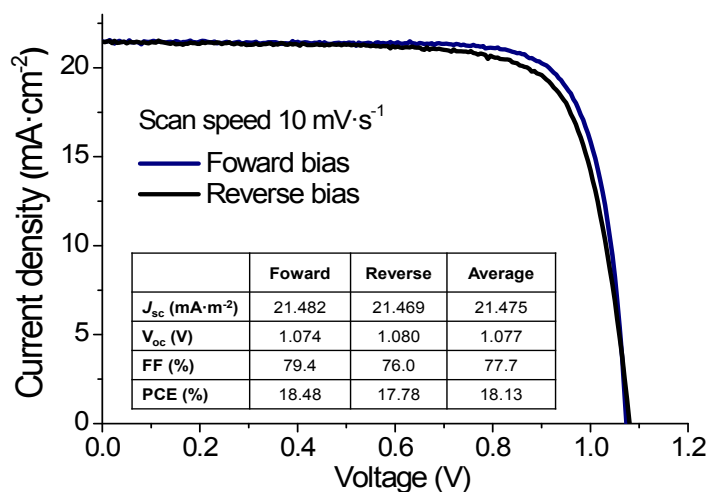


Fig. S6. Hysteresis on the $J-V$ curve obtained for a typical high efficient cell measured under AM 1.5G illumination in ambient atmosphere under forward and reverse bias. The cell was measured without encapsulation at a constant rate $10 \text{ mV}\cdot\text{s}^{-1}$. No anti-reflective coating was used during the measurement.

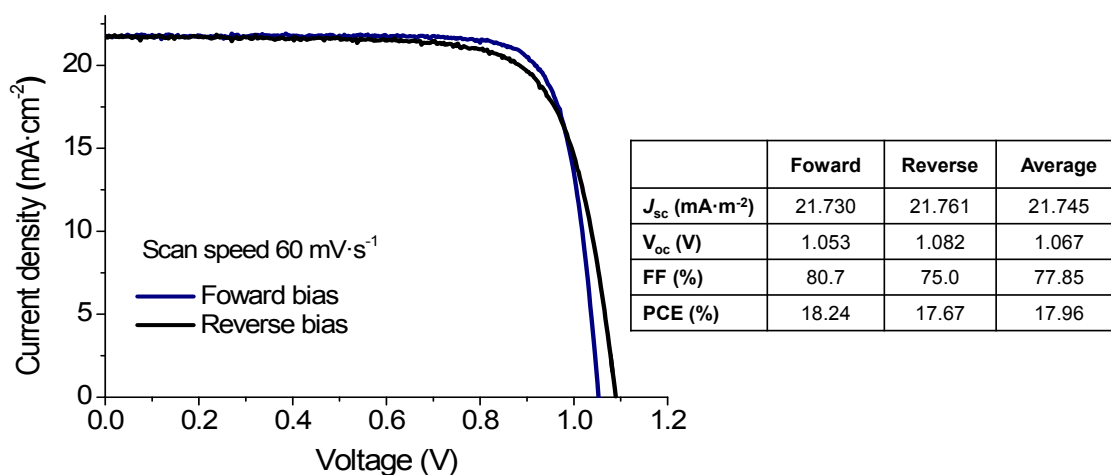


Fig. S7. $J-V$ curve measured for one of our high efficient cells under AM 1.5G illumination in ambient atmosphere. The cell was measured without encapsulation at a constant rate $60 \text{ mV}\cdot\text{s}^{-1}$. Very low hysteresis is detected under these conditions. During forward bias it exhibited a FF $\sim 80.7\%$, which, from our knowledge, represents a record value for PSC based on NIP structure and stays very close to the theoretical limit.

7. Initial time-dependent performance test.

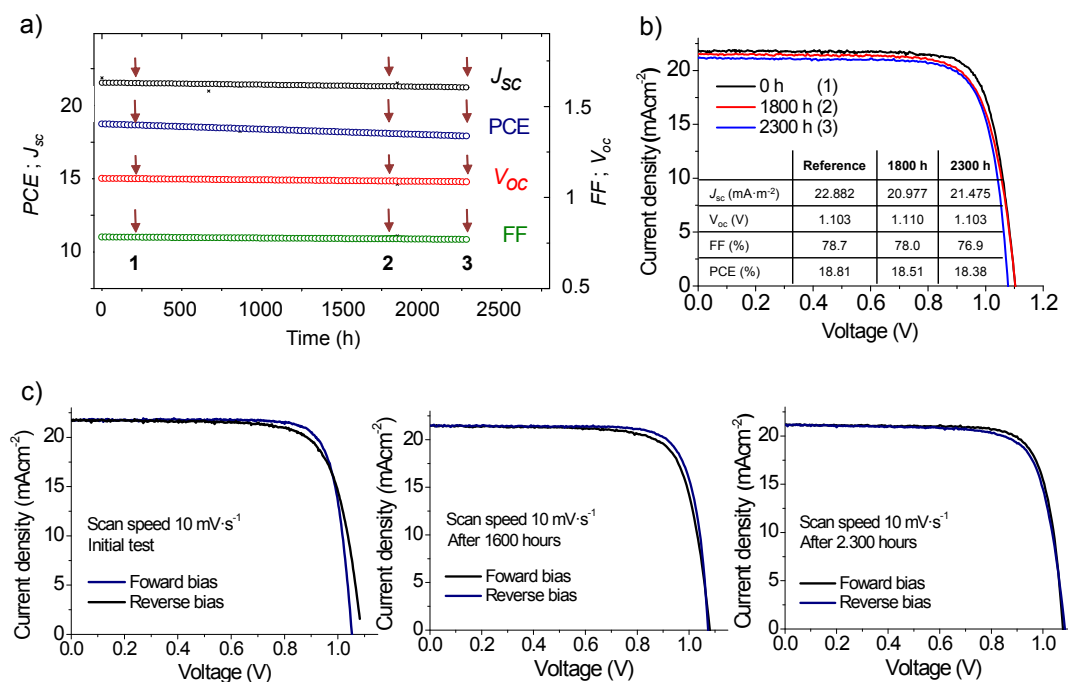


Fig. S8. Initial stability test of one typical high efficient solar cell during more than 2200 hours. (a) The data show stability even after being stored without any encapsulation in dry-air. The curves corresponds to the dates marked with arrows (1 - 3) in the stability graph shown in (a) ($t = 0, 1.800$ and 2.300 hours). (b) Evolution of the $J-V$ curves with time measured under AM 1.5G illumination in ambient atmosphere. (c) $J-V$ hysteresis obtained for the curves shown in graph (b).

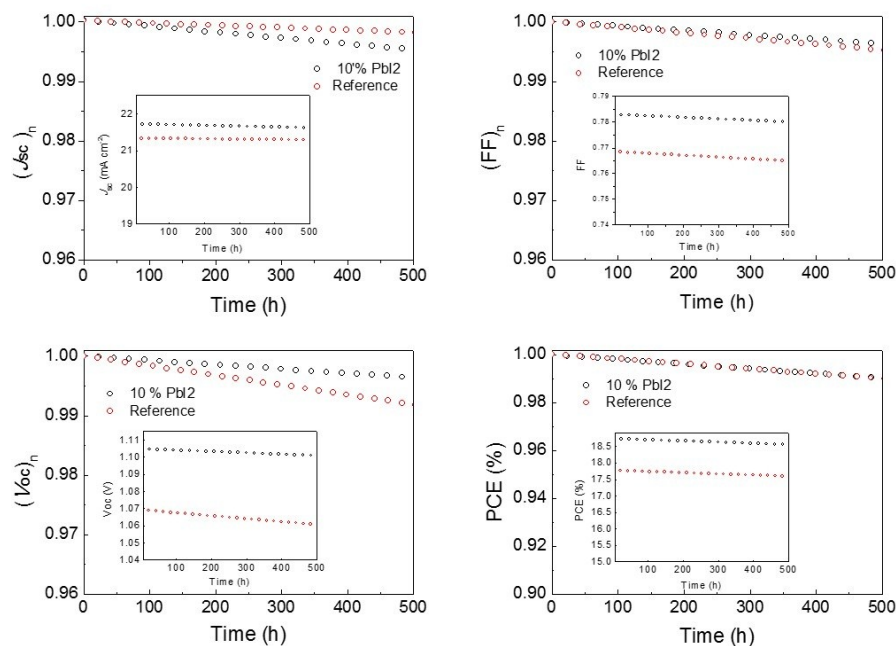


Fig. S9. Evaluation of the solar cell parameters (J_{sc} , FF , V_{oc} and PCE) obtained for the reference cell (steochimetric ratios between PbI_2 and CH_2NH_3I precursors) and one of the high efficient solar cells during their first 500 hours after preparation. The main graphs show the normalized parameters obtained from both cells to facilitate their comparison, while the inset shows the absolute values of J_{sc} , FF , V_{oc} and PCE for each cell.

Notes and references

1. L. Etgar, P. Gao, Z. Xue, Q. Peng, A. K. Chandiran, B. Liu, M. K. Nazeeruddin and M. Grätzel, *Journal of the American Chemical Society*, 2012, **134**, 17396-17399.
2. Jeon, N. J.; Noh, J. H.; Kim, Y. C.; Yang, W. S.; Ryu, S.; Seok, S. I. *Nat. Mater.* 2014, 13, 897.
3. Moehl, T.; Im, J. H.; Lee, Y. H.; Domanski, K.; Giordano, F.; Zakeeruddin, S. M.; Dar, M. I.; Heiniger, L.-P.; Nazeeruddin, M. K.; Park, N.-G.; Gratzel M. J. *Phys. Chem. Lett.* 2014, 5, 3931.