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Supporting Information

Improved efficiency and reduced hysteresis in ultra-stable fully-printable mesoscopic perovskite solar cells through incorporation of CuSCN in the perovskite layer

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General Methods

All experiments were performed under ambient conditions in air unless stated otherwise. Solvents and chemicals were purchased from commercial suppliers and used as received. XRD diffraction experiments of thin films were performed on a Bruker D8 Advance diffractometer operated in Bragg-Brentano geometry.

Device preparation

Printed mesoscopic substrates for fabricating perovskite solar cells were obtained from Solaronix SA (Aubonne, Switzerland). The substrates were heated to 400 °C for 30 minutes and then cooled down to room temperature prior to use. Polyimide impregnation masks were applied to the substrates to define the size of the perovskite film. The perovskite precursor solution was made by dissolving 0.55g PbI_2 (TCI), 0.19g methylammonium iodide (Greatcell), 0.015 g 5-aminovaleric acid hydroiodide (Greatcell) and the corresponding amount of CuSCN (Sigma) in 1 ml gamma-butyrolactone (Sigma) at 75°C. The solution was then cooled down to room temperature prior to use. The infiltration of the precursor solution was done by dropping 6µl of perovskite solution onto the substrate and letting the solution infiltrate the mesoporous structure for 30 min at room temperature in inert atmosphere. Afterwards the substrate was transferred into a temperature-controlled oven allowing the perovskite to crystallize at 50 °C for 1h. The finished solar cells were then exposed to 75% relative humidity at 40 °C for 5 days to reach their final efficiency. Solar cells used for stability testing were sealed using a glass slide with a Surlyn gasket.

Preparation of perovskite films for characterization

Perovskite films for SEM top-view, XRD, PL and SIMS measurements were fabricated by using substrates without the conductive carbon electrode layer: FTO/c-TiO_2/m-TiO_2/m-ZrO_2. The perovskite films were processed the same way as for the device preparation.

Device characterization

The photovoltaic device performance was analyzed using an Oriel AAA solar simulator (Newport) producing 1 sun AM 1.5G ($100 Wcm^{-2}$) sunlight. Current-voltage (J-V) curves were measured in ambient conditions with a potentiostat (Keithley). The light intensity was calibrated with an NREL certified KG5 filtered Si reference diode. The solar cells were masked with an aperture of 0.16 cm^2 to define the active area. The J-V curves were recorded scanning at 5 mV s^{-1}.

PL mapping

Photoluminescence mapping was performed using a Renishaw InVia Raman microscope. The PL map was recorded with a 532 nm green laser with a spot size of around 400 nm.

ToF-SIMS analysis

Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) analyses were performed using a ToF-SIMS V instrument (IonTof, Münster (Germany)) with bismuth (Bi^+) as the primary ion source (30 keV, 1 pA pulsed at 10 kHz). A low-energy cesium Cs^+ ion beam (1 keV, 50 nA) was used to sputter the sample in between two successive raster scans with the Bi^+ analysis beam. The analysis area was 50 x 50 μm^2 and the sputter area was 100 x 100 μm^2 at a resolution of 256 x 256 pixels. The 3D image is the result of the compilation of 2D maps, corresponding to the overall depth of few hundreds of nanometers.

HIM–SIMS analysis:

Analytical information and secondary electron images of the perovskite absorber layer were obtained with a Secondary Ion Mass Spectrometry (SIMS) system specifically developed at LIST for the ORION NanoFab Helium Ion Microscope (HIM) (ZEISS, Peabody (USA)) [1,2]. The spectrometer was tuned for the simultaneous detection of the $^{65}Cu^+$ (m/z = 65), $^{91}Zr^+$ (m/z= 91) and $^{208}Pb^+$ (m/z =208) signals in the positive polarity. The SCN^- (m/z=58) cluster has been detected in negative secondary polarity. The maps were realized in a matrix of 512x512 pixels with a counting time of 3 ms/pixel for a field of view of 20 x20 μm^2.

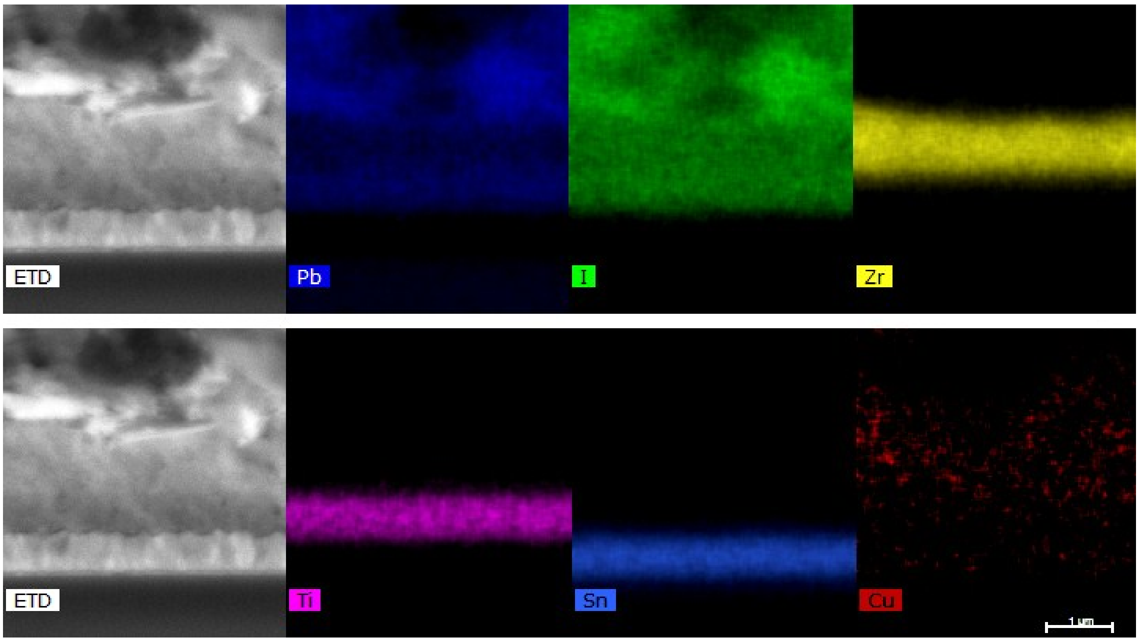

Figure S1 Elemental analysis (EDX) performed on a cross-section of a device fabricated using 8 mol% of CuSCN as additive.

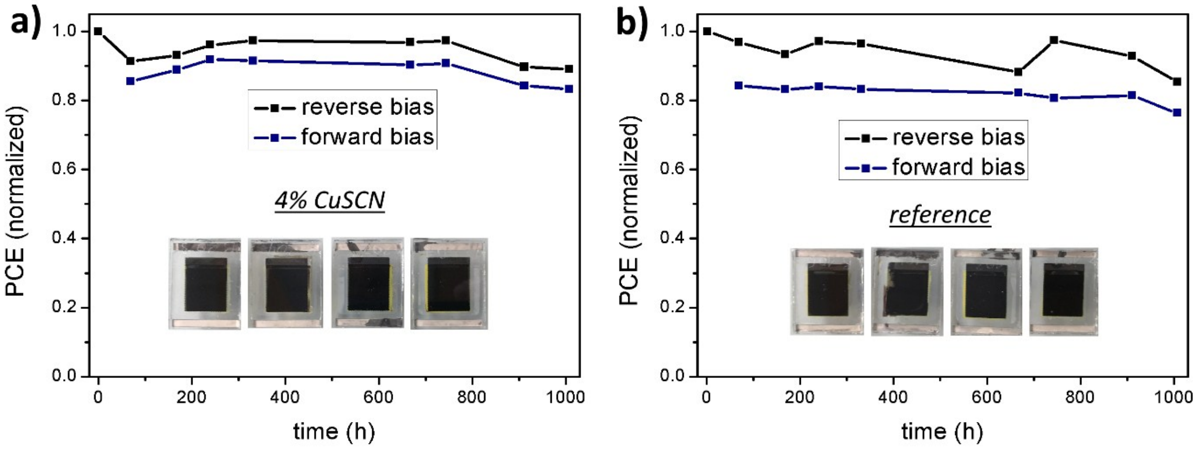

Figure S2 Stability of perovskite solar cells with (left) and without CuSCN (right). Incapsulated devices were kept under constant illumination at 100mW cm^{-2} simulated sunlight for 1000h. The data show an average over 4 devices. The stability was found to be similar between 4% CuSCN and the reference configuration with a loss of efficiency of less than 10%.

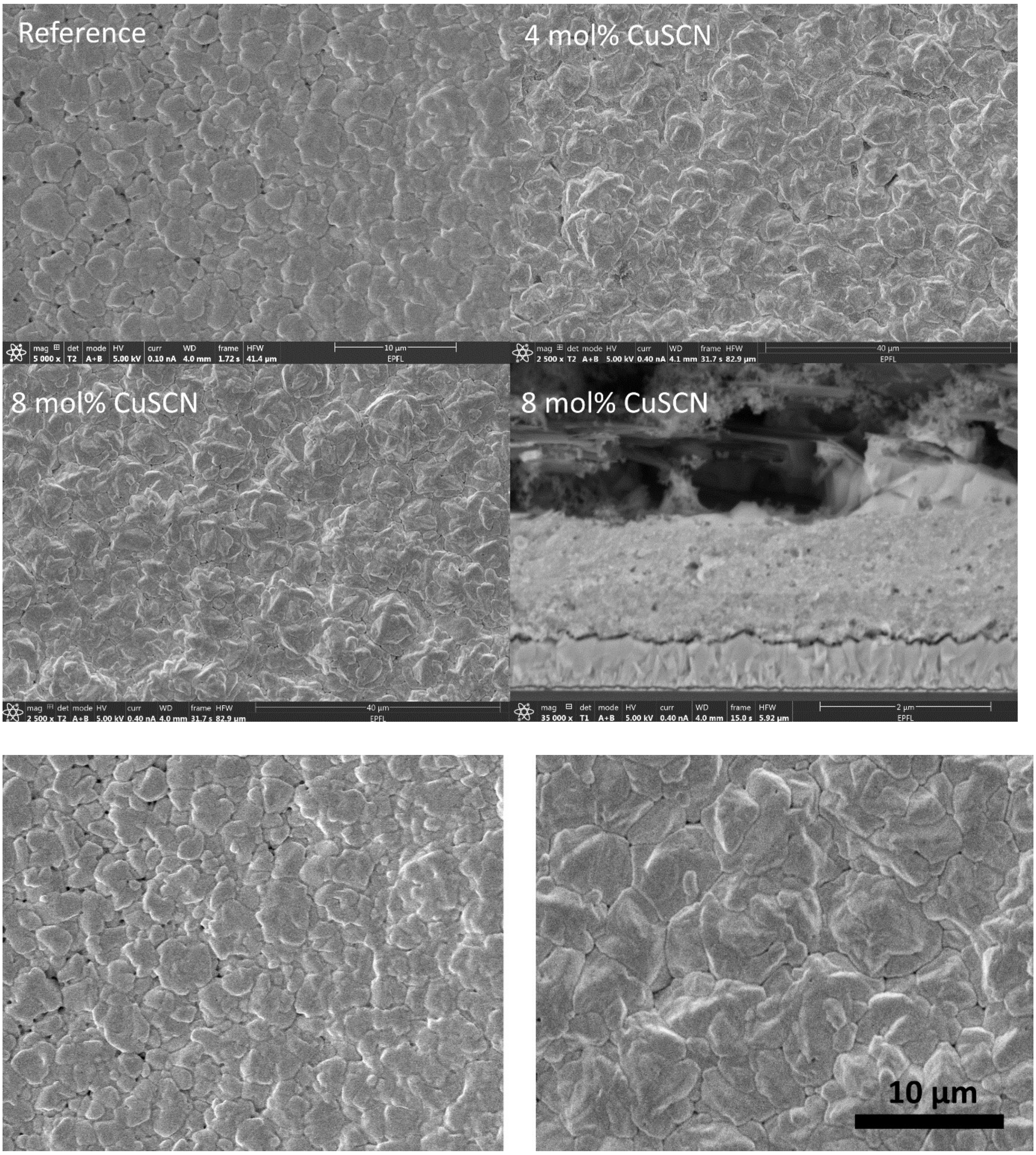

Figure S3 SEM top-view and cross-section images of samples with different amount of CuSCN added to the perovskite (top). Larger grain size has been observed for perovskite samples containing CuSCN (bottom right) compared to the pristine perovskite (bottom left).

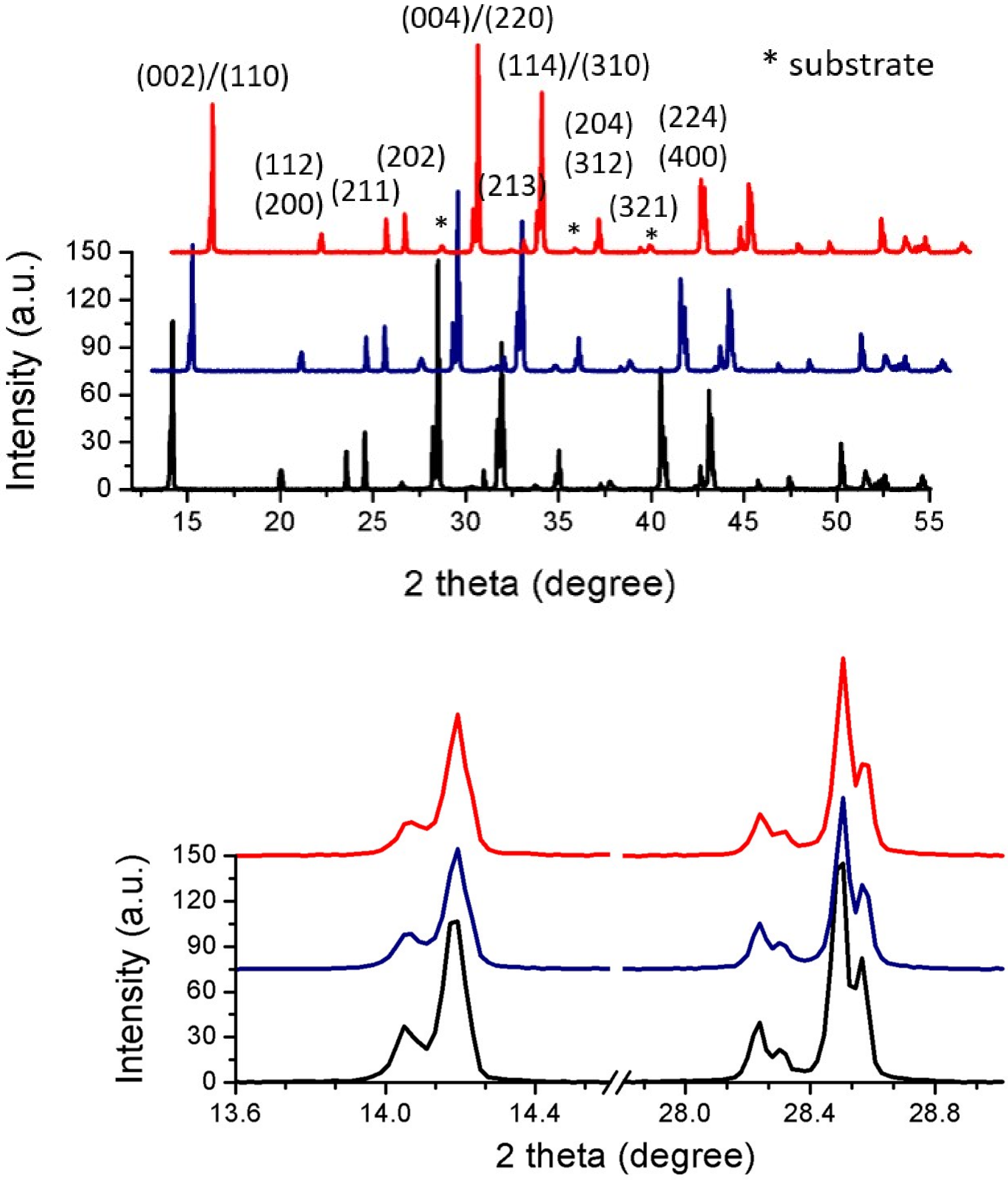

Figure S4 (top): XRD pattern of perovskite films with different amounts of CuSCN added. Reference (black), 4 mol% CuSCN (blue), 8 mol% CuSCN (red). Relevant perovskite peaks have been indexed. (bottom): Detailed view of the perovskite peaks at around 14° and 28.5°.

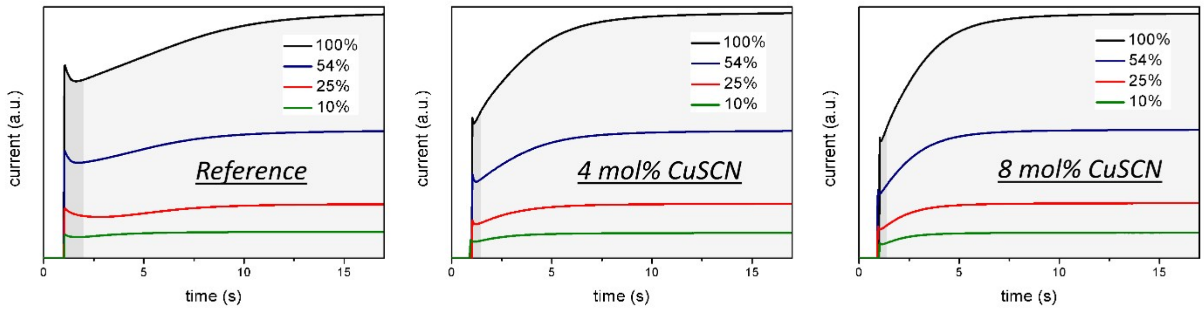

Figure S5 Current transient measurements on solar cells with different amount of CuSCN incorporated into the perovskite layer.

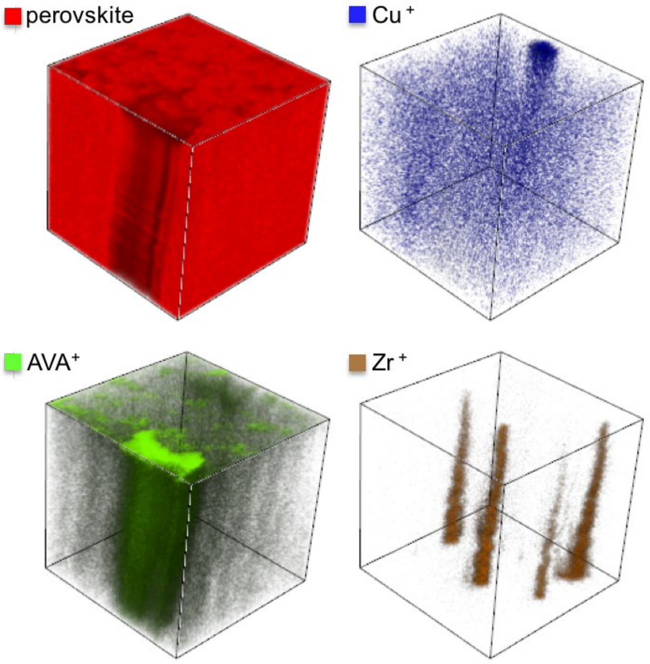

Figure S6 3D TOF-SIMS analysis of the perovskite thin film containing the aminovaleric acid (AVA) and CuSCN additives (on a TiO_2/ZrO_2 substrate). The analyzed slab measures 50x50μm^2 is a few hundreds nm deep. The perovskite signal is a combination of the secondary ion signal from MA^+, Pb_2^+, Cs_2I^+ ions (the Cs implantation comes from the primary Cs^+ ion beam used for the analysis).

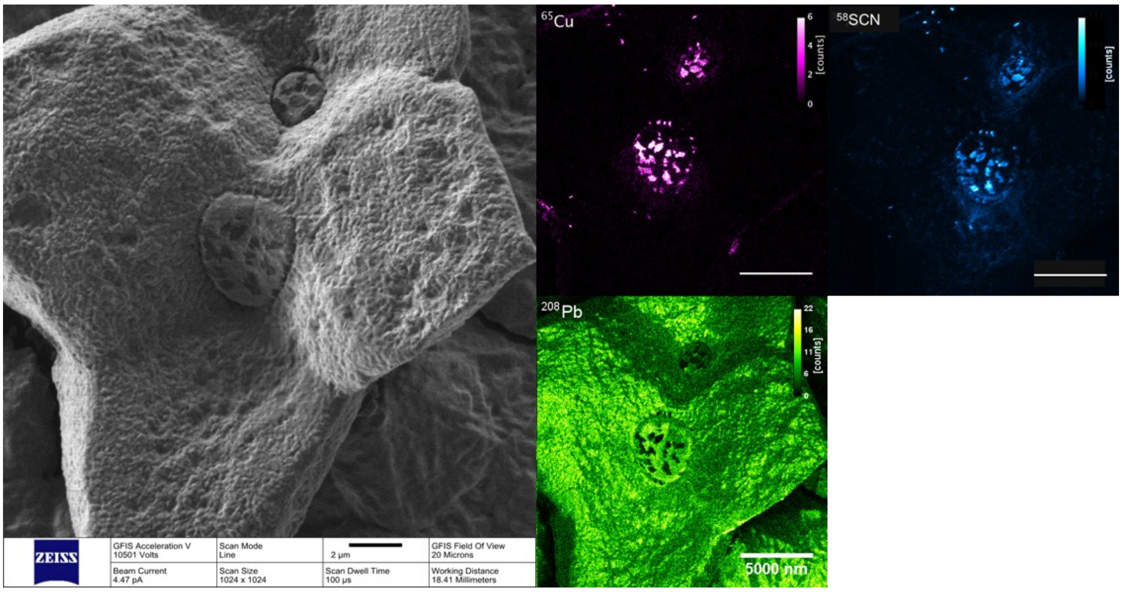

Figure S7 Secondary Electron (SE) images from Helium Ion Microscopy (HIM) of the island observed in the perovskite thin film. Secondary Ion Mass Spectrometry (SIMS) imaging of copper, lead and SCN cluster. The scale bar corresponds to 5 µm.

Maximum power point tracking (MPPT)

Sample	**Voltage**	**Current**	**PCE**
Reference	661 mV	19.4 mA/cm^2	12.8 %
4 mol% CuSCN	695 mV	20.2 mA/cm^2	14 %
8 mol% CuSCN	666 mV	18.9 mA/cm^2	12.6 %