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A Low Viscosity, Low Boiling Point, Clean Solvent System for the Rapid Crystallisation of Highly Specular Perovskite Films

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Supporting Information

Materials and Methods:

Solvent preparation

The acetonitrile/methylamine (ACN/MA) composite solvent can be prepared through various routes. In this work, we have two different methods of introducing the methylamine into the ACN. For thin film and device studies, a solution of MA in ethanol (Sigma Aldrich, 33 wt%) was placed into an aerator which was kept in an ice bath. A carrier gas, N_2, was then bubbled into the solution, thus degassing the solution of MA. The MA gas which was produced was then passed through a drying tube filled with a dessicant (Drietire and CaO), before it was bubbled directly into the ACN (Sigma Aldrich) which contained the perovskite precursors (1 MAI: 1.06 M PbI_2) at a concentration of 0.5 M. The gas was bubbled into the black dispersion until the perovskite particles were completely dissolved resulting in a clear, light yellow solution as shown in the main manuscript (Figure 1). A schematic of the set-up is shown below.

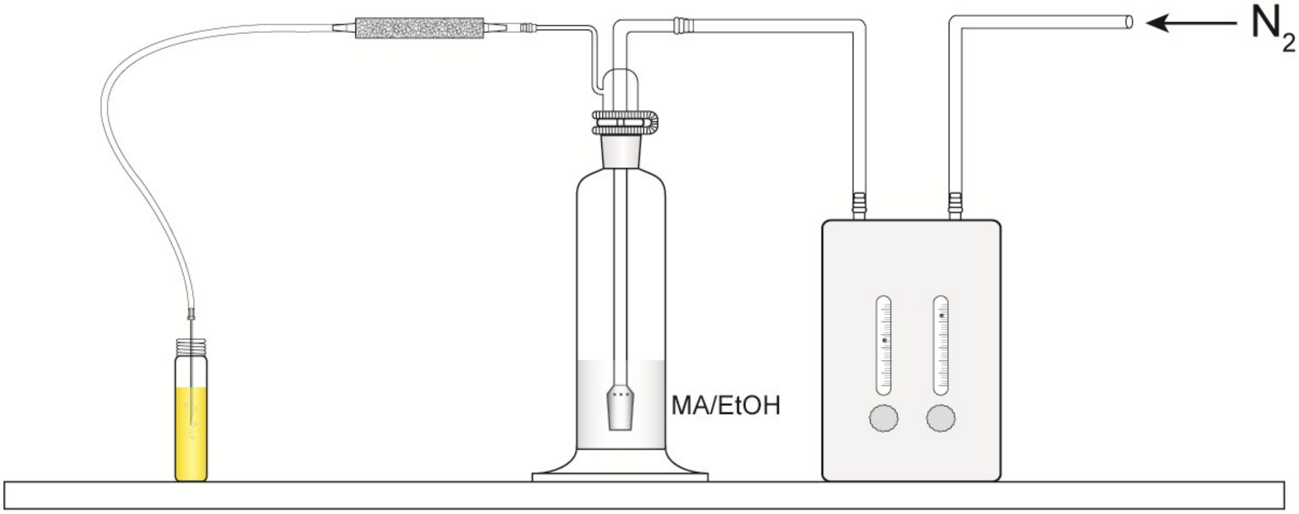


Figure S1: Schematic of the apparatus used for infusing MA into the ACN solvent to create the perovskite precursor solution.

After all particulates in the solution were dissolved, the vial was sealed with a septum cap and stored at 5 °C until needed. The solution can be kept for up to at least 4 months under these conditions without any noticeable loss in the performance of the subsequently fabricated devices. The solution was taken from the stock as needed, after which the vial was resealed and returned to the refrigerator.

For solvent characterisation, the solvent was prepared by condensing pure MA gas into the ACN. While this allows for a maximum concentration of 24 wt % to be achieved, this may represent a non-equilibrium concentration. For all solvent characterisations, the concentration used was 15 wt %. In this case, the mixed solvent was prepared as follows; acetonitrile was placed in a round bottom flask on a schlenk line and degassed by 3 cycles of freeze, pump, and thaw. The flask was then placed in a cooling bath of ethylene glycol and dry ice at -15 ^{o}C with the gas inlet tube beneath the liquid level of the acetonitrile. MA gas was introduced at a rate slow enough to ensure condensation on contact with the acetonitrile so that the MA was mixed with the acetonitrile in the liquid phase. At several points during the synthesis the apparatus was removed from the schlenk line and weighed to determine the added weight percentage of MA in acetonitrile. Aliquots of the solution were taken at each weight point to determine the density and test the dissolution of the precursor salts at different concentrations. At each weight point the solution was allowed to heat up to room temperature and the pressure monitored for the release of MA gas; the maximum concentration was determined as the point at which MA gas came out of solution when heated to room temperature. In order to check that this method of solvent preparation was comparable to the use of the carrier gas, devices were fabricated using the solvent thus prepared, and yielded equivalent power conversion efficiencies.

Viscosity Measurements

Viscosity was measured using a Brookfield DVI viscometer in a cone and plate geometry at 20 ^{o}C. Samples were tested at multiple rotation speeds and exhibited Newtonian behaviour.

Fabrication of n-i-p Devices

Briefly, FTO-coated glass sheets (7 Ω cm^{-1} Hartford Glass) were etched with zinc powder and HCl (3M) to obtain the required electrode pattern. The sheets were then washed with soap (2% Hellmanex in water), deionized water, acetone, and methanol, and finally treated under oxygen plasma for 10 min to remove the last traces of organic residues. All chemicals were purchased from Sigma Aldrich and used as received unless otherwise stated. A 100 nm thick compact layer of TiO_2 was then deposited on the glass using titanium isopropoxide (99.999% purity) diluted in anhydrous ethanol and sintered for 45 mins at 500°C. After the substrate was allowed to cool, a layer of C60 (10 mg/ml in 1,2-dichlorobenzene) or 1-Butyl-3-methylimidazolium tetrafluoroborate (0.01 wt % in MeOH) was deposited via spin coating at 3500 rpm for 30 s or 5000 rpm for 45 seconds respectively. The substrate was then heated at 80 C for 2 mins, and allowed to cool to room temperature before the deposition of the perovskite layer. After cooling, a 0.5 M solution of 1:1.06 MAI (Dyesol) to PbI_2 (99% purity) in the ACN/MA solvent was spincoated onto the substrate at 2000 rpm for 45 s, in dry air, resulting in the formation of a smooth, dense, perovskite layer. A post treatment of methylammonium chloride (MACl) was then carried out by dynamically spincoating 100 µl of MACl (Alfa Aesar, 5 mg/ml in isopropanol). The substrate was then heated at 100 C for 60 mins. After annealing, the substrates were allowed to cool to room temperature. The hole transporting material (HTM) 2,2′,7,7′-

tetrakis(N,N′-di-p-methoxyphenylamine)-9,9′-spirobifluorene (spiro-OMeTAD) was then dissolved in chlorobenzene with additives at a concentration of 30mM lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) and 80mM tert-butylpyridine (tBP). Lastly, 110 nm thick silver electrodes were evaporated onto the devices through a shadow mask, using a thermal evaporator.

Fabrication of p-i-n Devices

The FTO substrates and the hole-transporter (poly-TPD doped with 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ)) were prepared according to the method developed by Wang et al.[1] The perovskite film was deposited and treated in the same manner as above. A layer of phenyl-C61-butyric acid methyl ester (PCBM from Solenne BV, 20 mg/mL in chlorobenzene) was dynamically spincoated onto the perovskite film at 1.8 krpm for 30s, followed by annealing at 90°C for 10 mins. Once cooled to room temperature, a thin layer of bathocuproin (BCP from Alfa Aesar, 0.5 mg/mL in isopropanol) was dynamically spincoated at 4 krpm for 20s. Lastly, 110 nm thick silver electrodes were evaporated onto the devices through a shadow mask, using a thermal evaporator.

Fabrication of Large Area Perovskite Films

For the fabrication of the large area perovskite films, 1 ml of a 0.5 M $CH_3NH_3PbI_3$ solution in ACN was deposited onto the centre of the substrate which was then spun at 2000 rpm for 45 seconds. This process resulted in a highly specular perovskite film, which crystallises during spincoating.

Fabrication of Spectroscopy Samples

Spectroscopy samples were fabricated on cleaned, plasma etched glass. All samples were spin coated in dry air. For the $CH_3NH_3PbI_3$ samples, equimolar amounts of MAI (Dyesol) and PbI_2 (99 % purity) were dissolved in DMF or the ACN/MA mixed solvent at a concentration of 0.5 M. These solutions were then spincoated onto the cleaned glass at 2000 rpm for 45 s. In the case of the ACN/MA solvent, the samples were then annealed at 100 °C for a specific time ($0 \leq t_{anneal} \leq 75$ mins) while for the DMF, samples were annealed at the same temperature for 10 mins. For the ACN/MA samples, a post treatment of methylammonium chloride (MACl) was then carried out by dynamically spincoating 100 µl of MACl (Alfa Aesar, 5 mg/ml in isopropanol). For the $CH_3NH_3PbI_{3-x}Cl_x$ samples, MAI and $PbCl_2$ were dissolved in DMF at a 3:1 molar ratio, at a concentration of 38 wt %. The solution was then spincoated onto cleaned glass at 2000 rpm for 45 s, after which it was annealed at 100 °C for 2 hrs. Subsequent to the deposition of the perovskite layer, films were coated with a 1% solution of poly (methyl methacrylate). Films were typically stored in a desiccator in the dark for 12 hours before spectroscopic investigation.

Solar Cell Characterization

Solar cell performance was measured using a class AAB ABET solar simulator which was calibrated to give simulated AM 1.5 sunlight, at an irradiance of 100mW/cm^2. The irradiance was calibrated using an NREL-calibrated KG5 filtered silicon reference cell. Current-Voltage curves were recorded using a sourcemeter (Keithley 2400, USA). All solar cells were masked with a metal aperture which was used to define the active area of the devices, which in this case was 0.0912 cm^2 or 0.7 cm^2 as specified . All devices, like spectroscopy samples were stored in a desiccator in the dark for 12 hours prior to testing.

Optical Characterisation

Absorption spectra were recorded on a Varian Cary 300 Uv-Vis spectrophotometer. Steady-state and time-resolved PL measurements were acquired using a time-correlated single photon counting (TCSPC) setup (FluoTime 300 PicoQuant GmbH). Film samples were photoexcited using a 507nm laser head (LDH-P-C-510, PicoQuant GmbH) pulsed at frequencies between 0.3-10MHz, with a pulse duration of 117ps and fluence of ~30nJ/cm^2. The PL was collected using a high resolution monochromator and hybrid photomultiplier detector assembly (PMA Hybrid 40, PicoQuant GmbH).

Microscopy

The AFM images were obtained using a ThermoMicroscope M5 in contact mode and scanning over a range of 5 μm by 5 μm at a resolution of 256 × 256 data points. The surface roughness was measured as the root mean-squared roughness over the scanning area.

A field emission SEM (Hitachi S-4300) was used to acquire SEM images. The instrument uses an electron beam accelerated at 10–30 kV, enabling operation at a variety of currents.

Thickness Homogeneity

We measured thicknesses using a spectral reflectance instrument (F20, Filmetrics). The data was fitted with a model consisting of a $Si/SiO_2/MAPbI_3$/air optical stack. The goodness of the fit was above 98 % and the optical constants for $MAPbI_3$ were taken from Loeper et al.[2]

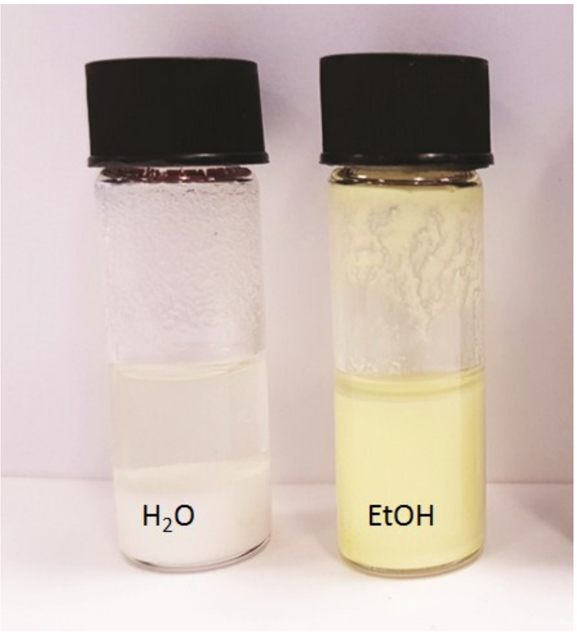


Figure S2: Dispersions of perovskite precursors in solvent mixtures of H_2O/MA and ethanol (EtOH)/MA.

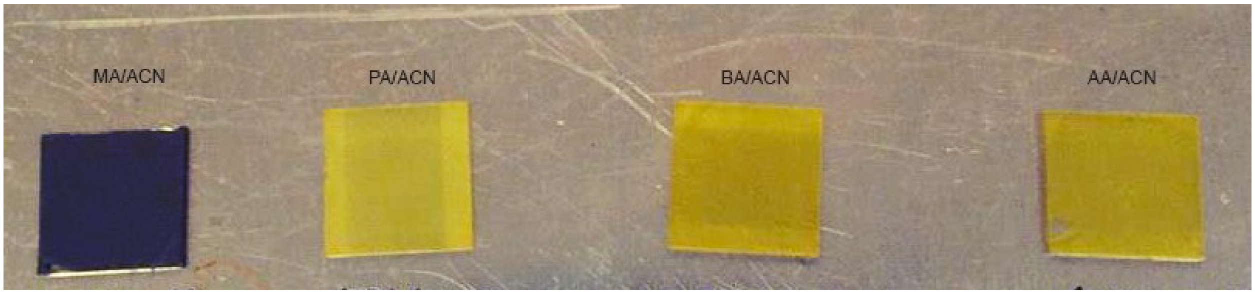


Figure S3: Films spincoated from ACN/MA, propylamine (PA)/ACN, butylamine (BA)/ACN and pentylamine (AA)/ACN.

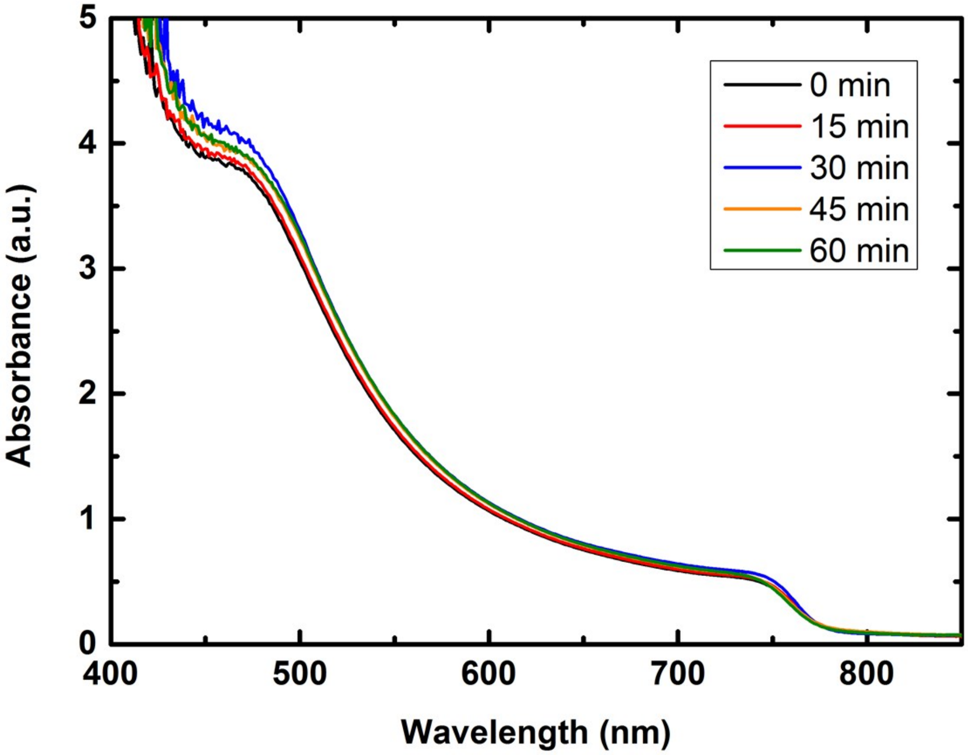


Figure S4: Dependence of the absorbance of $CH_3NH_3PbI_3$ films, deposited from an ACN/MA solvent, on annealing time.

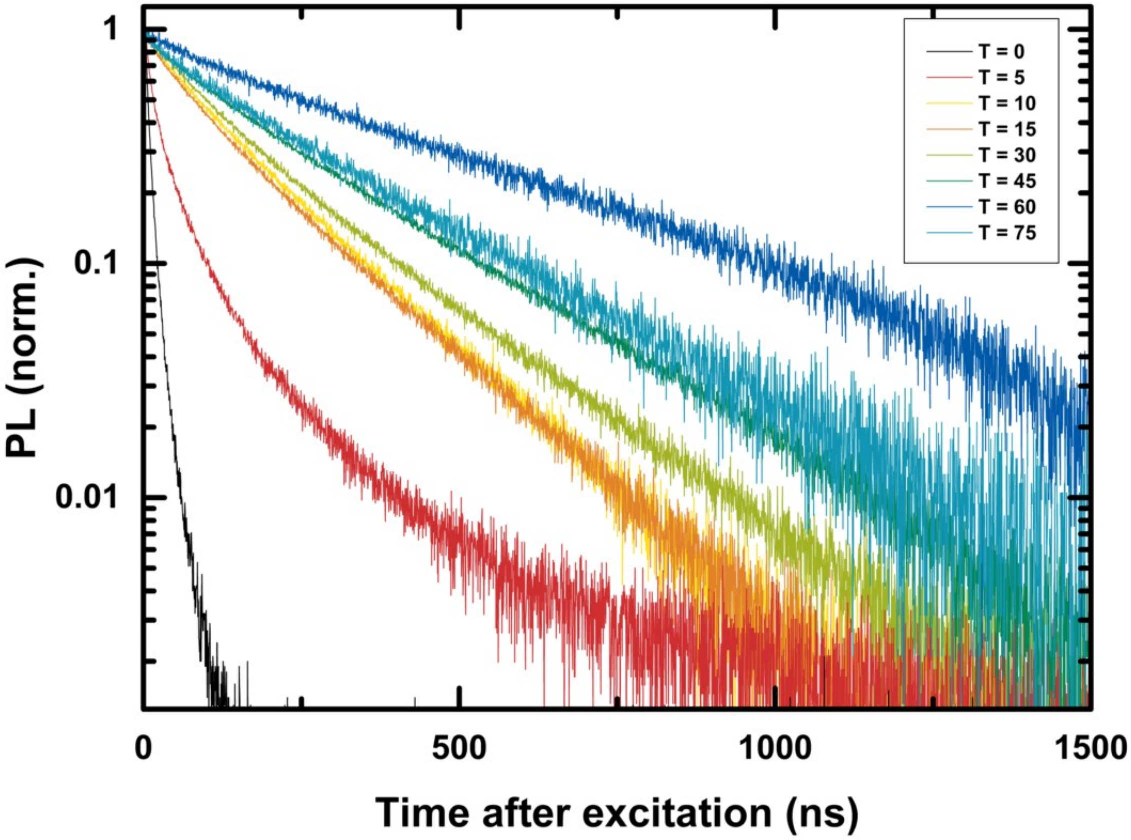


Figure S5: Photoluminescence decays of $CH_3NH_3PbI_3$ films with different annealing times. All films were deposited from a precursor solution in ACN/MA.

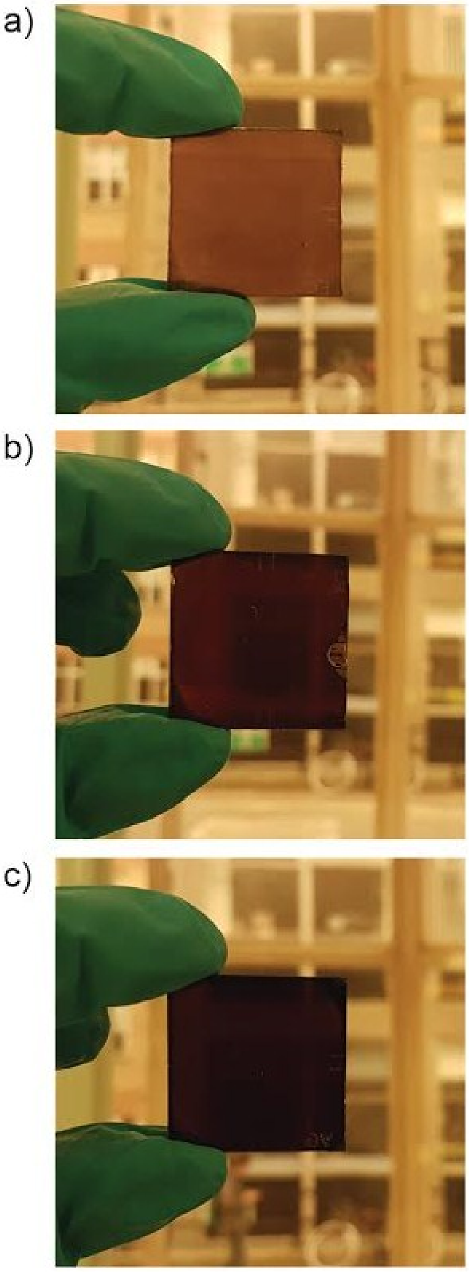


Figure S6: Films of $CH_3NH_3PbI_3$ perovskite spincoated from (a) an equimolar solution of MAI and PbI_2 in DMF (b) an equimolar solution of MAI and PbI_2 in DMF/DMSO, with solvent quenching (chlorobenzene) and (c) a 0.5 M solution of MAI: PbI_2 (1:1.06) in ACN/MA.

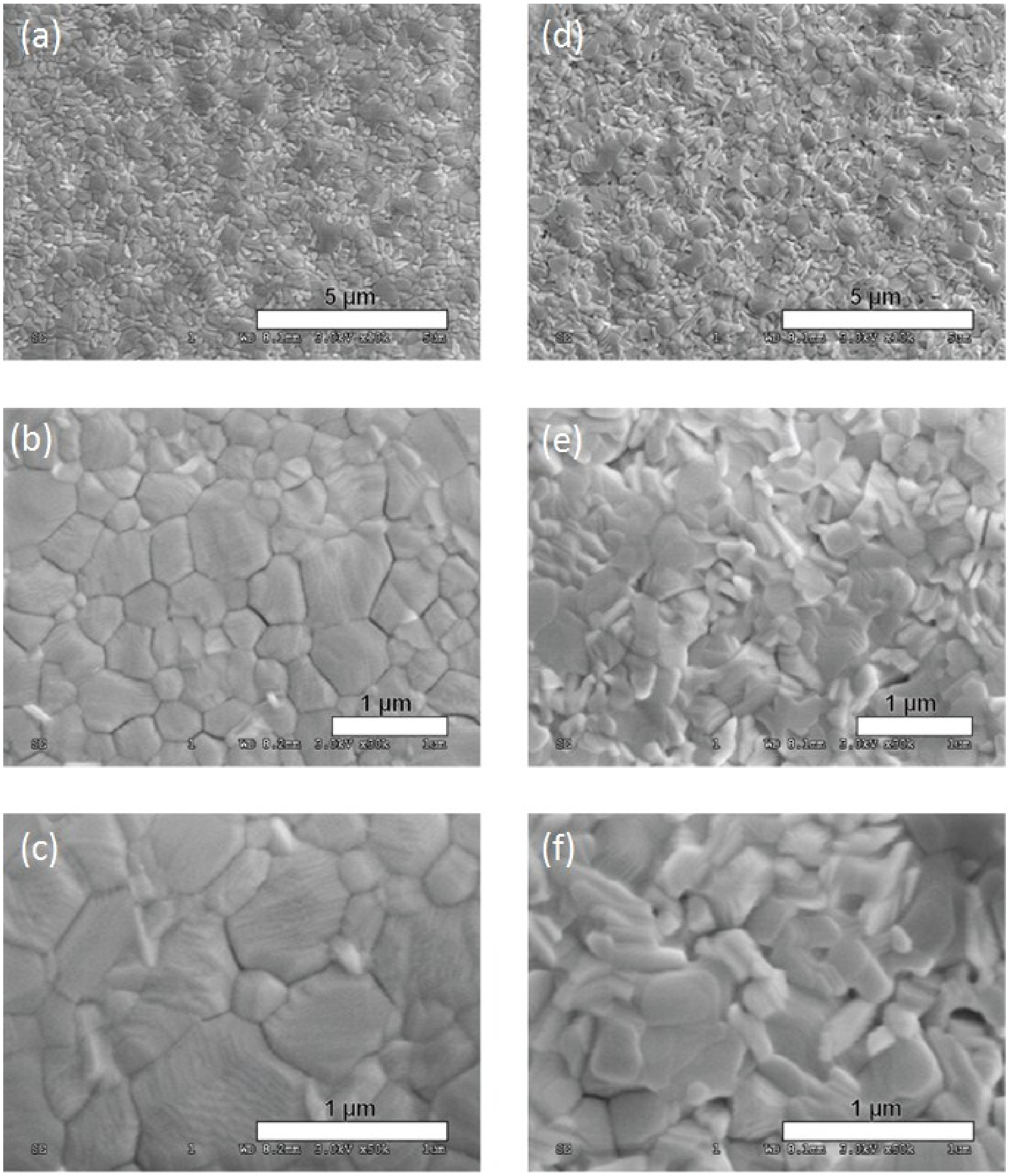


Figure S7: SEM images of $CH_3NH_3PbI_3$ films which were deposited from precursor solutions made with the ACN/MA solvent. (a)-(c) Bare films without MACl post treatment. (d)-(f) Films which have been subjected to a post treatment of MACl.

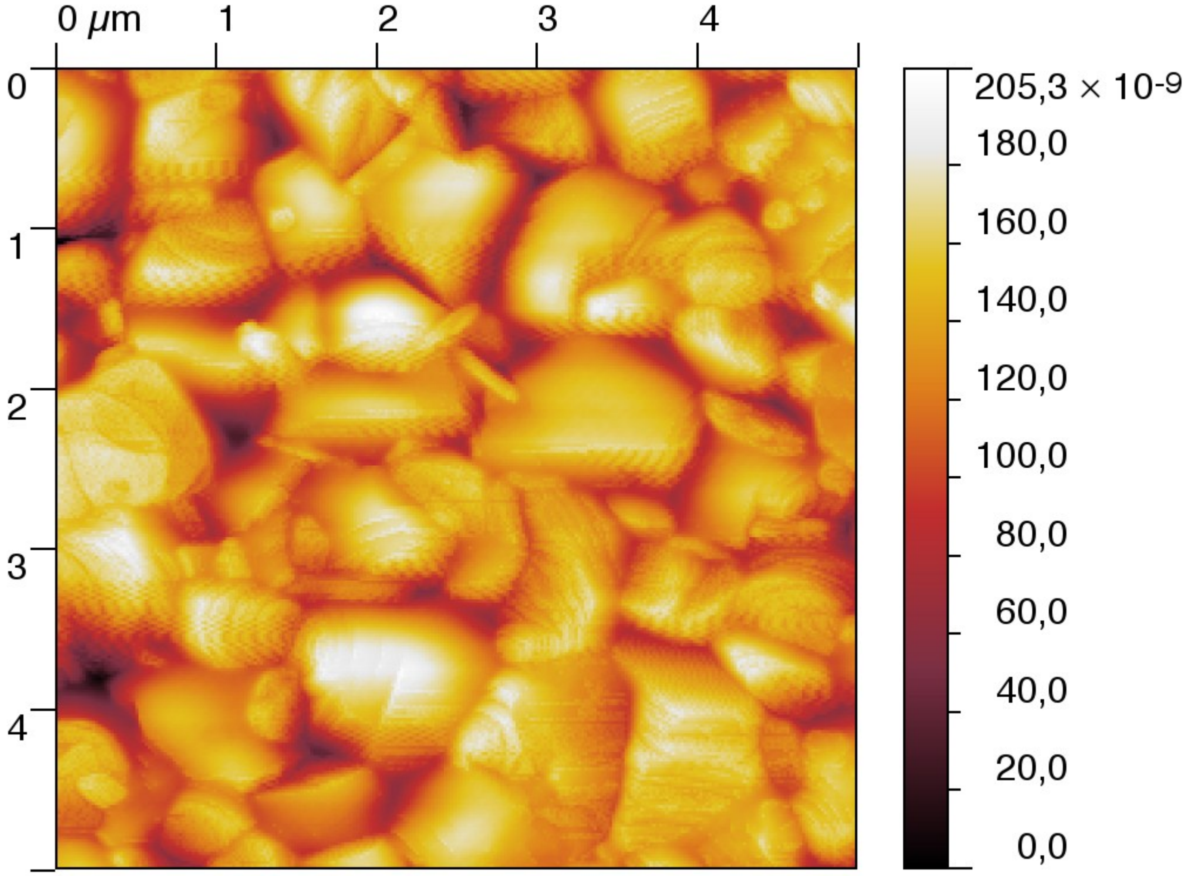
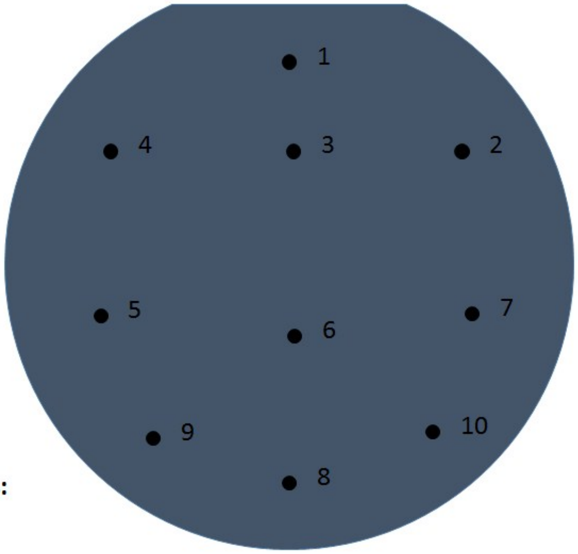


Figure S8: An AFM image of a film of $CH_3NH_3PbI_3$ fabricated using a solvent mixture of 4:1 DMF/DMSO, with solvent quenching. The measurement was taken over a 5 μm x 5 μm area in contact mode. The rms value for this measurement is 26.3 nm.

Spot #	$MAPbI_3$	SiO_2
1	326.3	34.05
2	332.1	31.34
3	328.5	37.17
4	325.2	32.24
5	324.3	33.92
6	330.9	40.00
7	328.5	34.45
8	345.9	31.84
9	325.5	33.70
10	328.8	32.72



Filmetrics parameters:
n, k from Loeper et al
$Si/SiO_2/MAPbI_3$/air
SiO_2, $MAPbI_3$ varied
range: 330-1100nm
Spectrum matching: robust

Results:
$MAPbI_3$ avg = 329.6 nm, sdev = 6.25 nm
SiO_2 avg = 34.14 nm, sdev = 2.64
Goodness of fit > 98%

Figure S9: Thickness Homogeneity Measurements.

The $CH_3NH_3PbI_3$ film was spincoated from that ACN/MA solution onto a Si substrate of 10 cm diameter. The variation in film thickness was then investigated by probing 10 different spots on the film. The results of this investigation are summarised in Fig.9, where the thickness variation across the entire film was found to be ± 6.25 nm for a 330 nm thick film.

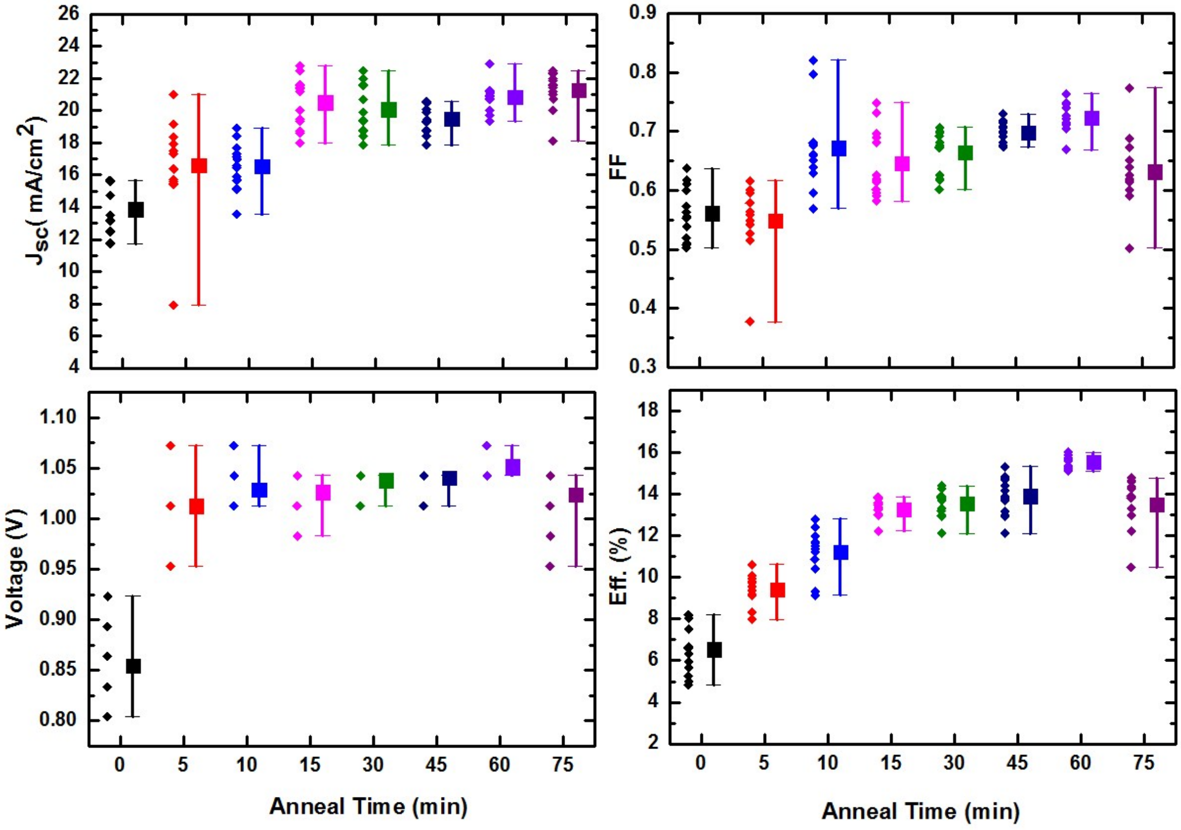


Figure S10: Evolution of device performance with increasing annealing time.

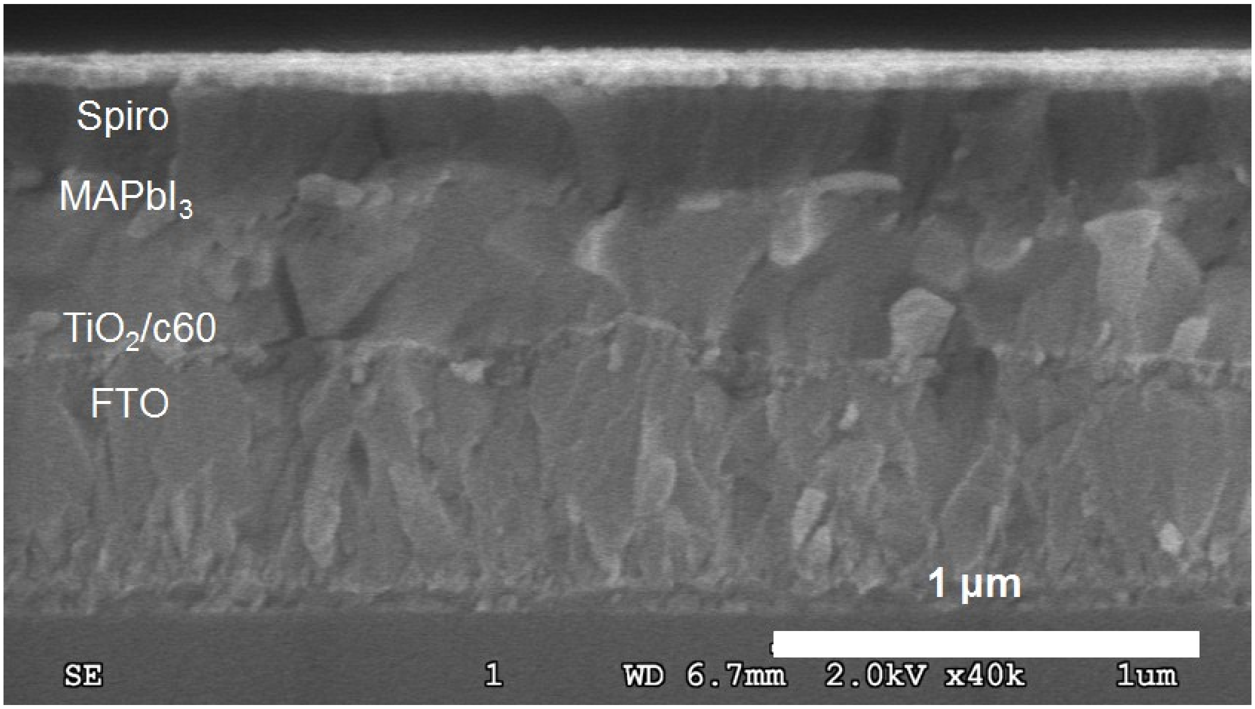


Figure S11: Cross-Sectional SEM image of a device fabricated using the ACN/MA solvent system.

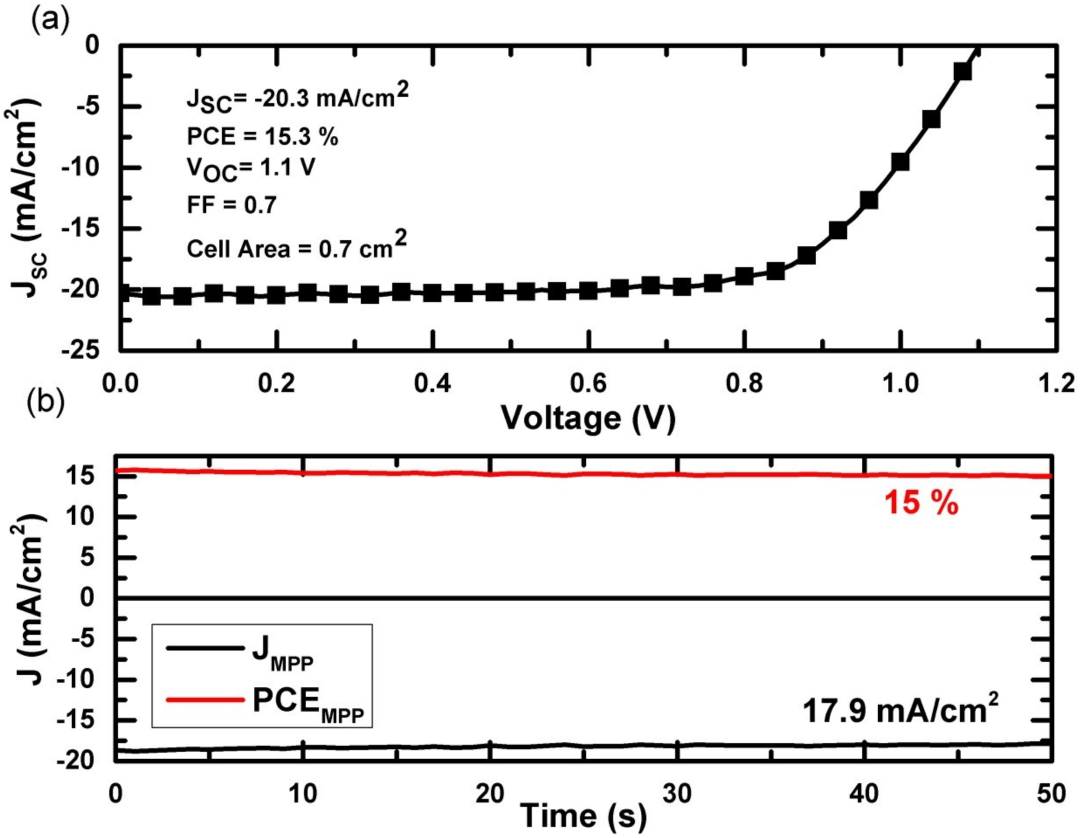


Figure S12: Current-Voltage curve of a 0.7 cm^2 p-i-n device, where the active layer is fabricated using the ACN/MA compound solvent. The JV curve was fit to a characteristic diode equation as outlined in Cristoforo et al.,[3] in order to extract R_s and R_{sh} which gave values of 1.7 Ω·cm^2 and 1186 Ω·cm^2 respectively.

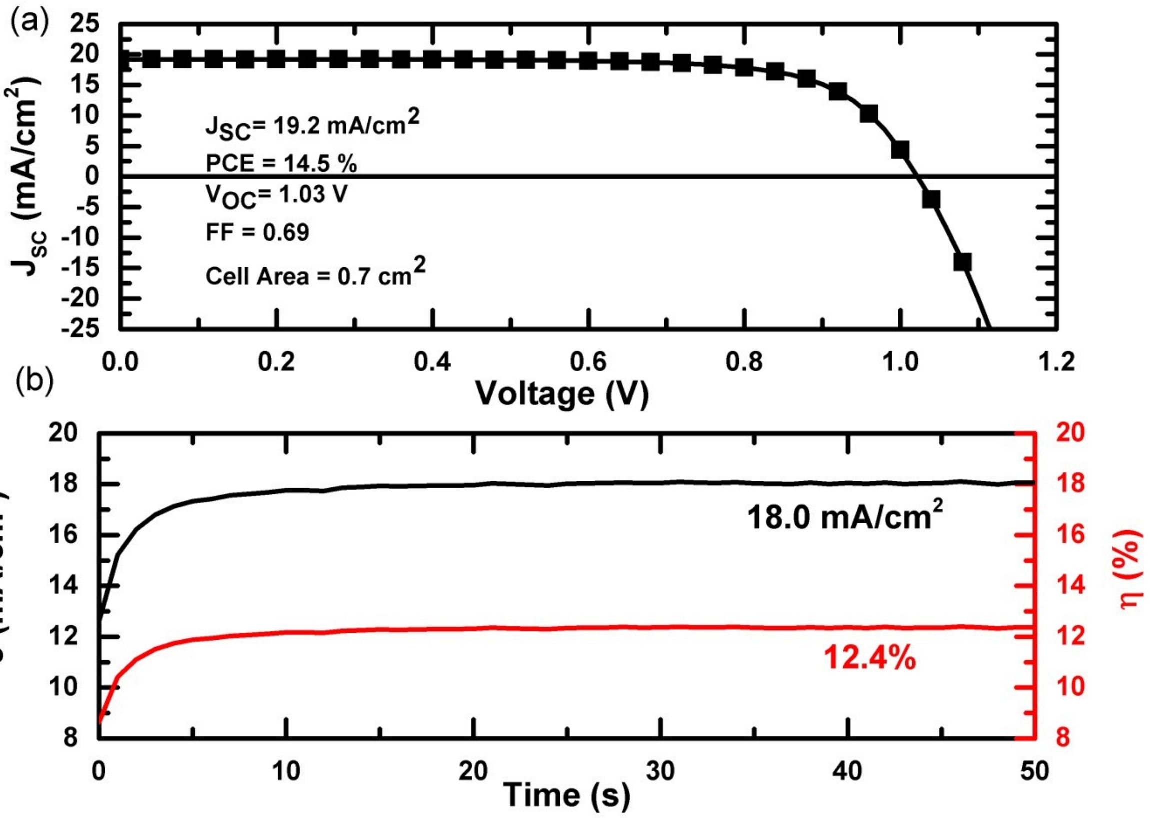


Figure S13: Current-Voltage curve of a 0.7 cm^2 n-i-p device, where the active layer is fabricated using the ACN/MA compound solvent. The JV curve was fit to a characteristic diode equation as outlined in Cristoforo et al.,[3] in order to extract R_s and R_{sh} which gave values of 1.5 Ω·cm^2 and 1862 Ω·cm^2 respectively.

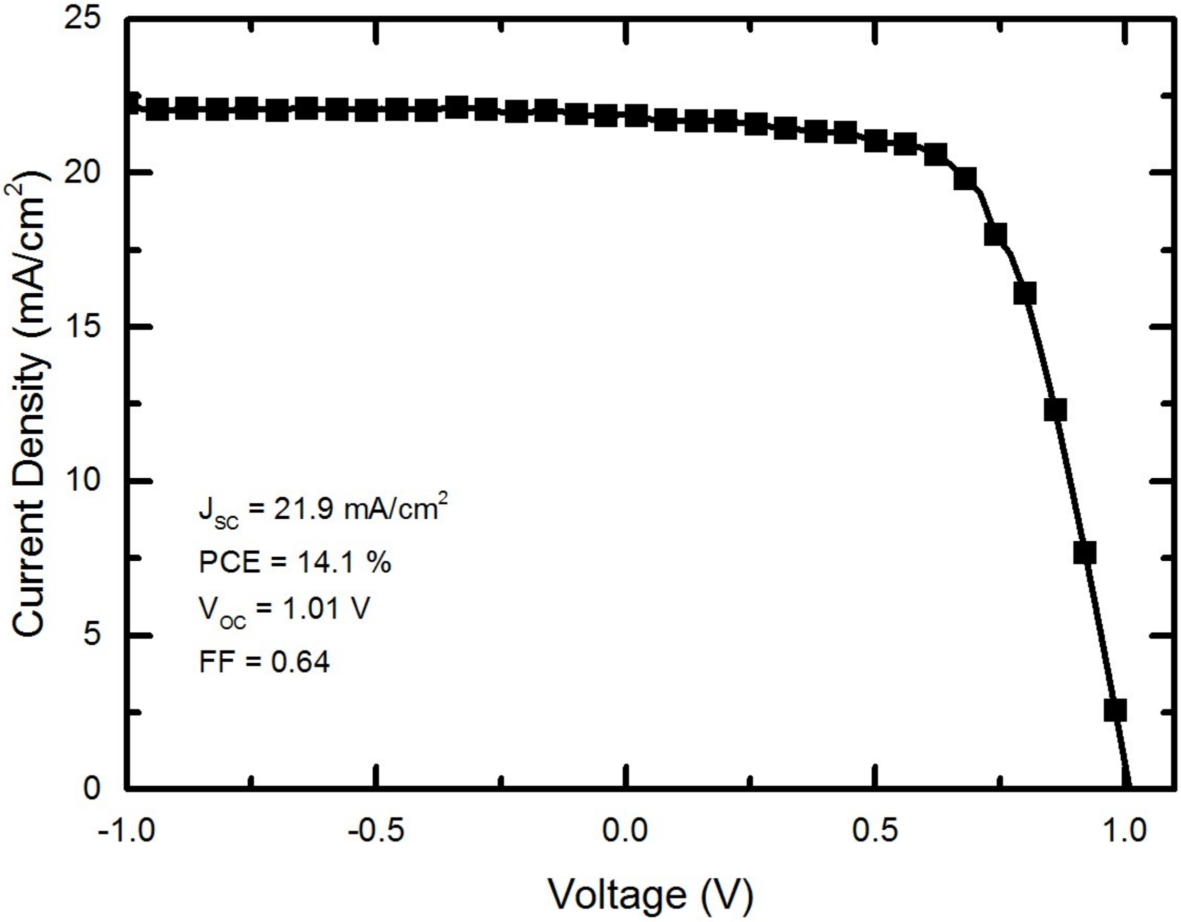


Figure S14: Current-Voltage curve of a 0.7 cm^2 device scanned from -1V.

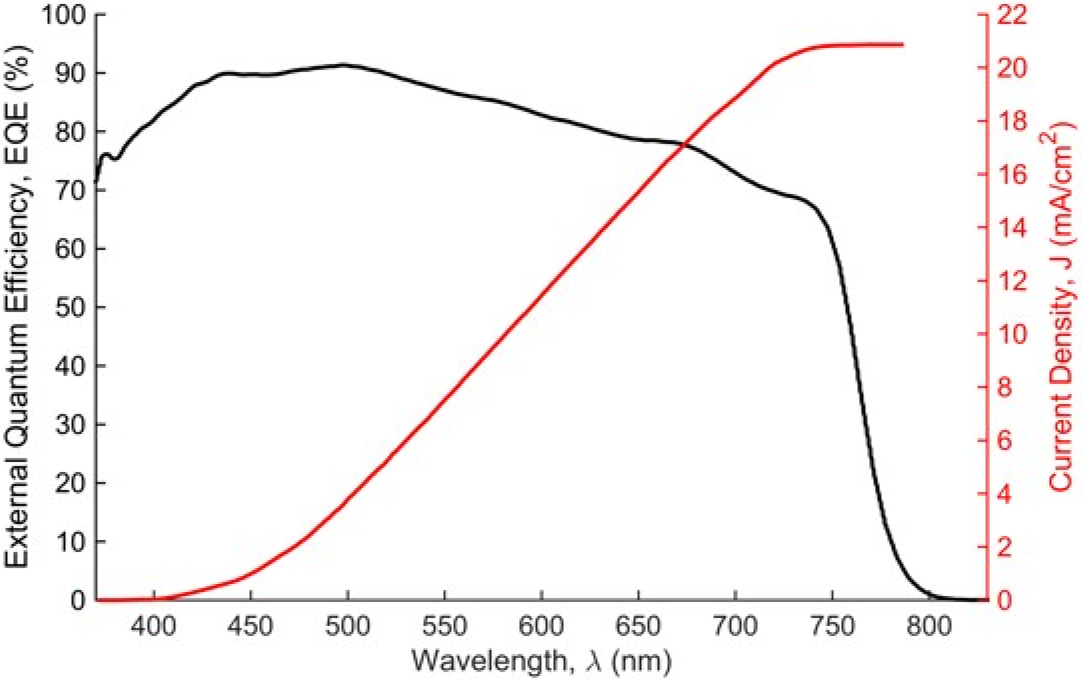


Figure S15: External Quantum Efficiency of the champion 19.0 % device, with an integrated J_{SC} of 20.8 mA/cm^2.

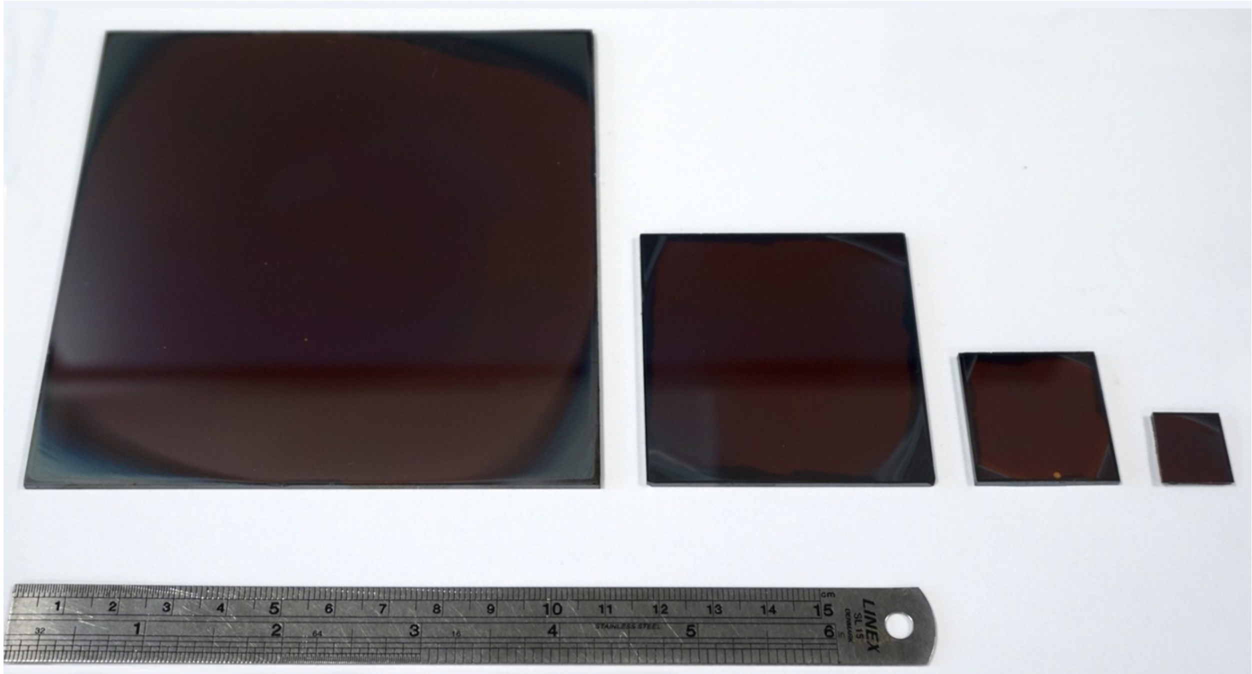


Figure S16: Films of $CH_3NH_3PbI_3$ spincoated from an ACN/MA solution. Substrates range from 1.44 cm^2 to 125 cm^2 (left to right).

References:

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3. M. Christoforo, E. Hoke, M. McGehee, and E. Unger, *Photonics*, 2015, **2**, 1101–1115.