Highly Crystalline Methylammonium Lead Tribromide Perovskite Films for Efficient Photovoltaic Devices

Nakita K. Noel,[1,2]* Bernard Wenger,[1] Severin N. Habisreutinger,[1†] Jay B. Patel,[1] Timothy Crothers[1] Zhiping Wang,[1] Robin J. Nicholas,[1] Michael B. Johnston,[1] Laura M. Herz,[1] Henry J. Snaith.[1]*

[1] Clarendon Laboratory, Department of Physics, University of Oxford, Parks Road, Oxford, OX1 3PU, UK.

[2] Department of Electrical Engineering, Princeton University, 41 Olden Street, Princeton, NJ, 08544, USA

Corresponding Authors: *nnoel@princeton.edu; henry.snaith@physics.ox.ac.uk

Current Address:

[†] National Renewable Energy Laboratory, Chemistry and Nanoscience Center, 15013 Denver West Parkway, Golden, USA

Supporting Information

Materials and Methods

Preparation of HPbBr$_3$:

To form a stable solution of MAPbBr$_3$ in the ACN/MA, we have used HPbBr$_3$ as the lead source. This was done through a modification of the synthesis of HPbI$_3$ described by Wang et al.[1] Briefly, PbBr$_2$ (98%, Alfa Aesar) and HBr (Sigma Aldrich) were added to DMF at 1:1.5 molar ratio. The solution was stirred at 50 °C for 3 hours until complete dissolution occurred, and a supersaturated solution was formed. The solution was then left to cool down naturally and then placed in the fridge overnight. The precipitate was then filtered and the supernatant discarded. The product was then dried at 40 °C and kept in a desiccator until use.

Preparation of the Precursor Solution:

Equimolar quantities of HPbBr$_3$ and CH$_3$NH$_3$Br (Dyesol Ltd.) were combined in a vial and anhydrous acetonitrile (Sigma Aldrich) was added, causing the formation of a yellow-orange powder. The powder was then dissolved by bubbling methylamine (33 wt% in EtOH, Sigma Aldrich) into the dispersion, as has been described elsewhere.[2] When the precursors were

completely dissolved, the solution was then filtered and kept in the refrigerator at 5 °C until required.

Preparation of $CH_3NH_3PbBr_3$ films for Spectroscopy:

Glass or quartz substrates were first washed with soap (2% Hellmanex in water), deionized water, acetone, ethanol and isopropanol, and finally treated under oxygen plasma for 10 min to remove the last traces of organic residues. The $CH_3NH_3PbBr_3$ precursor solution was spin-coated onto the substrate at 2000 rpm for 45 s in a nitrogen-filled glovebox. This results in the crystallization of a dense, thin film of $CH_3NH_3PbBr_3$. The substrates were then annealed at 100 °C for 45 min and subsequently allowed to cool down to room temperature. For treated films, choline chloride (Sigma Aldrich) was dissolved in isopropanol at the desired concentration (1, 5 or 10 mg/ml) and spin-coated onto the cooled perovskite film at 5000 rpm for 30 s. The films were then annealed for a further 10 mins at 100 °C. After the deposition of the perovskite layer, films were coated with a 1 wt.% solution of poly methyl methacrylate (Sigma Aldrich). Films were typically stored in a desiccator in the dark for 12 hours before spectroscopic investigation.

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 405 nm laser head (LDH-P-C-510, PicoQuant GmbH) pulsed at frequencies between 0.3-

10 MHz, 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).

Optical Pump Teraherz Probe Spectroscopy

Optical-pump THz-probe (OPTP) measurements were conducted using a Spectra Physics Tsunami-Empower-Spitfire Pro Ti:Sapphire regenerative amplifier. The amplifier provided pulses with a duration of 40 fs at a repetition rate of 1.1 KHz, and a centre wavelength of 800 nm. A 400 nm optical pump pulse was obtained by frequency doubling this output in a beta barium borate crystal. THz-probe pulses were generated using optical rectification in a 450 μm (110)-GaP crystal and were detected with electro-optic sampling in a ZnTe crystal (0.2 mm (110)-ZnTe on 3 mm (100)-ZnTe). Perovskite samples for THz mobility measurements were deposited on z-cut quartz substrates and measured in an evacuated chamber. Charge-carrier mobility values were determined by recording the percentage change in THz transmission caused by the optical-pump pulse, using excitation energies ranging from 4 -19 μJ/cm^2, as described previously.[3]

Device Fabrication:

Planar heterojunction solar cells were fabricated utilising previously published methods. Concisely, FTO-coated glass sheets (7Ωcm^{-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, ethanol and isopropanol, and finally treated under oxygen plasma for 10 min to remove the last traces of organic residues. A compact layer of SnO2 was then deposited on the glass using a modified version of the methodology presented by Anaraki et al.[4] Briefly, $SnCl_4.5H_2O$ was dissolved in isopropanol at a concentration of 0.05M and stirred at room temperature for 30 min. The solution was then spin-coated onto the substrates at 3000 rpm, after which the substrates were annealed at 180˚C for 1 hour before being left to naturally cool down to room temperature. The substrates were then immersed in a chemical bath, which consisted of $SnCl_2·2H_2O$ (Sigma-Aldrich) in deionised water (0.012 M), 20.7 mM urea (Sigma-Aldrich), 0.15 M HCl (Sigma-Aldrich) and 2.87 µM 3-mercaptopropionic acid (Sigma-Aldrich). The substrates were kept in an oven at 70 °C for 180 min, after which they were sonicated in deionised water for 2 minutes. They were then washed with ethanol and annealed at 250 °C for 60 min. After the substrates were cooled down to room temperature, the $CH_3NH_3PbBr_3$ films were deposited as described above, with or without the passivation treatment as required. Subsequently, the single-walled carbon nanotubes (SWNTs) were deposited dynamically through drop by drop spin coating (3000 rpm for 90 s). The hole transport material (HTM) was then dissolved in chlorobenzene (85 mg/mL with 80 mol % tBP), and was spin coated onto the perovskite substrates at 2000 rpm. 80 nm thick gold electrodes were then deposited under high vacuum (10^{-6}) through a shadow mask.

Current-Voltage Characterisation

Solar cell performance was measured using a class AAB ABET sun 2000 solar simulator that was calibrated to give simulated AM 1.5 sunlight at an irradiance of 100 mW/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 that was used to define the active area of the devices, which in this case was 0.0925 cm^2. All devices were stored in a desiccator in the dark for 12 h prior to testing.

External Quantum Efficiency Measurements

External quantum efficiency (EQE) was measured via custom build Fourier transform photocurrent spectrometer based on a Bruker Vertex 80v Fourier Transform Interferometer. Devices were illuminated with an AM1.5 filtered solar simulator. Devices were calibrated to a Newport-calibrated reference silicon solar cell with known external quantum efficiency. The devices were masked with a metal aperture with a defined active area, 0.0919 cm^2.
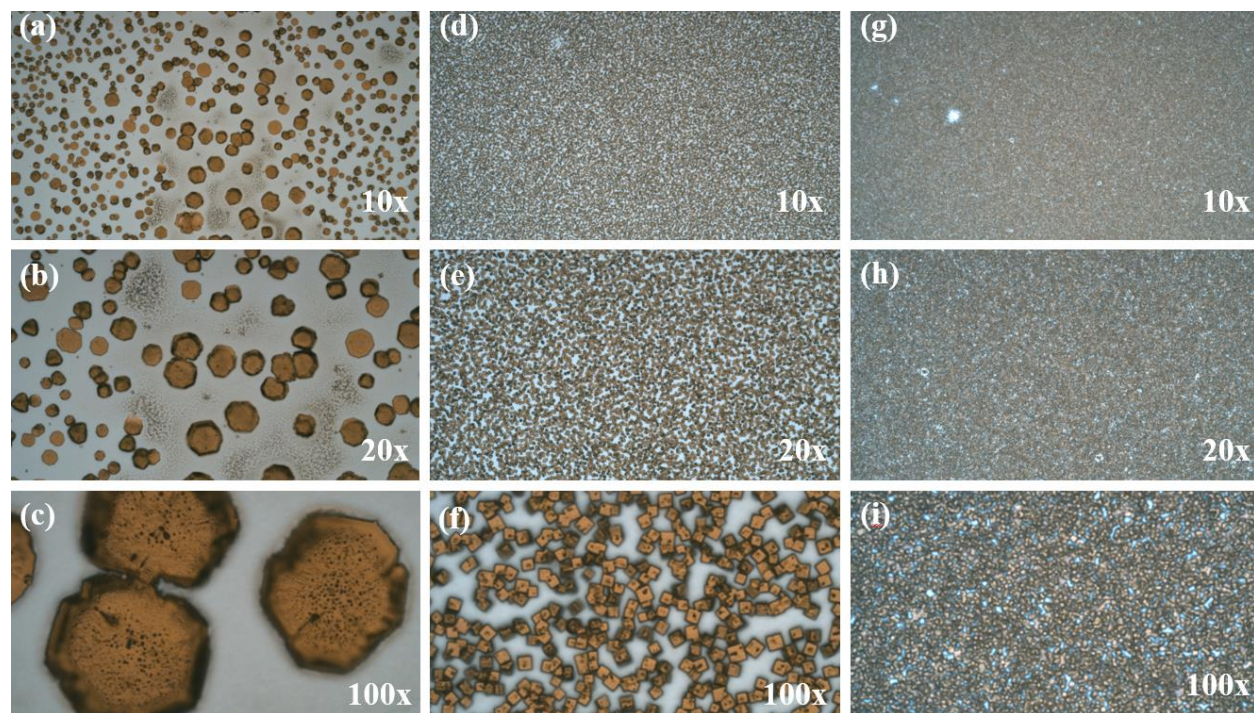
Figure S1: Optical microscope images of $CH_3NH_3PbBr_3$ films deposited from (a)-(c) neat DMF, (d)-(f) DMF + 50 µL HBr and (g)-(i) DMF + 100 µL HBr.
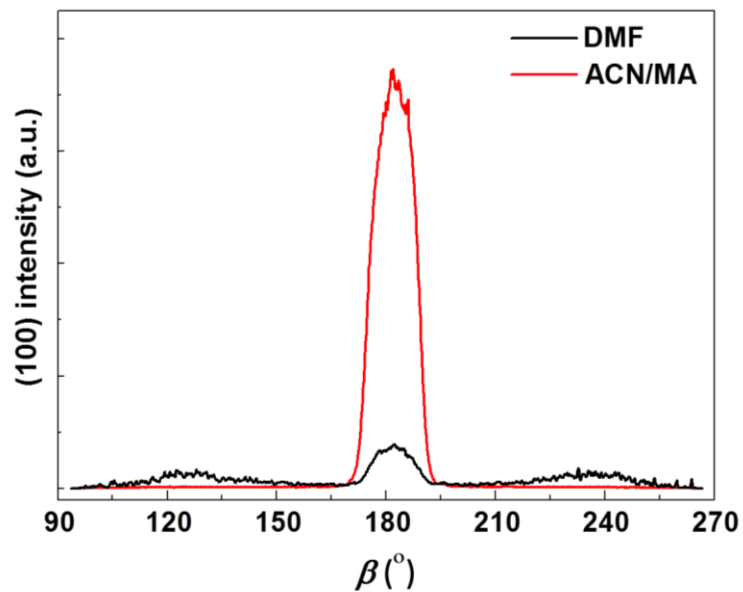
Figure S2: 100 diffraction peak intensity versus azimuthal angle β of the $CH_3NH_3PbBr_3$ films deposited from DMF and ACN/MA solvents.
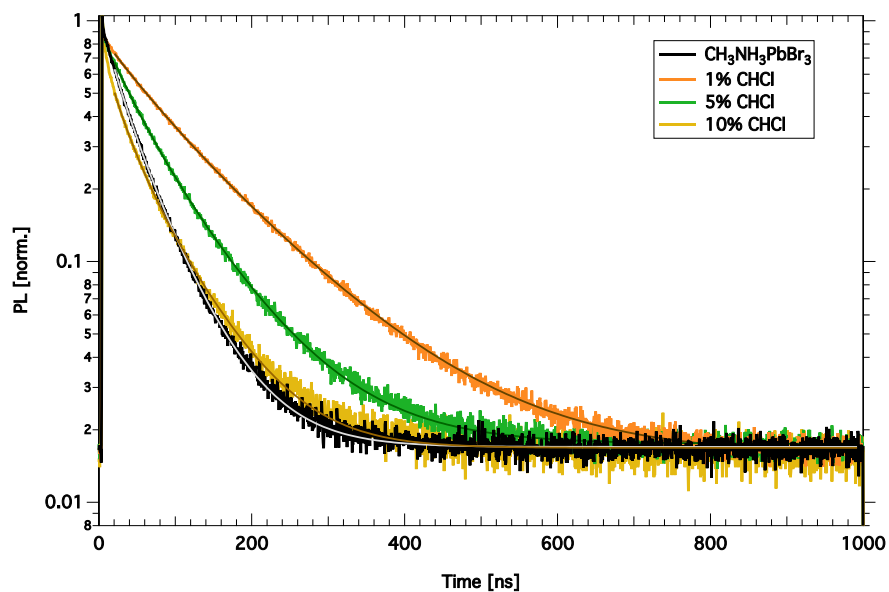

Figure S3: Photoluminescence decays of Figure 3b with monoexponential fits of the decay tails. The corresponding lifetimes are listed in Table S1.

	τ_{nr} [ns]	μ [cm^{2}V^{-1}s^{-1}]	D [cm^{2}s^{-1}]	L_D [µm]
ctrl	47	17.8	0.457	1.47
1% CHCl	111	17.3	0.444	2.22
5% CHCl	79	14.5	0.372	1.71
10% CHCl	51	13.7	0.352	1.34

Table S1: Summary of non-radiative lifetimes (τ_{nr}), THz mobility (μ), diffusion coefficients (D) and diffusion lengths (L_D).

To obtain quantitative information from the time-resolved photoluminescence measurements, we fit the tails of the decay with a single exponential function. At low carrier density, the recombination kinetics are usually governed by pseudo-first order non-radiative recombination processes. Here, we find good agreement with a single exponential decay and therefore can extract a non-radiative lifetime τ_{nr} from the fits. We then calculate the diffusion length $L_D = \sqrt{D \, \tau_{nr}}$, where D is the diffusion coefficients estimated from Einstein's relation $D = \frac{\mu \, k_B T}{e}$ where μ is the THz mobility, k_B Boltzmann's constant, T temperature and e the elementary charge.
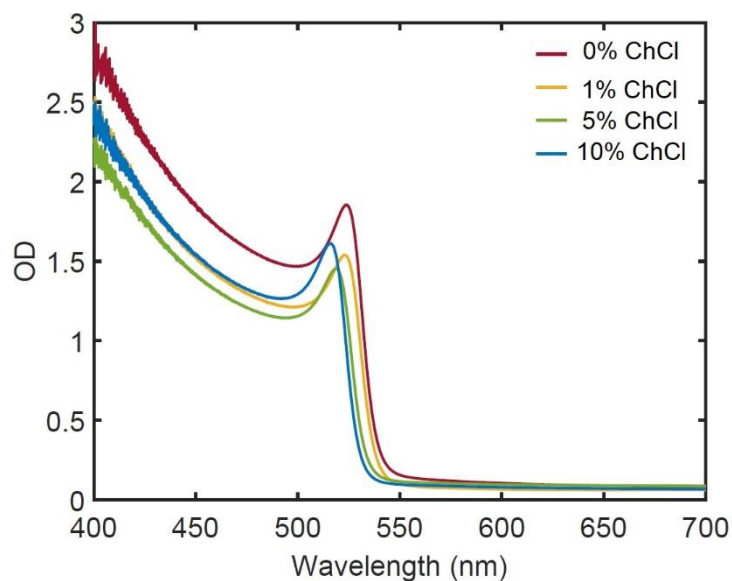
Figure S4: UV-Vis absorption spectra of neat and passivated MAPbBr$_3$ films. Films were subjected to a post treatment of choline chloride dissolved in isopropanol at 1, 5 and 10 mg/ml.
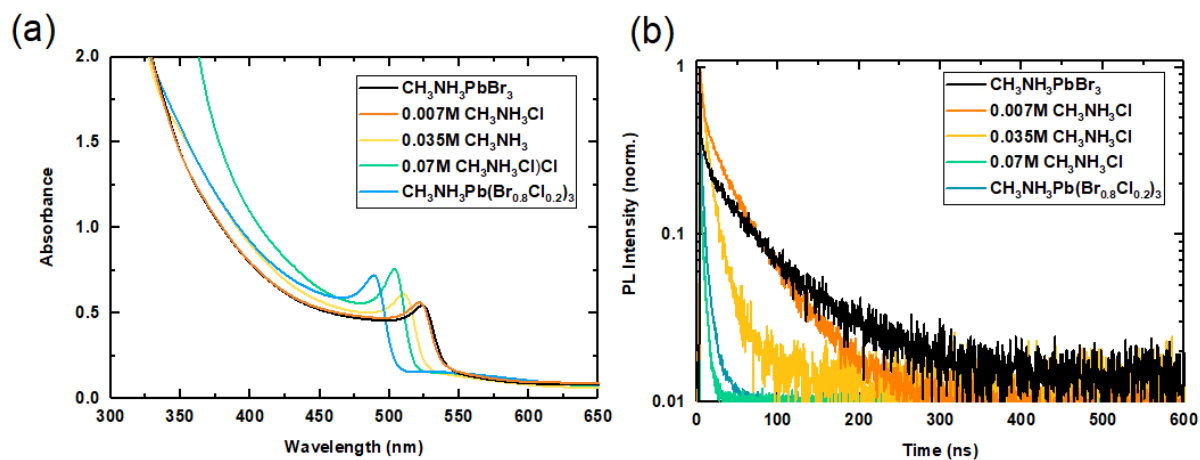

Figure S5: (a) UV-Vis absorption spectra and (b) Photoluminescence decays of CH$_3$NH$_3$PbBr$_3$ films subjected to post treatments of CH$_3$NH$_3$Cl dissolved in isopropanol.
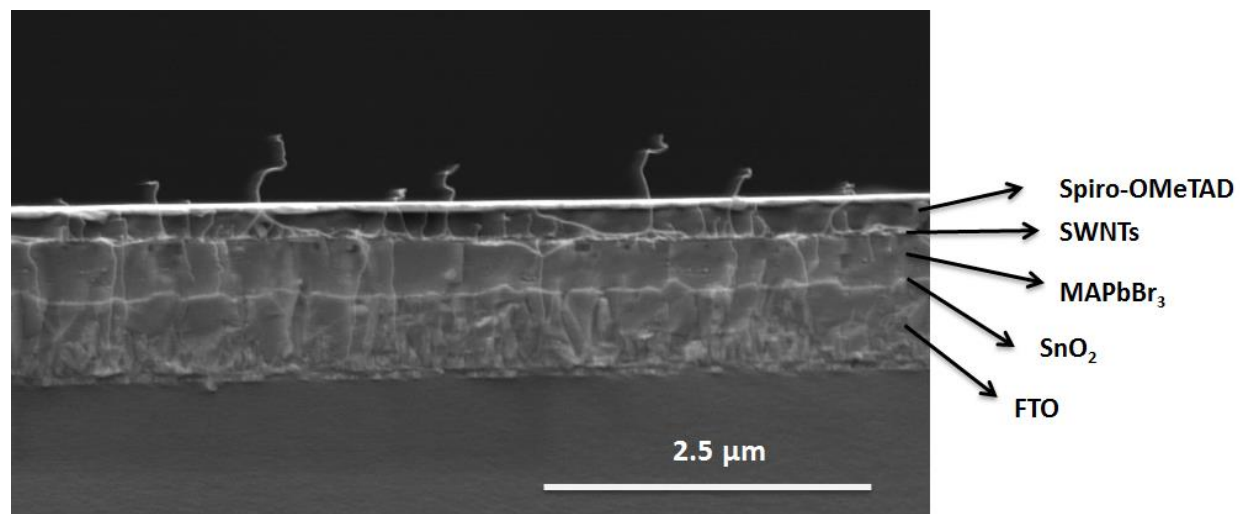
Figure S6: Cross-sectional scanning electron microscope (SEM) image of a typical CH₃NH₃PbBr₃ solar cell where the active layer has been deposited from the ACN/MA solvent system.
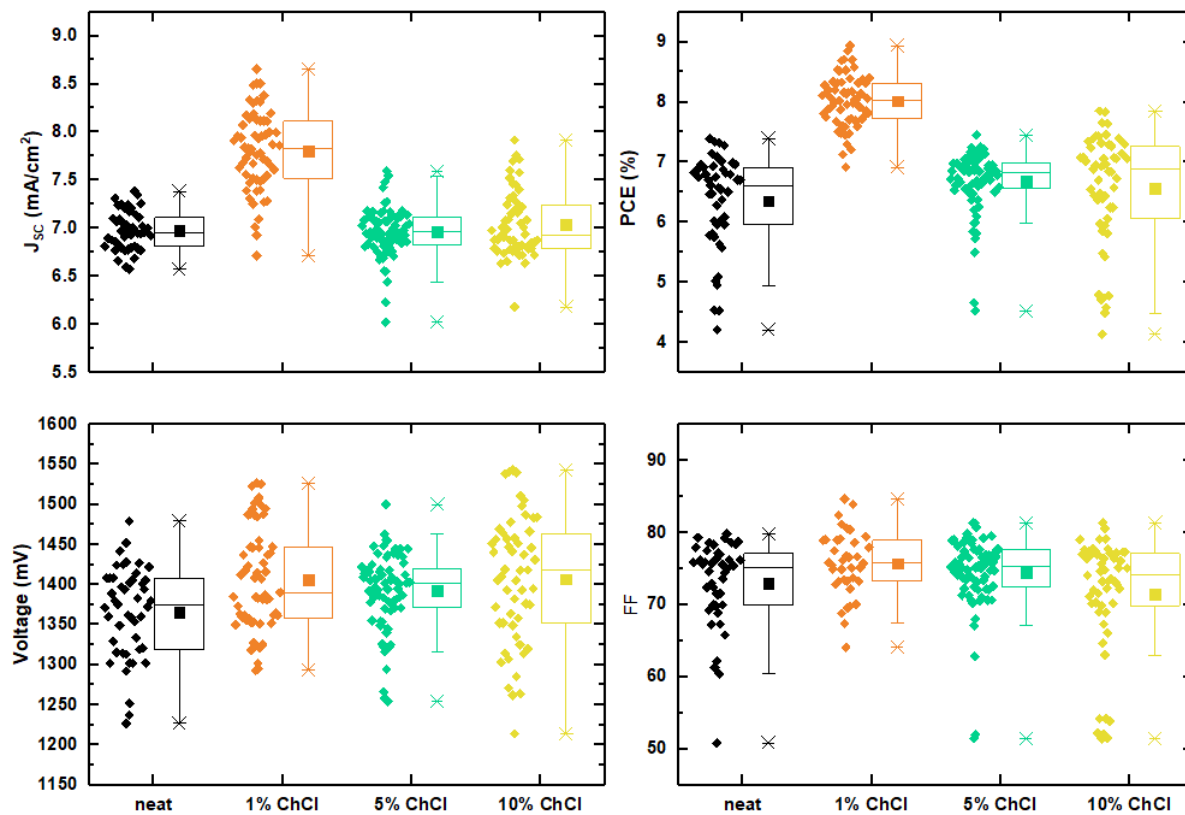
Figure S7: Device performance parameters of a batch of $CH_3NH_3PbBr_3$ devices, both neat and passivated with varying concentration of choline chloride (ChCl).

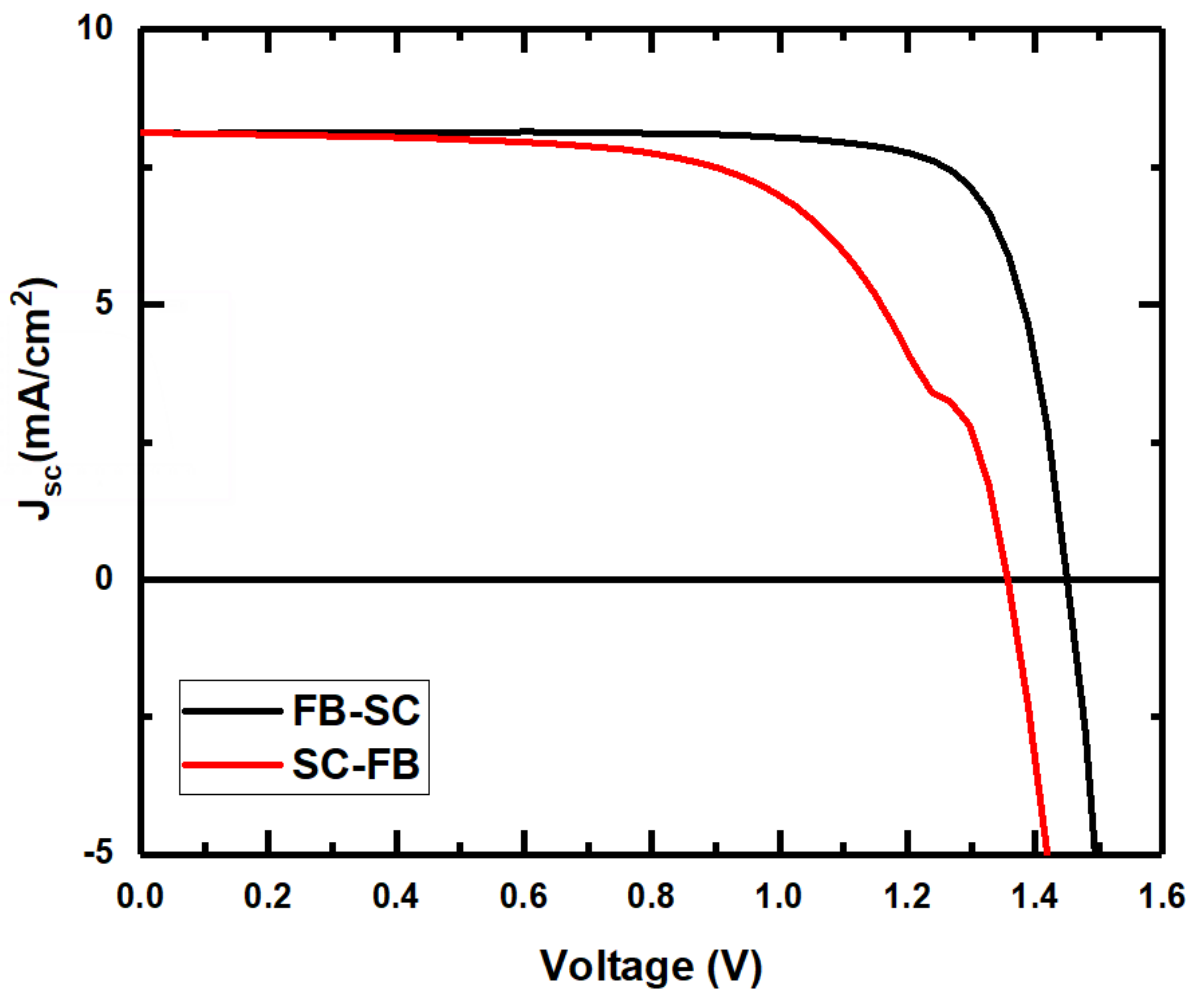**Figure S8:** Current-Voltage characteristics of a typical CH₃NH₃PbBr₃ device. SC-FB denotes the forward scan, from short circuit to forward bias, while FB-SC denotes the reverse scan, from forward bias to short circuit.
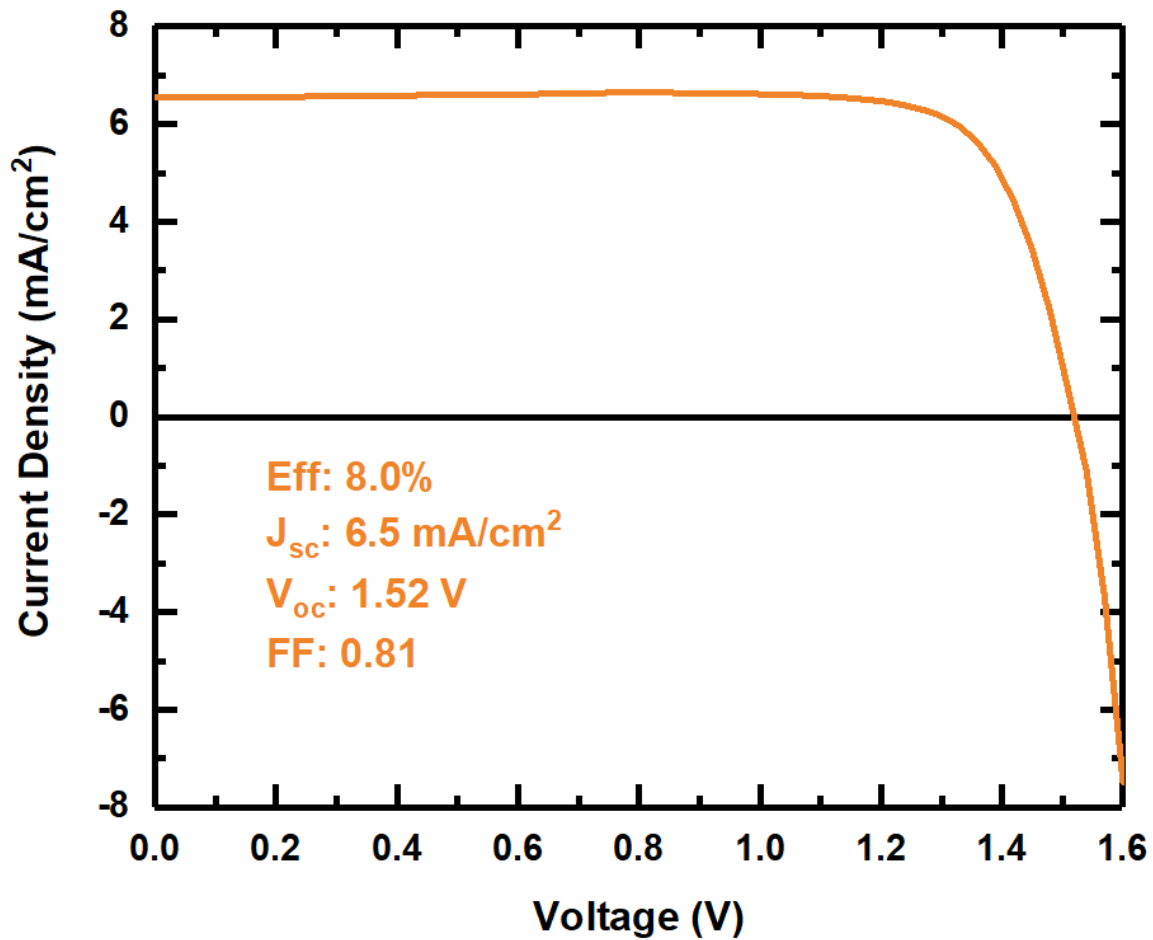
Figure S9: Current-Voltage characteristics of a high voltage $CH_3NH_3PbBr_3$ device, where the perovskite film was treated with a 1 wt.% solution of choline chloride (ChCl) in isopropanol.
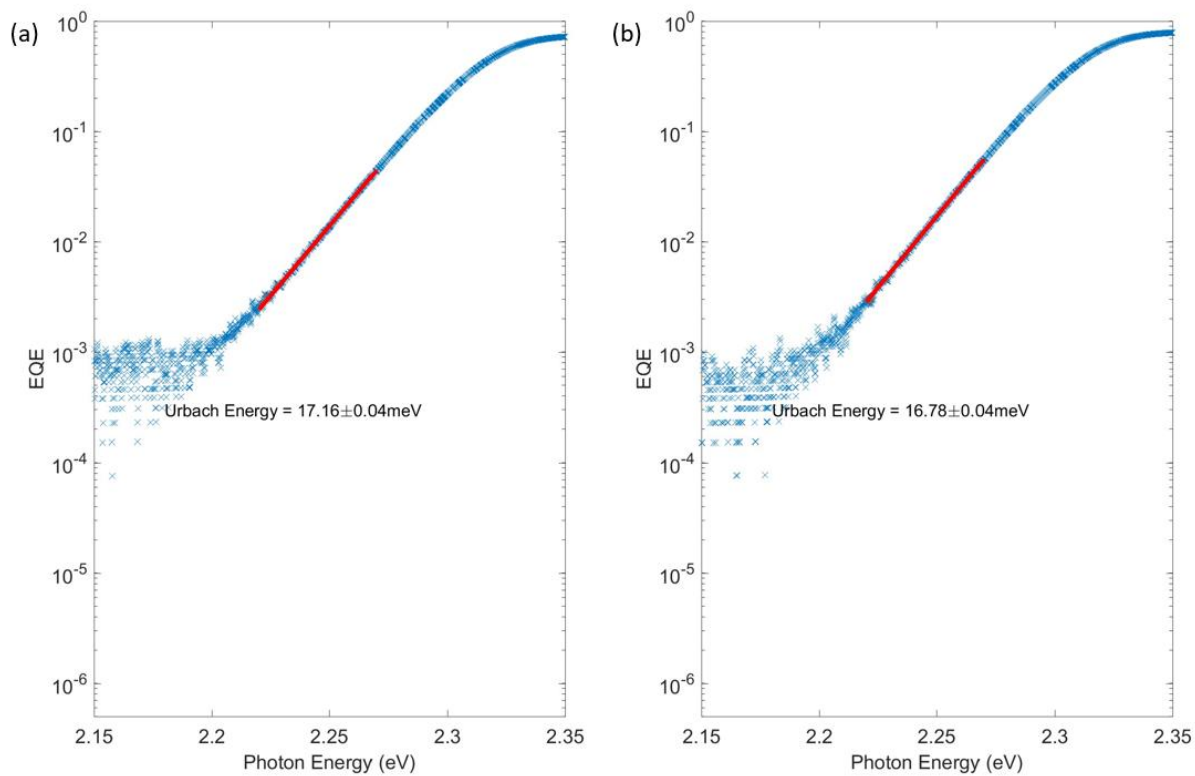
Figure S10: Determination of the Urbach energies of $CH_3NH_3PbBr_3$ devices made from (a) neat and (b) choline chloride treated perovskite films. Raw data is represented by blue crosses, and the fit is depicted with the solid red line.
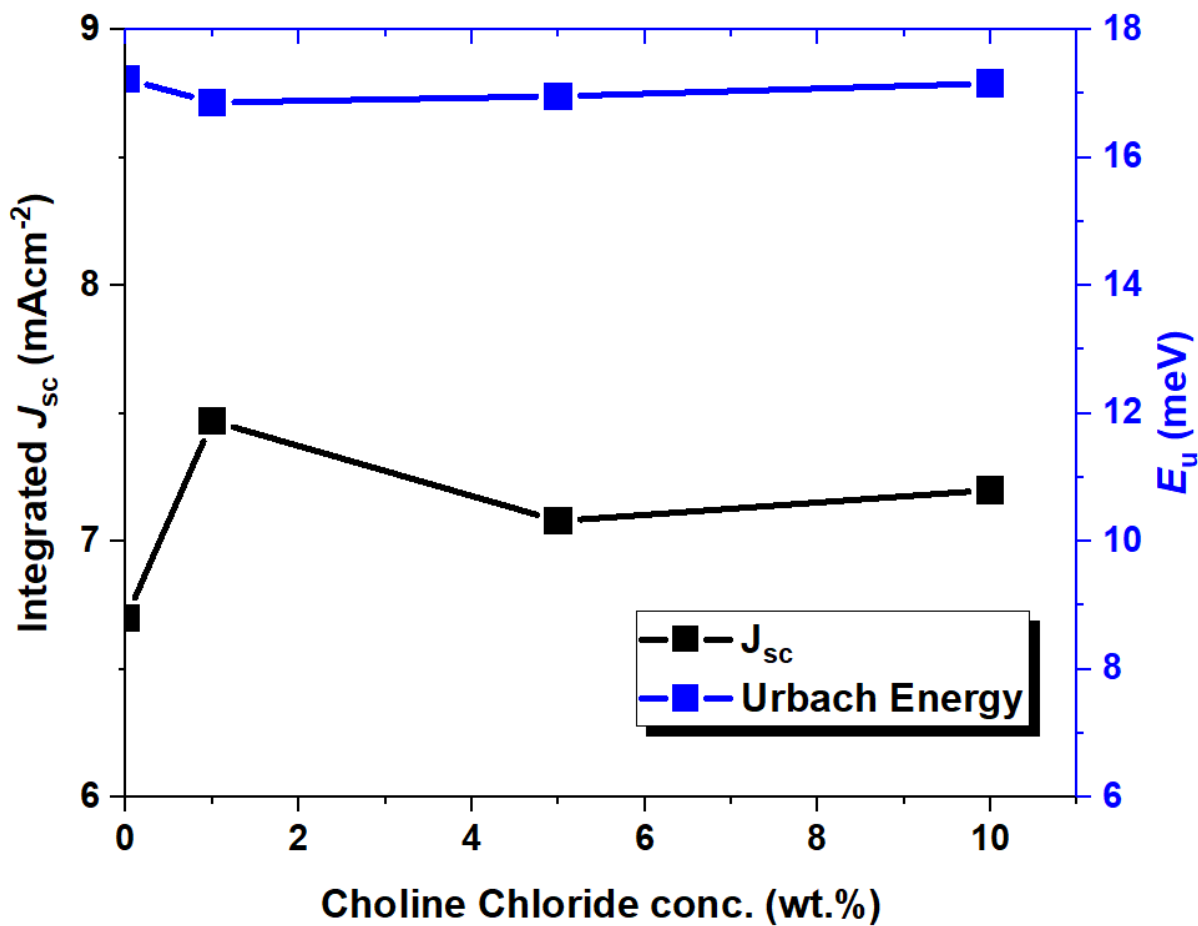
Figure S11: Integrated current density vs. choline chloride concentration for neat and treated CH$_3$NH$_3$PbBr$_3$ perovskite solar cells.

References

[1]   F. Wang, H. Yu, H. Xu, N. Zhao, *Adv. Funct. Mater.* **2015**, *25*, 1120.

[2]   N. K. Noel, S. N. Habisreutinger, B. Wenger, M. T. Klug, M. T. Horantner, M. B. Johnston, R. J. Nicholas, D. T. Moore, H. J. Snaith, *Energy Environ. Sci.* **2017**, *10*, 145.

[3]   T. W. Crothers, R. L. Milot, J. B. Patel, E. S. Parrott, J. Schlipf, P. Müller-Buschbaum, M.

B. Johnston, L. M. Herz, *Nano Lett.* **2017**, *17*, 5782.

[4]   E. H. Anaraki, A. Kermanpur, L. Steier, K. Domanski, T. Matsui, W. Tress, M. Saliba, A.

Abate, M. Gratzel, A. Hagfeldt, J.-P. Correa-Baena, *Energy Environ. Sci.* **2016**, *9*, 3128.