Supporting Information for:

"Single-Crystal-Like Optoelectronic-Properties of MAPbl₃ Perovskite Polycrystalline Thin Films "

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Experimental Details:

Perovskite Synthesis: The perovskite synthesis was performed in a nitrogen-filled glovebox. In all cases a 62 wt% perovskite precursor solution was used. PbAc₂x3H₂O (99.995 % purity, Sigma Aldrich) was mixed with methylammonium iodide (MAI, Dyesol) in a molar ratio of 1:3. The main solvent used was dimethylformamide (DMF, Sigma Aldrich) and the used additive was tetrahydrothiophene-1oxide (THTO, Alfa Aesar). For the solution preparation, it is very important to first add both precursors in the same vial and mix them until the mixture turns yellow to form the intermediate phase (IP) before dissolving it. The mixture can be easily dissolved at RT and should not be heated at any time, since heat destroys the IP very fast, which changes crystallization dynamics. For perovskite deposition, the solution was spin-coated dynamically at 5000 rpm for 3 min. Here, it is very important to use the minimum amount of solvent to cover the substrate. In our case, we used 50 μ L for substrate dimensions of 3cmx3cm. After spin-coating the film appears bright yellow and after 10 min of staying at RT, the films turn to the bright orange IP. After the IP was formed the film was transferred to the hotplate and annealed at 130 °C for 5 min to crystallize the perovskite. We have to note that the atmosphere in the glovebox is very crucial for perovskite nucleation and crystal growth, such as antisolvents like chlorobenzene (CB) can induce a faster perovskite nucleation and lead to smaller grain sizes.

Device fabrication: Fluorine-doped tin oxide (FTO, Pilkington, 7 Ω /sq) substrates were etched with 2 M HCl and zinc powder and cleaned in 2 % Hallmanex detergent, acetone, ethanol and were plasmacleaned in nitrogen plasma before deposition of charge transport layers.

A sol-gel approach was used to deposit the TiO₂ layer with a solution containing 0.23 M titanium isopropoxide (Sigma-Aldrich, 99.999 %) and 0.013 M HCl in isopropanol (IPA). The solution was spin-coated dynamically on top of the substrate at 2000 rpm for 45 s, dried at 150 °C for 10 min and annealed at 500 °C for 45 min. Afterwards, the substrates were transferred into a glovebox and a C_{60} monolayer with 0.5 mg/ mL 4-(1',5'-Dihydro-1'methyl-2'H-[5,6]fullereno-C60-Ih-[1,9-c]pyrrol-2'-yl)benzoic acid solution in CB (Sigma Aldrich) was spin-coated with 2000 rpm for 30 s on top and dried at 100 °C for 5 min. To achieve a better wetting of the perovskite solution, a 0.2 wt% IPA solution of Al_2O_3 nanoparticles (Sigma-Aldrich, < 50 nm particle size, 20 wt% in IPA) was deposited on top of C_{60} at 2000 rpm for 30 s and dried at 130 °C for 5 min.

The perovskite was deposited on top and a spiro-OMeTAD (99.6 % purity, Borun New Materials Technology Ltd.) layer afterward. We used a 75 mg/mL spiro-OMeTAD solution in CB with 3 vol% of 170 mg/mL bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI, Sigma-Aldrich) in acetonitrile (Sigma-Aldrich, anhydrous, 99.8%) and 1 vol% 4-*tert*-butylpyridine (TBP, Sigma-Aldrich, 96%). The solution was spin-coated at 1500 rpm for 45 s. The devices were stored for one day in a desiccator to oxidize the Li-TFSI additive in spiro-OMeTAD. To finalize the devices, a 40 nm thick Au counter electrode was thermally evaporated under high vacuum conditions (<10⁻⁷ mbar) through a metal aperture leading to devices in the range of 0.10 cm². The active area was determined with a 0.083 +- 0.001 cm² metal aperture.

Characterisation:

X-ray diffraction (XRD): Every XRD analysis was operated with a Cu K_{α} X-ray source. Films were deposited on TiO₂-coated FTO- coated glass and scans were obtained using a Bruker D8 Discover X-ray diffractometer with a position-sensitive detector (LynxEye) in Bragg-Brentano geometry. 2 θ scans from powder X-ray diffraction (PXRD) were obtained with an STOE Stadi MP diffractometer equipped with a DECTRIS MYTHEN 1 K solid-states trip detector.

Grazing Incidence Wide Angle X-ray Scattering (GIWAXS): GIWAXS data on the perovskite films was acquired with a Ganesha 300XL SAXS-WAXS system with a Cu K_{α} X-ray source. The incident angle was set to 0.4 ° which is well above the critical angle of MAPbl₃ so that the X-ray beam can penetrate the entire film. The measurement time was 10 h if not stated otherwise and the scattering signal was recorded with a Dectris Pilatus 300k pixel detector with automatic flat field correction positioned 106 mm behind the sample. Data treatment and reduction including solid-angle, efficiency, and polarization correction and reshaping of 2D images was conducted with the Matlab software GIXSGUI by Argonne National Laboratory. ¹

Scanning Electron Microscopy (SEM): A scanning microscope (FEI Helios NanoLab G3 UC) was used to acquire SEM images of perovskite layers prepared on TiO₂-coated FTO glass.

Transmission Electron Microscopy (TEM): TEM was performed on an FEI Titan Themis equipped with a field emission gun operated at 300 kV.

Device Characterization: Photovoltaic device performance was measured with a Keithley 2400 source meter in the air at 25 °C under illumination by a Newport Oriel Sol2A solar simulator, which was calibrated to 100 mW/cm⁻² with a Fraunhofer ISE certified silicon cell with a mismatch factor of 1.01.

The active area of the solar cell was defined with a square metal aperture mask of 0.0831 cm^2 . The devices were pre-biased at 1.5 V for 5 sec and measured with a scan speed of 0.2 V/s from 1.5 V to 0 V and back to 1.5 V.

To calculate the short circuit current from the EQE measurement, the AM 1.5G reference irradiance spectrum provided by the American Society for Testing and Materials was used (ASTM G173-03).



Time-of-Flight Measurement (TOF):

Scheme S1. Scheme of the experimental ToF setup. The generation of charges in the MAPbl₃ films is induced upon low-intensity pulsed laser excitation at 540 nm. The laser system consists of an optical parametric oscillator (OPO), pumped by a solid-state Nd: YAG laser with a repetition rate of 20 Hz and a pulse width of 7 ns. Perovskite thin films, contacted in a lateral architecture and top-coated with a thin PMMA layer to prevent moisture-induced degradation, were illuminated from the semitransparent glass/gold side at the margin of one contact by focusing the laser through a microscope objective (spot diameter approximately 2 μ m). An external DC field was applied through the Au electrodes exclusively during the measurement of the transient (timeframe of approximately 1 s). The



Figure S1: PXDR Analysis: a) comparison of the precursors MAI and anhydrous PbAc₂ with the mixture of both, which does not form a new phase; b) comparison of in water fully converted new phase from (hydrated) PbAc₂•3H₂O and MAI needle-shaped bright yellow crystallites and the powder scratched off from deposited film from precursor solution with 13 vol% THTO. Both agree very well with a calculated pattern in the P222 structure type; c) comparison of the precursors MABr and hydrated PbAc₂ with resulting new compound from mixing both solids which also agree with an orthorhombic structure type; d) SEM images of the synthesized needles of the IP.



Figure S2: In-situ XRD of spin-coated films, before and while annealing: a) film prepared from DMF solution; b) films prepared from DMF-based solution containing 20 vol% DMSO; c) films prepared from DMF based solution containing 9 vol% THTO; d) films prepared from DMF-based solution containing 13 vol% THTO; e) films prepared from DMF-based solution containing 13 vol% THTO; e) films prepared from DMF-based solution containing 13 vol% THTO; e) films prepared from DMF-based solution containing 13 vol% THTO; e) films prepared from DMF-based solution containing 13 vol% THTO; e) films prepared from DMF-based solution containing 30 vol% DMSO, Pb₃I₈ complex appears in XRD at 6.6°, 7.2°, 9.2° agreeing with [²].



Figure S3: SEM top-view images of films deposited on TiO_2/FTO -coated glass. a) intermediate phase 1 day after deposition; b) perovskite converted at RT over 1 week from intermediate phase; c) perovskite deposited from solution with 13 vol% THTO and annealed at 100 °C; d) perovskite deposited from solution with pure DMF solution (0 vol% THTO).



Figure S4: 2D GIWAXS investigation: a) 2D GIWAXS pattern of samples prepared from 13 vol% THTO solvent additive to the precursor solution, the boxes mark the positions for the cuts around the (002) and (004) reflection presented in b) Voigt functions were fitted at 44.8(3)° with FWHM = 2.0(7)° showing extremely narrow peaks and hence very narrow distribution of crystal orientations; c) 2D GIWAXS pattern of a film produced with pure DMF solvent (measured for 1 h).



Figure S5: XRD investigation of MAPbI₃ films prepared from different THTO concentrations.



Figure S6: TEM investigation of solar cell cross-section with on top, the image of full lamella composited from 21 images which were taken from left to right and the marked investigated areas underneath. Areas investigated with HRTEM are marked with a-n and correspond to the left to right direction of the cross-section in the downwards directions. Extracted FFTs of the HRTEMs are included with arrows in white indicating the area of the extracted FFT.



Figure S7: EDX mapping in TEM.



Figure S8: ToF analysis data: a) Extracted transit times for electrons from ToF analysis for perovskite films deposited with different THTO concentrations; b) Voltage series for 13 vol% THTO sample for a proof-of-principle for the acquired data in c); c) Voltage series for fixed gap sizes with 26 vol% THTO sample; c) representative transients for different electrode spacing for 13 vol% THTO sample.



Figure S9: a+b) JV curves of devices in different device architecture with straight lines for forward scan and dashed lines for reverse scan; c+d) Steady state power output under applied bias for different perovskite films and device architectures; e) EQE of a device with a perovskite film from 13 vol% THTO in the device architecture: $FTO/TiO_2/C_{60}/AI_2O_3/MAPbI_3/Spiro-OMeTAD/Au$.



Figure S10: a) Transmittance spectrum obtained from a film synthesized with 26 vol% THTO; b) photo of the same film.

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