Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2022

Preserving the Stoichiometry of Triple-Cation Perovskites by Carrier-Gas-Free Antisolvent Spraying

*Oscar Telschow[1,2], Miguel Albaladejo-Siguan[1,2], Lena Merten,[3] Alexander D. Taylor[1,2], Katelyn P. Goetz[1,2], Tim Schramm[1,2], O. V. Konovalov[4], M. Jankowski[4], Alexander Hinderhofer,[3] Fabian Paulus,[2] Frank Schreiber[3] and Yana Vaynzof[1,2]**

1. Integrated Center for Applied Physics and Photonic Materials, Technische Universität Dresden, Nöthnitzer Straße 61, 01187 Dresden, Germany

2. Center for Advancing Electronics Dresden (cfaed), Technische Universität Dresden, Helmholtzstraße 18, 01069 Dresden, Germany

3. Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen, Germany.

Corresponding Author

* E-mail: yana.vaynzof@tu-dresden.de

EXPERIMENTAL SECTION

Materials

Pre-cut glass 12x12 mm^2 substrates with a precoated central stripe of indium tin oxide (ITO) by Psiotec Ltd. were used as a substrate for device fabrication. Perovskite precursor solution was created with PbI_2 and $PbBr_2$ from TCI, CsI from Alfa Aesar and MAI (CH_3NH_3I) and FAI ($HC(NH_2)_2I$) from Greatcell Solar Materials. PCBM was purchased from Solenne BV and MeO-2PACz from TCI. BCP, TFT and all solvents were purchased from Sigma Aldrich. The materials, solvents and solutions were stored in a dry nitrogen atmosphere.

Solution preparation

MeO-2PACz was dissolved in anhydrous EtOH and the solution was sonicated for 15 min at 30 °C to 40 °C. The 1 mmol L^{-1} solution for spin coating was diluted from a 10 mmol L^{-1} stock solution.

The perovskite precursor solution was prepared in a sequential solution method, to assure a 1.155 M solution that is exactly stoichiometric. In the first step, the component salts were weighed into adequate vials. Then the inorganic salts, CsI, PbI_2 and $PbBr_2$, were dissolved in dimethylsulfoxide (DMSO) in the first case and a 4:1 mixture by volume of anhydrous *N,N*-dimethylformamide (DMF) to DMSO in the two latter cases at 180°C. After the salts dissolved completely and the solutions had cooled down, the CsI and $PbBr_2$ solutions were added to the PbI_2 solution in a volume ratio of 0.05:0.15:0.85 to obtain a 1.1 M inorganic stock solution of $Cs_{0.05}PbI_{1.75}Br_{0.3}$.

In a molar ratio of 0.95:1 the inorganic stock solution was added into vials with correctly weighed amounts of FAI and MAI. Then, the solution from the MAI vial was added into the FAI solution in a volume ratio of 1:5 MAI to FAI, yielding a 1.1 M solution of $Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.9}Br_{0.1})_3$.

For the electron transport layer (ETL), PCBM was dissolved in anhydrous chlorobenzene (CB) in an amber vial with a concentration of 20 mg mL^{-1}. To ensure the dissolution, the mixture was stirred in a nitrogen filled glovebox overnight with a magnetic stirring bar at 70 °C. Afterwards, the solution was filtered through a 0.45 µm PTFE syringe filter.

As a hole-blocking layer (HBL), Bathocuproine (BCP) was deposited by means of a 0.5 mg mL^{-1} solution in anhydrous IPA. The solution was prepared by stirring overnight at 70 °C via a magnetic stirring bar under inert atmosphere.

Device Fabrication

Photoresist was removed from the pre-patterned ITO substrates by rinsing with acetone (ACE) and deionized water (DIW), they were sonicated in soap water for 7 min at 40 °C. Afterwards the substrates were sequentially rinsed with and subsequently sonicated for 7 min at 40 °C in DIW, ACE and isopropyl alcohol (IPA) before being blown dry with nitrogen.

To finish off the cleaning process, the substrates were exposed to an oxygen plasma for 10 min, placed in samples boxes and transferred to a humidity-controlled glovebox (GB), where the hole-transport layer (HTL) and perovskite film were coated.

To fabricate the MeO-2PACz HTL, 35 µL of solution was spin-coated statically onto the substrate at 3000 RPM for 15 s, forming a self-assembled monolayer (SAM). Afterwards, the substrates were annealed for 10 min at 100 °C.

To create the perovskite film, 35 µL of the precursor solution was applied to the substrate before running a two-step spin-coating program. At first the substrate was spun at 1000 RPM for 10 s, then at 5000 RPM for 30 s. Anhydrous TFT (α,α,α-Trifluorotoluene) was applied to the spinning sample 10 s prior to the end of the fast spinning step.

In a nitrogen-atmosphere glovebox, 20 µL of PCBM solution were applied per sample. About 5 s to 10 s into a 30 s spinning process at 2000 RPM, the solution was cast dynamically with the pipette tip as close as possible to the sample. Finally, the samples were annealed for 10 min at 100 °C on a hotplate.

After cooling down, the samples were coated with BCP. 40 µL of solution were spin-coated dynamically during a 30 s, 4000 RPM spinning routine after 5 s to 10 s.

To form a top contact, 80 nm of 99.99 % pure silver (Ag) were deposited onto the samples by thermal evaporation from tungsten resistance-heated boats. Silver pellets were purchased from Kurt J. Lesker Company. The device area is set as the overlap of Ag contact and ITO stripe to be 4.5 mm^2. The deposition was executed in three steps, varying in deposition rate. The first 5 nm were evaporated at 0.01 nm s^{-1} in order to not harm the HBL and ETL. The next 25 nm were evaporated at 0.03 nm s^{-1} and the subsequent 50 nm were evaporated at 0.1 nm s^{-1}.

Adjusting the amount of deposited TFT

In this work, we utilised a pump spray bottle to dispense the antisolvent. In short, a pump mechanism creates a overpressure inside the spraying bottle and forces the antisolvent to leave the container through a thin pipe and a double conical nozzle at the top of the bottle, resulting in a uniform dispensing of the solvent into a fine mist. The spraying bottle was purchased from WUXI YIZHAO NETWORK TECHNOLOGY CO., LTD with a capacity of 30 mL.

A custom-made holder fixed the height and orientation of the spraying nozzle and thereby the spray cone with respect to the substrate to yield reproducible antisolvent deposition. The antisolvent was sprayed from either 1 cm or 2 cm height. To compare the investigated spraying of antisolvent with pipetting, the amount of antisolvent reaching the sample was determined. Calculations based on the opening angle of the spray cone and the weight loss of the spraying bottle per activation led to an calculated amount of 58 µL of TFT landing on the sample when spraying 2 times from 2 cm height and 210 µL of TFT when spraying 2 times from 1 cm above. Experimental validation agreed with these estimations, with variations of 10 µL to 20 µL observed. Therefore, spraying from 2 cm was compared to pipetting of 60 µL and spraying from 1 cm compared to pipetting of 200 µL antisolvent, respectively.

J-V characterization

The J-V setup uses an ABET TECHNOLOGIES Sun 3000 AAA solar simulator, shining light onto the electrical connection sample holder. Currents were measured with a Keithley 2450 SMU. To properly simulate solar AM 1.5 illumination and account for the spectral mismatch between solar simulator, solar spectrum, reference cell and DUI, the intensity was calibrated prior to every measurement with a NIST-traceable reference Si solar cell with a known spectral response. The resulting mismatch factor was approximately 1.1. Each sample contains 8 pixels with a pixel area of 1.5 mm × 3 mm. Under illumination, the current was measured during a voltage sweep from 1.2 V to 0 V and back with a step size of 0.025 V and a dwell time of 0.1 s after 2 s of light soaking at 1.2 V.

GIWAXS (Grazing-incidence wide-angle X-ray scattering)

The GIWAXS measurements were performed at the surface scattering instrument of ID10 beamline of the European Synchrotron Radiation Facility (ESRF), Grenoble (France). The GIWAXS data was recorded at the ESRF beamline ID10 with a photon energy of E = 22 keV. To account for preferred orientations, commonly found in perovskite thin films, we used GIWAXS to record reciprocal space maps by employing a 2D Pilatus 300 K detector. All measurements were performed under a nitrogen atmosphere. Incidence angles were varied from 0° to 0.3° to adjust the probing depth from few nanometers to hundreds of nanometers.

Scanning electron microscopy (SEM)

For SEM measurements the InLens detector of a ZEISS GeminiSEM 500 was utilized to yield images with a 5 nm resolution using 1.5 kV landing energy electrons on samples consisting of the HTL and perovskite layer. The samples were grounded using conductive silver paste on the ITO stripe to avoid sample charging.

UV-vis measurements

Absorption in the ultraviolet and visible range was measured with a SolidSpec-3700 spectrophotometer from SHIMADZU. After running a background measurement, a substrate with HTL and perovskite layer was placed in one beam path, while a similar substrate coated with only the HTL was placed in the reference beam path. The spectrum was measured from 850 nm to 400 nm with a step size of 2 nm and a time constant of 1 s.

Photoluminescence and PLQE

To measure PLQE, the samples were fixed in the beam path of a 532 nm laser operated at 5 mW inside a calibrated Labsphere 6 inch QE sphere integration sphere and measured utilizing an Ocean Optics QE65 Pro spectrometer, following the procedure described by De Mello *et al.*[1]

During the measurement the integration sphere was flushed with nitrogen in order to prevent oxygen or water molecules in ambient air from interacting with the perovskite surface. The samples were coated with HTL, perovskite, ETL and HBL.

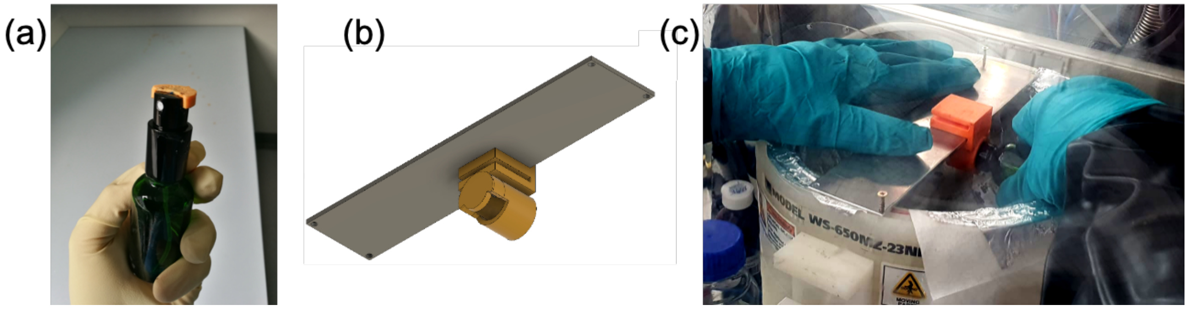

Figure S1. (a) a photograph of the spraying bottle, (b) schematic of the spraying bottle holder and (c) a photograph depicting the spraying procedure during spin-coating.

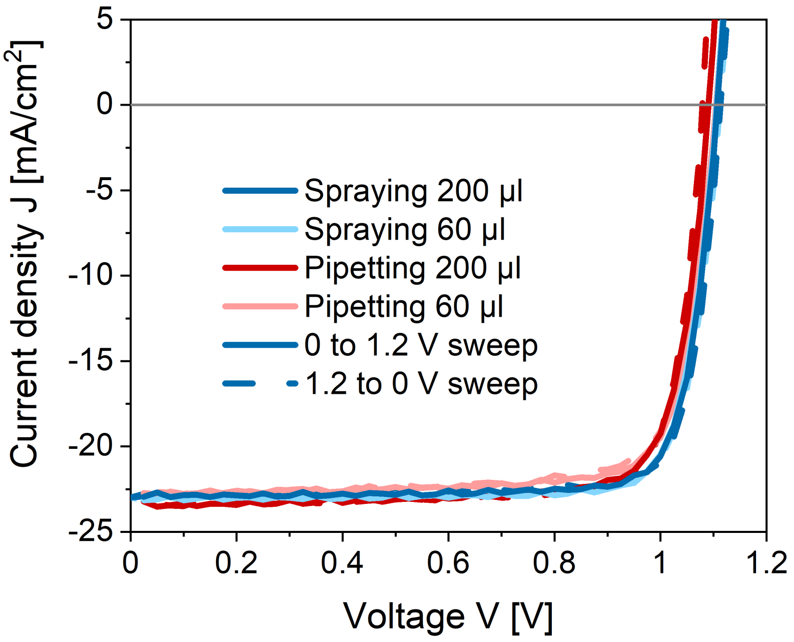

Figure S2. J-V characteristics of the champion sprayed and pipetted devices. Both reverse and forward scan directions are displayed.

Table S1. Photovoltaic performance parameters of champion solar cells whose performance is shown in Figure S1.

Setting	**Sweep**	**V_{OC} (V)**	**J_{SC} (mAcm^{-2})**	**FF (%)**	**PCE (%)**
Pipetting 60 µL	Forward	1.10	22.69	80.03	20.06
	Reverse	1.11	22.69	78.17	19.68
Pipetting 200 µL	Forward	1.09	23.52	79.36	20.35
	Reverse	1.08	23.52	80.99	20.55
Spraying 60 µL	Forward	1.11	22.99	82.71	21.03
	Reverse	1.11	22.99	82.20	21.01
	Forward	1.11	23.00	82.42	20.97

Spraying 200 µL	Reverse	1.11	23.00	81.87	20.95

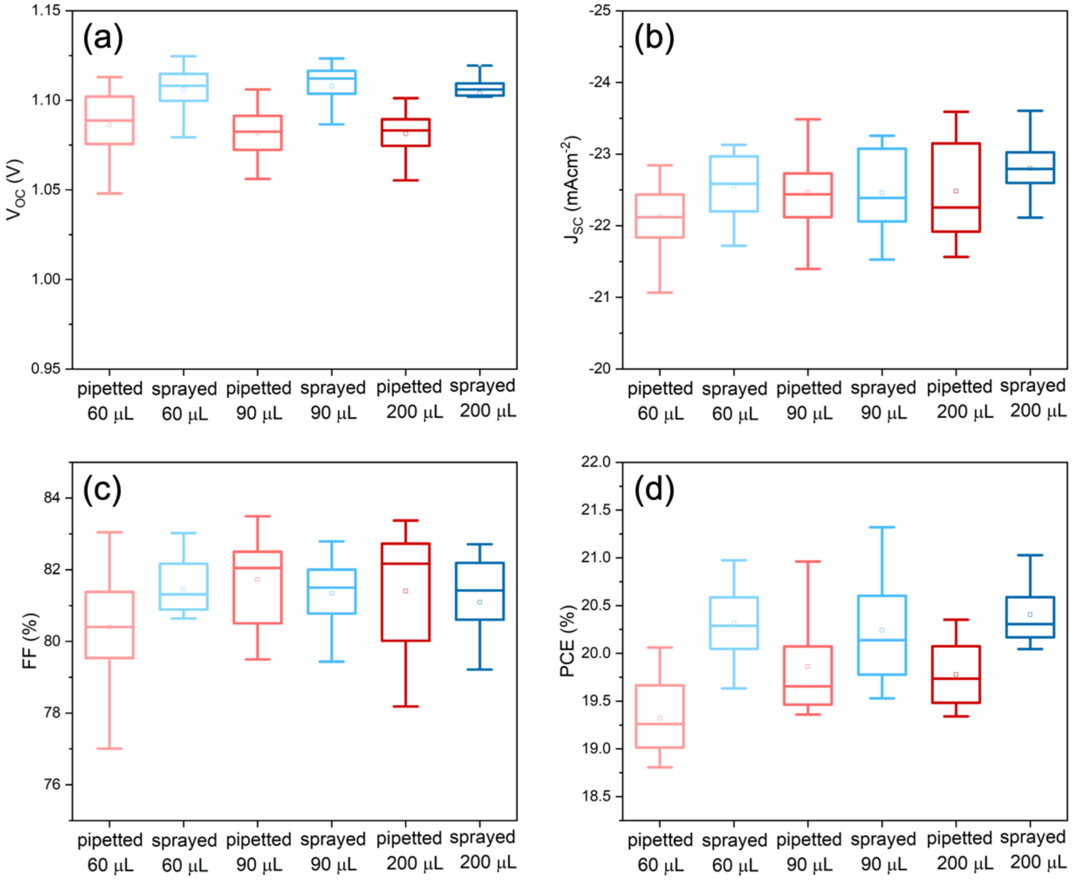

Figure S3. (a) V_{OC}, (b) J_{SC}, (c) FF and (d) PCE of devices with either pipetted or sprayed antisolvent with 60, 90 and 200 µL.

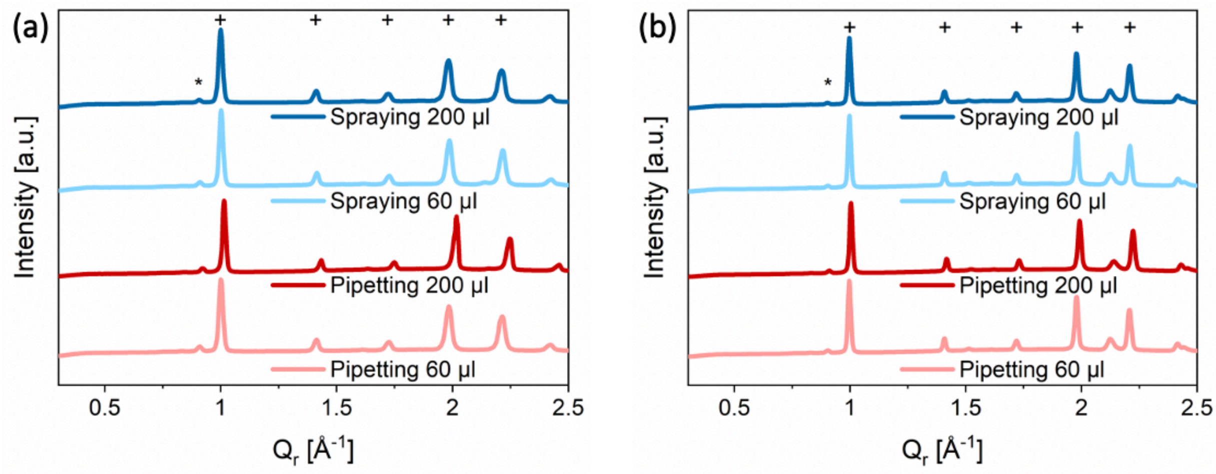

Figure S4. Radial profiles of (a) surface and (b) bulk of triple cation perovskite films fabricated by either pipetting or spraying 60/200 µL antisolvent. Peaks are labeled with (+) for triple cation and (*) lead iodide. Unlabeled peaks originate from the ITO substrates.

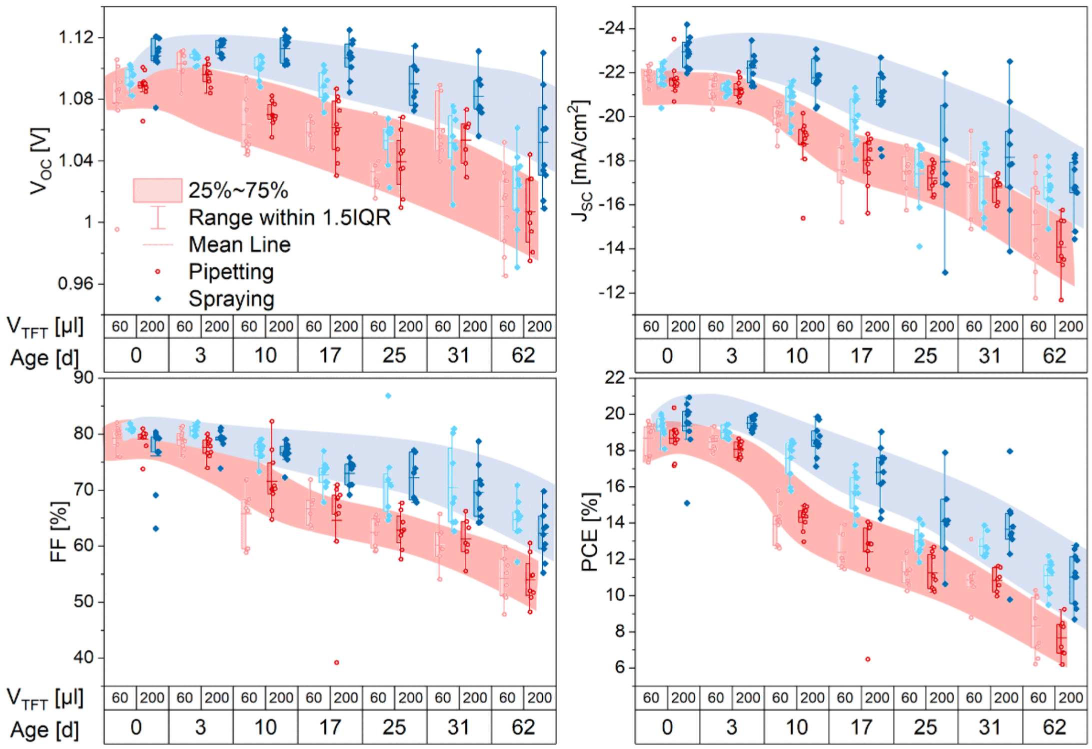

Figure S5. Evolution of the photovoltaic parameters of pipetted and sprayed devices over a period of 62 days. The unencapsulated solar cells were left in the ambient in the dark between measurements.

References

---

(1) J. C. de Mello, H. F. Wittmann, R. H. Friend, Adv. Mater. 1997, 9 (3), 230.