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Enhanced Grain-boundary Emission Lifetime and Additive Induced Crystal Orientation in One-Step Spin-Coated Mixed Cationic (FA/MA) Lead Perovskite Thin Films Stabilized by Zinc Iodide Doping

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13 October 2017

Enhanced Grain-boundary Emission Lifetime and Additive Induced Crystal Orientation in One-Step Spin-Coated Mixed Cationic (FA/MA) Lead Perovskite Thin Films Stabilized by Zinc Iodide Doping

Loreta A. Muscarella, Dina Petrova, Rebecca Jorge Cervasio, Aram Farawar, Olivier Lugier, Charlotte McLure, Martin J. Slaman, Junke Wang, Elizabeth von Hauff, René M. Williams

SUPPORTING INFORMATION

A:

Additional information in order of appearance in the main text.

B:

Experimental details

INDEX

A: Additional information in order of appearance in the main text.

- 1) Description of tests performed with other dopants.
- 2) Picture of “silicon-like” appearance of thick layer.
- 3) Data on optimization of CPACl concentration.
- 4) Data on aging without loss of XRD features after 60 days
- 5) Stability of layer on PEDOT-PSS.
- 6) XRD showing the lattice contraction (from 6.343 Å (with 3-CPACl) to 6.280 Å (with 3-BPABr).
- 7) Solid-solid reaction completed by ambient grinding
- 8) EDX of thin films
- 9) Confocal Laser Scanning Microscopy without the CPACl additive.
- 10) Solar cell parameters and information.

B: Experimental details***1. Instruments***

XRD.

Confocal microscopy.

UV-Vis absorption.

Time resolved emission.

Steady state emission.

IR.

SEM-EDX.

2. Materials

Chemicals

Substrates and sealing

3. Procedures

ITO cleaning.

Precursor solutions.

Spin-coating conditions and procedure and annealing of spin-coated films

Storage of films.

Sealing of films.

Fabrication perovskite solar cells

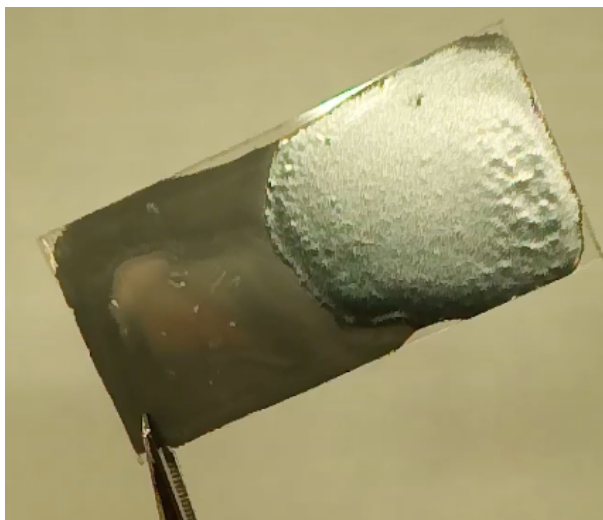
A: Additional information in order of appearance in the text

Description of how other dopants led to rapid aging or instable films.

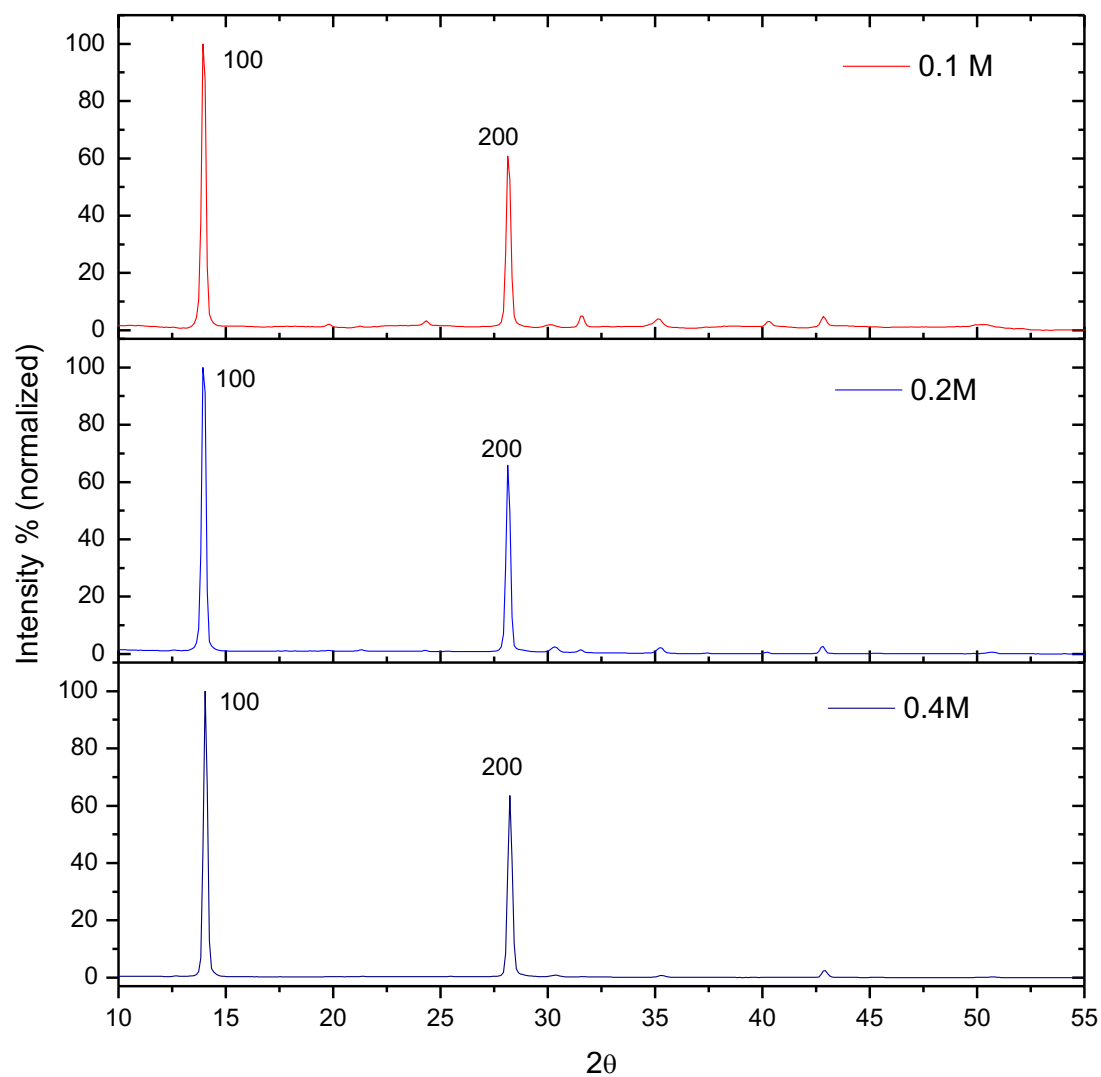
In a typical experiment, a precursor solution containing perovskite components and a dopant was made and drop-casted or spin-coated on a cleaned glass substrate.

The layer was left under ambient conditions and visually monitored for colour changes into a yellow or white phase.

These colour changes would occur within minutes or hours, or a few days, depending on the components.



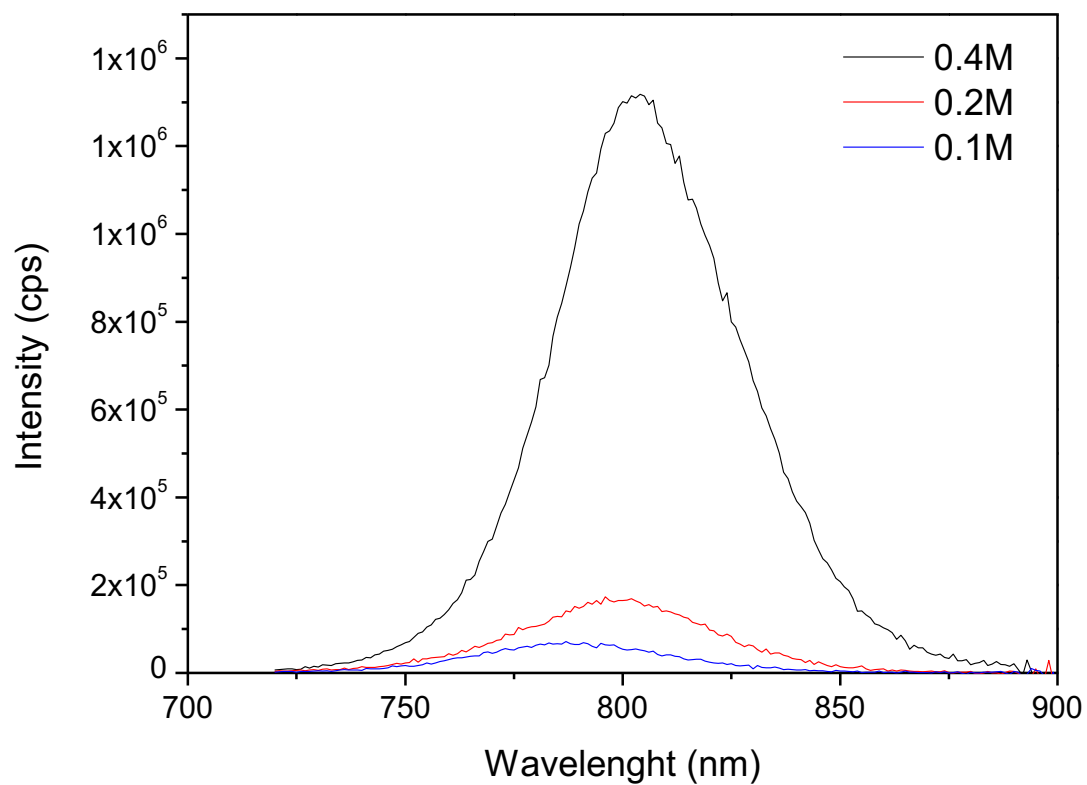
Drop casted thick film showing a shiny silvery, “silicon-like” appearance (top-right).



XRD of several thin films, showing the effect of increased additive concentration, from 0.1 to 0.4 M CPACI.

At a 0.4 M concentration in the precursor solution, the films produced show the most intense 100 and 200 diffractions.

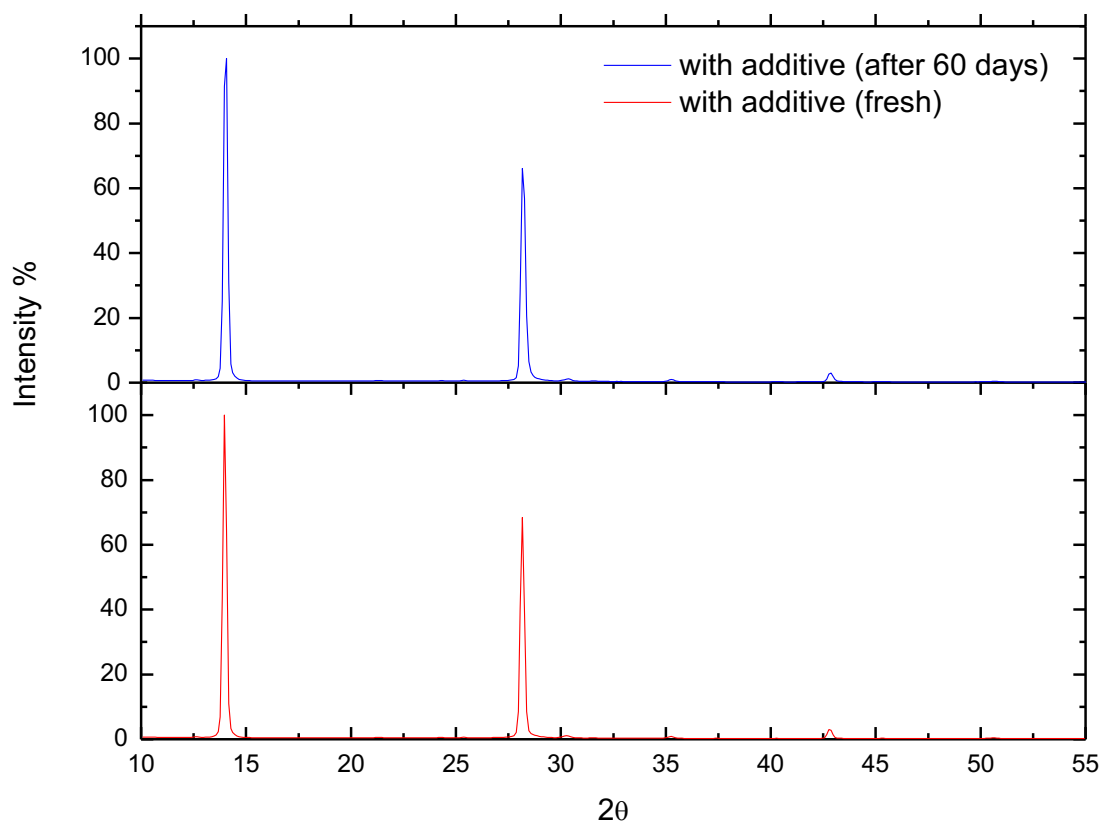
At higher concentrations, the films had an orange colour after spin coating and annealing.



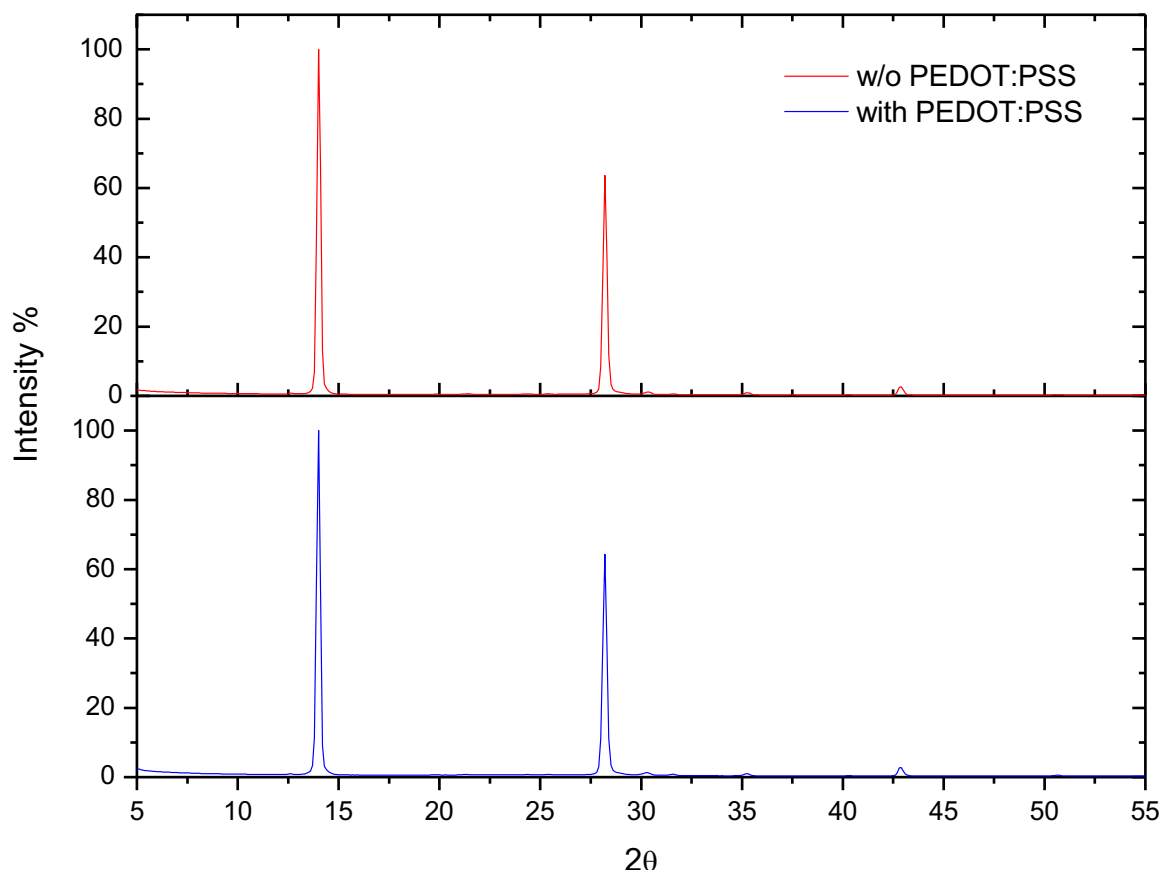
PL intensity as a function of additive concentration. from 0.1 to 0.4 M CPACI.

At a 0.4 M concentration in the precursor solution. the films produced show the most intense photoluminescence.

At higher concentrations, the emission peak was shifted to the blue and decreased at 800 nm.

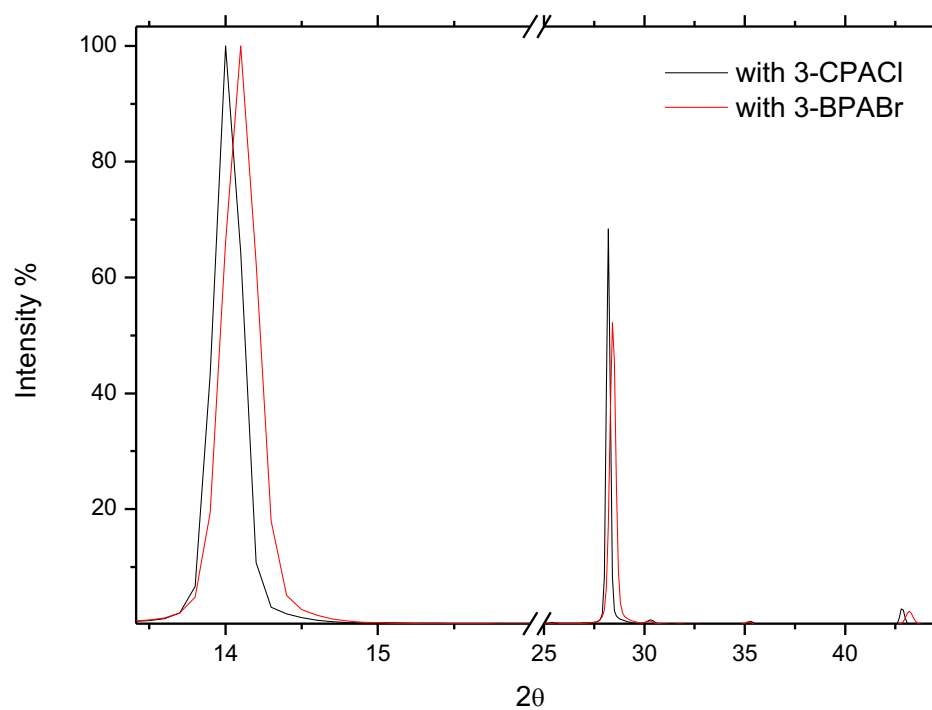


XRD of a freshly made thin film of $(\text{FA}_{0.85}\text{MA}_{0.15})(\text{Pb}_{0.975}\text{Zn}_{0.025})(\text{I}_{2.85}\text{Br}_{0.15})$ -[CPACl] on ITO as well as XRD of the same identical film after 60 days storage at ambient conditions.



Comparison of XRD of $(\text{FA}_{0.85}\text{MA}_{0.15})(\text{Pb}_{0.975}\text{Zn}_{0.025})(\text{I}_{2.85}\text{Br}_{0.15})\text{-[CPACl]}$ on ITO/PEDOT:PSS (in blue) with that of $(\text{FA}_{0.85}\text{MA}_{0.15})(\text{Pb}_{0.975}\text{Zn}_{0.025})(\text{I}_{2.85}\text{Br}_{0.15})\text{-[CPACl]}$ on ITO (in red).

The same diffraction pattern is observed when PEDOT:PSS is present.



Effect of additive on XRD.

Comparison between $(\text{FA}_{0.85}\text{MA}_{0.15})(\text{Pb}_{0.975}\text{Zn}_{0.025})(\text{I}_{2.85}\text{Br}_{0.15})$ -[CPACl] (in black) XRD and $(\text{FA}_{0.85}\text{MA}_{0.15})(\text{Pb}_{0.975}\text{Zn}_{0.025})(\text{I}_{2.85}\text{Br}_{0.15})$ -[BPABr] (in red) XRD.

Small unit cell contraction upon bromide incorporation. Orientation is maintained.

Solid-solid reaction completed by ambient grinding

In a typical experiment the following components were weighted and put together in a vial:

PbI_2 : 461 mg; FAI: 175 mg, MABr: 20; ZnI_2 : 8 mg; 3-CPACl: 26 mg

The mixture was shaken for around one minute, left to sit for ten minutes, and then ground using a pestle and mortar.

Figures 1, 2, 3 and 4 show the mixture before shaking, after shaking, 10 minutes after shaking and after grinding in a pestle and mortar respectively.



Figure 1

Before shaking



Figure 2

Direct after shaking



Figure 3

10 minutes after shaking



Figure 4

After grinding

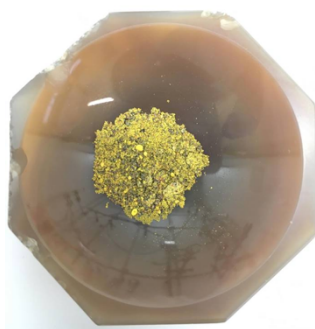


Figure 5

Before grinding

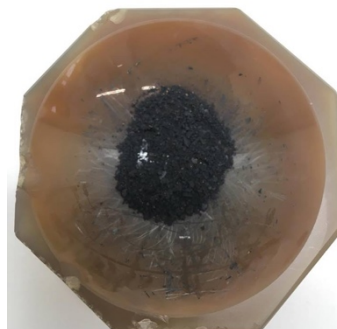
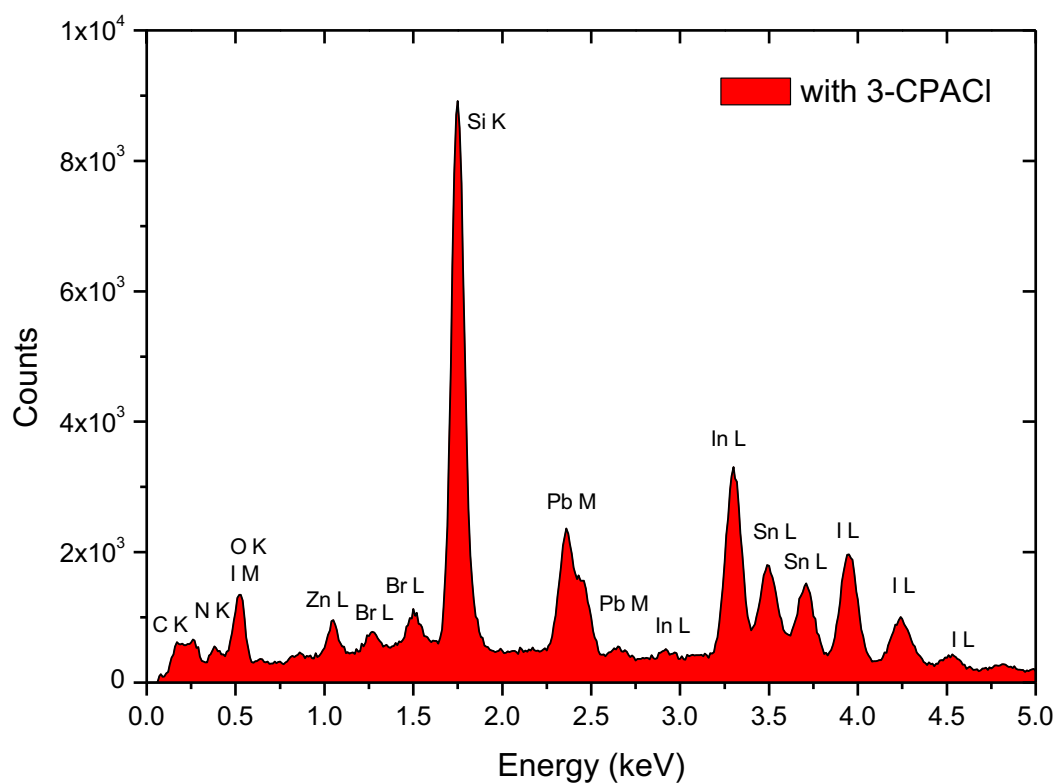


Figure 6

After grinding

The addition of FAI appears to initiate the reaction (with the PbI_2).



EDX related to the SEM of picture 2 in the main text. The EDX clearly shows the presence of Zn, Br, Pb and I, next to signals related to ITO on glass (In, Sn, O, Si).

Extra information:

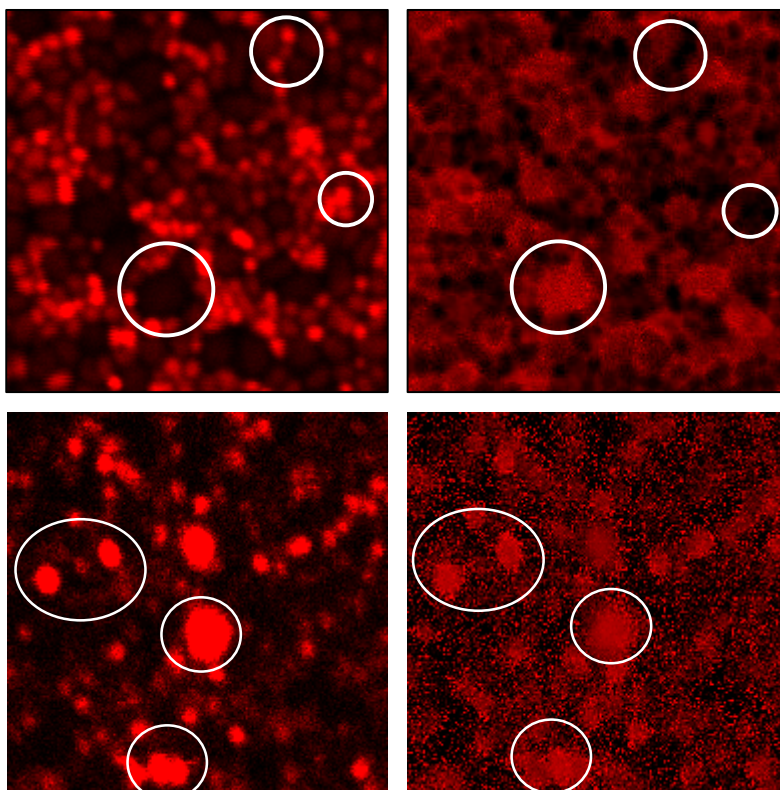
(0.840 keV = Zn L, 1.270 keV = Br L, 3.700 keV = Sn L, 4.230 keV = I L, 4.510 keV = I L).

Carbon (C) and nitrogen (N) signals are in agreement with the presence of FA and MA.

It can be noted that no clear signals related to Cl are present.

Cl is expected at 0.18, 0.23, 2.63 and 2.82 keV

The emissive shell is also indicated by the K or L extension.

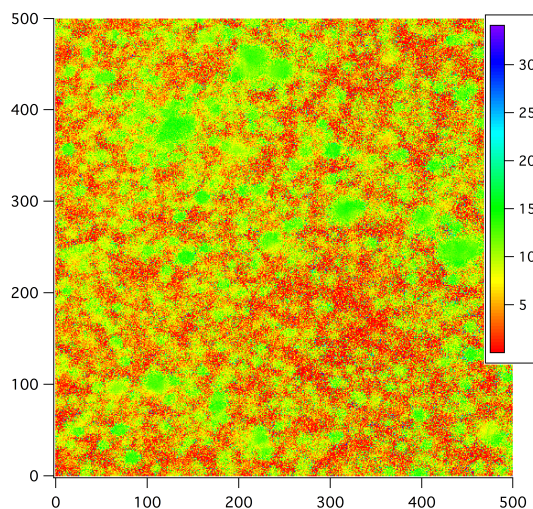


Comparison of CLSM of Zn(II) doped material made with the CPACl additive (top) with the material that does not contain the additive.

The lower picture shows the correspondance between high PL intensity and long PL lifetime.

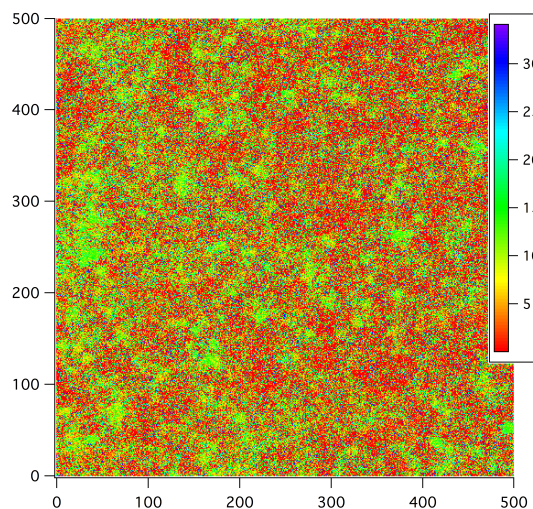
The top picture shows the special inverted behaviour with a low PL intensity and long PL lifetime.

A



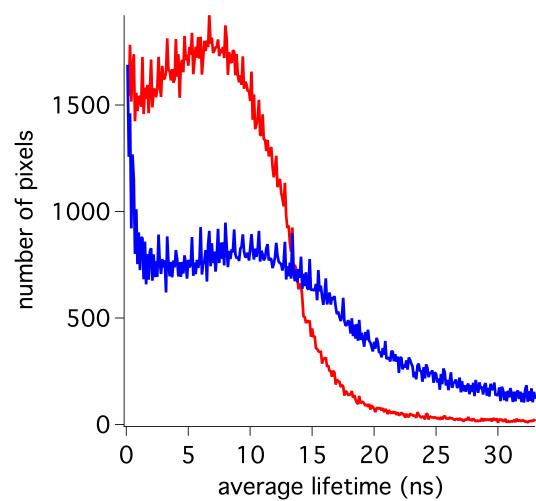
CLSM without CPACI additive

B



with additive

C

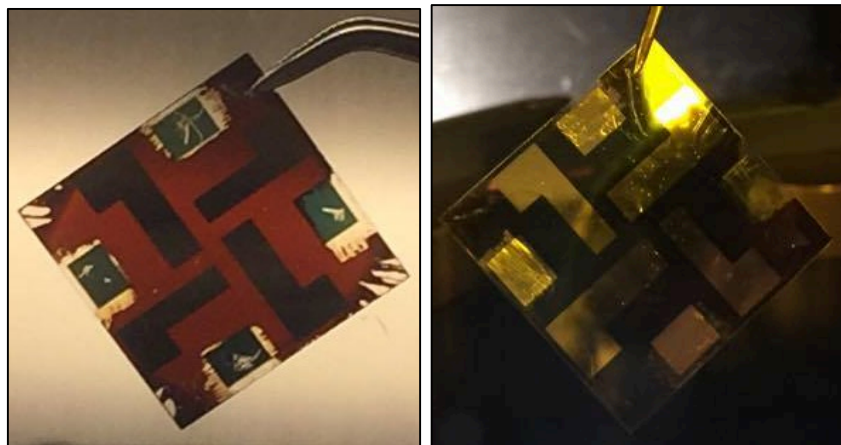


Figures present PL lifetime imaging of a $20 \times 20 \mu\text{m}$ layer of our perovskite layer on ITO without additive (A) and processed with 3-CPACI, (B) showing that even though the average lifetime of these two sample is almost the same (around 12 ns) the 3-CPACI sample shows an enhanced carrier lifetime giving a larger percentage of spots with a longer lifetime around 25 ns (blue spots, right figure). Green domains, which represent a lifetime around 15 ns, are less and more organized (green spots) in the case of the film made with 3-CPACI, surrounded by objects (crystals) with a longer lifetime (blue spots).

Figure C shows a histogram of the average lifetimes from (A) and (B), clearly showing that the film made with the CPACI additive has a larger fraction of long lived emission (blue line).

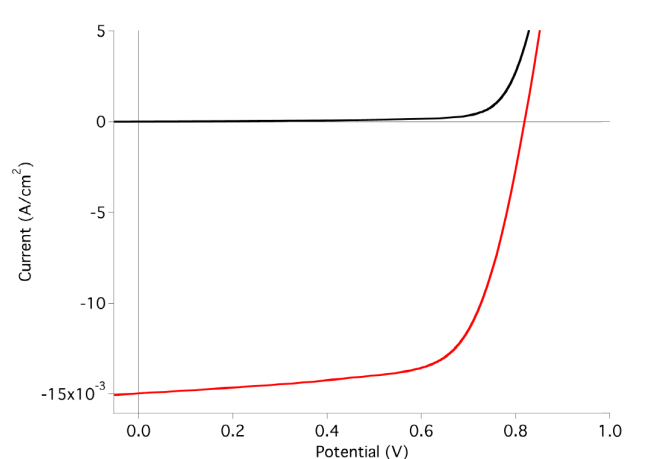
Solar cell parameters and information

Solar cell devices were fabricated using our material with 2.5% ZnI_2 processed with 3-CPACl as additive. Stacks were made-up in the configuration of ITO/PEDOT:PSS/ Perovskite/PCBM/LiF/Al At the end of fabrication, a solar cell looks like in the *Figure below*.



Typical perovskite solar cells devices made at TU/e.

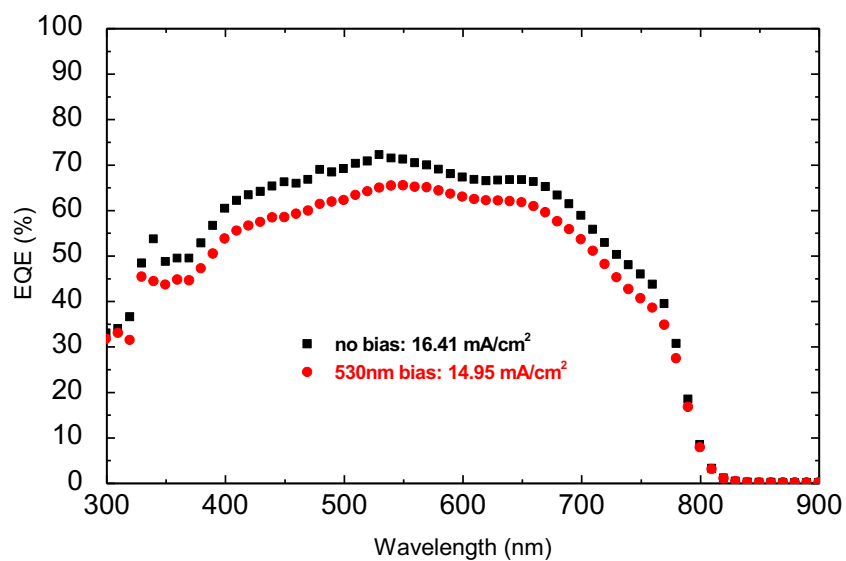
The solar cells from the solution processed with 3-CPACl have an average PCE of 7.80% ($V_{oc} = 0.83$ V. $J_{sc} = 14.01$ mA/cm^2 and $FF = 0.662$) and good repeatability. Furthermore, the highest PCE obtained from this solution was 8.79% along with the V_{oc} , J_{sc} and FF of 0.83V, 14.90 mA/cm^2 , and 0.71 respectively as it shown *below*.



Obtained device data (21 devices). In bold the “hero-device” and underlined, the highest values of the individual parameters (implying 10.6 % could be attainable with this thickness of layer).

cell		J _{sc}	V _{oc}	FF	PCE(down)		J _{sc}	V _{oc}	FF	PCE (up)
		mA/cm ²	V		%		mA/cm ²	V		%
1	a2	12.30	<u>0.89</u>	0.65	7.14					
	b2	12.50	0.89	<u>0.76</u>	8.53		12.10	0.89	0.57	6.09
2	a1	14.10	0.85	0.65	7.84		14.70	0.85	0.67	8.38
	b1	13.50	0.83	0.63	6.99		13.70	0.83	0.60	6.83
	a2	14.30	0.83	0.68	8.05		14.80	0.83	0.68	8.34
	b2	14.40	0.85	0.72	8.76		14.00	0.84	0.66	7.78
3	a1	13.60	0.84	0.64	7.28		14.30	0.85	0.63	7.64
	b1	14.10	0.85	0.69	8.26		14.40	0.85	0.65	7.96
	a2	14.70	0.84	0.68	8.40		15.40	0.84	0.68	8.72
	b2	14.10	0.84	0.73	8.64		13.80	0.83	0.66	7.58
4	a1	14.50	0.82	0.59	7.07		<u>15.60</u>	0.81	0.65	8.16
	b1	14.40	0.82	0.63	7.43		14.80	0.80	0.63	7.44
	a2	14.60	0.82	0.66	7.85		15.10	0.82	0.69	8.50
	b2	14.90	0.83	0.71	8.79		14.80	0.81	0.69	8.22
8	a1	14.30	0.80	0.59	6.78		15.50	0.81	0.67	8.41
	b1	15.10	0.82	0.67	8.32		15.10	0.81	0.66	8.00
	a2	14.90	0.81	0.66	7.98		15.40	0.81	0.69	8.65
	b2	14.40	0.80	0.64	7.43		14.30	0.79	0.59	6.61
9	a1	13.40	0.81	0.60	6.47		14.30	0.82	0.61	7.22
	b1	14.10	0.82	0.65	7.51		14.30	0.82	0.61	7.21
	b2	13.90	0.81	0.60	6.78		13.80	0.80	0.54	5.94

The EQE of this device was as high as 70% with a 10% loss under one sun. This is probably due to trap sites in the perovskite layer given by an un-optimized process of thin film fabrication for solar cell applications. This tells us more process optimization can be done in the following studies.



EQE of the planar solar cell with highest PCE based on perovskite film from CPACI additive-containing precursor solution.

2 Experimental details

2A Instruments

X-ray diffraction of thin films

XRD spectra of perovskite thin film samples coated on ITO substrates were acquired using a Bruker D8 Discover with VANTEC-1 detector and Cu source. A 40 kV voltage was used in a range of 5.0-55.0 degrees with a 0.1 increment and a speed of 30 sec/step. Data analysis was made using PDXL software.

UV-Vis Spectroscopy

To acquire absorbance measurements of thin films an Agilent/HP 8453 UV-Visible Spectrophotometer with single-beam, microprocessor-controlled and collimating optics was used. The range of acquisitions is from 200 nm to 1100 nm.

Profilometer

To measure step-heights of thin films a Dektak 150 from Veeco was used. Setting parameters chosen are 10 mg with LIS 3 sensor as stylus force and 120.000 point per scan.

Confocal Microscopy

To acquire confocal microscopy images of thin films a Micro Time 200 from PicoQuant “Time-resolved Confocal Fluorescence Microscope with Unique Single Molecule Sensitivity” was used, with a 100 × objective and NA = 1.4. A supercontinuum white light laser [SuperContinuum NKT Photonics laser operating at 9MHz] was used with a 530-550 nm bandpass filter. 560 nm excitation wavelength with a laser power of 1% and 5%, respectively 0.008 μW and 0.04 μW, were used to irradiate perovskite thin films. Beam diameter was 200 nm (FWHM) with a Gaussian beam profile. Detection range was between 595 and 900 nm. A 560 nm notch filter was applied. Optical resolution is 0.2 μm (in x-y plane). Pixel-size is 50 nm. For a Z-scan this was 80 nm (pixel-size).

Samples were prepared identically to those for photoluminescence measurements on ITO. The glass side of the substrate was oil-immersed. (air/perovskite/ITO/glass/oil).

Photoluminescence

To acquire photoluminescence emission spectra from thin films a Spex FluoroMax-3 was used. The emission spectra were performed with an excitation wavelength of 550 nm and slit-widths of 3.0 nm in a Front Face (FF) geometry. All spectra were corrected for the detector’s wavelength-dependent response.

Optical Microscope

To capture images in transmittance and reflectance mode of perovskite thin films an Olympus BX60 equipped with a 4, 10, 20 and 40 × dry objectives and a 100 × oil objective was used.

Evaporation Chamber and Solar Cell Simulator

To evaporate electrodes a One MBraun four-source thermal evaporator in glovebox was used. Co-evaporation can be done in this evaporator. Different speeds were used to evaporate electrodes: 1 nm of LiF from crucible at 0.2 Å/s, 100 nm of Aluminium at 2 Å/s for the first 10 nm and 5 Å/s to complete the evaporation. The glove box has also electric feedthroughs which allow J-V measurement of the solar cell devices inside the glovebox. A Newport 150 W solar simulator and computer controlled Keithley 2400 for solar cell efficiency measurement was used.

Performed at TuE in the group of Prof. Dr. Ing. René A. J. Janssen by Junke Wang.

FE-SEM with EDAX:

A Field Emission SEM, Jeol JSM-6301F, equipped with a EDAX: Genesis Apex2 system (Apollo 10+) detector for elementary analysis was used. Electron beam acceleration in the range of 10 kV to 30 kV in high vacuum and a variable magnification until 65000 × were used.

Spin Coater

To form thin films by spin coating a B.L.E spin coater Delta 10 was used. It was used varying rpm and time of spinning depending on the viscosity, concentration and composition of the precursor solution used. No acceleration factor was applied.

UV-Ozone Photoreactor

During the procedure of cleaning glass/ITO plates, to remove organic contaminants from ITO/glass surface, a UVP UV-Ozone Phoreactor PR-100 was used.

Infrared Spectroscopy

For IR measurement of solid samples an ALPHA Platinum with ATR single reflection diamond module from Bruker was used. The acquisition range was set from 4000 cm⁻¹ to 400 cm⁻¹. ALPHA ATR is characterized by high sensitivity DLATGS detector, Rocksolid interferometer. The spectral resolution was adjusted in a range from 0.8 cm⁻¹ to 2 cm⁻¹ in 23 scans. Data are elaborated by OPUS 6.5.

Profilometer

To measure step-heights for thin films a Dektak 150 from Veeco was used. Setting parameters chosen are 10 mg with LIS 3 sensor as stylus force and 120.000 point per scan.

MATERIALS

CHEMICALS

For synthesis of lead-based perovskites precursor solutions were used Methylamine Hydrobromide (MABr, TCI, CAS 6879-37-5, purity >98%, MW. 111.97g/mol), Methylamine Hydroiodide (MAI, TCI, CAS 14965-49-2, purity >98%, MW. 158.97g/mol), Lead iodide (PbI₂, Sigma Aldrich, CAS 10101-63-0, purity of 99%, MW. 461.01 g/mol), Formamidine Hydroiodide (FAI, TCI, CAS 879643-71-7, purity >98%, MW. 171.97 g/mol),

To enhance stability were used also Zinc (II) iodide (ZnI₂, Sigma Aldrich, CAS 10139-47-6, purity of 98%, MW. 319.18 g/mol), Tetramethylammonium iodide (tMAI, Sigma Aldrich, CAS 75-78-1, purity of 99%, MW. 201.05 g/mol), Palladium(II) iodide (PdI₂, Sigma Aldrich, CAS 7790-38-7, purity of 97%, MW. 360.23 g/mol), Palladium(II) bromide (PdBr₂, Sigma Aldrich, CAS 13444-94-5, purity of 99%, MW. 266.23 g/mol).

As solvents were used Dimethylsulfoxide (DMSO, Merk Millipore, CAS 67-68-5, MW. 78.13 g/mol), N,N-dimethylformamide (DMF, Biosolve Chimie SARL, CAS 68-12-2, purity 99.8%, MW. 73.10 g/mol), 1-Methyl-2-pyrrolidinone (NMP, CAS 872-50-4, MW. 99.13 g/mol), γ -Butyrolactone (GBL, CAS 96-48-0, purity \geq 99% GC, MW. 86.09 g/mol). The DMSO and GBL were tested but best results were obtained with DMF.

As antisolvent were used Toluene (Biosolve Chimie SARL, CAS 108-88-3, Purity 99.7%, MW. 92.14 g/mol), Chlorobenzene (Aeros Organics, CAS 108-90-7, Purity 99.9%, MW. 112.56 g/mol), Diethyl ether (DEE, Biosolve Chimie SARL, CAS 60-29-7, MW. 74.12g/mol), Dichloromethane (DCM, Biosolve Chimie SARL, CAS 75-09-2, MW. 84.93g/mol), Anisole (Sigma Aldrich, CAS 100-66-3, Purity 99.7%, MW. 108.14 g/mol), Ethyl Acetate (EA, Biosolve Chimie SARL, CAS 141-78-6, Purity 99.9%, MW. 88,11 g/mol), Diisopropyl ether (DIE, Biosolve Chimie SARL, CAS 108-20-3, Purity 99 %, MW. 102.77 g/mol). Ethylacetate gave best results.

As additives were used Hydriodic acid (HI, Sigma Aldrich, 57 wt. %, distilled, 99.999% trace metals basis, MW. 127.91 g/mol), tin(II) chloride (SnCl₂, Sigma Aldrich, CAS 7772-99-8, purity of 99%, MW. 189.62 g/mol), Ammonium Chloride (NH₄Cl, Sigma Aldrich, CAS 12125-02-9, purity of 99.5%, MW. 53.49 g/mol), 3-chloropropylamine hydrochloride (3-CPACl, Sigma Aldrich, CAS 6276-54-6, purity of 98% trace metals basis, MW. 130.02 g/mol), 3-Bromopropylamine hydrobromide (3-BPABr, Sigma Aldrich, CAS 5003-71-4, purity of 98%, MW. 218.92 g/mol), Benzylamine hydrochloride (BACl, Sigma Aldrich, CAS 3287-99-8, MW. 143.61 g/mol), 1,3-dichloropropane (DCP, ACROS Organics™, CAS 142-28-9, purity of 98.5%, MW. 112.99 g/mol), 1,4-dichlorobutane (DCB, ACROS Organics™, CAS 110-56-5, purity of 99%, MW. 127.01 g/mol), 1,6-dichlorohexane (DCH, ACROS Organics™, CAS 2163-00-0, purity of 98%, MW. 155.07 g/mol), Sodium iodide (NaI, Sigma Aldrich, CAS 7681-82-5, Purity 99.999% trace metals basis, MW. 149.89 g/mol).

As HTL were used Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, Sigma Aldrich, 0.14% PEDOT and 2.6% PSS, 2.8 wt% dispersion in H₂O), N²,N²,N^{2'},N^{2'},N⁷,N⁷,N^{7'},N^{7'}-octakis(4-methoxyphenyl)-9,9'-spirobi[9H-fluorene]-2,2',7,7'-tetramine (Spiro-MeOTAD, Sigma Aldrich, CAS 207739-72-8, Purity 99%).

Cleaning of substrates

For the cleaning procedure of glass/ITO substrates were used Deionized Water, Acetone (C₃H₆O, Biosolve Chimie SARL, CAS 67-64-1, MW. 58.08 g/mol), 2-Propanol (C₃H₈O, Emplura, CAS 67-63-0, purity GC, MW. 60.1 g/mol).

Substrates

Four different types of transparent conductive oxides were used, respectively large ITO, small ITO, patterned ITO and thick TCO:

PGO: 2.5 x 2.5 cm² un-patterned ITO substrates, with a thickness of 1.1 mm. On polished HQ Float Glass substrate.

(CEC010P, ITO-coating (≤ 10 Ohms/sq.) coated on polished glass substrate: - thin SiO₂ passivation layer between Substrate and ITO - dim.: 25 mm (+/-0.25) x 25 mm (+/-0.25) - thickness 1.1mm (+/-0.1) - CNC precision-cut, no bevel).

(Präzisions Glas & Optik GmbH, <https://www.pgo-online.com/>)

Ossila: 1.5 x 2 cm² unpatterned ITO substrates, Ossila, with a thickness of 1.1 mm.

(ITO Glass Substrates (Unpatterned) Code: S111)

(<https://www.ossila.com/products/ito-glass-substrate>)

Naranjo: 3 x 3 cm² patterned ITO was purchased from Naranjo Substrates, thickness of 1 mm.

(<http://www.naranjosubstrates.com/>).

Mansolar: Conductive glass electrodes (counter electrodes). 4 x 2 cm² thickness of 3 mm.

(<https://www.mansolar.nl/supplies/12-conductive-glass-electrodes-counter-electrodes.html>)

As substrate for the drop-cast deposition of precursor solutions (cut) Microscope Glass slides Thermo Scientific Menzel-Gläser c.a./env. 76 x 26 mm. were used. These were also used as first tests for optimizing the spin-coating procedure.

Sealing

To seal stacked layers we used “Pattex power epoxy” (5 min.) or “Loctite glass”.

2C PROCEDURES

Cleaning of ITO/glass substrates

A very important step to form high quality perovskite thin films by spin coating is the cleaning procedure of substrates. It is possible to use different types of substrates: ITO (indium tin oxide), FTO (fluorine tin oxide) or glass. In all cases, it is necessary a systematic cleaning procedure to obtain homogeneous films and avoid cracks on thin films.

First, substrates have to be washed with water and then sonicated in an ultrasonic bath^[1] with deionized water for 15 minutes. The same procedure has to be done with acetone and then with 2-propanol. Later, substrates are dried with an airflow and then treated with ozone for 30 minutes.^[2]

Before spin coating, a N₂ flow is blown over the surface to remove dust or particles.

When forming films by drop casting, the cleaning procedure is also important, especially for visual stability monitoring.

Preparation of precursor solution of FA_{0.85}MA_{0.15}PbBr_{0.15}I_{2.85}

The procedure is referred to room temperature and atmospheric pressure.

For the preparation of FA_{0.85}MA_{0.15}PbBr_{0.15}I_{2.85}, FAI (0.001 mol, 175.36 mg), PbI₂ (0,001 mol, 461.01 mg), MABr (2·10⁻⁴ mol, 20.15 mg), are weighted into a 5 mL vial. A stirrer and 1 mL of DMF are added. The mixture is sonicated in order to perfectly dissolve reagents.

Preparation of precursor solution of (FA_{0.85}MA_{0.15})(Pb_{0.975}Zn_{0.025})(I_{2.85}Br_{0.15})-[CPACl]

The procedure is referred to room temperature and atmospheric pressure. This precursor solution is 1 M in PbI₂ and 1.2 M in total ammonium cation concentration.

For the preparation of the precursor solution of the perovskite doped with 2.5% ZnI₂ and crystal oriented by the CPACL additive the following amounts were used in a typical experiment: 461.01 mg of PbI₂, 175.36 mg of FAI, 20.15 mg of MABr, 7.97 mg of ZnI₂, 52 mg of 3-CPACl are weighted into a 5 mL vial. A stirrer and 1 mL of DMF are added. The mixture is sonicated in order to perfectly dissolve reagents. The precursor solution is stable for several weeks, however, after several months it can become orange and deteriorates.

This type of preparation-method was also used for precursor solutions using other percentages of ZnI₂ or dopants.

Procedure to spin coating with One-Step Deposition with anti-solvent dripping/spraying

Thin films were deposited on cleaned ITO-coated glass (or other substrate) by spin-coating 0.1 mL of precursor solution (for 2.5 x 2.5 cm²) at 3500 rpm for 30 seconds under ambient conditions (no acceleration factor was applied). One-step deposition method with sprayed appropriate anti-solvent (ethylacetate) was used. After 15 seconds from start of the spin-coating programme, 0.4 mL of Ethyl Acetate (EA) was sprayed within ~0.5 second over the precursor perovskite layer at a fixed height of 4 centimetres between the needle tip and the surface. A metal gasket from an HPLC setup was used as a height fixation. Films were annealed for 5 minutes at 70°C and for 15 minutes at 100°C using a multi-step annealing in ambient conditions. Layer temperature was checked during annealing with a IR remote temperature sensor. (Infrared-thermometer VOLTcraft IR 500-8S Optics (thermometer) 8:1 -50 tot +500 °C).

Syringe and needle use for anti-solvent: 2-part single-use syringes (1 mL, Norm-Ject), single-use needles (0.5 x 16 mm, 25 G 5/8", Braun), for the anti-solvent "dripping".

At last, films are protected in a desiccator and used for further analysis. (Some films were stored under ambient conditions). In the *Table* below it is possible to see names and properties of all anti-solvents tested. Ethylacetate resulted in the best-looking films.

Antisolvent	Molecular Weight (g/mol)	Density (g/mL 25 °C)	Boiling Point (°C)	Vapor pressure mmHg, 20°C)	Viscosity (mPa·s, 25°C)	Dipole Moment (D)	Dielectric Constant (ε)
Toluene	92.14	0.87 (20 °C)	111	210	0.590 (20°C)	0	2.3
Diethylether	74.12	0.7134	34.6	440	0.224	1.15	4.33
Chlorobenzene	112.56	1.106	131	11.8	0.799 (20 °C)	3.62	1.54
Dichloromethane	84.93	1.3266 (20°C)	39.6	4297	0.413	1.60	9.1
Ethyl Acetate	88.10	0.90 (20°C)	77	73	0.426	1.78	6.02

Table . List of antisolvents used and their properties.

Procedure for drop casting

The precursor solution is heated and stirred for 30 minutes at 70 °C to have the same temperature of the heated glass/ITO plates, heated at the same temperature. 0.1 mL of precursor solution (or one drop) is added carefully over a glass/ITO substrate and then heated at 70 °C until evaporation of the solvent. After thermal annealing at 100 °C for 30 minutes, thin films are protected against moisture from the air by storage in a desiccator, unless specified otherwise.

Sealing of layer

Some layers were heated for 10 min. at 80 °C, stacked and clamped with a clamping screw (perovskite layers facing each other) and sealed on the edges with epoxy or glass glue. These layers can be stable for multiple months up to (at least) one year. These layers are being exposed to windowsill conditions.

Fabrication perovskite solar cells (performed at Eindhoven University (TuE) in the group of Prof. Dr. Ir. René A. J. Janssen, by Junke Wang.

Devices were fabricated outside of glovebox in the configuration of ITO/PEDOT:PSS/Perovskite/PCBM/LiF/Al. ITO (Naranjo) substrates are cleaned sequentially with deionized water, acetone, and isopropanol in an ultrasonic bath for 15 minutes. After drying under air stream, substrates were further cleaned by an ozone plasma treatment for 30 minutes. In this stack, PEDOT:PSS is first spin-coated onto the substrates at 3000 rpm for 60 second and annealed at 100 °C for at least 15 minutes. Then the precursor solution is spin coated at 3000 rpm for 30 seconds (anti-solvent sprayed after 15 s) and then annealed at 100 °C for 20 minutes. Afterward, the PCBM (20 mg/mL in chlorobenzene: chloroform 1:1) is then deposited on top of the perovskite layer by spin coating at 1000 rpm for 60 seconds. 1 nm-thick of LiF and 100 nm-thick of Al are finally evaporated under high vacuum ($<2 \cdot 10^{-6}$ Torr) through a shadow mask at the rate of 2 Å/s.

Author contributions:

Loreta A. Muscarella discovered the effect of the additive and did most of the experimental work described in this manuscript. Olivier Lugier made the first perovskite materials in our lab. Rebecca Jorge Cervasio discovered the stabilizing effect of ZnI₂. Aram Farawar optimized the spin-coating procedure. Dina Petrova performed the confocal microscopy. Charlotte McLure performed the solid-solid reaction. Martin J. Slaman performed the SEM, EDX and XRD. Junke Wang made and measured the solar cells at TuE. Elizabeth J. von Hauff contributed with valuable discussions and comments on the manuscript.

René M. Williams initiated and supervised the research, and wrote the manuscript.

¹ E. S. Lee, J. H. Choi, H. K. Baik, “*Surface cleaning of indium tin oxide by atmospheric air plasma treatment with the steady-state airflow for organic light emitting diodes*”, *Surface and Coatings Technology*, **2007**, 201, 9-11, 4973-4978

² S. So, W. Choi, C.Cheng et al. “*Surface preparation and characterization of indium tin oxide substrates for organic electroluminescent devices*”, **1999**, *Appl Phys A*, 68, 447