Preparation of mixed-ion and inorganic perovskite solar cells using water and isopropanol as solvents for solar cell applications

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Cs_{1-y}FA_yPbI₃ and Cs_{1-y}FA_yPbBr₃ perovskite characterisation

Samples for this analysis were prepared similarly to what is described in the experimental section in the main manuscript. Briefly, we spin-coated a metal nitrate solution, with the respective Cs/Pb ratios, directly onto FTO glass and dried at 70 °C. These metal nitrate films were then dipped for 60 minutes in their respective solutions and heated for 30 min at 100 °C. The iodine perovskite films were additionally heated for 10 min at 185 °C prior to characterisation due to the tendency of the light active phase to revert to the δ -perovskite phase with prolonged ambient air exposure. The full X-ray diffractograms of these films are presented here below in Figure S1, as well as in Figure S9 for the pure CsPbBr₃. In Figure S2, the full transmittance and reflectance spectra for all the films is presented and in Figure S6 the stead-state photoluminescence for the same films can be observed.



Figure S1: X-ray diffractograms of the metal nitrate films (left), resulting iodide (middle) and resulting bromide perovskite films (right). All films were deposited directly onto FTO glass and measured in the same manner as described by the experimental section in the manuscript.



Figure S2: UV-Vis transmittance and reflectance spectra of the metal nitrate films (left column), resulting iodide (middle column) and resulting bromide perovskite films (right column). No CsPbI₃ was made.



Figure S3: Steady-state photoluminescence of the resulting iodide and bromide perovskite films. The iodide perovskite were measured with an excitation wavelength of 620 nm while the bromide perovskites were excited at 470 nm. The signal/noise ratio for the iodide spectra is low due to detector limitations in that specific wavelength region.





Figure S4: Transient photoluminescence spectra of the $Cs_{1-y}FA_yPbI_3$ and $Cs_{1-y}FA_yPbBr_3$ perovskite films measured in a nanosecond laser setup with a CCD camera. The iodide perovskites the films were excited at 620 nm and the bromides at 470 nm. For the iodide perovskite spectra, some amount of scattered laser signal can be observed at 620 nm as well as an artefact ~730 nm, both are marked with an asterisk.

As mentioned in the main text, we imaged and measured these films by using a scanning electron microscope in combination with energy dispersive spectroscopy (SEM/EDS). In Figure S3 an SEM image, along with two EDS maps, of the $1:0.1 \text{ Pb}(\text{NO}_3)_2:\text{CsNO}_3$ film is presented as an example to see the uniform distribution of lead and caesium in the film. Furthermore, the elemental compositions of the metal nitrate as well as the resulting iodide and bromide perovskite films can be observed in Table S1 and Table S2.



Figure S5: Scanning electron microscopy SE2 detector image (left) of a 1:0.1 $Pb(NO_3)_2$:CsNO₃ film along with the respective energy dispersive spectral maps for lead (middle) and caesium (right).

Table S1: Expected Cs/Pb ratio as determined from the solution concentrations vs. the measured ratio in the metal nitrate films as determined by EDS.

Expected	Measured	
Cs/Pb ratio	Cs/Pb ratio	
0.1	0.075	
0.2	0.16	
1	0.95	

Table S2: Expected composition of the iodide and bromide perovskites resulting from the metal nitrate films as determined from the solution concentrations vs. the measured composition of the respective perovskite films as determined by EDS. The Cs/Pb ratio was only determined from bromide perovskites because of iodide-caesium overlap in iodide perovskites.

Functed Composition	X/	X/Pb		
	ŀ	Br⁻		
FAPbX ₃	2.4	3.8	-	
$Cs_{0.1}FA_{0.9}PbX_3$	2.4	3.5	0.05	
$Cs_{0.2}FA_{0.8}PbX_3$	2.6	3.7	0.15	
CsPbX ₃		3.3	0.98	

X-ray photoelectron spectroscopy

Due to the low conductivity of the precursor, the sample was charging causing a shift by about 0.6 eV (shift of adventitious carbon). In order to characterise the complete surface composition of the perovskite film we also fitted the Cs3d, I3d, O1s, Pb4f, Br3d and Cs4d peaks. The calculated ratios, relative to the area of the Pb4f peak, are presented in Table S3 and the respective peak fits are presented in Figure S4.

Table S3: Electron binding energy peak positions of the respective elements, as measured by hard X-ray photoelectron spectroscopy, for both the perovskite and the metal nitrate precursor film.

	Perovs	Metal nitrate film	
	Peak position (eV)	Relative ratio to Pb4f	Peak position (eV)
Br3d	68.6	0.22	N/A
Cs4d	75.9	0.05	N/A
Pb4f	138.6	1	140.1
C1s	285.0	0.49	285.5
	286.7	0.19	
	288.5	0.72	
	289.4	0.27	
N1s	400.9	2.01	408.3
Ті2р	N/A	N/A	458.9
01s	533.3	0.22	533.5
			530.2
I3d	619.4	4.30	N/A
Cs3d	724.9	0.04	725.5



Figure S6: Enhanced X-ray photoelectron spectra of the binding energy regions for the respective elements. The perovskite (blue) and metal nitrate precursor (orange) film signals were fitted with Voigt functions for quantification (green). The precursor fits are only for illustration and could not be used for estimating concentrations due to sample charging. All spectra are normalised to the Pb4f peak area and calibrated against an Au4f standard.

As mentioned in the main text, and presented in Figure S5, the O1s signal from the perovskite film prepared by using a metal nitrate precursor was compared to the O1s signal from a conventionally prepared (1-step) perovskite film. It is apparent from the data, the O1s signals are more or less identical. The 1-step perovskite film was prepared, inside glovebox with a nitrogen atmosphere, from a perovskite precursor solution with a mixture of DMF and DMSO as solvents and by using the so-called anti-solvent method.¹



Figure S7: The Pb4f spectra and O1s X-ray photoelectron spectra of 1-step prepared (orange) and metal nitrate precursor prepared (blue) perovskite films. The 1-step sample was measured at the same beamline with the same photon and pass energy. O/Pb ratio in the 1-step film is 0.18 and 0.24 in the metal nitrate prepared film. The spectra were calibrated against an Au4f standard and normalised against the Pb4f peak area.

Cs_yFA_{1-y}Pb(I_xBr_{1-x})₃ characterisation

Here below we present UV-Vis absorbance, XRD, SEM images along with photographs of perovskite films from the solar cell optimization of $Cs_{10}FA_{90}Pb(I_{0.83}Br_{0.17})_3$. However, we must note that the chemicals used for preparing these films were of a different batch than the chemicals used for the solar cell optimisation.



Figure S8: Characterisation of films prepared in the same way as in Table 1 in the manuscript. Top Left: XRD patterns of the metal nitrate precursor films prepared with different precursor solution concentrations as well as the resulting perovskite film. Top Right: UV-Vis absorbance of the same films. Bottom row: Topographic SEM images of the resulting perovskite films after 90 minute dipping in 40 mM organic-halide salt bath.



Figure S9: Photographs of the perovskite films obtained by using different precursor solution concentrations (from left: 1.00, 1.25, 1.50, 1.75 and 2.00 M) after 90 minute dipping in 40 mM organic-halide salt bath while in the bath (top) and after annealing at 100 °C for 10 min (bottom).



Figure S10: Characterisation of films prepared in the same way as in Table 2 in the manuscript. Top Left: XRD patterns of the resulting perovskite film prepared with different organic-halide salt bath concentrations. Top Right: UV-Vis absorbance of the same films. Bottom row: Topographic SEM images of the resulting perovskite films, prepared from 1.5 M precursor solution, after 90 minute dipping in X mM organic-halide salt bath.



Figure S11: Photographs of the perovskite films obtained from a 1.5 M precursor solution and by using different organichalide salt bath concentrations (from left: 30, 40, 45, 50 and 55 mM) after 90 minute dipping while in the bath (top) and after annealing at 100 °C for 10 min (bottom).

For Figure S12, and SE2 detector was used (complimentary to the conventional InLens detector) in the SEM instrument. The SE2 detector benefits from greater topological contrast but has lower resolution compared to the InLens. From the SE2 images one can see that the needle like structures, observed in the InLens images, protrude from the film surface. One can also see, due to an even grayscale contrast, that the perovskite film obtained after 10 minute dipping has the most even surface.



Figure S12: Characterisation of films prepared in the same way as in Table 3 in the manuscript. Top Left: XRD patterns of the perovskite film prepared from 1.5 M precursor solution and a 40 mM dipping-bath concentration but different dipping times. Top Right: UV-Vis absorbance of the same films. Middle row: Topographic SEM images of the resulting perovskite films after X minute dipping in 40 mM organic-halide salt bath. Bottom row: Topographic SE2 SEM images of the same perovskite films. The SE2 detector gives greater topological contrast.



Figure S13: Photographs of the perovskite films obtained by using different dipping-bath times (from left: 5, 10, 30, 60 and 90 min) in 40 mM organic-halide salt bath after annealing at 100 °C for 10 min.

Cs_yFA_{1-y}Pb(I_xBr_{1-x})₃ solar cells

In Figure S7 we present the current-voltage (IV) curves for perovskite solar cells prepared from two different metal nitrate solutions and in Table S4 their parameters can be observed. The concentration is relative to the $Pb(NO_3)_2$ amount in the water solutions and both solutions included an added 10% CsNO₃ by mole relative to the lead. The metal nitrate films were dipped in a 40 mM 83:17 FAI:FABr solution for 90 minutes.



Figure S14: IV-curves for perovskite solar cells prepared from a 1.5 M (left) and 1.75 M (right) $Pb(NO_3)_2$ solutions. Both solutions included a 10% CsNO₃ additive. The cells were scanned in both directions at 10 mV/s (red curves) and the average of those curves taken (black curve). The 1.75 M cell was also measured fast at 50 mV/s (blue curve) and the dark scan is also presented (red dotted curve).

Table S4: IV-parameters for perovskite solar cells prepared from a 1.5 M and 1.75 M $Pb(NO_3)_2$ solutions. Both solutions included a 10% CsNO₃ additive. The scan speed was 10 mV/s and the mask size 0.126 cm².

C_{pre}	Scan	V _{oc}	J_{sc}	FF	PCE
(M)		(V)	(mA cm ⁻²)		(%)
1.5	OC -> SC	0.97	18.9	0.66	12.0
	SC -> OC	0.94	18.7	0.65	11.4
	Average	0.96	18.8	0.66	11.7
1.75	OC - > SC	0.98	19.2	0.62	11.7
	SC -> OC	0.96	19.0	0.6	10.9
	Average	0.97	19.1	0.61	11.3

After the optimisation we made a total of 35 solar cells with a 1.5 M Pb(NO₃)₂ and 10% CsNO₃. Dipping bath concentrations were optimised to 40 mM and the dipping time to 10 min. In Figure S8 we present an IV-curve of the champion cell measured from that batch and in Table S5 the IV-parameters of the champion, as well as the average parameters for all 35 cells measured at a scan speed of 50 mV/s, are presented. As apparent from the IV-curve, the champion cell in the back-scan had some hysteresis issues which are most likely related to an imperfect TiO₂ blocking layer in that substrate as can be observed from the current leakage in the dark scan curve.



Figure S15: IV-curve of the champion solar cell obtained from a batch of 35 devices with $Cs_{10}FA_{90}Pb(I_{0.83}Br_{0.17})_3$ where the perovskite was prepared using a 1.5 M $Pb(NO_3)_2$ solution and dipped for 10 min into a 40 mM FAI:FABr bath. Red curves are scans measured at 10 mV/s and the black curve is the average of the two scan directions. Blue curve is a fast scan at 50 mV/s and the dark scan curve is also included.

Table S5: Average IV-parameters of all 35 devices with $Cs_{10}FA_{90}Pb(I_{0.83}Br_{0.17})_3$ where the perovskite was prepared using a 1.5 $M Pb(NO_3)_2$ solution and dipped for 10 min into a 40 mM FAI:FABr bath, as well as the IV-parameters for the IV-curve presented in Figure S8

Scans	Scan speed (mV/s)	V _{oc} (V)	J _{sc} (mA cm⁻²)	FF	PCE (%)
(35x)	50	0.94 ± 0.1	19.5 ± 2.1	0.62 ± 0.07	11.3 ± 2.2
Champion	50	1.00	21	0.69	14.5
OC -> SC	10	1.01	20.0	0.69	13.9
SC -> OC	10	0.99	18.9	0.54	10.2
Average		1.00	19.5	0.63	12.1

In Table S6 and Table S7 we report the IV-parameters for two other batch tests with different lead (II) nitrate solution concentrations. In both cases, 10% CsNO₃ was used and a 40 mM 83:17 FAI:FABr dipping solution where the nitrate film was dipped for 90 minutes.

Table S6: IV parameters for a lead (II) nitrate solution concentration test. A total of 29 devices were measured.

Pb(NO ₃) ₂	V _{oc}	J_{sc}	FF	PCE
conc. (M)	(V)	(mA cm ⁻²)		(%)
1.4	0.81 ± 0.12	15.0 ± 1.6	0.60 ± 0.08	7.3 ± 2.0
1.6	0.87 ± 0.04	15.7 ± 2.7	0.58 ± 0.06	7.8 ± 1.5
1.8	0.95 ± 0.02	18.9 ± 0.5	0.61 ± 0.03	10.8 ± 0.9

Pb(NO ₃) ₂	V _{oc}	J_{sc}	FF	PCE
conc. (M)	(V)	(mA cm ⁻²)		(%)
1.4	0.81 ± 0.05	15.5 ± 2.3	0.61 ± 0.05	7.7 ± 1.9
1.5	0.86 ± 0.02	17.4 ± 1.3	0.61 ± 0.05	9.2 ± 1.4
1.6	0.85 ± 0.02	17.7 ± 1.0	0.64 ± 0.02	9.5 ± 0.6
1.7	0.84 ± 0.02	17.2 ± 2.2	0.61 ± 0.02	8.8 ± 1.2
1.8	0.85 ± 0.02	17.3 ± 0.8	0.60 ± 0.02	8.9 ± 0.6

Table S7: IV parameters for a lead (II) nitrate solution concentration test. A total of 59 devices were measured.

CsPbBr₃

As mentioned in the manuscript, we synthesised inorganic CsPbBr₃ perovskite solar cells. An equimolar ratio of the lead (II) nitrate and caesium (I) nitrate was dissolved in water to reach a 1.5 M concentration for each component. This solution was spin-coated onto mesoporous TiO_2 substrates. The halide was then introduced by mixing concentrated hydrobromic acid (HBr) with an organic solvent to reach a concentration of ~40 mM. The organic solvents tested were isopropanol, toluene, chlorobenzene and anisole. The acid was only fully miscible in isopropanol and slightly in anisole. The CsPbBr₃ formed in all four solvents but the best solar cell was obtained from the sample dipped in toluene. However, for material characterisation we used the sample obtained from the isopropanol bath. The IV-curve for the champion cell is presented in Figure S9 and its IV-parameters in Table S8.



Figure S16: IV-curve for the champion $CsPbBr_3$ solar cell obtained from dipping an equimolar lead and caesium nitrate film into HBr mixed to toluene. Scan speed is 50 mV/s and the cell was measured in both directions (red curves) and the average taken (black curve).

Table S8: IV-parameters for the champion CsPbBr₃ solar cell presented in Figure S17.

CsPbBr ₃	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF	PCE (%)
OC -> SC	1.16	4.5	0.63	3.3
SC -> OC	1.16	4.6	0.47	2.5
Average	1.16	4.6	0.55	2.9



Figure S18: Full X-ray diffractogram of the CSPbBr₃ perovskite prepared from a metal nitrate film and using HBr mixed in isopropanol as a halide bath. Interestingly one can also observe some amount of $CsPb_2Br_6$ here.

References:

1 J. T. Jacobsson, J. P. Correa Baena, M. Pazoki, M. Saliba, K. Schenk, M. Grätzel and A. Hagfeldt, *Energy Environ. Sci.*, 2016.