## Fractional Deviations in Precursor Stoichiometry Dictate the Properties, Performance and Stability of Perovskite Photovoltaic Devices

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# **Supplementary Note 1:**

For the PbAc<sub>2</sub> recipe, the changes in stoichiometry were performed by adding a MAI/DMF stock solution into precisely known volumes of MAI:PbAc<sub>2</sub>/DMF perovskite solution. In order to perform controlled stoichiometric changes, it is necessary to know the total solid concentration in each of the solutions. Therefore, the density of the two solutions was determined in the following fashion:

For the MAI/DMF stock solution, 385.5 mg MAI was dissolved in 1 ml DMF (29 wt%). The density of this solution was determined (by weighing exactly known volumes) to be 1145 mg/ml, i.e. a solid concentration of 332.1 mg/ml MAI.

For the perovskite solution, carefully weighed amounts of MAI and PbAc<sub>2</sub> were dissolved in DMF at 42 wt% with a certain stoichiometry *y*. After addition of HPA (6.43 ul / 1 ml DMF) with a density of 1.206 mg/ml, the weight percentage of perovskite (MAI+PbAc<sub>2</sub>) decreases to 41.8%. The density for various stoichiometries was determined by weighing.

Once the density of the perovskite solution and the perovskite weight percentage are known, the solid concentration as well as the amount of  $PbAc_2$  per sample (40  $\mu$ l) can be calculated for each stoichiometry y. The weight of PbAc<sub>2</sub> in the remaining precursor solution was calculated for each step and suitable amounts of MAI/DMF stock solution were added to perform the desired changes in stoichiometry y (see **Table S1** for an example calculation, and **Fig. S13, S14** and **S16** for the results using this recipe). This is by far the most reproducible and accurate method to perform controlled stoichiometric changes and furthermore it allows the use of the same precursor solution for a complete batch. While changing the precursor stoichiometry is in principle also possible by weighing slightly different amounts of each of the precursors into individual solutions, our experience shows that human error when weighing various compounds in the same vial is often underestimated and that even with extreme care and attention, this method is less accurate than the one described above and used in this study. As the initial precursor weighing and the pipetting using calibrated Gilson Pipetman Microman E pipettes (for determining the density as well as performing changes in stoichiometry) both introduce small errors on the order of  $\sim 0.1\%$  and  $\sim 1\%$ , respectively, we were able to estimate the systematic error

for each stoichiometry *y*. As an example, using the values in **Table S1**, even in the extreme case that the actual volume per sample was 38 µl instead of the supposed 40 µl (5% relative error), the final stoichiometry after 5 variation steps would still be y = 3.0579 instead of y = 3.06 which represents an error of only  $\Delta y = 0.0021$  (see **Table S2**).

For the MAPI solvent quenching recipe, again the density of the perovskite solution and the stock solution, containing PbI<sub>2</sub>:MAI (0.95:1) and MAI (both dissolved in DMF/DMSO (4:1, v:v), with 42.96 wt % and 40 wt %, respectively), was determined by weighing to calculate the solid concentration in the solutions. Suitable amounts of stock solution were added to the starting perovskite solution to vary the stoichiometry  $z = PbI_2$ :MAI as presented in **Fig. S13** and **Fig. S15** (ESI†).

For the CsFAMA recipe, the parameter space for performing stoichiometric variations around the stoichiometric  $Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.9}Br_{0.1})_3$  (with  $z = Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}I:Pb(I_{0.85}Br_{0.15})_2 = 1$ ) is even bigger. In order to keep it simple, we varied the amount of excess Pb(I\_{0.85}Br\_{0.15})\_2, which represents the typical 'lead excess' in many publications, or the amount of excess FAI\_{0.83}MAI\_{0.17} in the precursor solution.

Same as for the PbAc<sub>2</sub> recipe, the density of the two stock solutions containing Pb(I<sub>0.85</sub>Br<sub>0.15</sub>)<sub>2</sub> and FAI<sub>0.83</sub>MAI<sub>0.17</sub> as well as that of the perovskite precursor solution Cs<sub>0.05</sub>(FA<sub>0.83</sub>MA<sub>0.17</sub>)<sub>0.95</sub>Pb(I<sub>0.9</sub>Br<sub>0.1</sub>)<sub>3</sub> (all dissolved in DMF/DMSO (4:1, v:v) with 31.2 wt%, 18 wt% and 43.3 wt%, respectively) was determined by weighing. Suitable amounts of stock solution were added to the perovskite solution to vary the stoichiometry  $z = Cs_x(FA_{0.83}MA_{0.17})_{100-x}I:Pb(I_{0.85}Br_{0.15})_2$  as presented in **Fig. S16**. The amount of Cesium is slightly decreasing upon the addition of the Cs-free stock solutions, however still remains between 0.045 < *x* < 0.05 for all investigated stoichiometries. The final nominal compositions can be written as Cs<sub>0.05</sub>(FA<sub>0.83</sub>MA<sub>0.17</sub>)<sub>0.95</sub>Pb(I<sub>0.9</sub>Br<sub>0.1</sub>)<sub>3</sub>,  $\Delta z_1$  Pb(I<sub>0.85</sub>Br<sub>0.15</sub>)<sub>2</sub> for an excess of lead or Cs<sub>0.05</sub>(FA<sub>0.83</sub>MA<sub>0.17</sub>)<sub>0.95</sub>Pb(I<sub>0.9</sub>Br<sub>0.1</sub>)<sub>3</sub>,  $\Delta z_2$  (FAI<sub>0.83</sub>MAI<sub>0.17</sub>) for an excess of organic with  $\Delta z_{1/2}$  representing the respective molar excess.

### Supplementary Note 2:

#### Modified Williamson-Hall method for microstrain estimation

Broadening and shifts in the XRD peak can be caused by either a reduction in the grain size (Scherrer broadening) and/or non-uniform strain (microstrain). We note that Scherrer broadening will only be significant when the grains are in the range of or less than 100nm, and as we will discuss later we do not expect this to be a significant contribution here. Strain is the relative change in size of an object with respect to its ideal size (or size before experiencing an external force). The microstrain in a crystalline material is a result of small fluctuations in the lattice spacing, induced by crystal imperfections/structural defects including dislocations, vacancies, stacking faults, interstitials, twinning, and grain boundaries.<sup>1,2,3</sup> By simply considering Braggs law for scattering of light of wavelength  $\lambda$ ,  $n\lambda = 2d\sin\theta$ , it is clear that small fluctuations in d (i.e.  $\Delta d$ ) will

result in small fluctuations, or broadening, in  $\theta$  when measuring the X-ray diffraction from the material. We quantify the extent of microstrain in our perovskite crystals by analysing the peak broadening in the diffraction patterns according to the modified Williamson-Hall method.<sup>2,4</sup> The effective observed d-space broadening ( $\Delta d_{obs}$ ) determined from the XRD peak width broadening, is a convoluted function of the Gaussian full width half maximum broadening in the 2 $\theta$  scan due to the instrument response ( $\Delta d_{ins}$ ), the grain size ( $\Delta d_{size}$ ) and the microstrain ( $\Delta d_{\varepsilon}$ ). These can be de-convoluted from the observed broadening, via,

$$\Delta d^{2}_{obs} = \Delta d^{2}_{\varepsilon} + \Delta d^{2}_{ins} + \Delta d^{2}_{size} \tag{1}$$

where the unit-less microstrain  $\varepsilon$  is defined as  $\varepsilon = (\Delta d_{\varepsilon}/d)$ , where d is the mean d-spacing.

For single crystals, the size effect induced peak width broadening can be neglected, hence if  $\Delta d^2_{size} \ll \Delta d^2_{obs}$  <sup>19</sup> and we can write,

 $(\Delta d^2_{obs} - \Delta d^2_{ins})^{1/2} \approx \varepsilon d.$ <sup>(2)</sup>

Therefore, the slope of  $(\Delta d^2_{obs} - \Delta d^2_{ins})^{1/2}$  versus *d*, gives the magnitude of the microstrain,  $\varepsilon$ , in the crystals.

### **References:**

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- 3. Williamson, G. . & Hall, W. . X-ray line broadening from filed aluminium and wolfram. *Acta Metall.* **1**, 22–31 (1953).
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## **Supplementary Tables:**

**Supplementary Table 1:** Example calculation for performing changes in stoichiometry: At the start, the solution with a stoichiometry of y = 2.96 contains 200 mg PbAc<sub>2</sub> with a perovskite (MAI+PbAc<sub>2</sub>) weight percentage of 41.8%. For each stoichiometry 2 samples (80 µl) are prepared. The density and the perovskite wt% was determined beforehand for all stoichiometries. Thus, the remaining weight of PbAc<sub>2</sub> after each variation step and with that the required amount of MAI/DMF stock solution (with 332.1 mg/ml MAI and 29 wt%) to obtain the desired stoichiometry could be calculated.

Stoichio-	Amount	Density	Perovskite	PbAc <sub>2</sub>	PbAc <sub>2</sub> per	Amount of	MAI/DMF				
metry, y =	of PbAc <sub>2</sub>	[mg/ml]	content	per 1	sample	MAI to change	solution to				
MAI:PbAc <sub>2</sub>	[mg]		[wt %]	ml [mg]	[mg]	<i>y</i> by 0.02 [mg]	add [µl]				
	Start: N	Start: Mix 200 mg PbAc_2 with 248.1 mg MAI and add 655.5 $\mu$ I DMF and 4.22 $\mu$ I HPA									
2.96 (x2)	200	1263	41.8	235.7	9.43		4.57				
2.98 (x2)	181.14	1261.5	41.73	234.1	9.36	1.52	<b>4</b> .10				
3.00 (x2)	162.42	1260	41.66	232.6	9.30	1.36	<b>3.63</b>				
3.02 (x2)	143.82	1258.5	41.6	231.1	9.24	1.21	<b>3</b> .16				
3.04 (x2)	125.34	1257	41.53	229.6	9.18	1.05	<b>2</b> .7				
3.06 (x2)	106.98	1255.5	41.46	228.1	9.12	0.90					

**Supplementary Table 2:** Error estimation using the same calculation as in Supplementary Table 1, but assuming that the actual volume per sample was (by error) 38  $\mu$ l instead of 40  $\mu$ l. The relative error for each step is calculated, yielding a total error of  $\Delta y = 0.0021$  for the last stoichiometry y = 3.06.

Stoichio-	Amount	Actual	PbAc <sub>2</sub> per	Actual	Aimed for	Actual	Relative				
metry, y =	of PbAc <sub>2</sub>	amount	sample	amount	stoichio-	stoichio-	error for this				
MAI:PbAc <sub>2</sub>	[mg]	[mg]	[mg]	[mg]	metry	metry	step $\Delta y$				
	Start: N	Start: Mix 200 mg PbAc_2 with 248.1 mg MAI and add 655.5 $\mu$ I DMF and 4.22 $\mu$ I HPA									
2.96 (x2)	200	200	9.43	8.96	2.98	2.9799	0.00010				
2.98 (x2)	181.14	182.08	9.36	8.90	3.00	2.9997	0.00023				
3.00 (x2)	162.42	164.28	9.30	8.84	3.02	3.0193	0.00038				
3.02 (x2)	143.82	146.6	9.24	8.78	3.04	3.0387	0.00058				
3.04 (x2)	125.34	129.04	9.18	8.72	3.06	3.0579	0.00083				
3.06 (x2)	106.98	111.6	9.12	8.67		Total error	0.0021				

**Supplementary Table 3:** EDX analysis at 10 kV. Atomic percentages of Glass/ITO/PEDOT:PSS/MAPbI<sub>3</sub> with various stoichiometries determined by EDX at an acceleration voltage of 10 kV. The values present an average of minimum 8 different spots on one sample and all perovskite layers were fabricated in the same batch. The signals from the 40 nm PEDOT:PSS (S), the ~150 nm ITO layer (Sn and In) and the glass substrate (Si) are clearly visible, showing that the whole perovskite bulk is probed. The corresponding I:Pb atomic ratios are presented in **Fig. S7**.

Element / y	С К [%]	N K [%]	ОК [%]	S L [%]	Si K [%]	ln L [%]	Sn L [%]	I L [%]	Pb M [%]
2.97	7.10	4.05	29.59	2.55	3.63	11.73	1.98	30.76	8.61
2.99	6.83	4.22	29.70	2.53	3.16	11.78	2.02	31.12	8.65
3.00	6.87	4.03	29.87	2.70	3.20	12.18	2.10	30.45	8.61
3.01	6.72	3.45	29.82	2.97	3.53	11.94	1.89	31.00	8.67
3.03	6.93	3.89	29.86	2.62	4.34	11.18	1.81	30.67	8.68
3.05	6.69	3.79	30.16	2.72	3.23	11.92	1.94	30.86	8.69

**Supplementary Table 4:** EDX analysis at 6 kV. Atomic percentages of Glass/ITO/PEDOT:PSS/MAPbI<sub>3</sub> with various stoichiometries determined by EDX at an acceleration voltage of 6 kV. The values present an average of minimum 8 different spots on one sample and all perovskite layers were fabricated in the same batch. No signal for Si, In and Sn is detected, showing that the interaction volume of the electron beam only just reaches the thin PEDOT:PSS layer and the main signal comes from regions of the perovskite layer closer to the film surface. The corresponding I:Pb atomic ratios are presented in **Fig. S7**.

Element / y	СК[%]	N K [%]	ОК[%]	S L [%]	Si K [%]	In L [%]	Sn L [%]	I L [%]	Pb M [%]
2.97	10.63	6.83	18.72	7.81	0	0	0	43.99	12.03
2.99	10.55	6.99	18.28	7.76	0	0	0	44.28	12.15
3.00	10.20	6.99	17.90	7.50	0	0	0	45.22	12.19
3.01	10.36	7.07	18.11	7.76	0	0	0	44.82	11.88
3.03	9.94	7.14	17.76	8.20	0	0	0	45.14	11.83
3.05	10.17	6.75	17.66	7.68	0	0	0	45.82	11.94

### **Supplementary Figures:**



**Figure S1. (a)** Representative J-V curves in reverse (solid lines) and forward (dotted lines) scan directions from the batch shown in the main text measured under simulated AM1.5G solar irradiance at 100 mWcm<sup>-2</sup>. (b) Representative dark J-V curves over the whole range of investigated stoichiometries.



Figure S2. (a) Representative EQE spectra of the devices shown in the main text. (b) UV-Vis measurements of various stoichiometries.



**Figure S3.** Normalized photovoltaic parameters of five batches with varying stoichiometry. The trend in (a)  $V_{OC}$ , (b)  $J_{SC}$ , (c) FF and (d) PCE with changing stoichiometry was observed in several batches. The absolute data of Batch 3 (blue) is shown in Fig.1 in the main text.



**Figure S4. (a)** Shift in XPS peak positions of Pb4f<sub>7/2</sub>, N1s and I3d<sub>5/2</sub> with changing stoichiometry and corresponding fits with slope d. (b) Ionization potential (left) and position of the MA+ peak w.r.t. to vacuum level (right) over stoichiometry and corresponding fits with slope d.



**Figure S5.** Schematic illustration of the possible quasi Fermi level splitting and the maximum obtainable  $V_{OC}$  for understoichiometric, stoichiometric and overstoichiometric perovskite layers. The position of the quasi Fermi level for holes,  $E_{F,h}$ , remains unchanged as the PEDOT:PSS/perovskite interface is not affected. The position of the quasi Fermi level for electrons,  $E_{F,e}$ , rises in energy as it is limited by the Fermi level of the metal electrode, which in our case is always at least an energetic distance  $\Delta$  below the conduction band at the surface. Reference 37 (main text) contains further information on the effect of such surface energetics changes on the device built-in potential and the open circuit voltage.



Figure S6. (a) Maximum attainable ELQE from ITO/PEDOT:PSS/MAPbI<sub>3</sub>/PCBM/BCP/Ag devices with various stoichiometries y. (b) EL spectra at a fixed current density of 200 mA/cm<sup>2</sup>.



Figure S7. I/Pb atomic ratio determined by EDX measurements performed at 10 kV (black) and 6 kV (red) as well as a fit to the corresponding XPS data in Fig. 2d.



**Figure S8.** Tracking of the photovoltaic parameters in reverse scan with dark storage in ambient atmosphere of Batch 2 in **Fig. S3**, (a) Voc, (b) J<sub>SC</sub>, (c) FF, (d) PCE, (d) SPO after 297 days and (e) hysteresis index.



**Figure S9.** Tracking of the photovoltaic parameters in reverse scan with dark storage in ambient atmosphere of Batch 1 in **Fig. S3**, (a) Vo<sub>C</sub>, (b) J<sub>SC</sub>, (c) FF, (d) PCE, (d) SPO after 245 days and (e) hysteresis index.



Figure S10. (a) Peak intensity and full width half maximum (FWHM) of the (110) peak for various stoichiometries. (b) Lattice constant over stoichiometry for the (110) and (220) planes.



**Figure S11.** (a) A modified Williamson-Hall plot of  $(\Delta d_{obs}^2 - \Delta d_{ims}^2)^{1/2}$  versus d spacing extracted from the corresponding diffraction profiles shown in Fig. 4c in the main text. The slopes of the solid lines from linear fits indicate the extent of microstrain for the different stoihciomteries. (b) Calculated microstrain of samples with different precursor ratios.



**Figure S12.** (a) Bandgap of ITO/PEDOT:PSS/MAPbI<sub>3</sub> with various stoichiometries calculated from Tauc-plots. (b) PDS measurements of Glass/MAPbI<sub>3</sub> with various stoichiometries. The Urbach energy (Eu) is determined by fitting the exponential decay of the absorbance with the equation shown in the graph.



**Figure S13. (a)-(d)** PV parameters in reverse scan of FTO/Poly-TPD/PbAc<sub>2</sub>/PCBM/BCP/Ag solar cells with variation of the  $y = MAI:PbAc_2$  ratio. See Experimental Section and Supplementary Note 1 for more details on solution and device preparation.



**Figure S14.** (a)-(d) PV parameters in reverse scan of FTO/Poly-TPD(F<sub>4</sub>-TCNQ)/MAPI/PCBM/BCP/Ag solar cells with variation of the z = MAI:PbI<sub>2</sub> ratio. See Experimental Section and Supplementary Note 1 for more details on solution and device preparation.



**Figure S15. (a)-(d)** PV parameters in reverse scan of ITO/SnO<sub>2</sub>-NP/PbAc<sub>2</sub>/Spiro-OMeTAD/Ag solar cells with variation of the  $y = MAI:PbAc_2$  ratio. See Experimental Section and Supplementary Note 1 for more details on solution and device preparation.



Figure S16. (a)-(d) PV parameters in reverse scan of  $FTO/SnO_2/PCBM/MAPI/Spiro-OMeTAD/Ag$  solar cells with variation of the  $z = MAI:PbI_2$  ratio. See Experimental Section and Supplementary Note 1 for more details on solution and device preparation.



**Figure S17.** (a) PCE (average of the reverse and forward scan) of FTO/Poly-TPD (F4-TCNQ)/CsFAMA/PCBM/BCP/Ag solar cells with  $C_{s0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.9}Br_{0.1})_3$  as active layer and variation of the  $z = Cs_{100-x}(FAI_{0.83}MAI_{0.17})_x$ : Pb(I<sub>0.85</sub>Br<sub>0.15</sub>)<sub>2</sub> ratio and (b) corresponding J-V curve of the champion pixel with z = 1.0085. See Experimental Section and Supplementary Note 1 for more details on solution and device preparation.



Figure S18. Preliminary storage stability investigation of PbAc<sub>2</sub>-based devices in the standard architecture (Fig. S15), showing that the initially most efficient overstoichiometric devices with y = 3.03 are degrading much faster when compared to the very stable devices with  $y \sim 2.99$ . The unencapsulated devices were stored in air in dark (~40-50% RH) between the measurements.