

# Intermediate-phase engineering via dimethylammonium cation additive for stable perovskite solar cells

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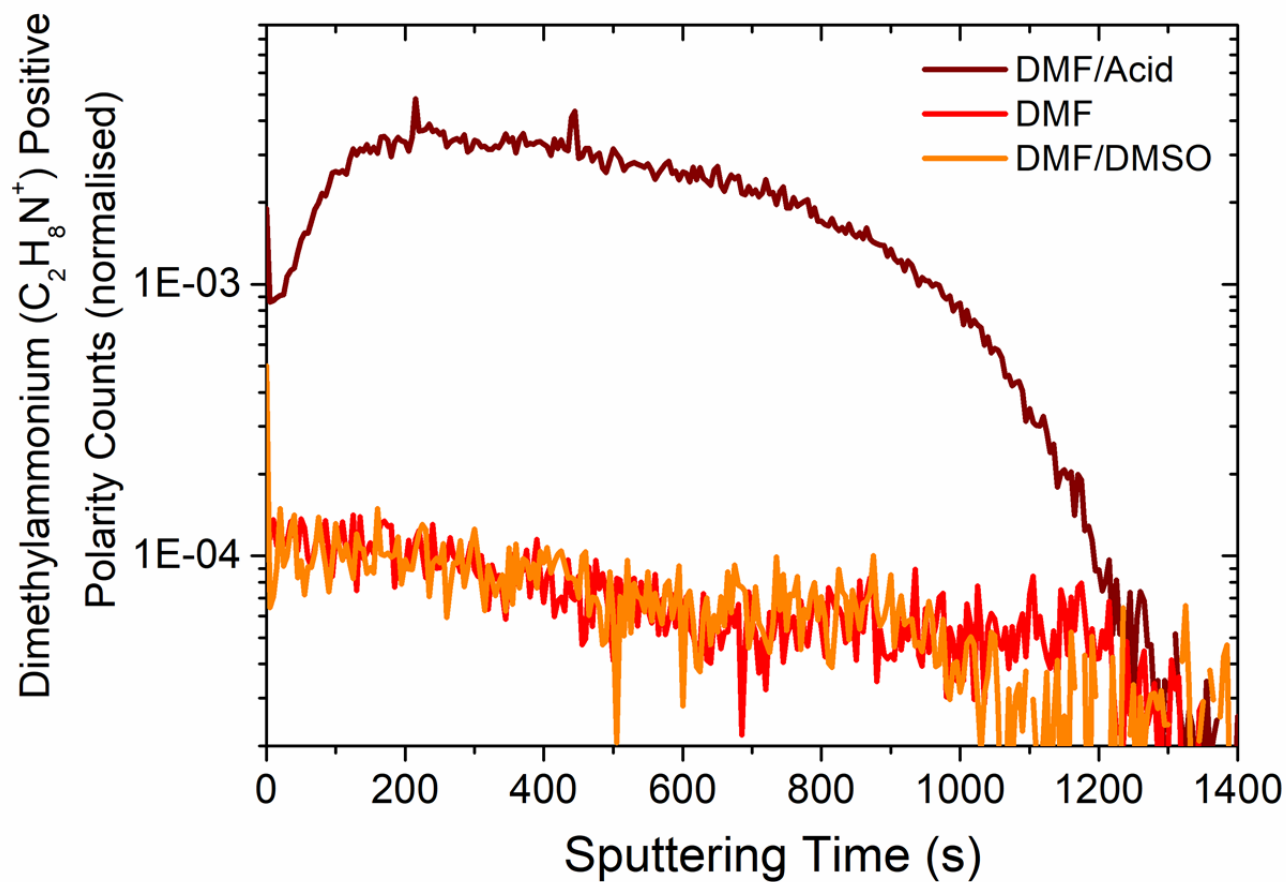
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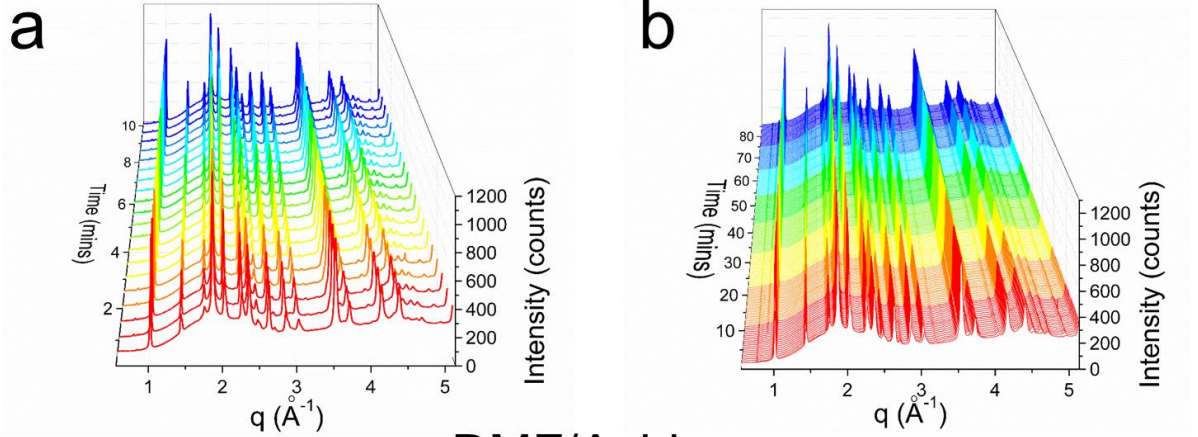
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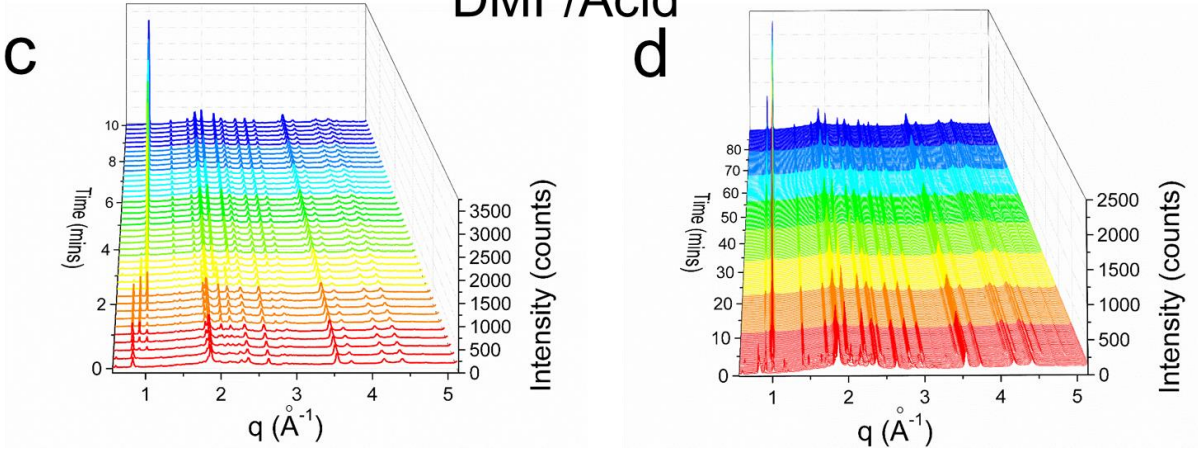


Supplementary Figure S1: Positive Polarity Time-of-flight secondary ion mass spectrometry (TOF-SIMS) detecting dimethylammonium  $C_2H_8N^+$  ions of (FA, Cs)Pb(Br, I)<sub>3</sub> films prepared using various fabrication methods after a 185 °C 90 mins annealing step.

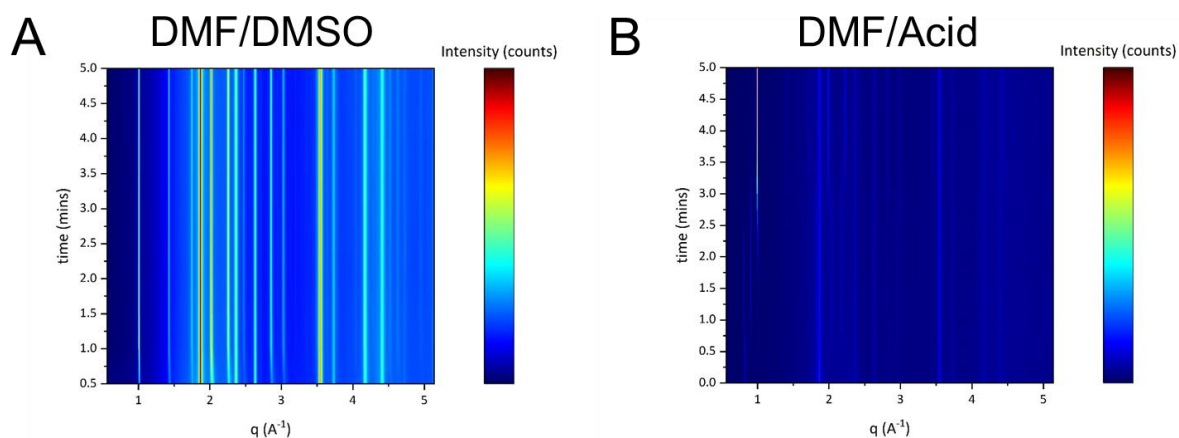
## DMF/DMSO



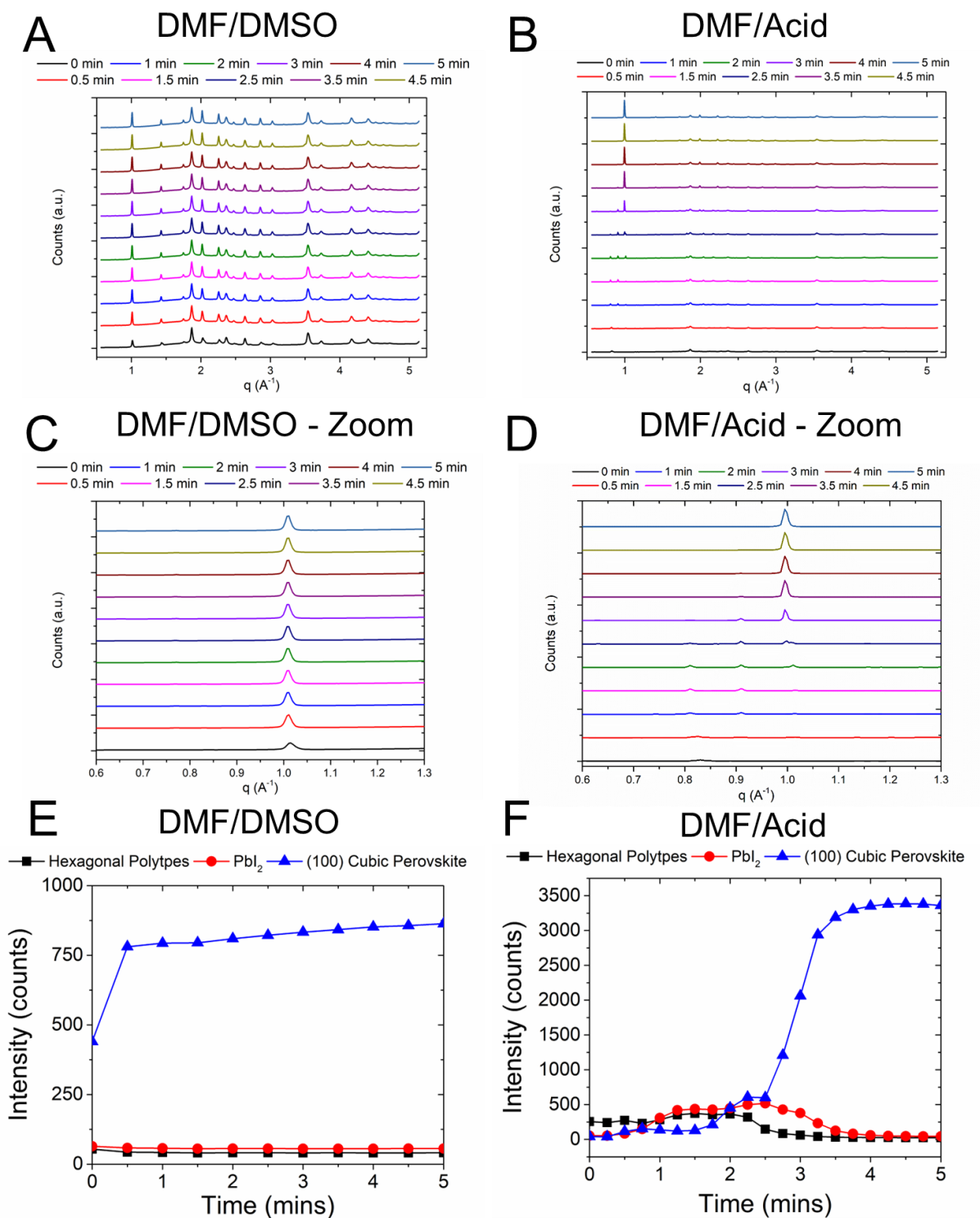
## DMF/Acid



**Supplementary Figure S2: In-situ crystallization of  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$  perovskite films comparing a low-temperature DMF/DMSO fabrication method to a high-temperature DMF/Acid fabrication method.** Wide-angle X-ray scattering (WAXS) data of a  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$  perovskite film fabricated with the DMF/DMSO and the DMF/Acid preparation method. The data shows a) the first 10 minutes and b) 90 minutes of annealing at 100 °C. Wide-angle X-ray scattering (WAXS) data of a  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$  perovskite film fabricated with the DMF/Acid method prepared with a “fully-aged” solution, which was aged for more than 72h after the addition of the HI/HBr additive. The data shows c) the first 10 minutes and d) 90 minutes of annealing at 185 °C. Annealing was done in a helium atmosphere with slight water/oxygen contamination.



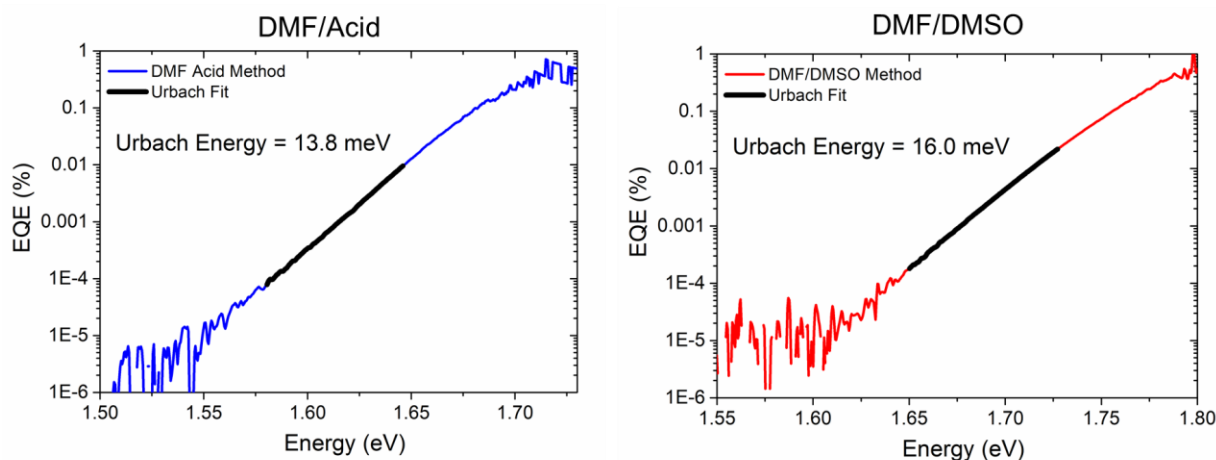
**Supplementary Figure S3: Wide-angle X-ray scattering (WAXS) 2D waterfall data of a  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$  perovskite film fabricated with a low-temperature DMF/DMSO and a high-temperature DMF/Acid fabrication method.** The data shows the first 5 minutes of a  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$  perovskite film fabricated with the **a)** DMF/DMSO fabrication method annealed at 100 °C **b)** DMF/Acid fabrication method annealed at 185 °C. The DMF/Acid method was prepared with a “fully-aged” solution, which was aged for more than 72h after the addition of the HI/HBr additive. Annealing was done in a helium atmosphere with slight water/oxygen contamination.



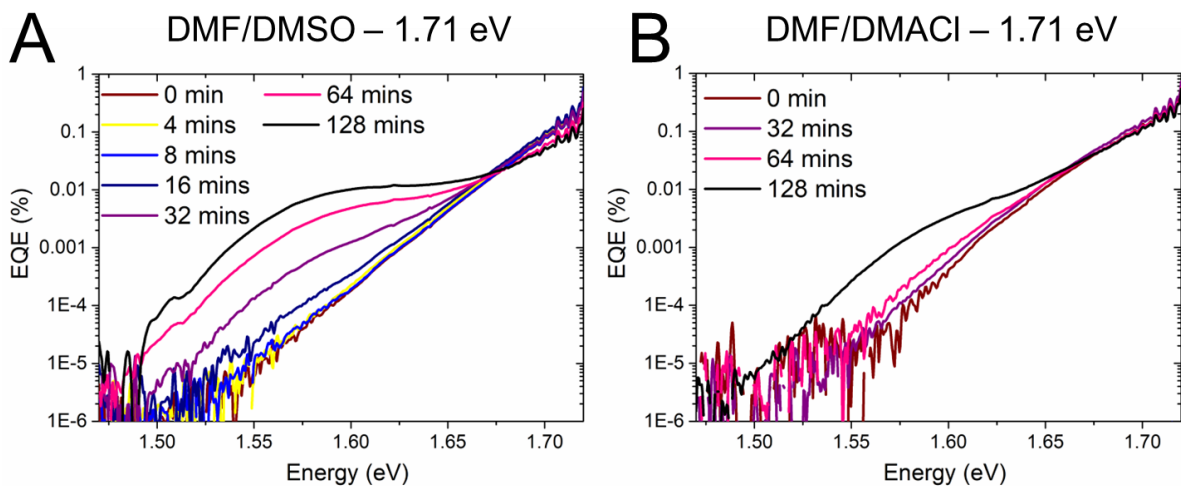
**Supplementary Figure S4: Wide-angle X-ray scattering (WAXS) 2D layered data and time-traces of individual diffraction peak of a  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$  perovskite film fabricated with a low-temperature DMF/DMSO and a high-temperature DMF/Acid fabrication method. The data shows the first 5 minutes of a  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$  perovskite film fabricated with the **A, C, E**) DMF/DMSO fabrication method annealed at  $100^\circ\text{C}$  **B, E, F**) DMF/Acid fabrication method annealed at  $185^\circ\text{C}$ . The DMF/Acid method was prepared with a “fully-aged” solution, which was**

aged for more than 72h after the addition of the HI/HBr additive. Annealing was done in a helium atmosphere with slight water/oxygen contamination.

We note that the DMF/acid route resulted in a  $\sim 50$  meV decrease in the bandgap of the pristine film in comparison to the DMF/DMSO route, possibly due to a halide exchange occurring during the crystallization process due to the hydrohalic acids. However, we note that Urbach energy stability improvement cannot simply be attributed to a narrower effective bandgap since the minority phase bandgap for the DMF/DMSO film stabilizes to 1.57 eV, which is 140 meV lower than the stabilized  $E_{g,minority}$  for the DMF/acid film. Furthermore, as shown on Fig. S6, for an identical 1.71 eV band gap, the DMF/DMSO  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.32}\text{I}_{0.64})_3$  perovskite film formed a minority phase narrow band gap material significantly faster than a 1.71 eV DMF/DMAcI  $\text{DMA}_{0.3}\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.32}\text{I}_{0.64})_3\text{Cl}_{0.3}$  perovskite film.

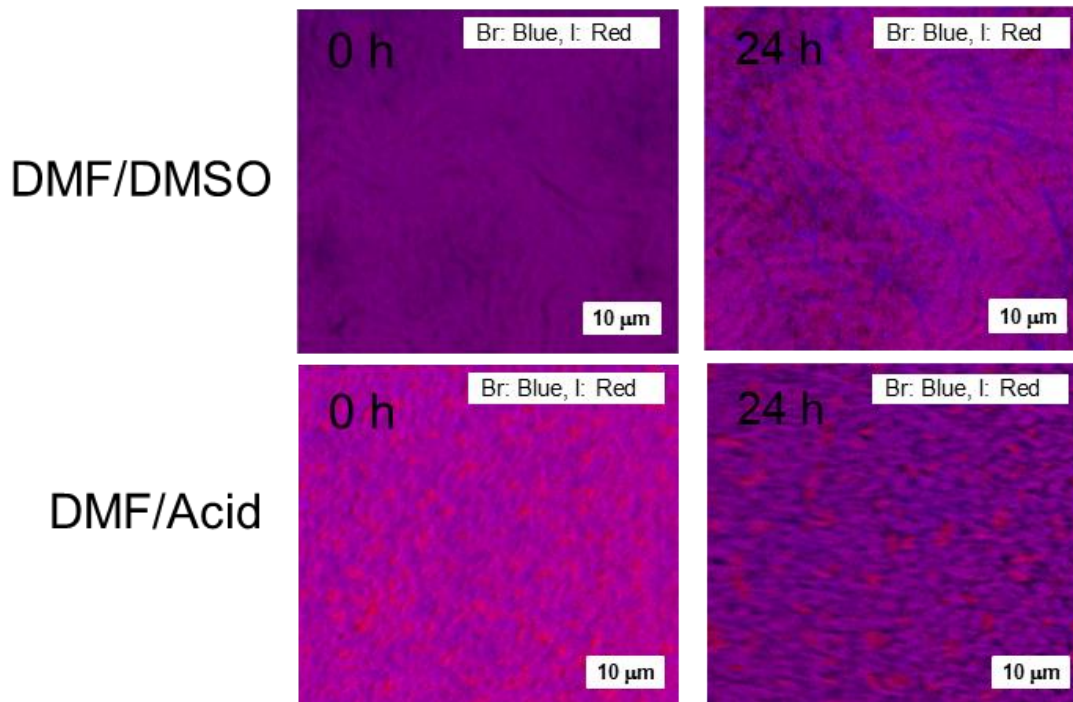


**Supplementary Figure S5: Semi-log plot of external quantum efficiency (EQE) at the absorption onset of A) a “DMF/Acid” film and B) “DMF/DMSO” film, measured using Fourier-transform photocurrent spectroscopy (FTPS) in short-circuit configuration.**



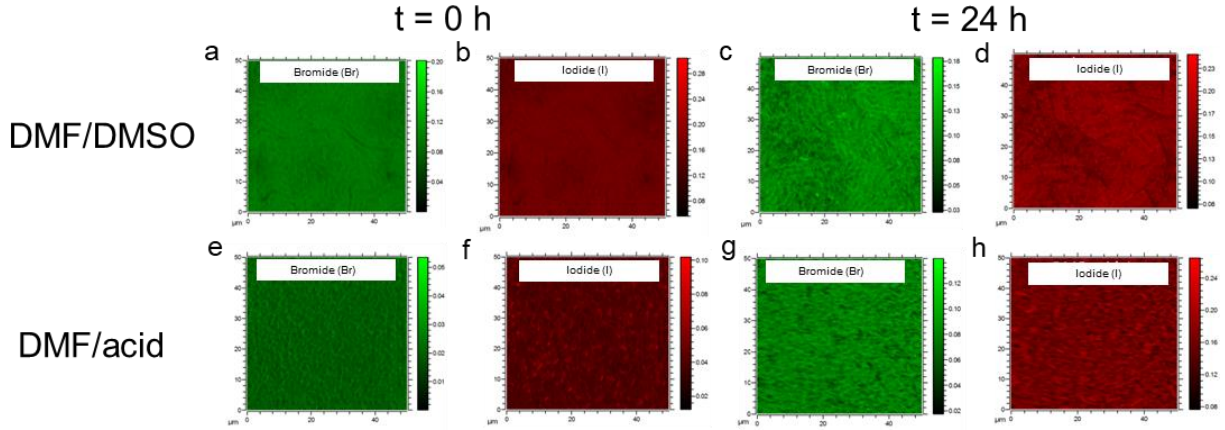
**Supplementary Figure S6: External quantum efficiency (EQE), measured via Fourier transform photocurrent spectroscopy for a solar cell with a) a 1.71 eV DMF/DMSO  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.32}\text{I}_{0.64})_3$  perovskite film, and with b) a DMF/DMACl  $\text{DMA}_{0.3}\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.28}\text{I}_{0.72})_3\text{Cl}_{0.3}$  perovskite film. For the EQE measurements, the devices were non-encapsulated and illuminated by a xenon-lamp simulated full-spectrum AM 1.5G,  $42 \text{ mW cm}^{-2}$  irradiance at open-circuit in air ( $\sim 45 \text{ RH}\%$ ) at room temperature.**

# Halide Segregation (I/Br)



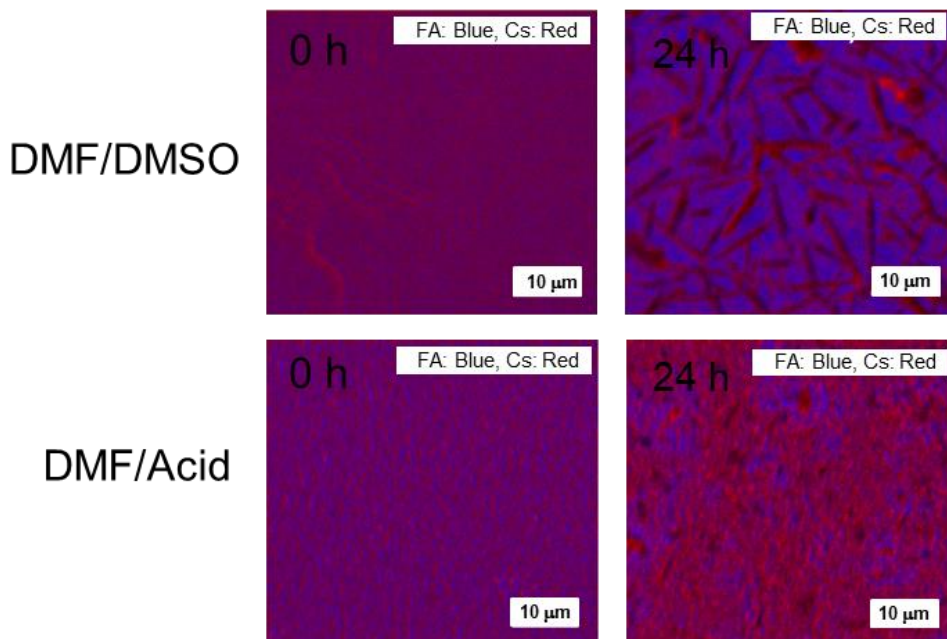
**Supplementary Figure S7: Formamidinium/caesium A-site cation segregation.** TOF-SIMS 2D mapping of Br (blue) and I (red) overlays for the (a) DMF/DMSO, (b) DMF/acid devices aged for 0 hours, and c) DMF/DMSO d) DMF/acid devices aged for 24 hours. The devices were then aged under AM 1.5G sunlight at maximum power point (MPP) in ambient air for 24 hours without encapsulation. All devices were fabricated with a FTO/SnO<sub>2</sub>/PC<sub>61</sub>BM/FA<sub>0.83</sub>CS<sub>0.17</sub>Pb(I<sub>0.6</sub>Br<sub>0.4</sub>)<sub>3</sub>/spiro-OMeTAD/Au architecture. The data was reconstructed to include data only from the perovskite absorber layer from a 3-D tomography dataset of the entire device stack. The images are based on a relative intensity scale for each species, which is shown for each individual image in **Fig. S8**.

## Halide Segregation (I/Br)



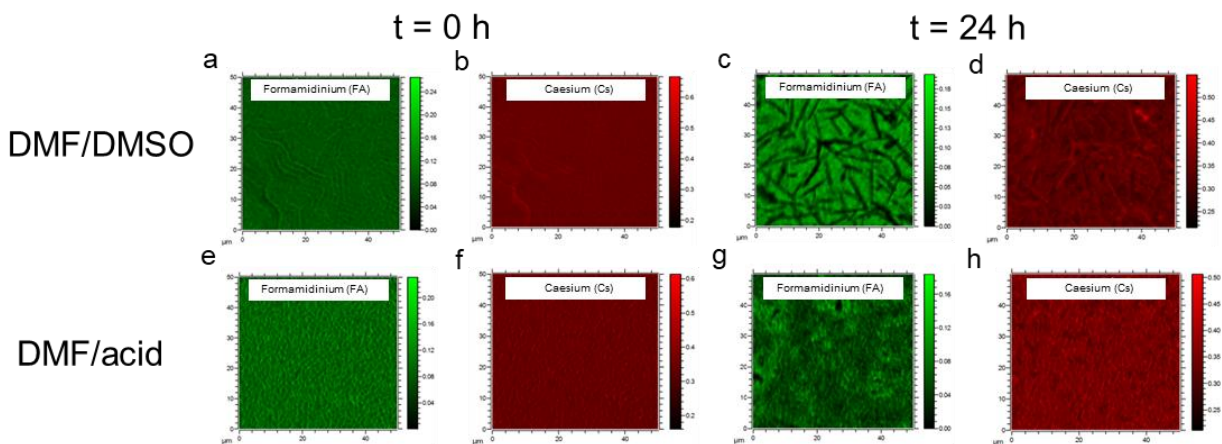
**Supplementary Figure S8: Light stability of individual halides measured using TOF-SIMS mapping.** TOF-SIMS 2D mapping of **a)** Br and **b)** I for the DMF/DMSO devices at  $t = 0$  h. TOF-SIMS 2D mapping of **c)** Br and **d)** I for the DMF/DMSO devices at  $t = 24$  h. TOF-SIMS 2D mapping of **e)** Br and **f)** I for the DMF/acid devices at  $t = 0$  h. TOF-SIMS 2D mapping of **g)** Br and **h)** I for the DMF/acid devices at  $t = 24$  h. The devices were aged under AM 1.5G sunlight at maximum power point (MPP) in ambient air for 24 hours without encapsulation. All devices were fabricated with a  $n-i-p$  FTO/SnO<sub>2</sub>/PC<sub>61</sub>BM/FA<sub>0.83</sub>CS<sub>0.17</sub>Pb(I<sub>0.6</sub>Br<sub>0.4</sub>)<sub>3</sub>/spiro-OMeTAD/Au architecture. The data was reconstructed to include data only from the perovskite absorber layer from a 3-D tomography dataset of the entire device stack. All the image sizes are 50 μm × 50 μm. The data were normalized to the total intensity measured at every pixel to minimize topographic effects on the image. Thus the scale at the right of each image is the normalized intensity ( $I_{\text{pixel } x} / I_{\text{total at pixel } x}$ ).

## Cation Segregation (FA/Cs)



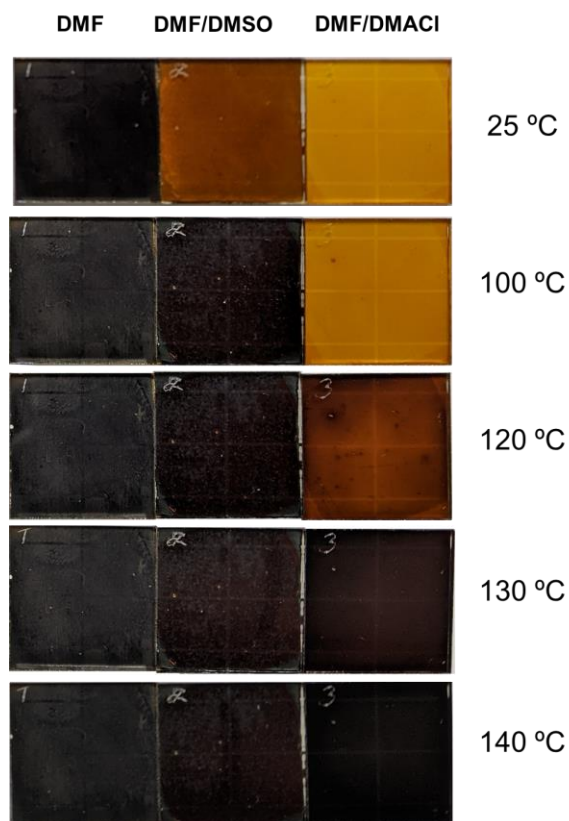
**Supplementary Figure S9: Formamidinium/caesium A-site cation segregation.** TOF-SIMS 2D mapping of FA (blue) and Cs (red) overlays for the (a) DMF/DMSO, (b) DMF/acid devices aged for 0 hours, and (c) DMF/DMSO (d) DMF/acid devices aged for 24 hours. The devices were aged under AM 1.5G sunlight at maximum power point (MPP) in ambient air for 24 hours without encapsulation. All devices were fabricated with a  $n$ -i-p FTO/SnO<sub>2</sub>/PC<sub>61</sub>BM/FA<sub>0.83</sub>Cs<sub>0.17</sub>Pb(I<sub>0.6</sub>Br<sub>0.4</sub>)<sub>3</sub>/spiro-OMeTAD/Au architecture. The data was reconstructed to include data only from the perovskite absorber layer from a 3-D tomography dataset of the entire device stack. The images are based on a relative intensity scale for each species, which is shown for each individual image in Fig. S10.

## A-site Cation Segregation (FA/Cs)

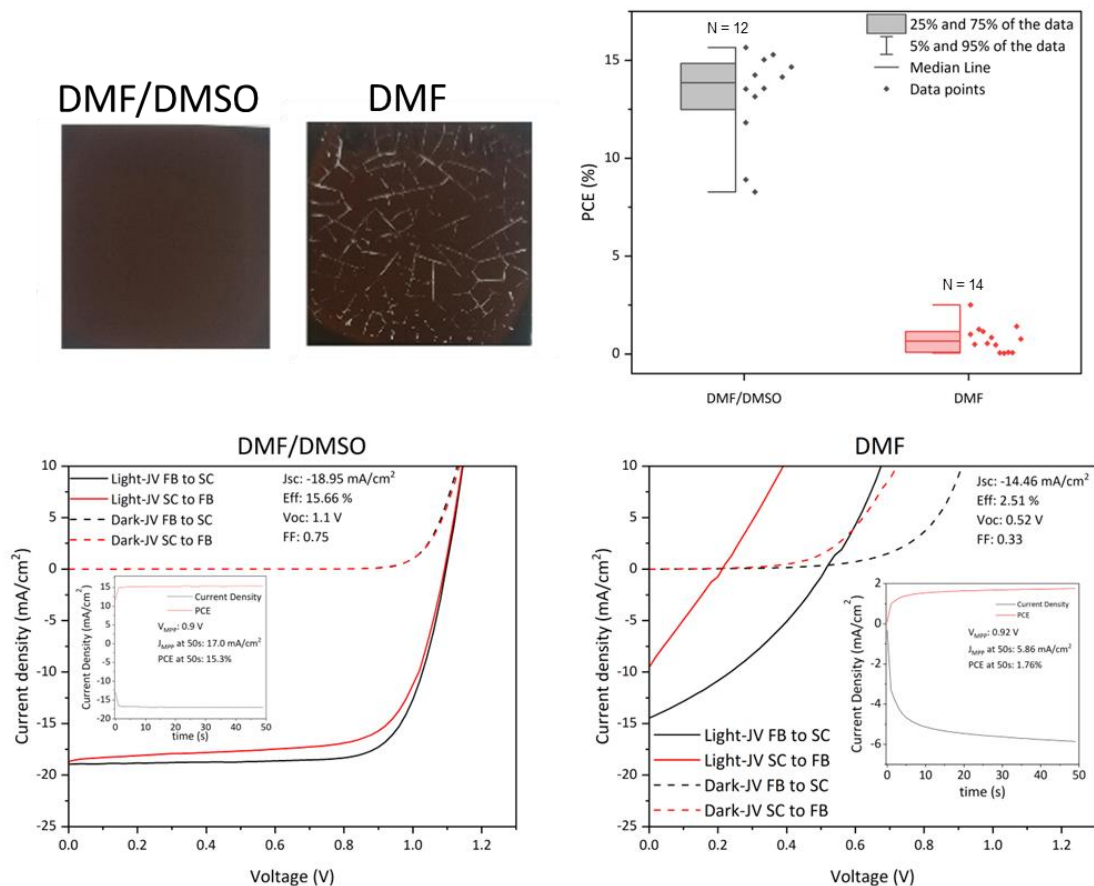
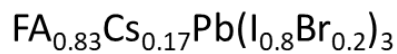


**Figure S10: Light stability of individual A-site cation measured using TOF-SIMS mapping.** TOF-SIMS 2D mapping of (a) FA and (b) Cs for the DMF/DMSO devices at  $t = 0$  h. TOF-SIMS 2D mapping of (c) FA and (d) Cs for the DMF/DMSO devices at  $t = 24$  h. TOF-SIMS 2D mapping of (e) FA and (f) Cs for the DMF/acid devices at  $t = 0$  h. TOF-SIMS 2D mapping of (g) FA and (h) Cs for the DMF/acid devices at  $t = 24$  h. The devices were aged under AM 1.5G sunlight at maximum

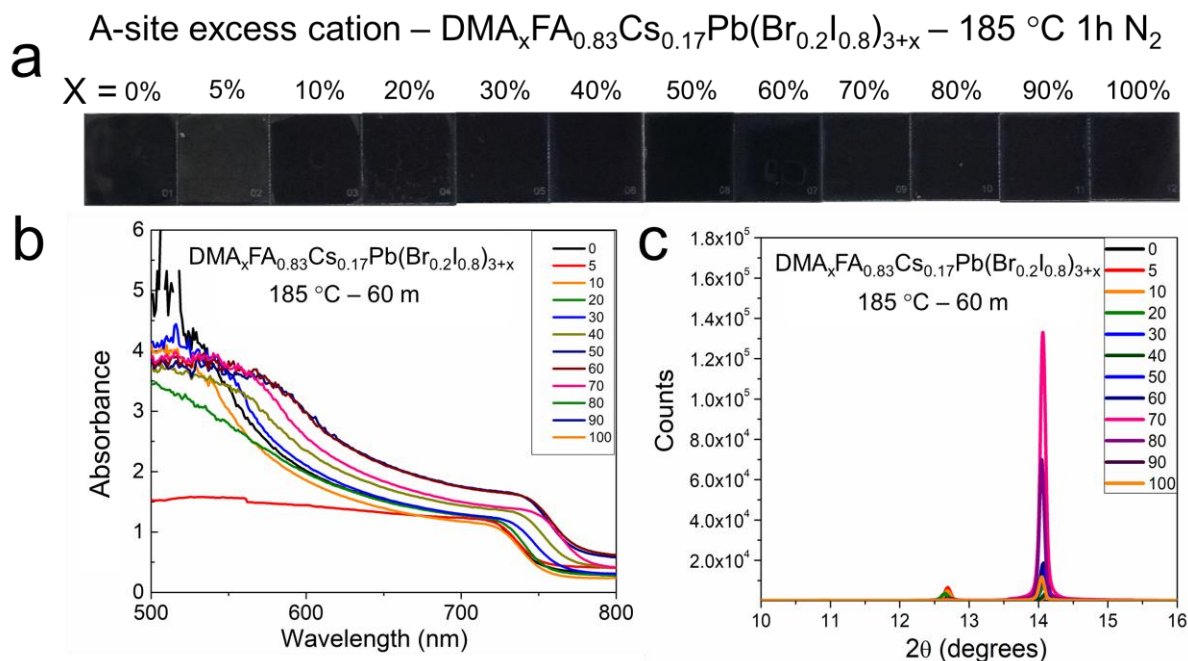
power point (MPP) in ambient air for 24 hours without encapsulation. All devices were fabricated with a n-i-p FTO/SnO<sub>2</sub>/PC<sub>61</sub>BM/FA<sub>0.83</sub>CS<sub>0.17</sub>Pb(I<sub>0.6</sub>Br<sub>0.4</sub>)<sub>3</sub>/spiro-OMeTAD/Au architecture. The data was reconstructed to include data only from the perovskite absorber layer from a 3-D tomography dataset of the entire device stack. All the image sizes are 50  $\mu\text{m}$   $\times$  50  $\mu\text{m}$ . The data were normalized to the total intensity measured at every pixel to minimize topographic effects on the image. Thus the scale at the right of each image is the normalized intensity ( $I_{(\text{pixel } x)} / I_{\text{total at pixel } x}$ ).



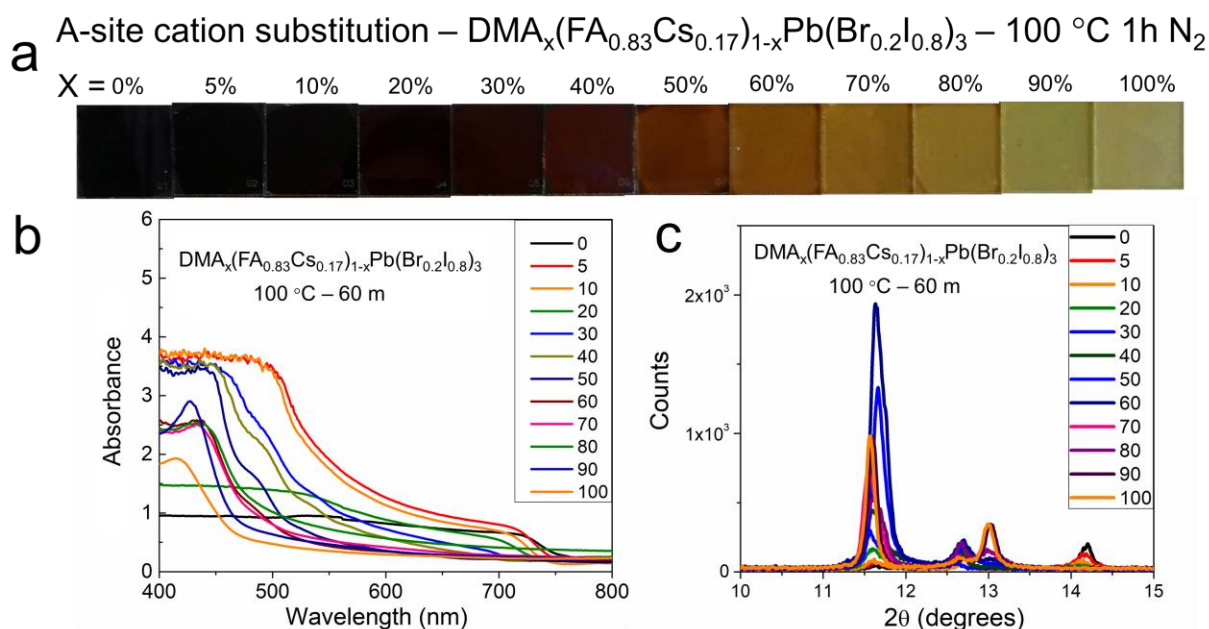
**Supplementary Figure S11: Impact of temperature on the various film preparation methods DMF, DMF/DMSO and DMF/DMAcI.** The films were heated at 25 °C, 100 °C, 120 °C, 130 °C and 140 °C for 1 minute in an air atmosphere. The neat DMF film appeared black immediately after spin coating, while the DMF/DMSO and DMF/DMAcI had a translucent appearance after spin coating and only at a temperature above 100 °C and 140 °C that these films appeared black. All images were captured on the FTO glass side.



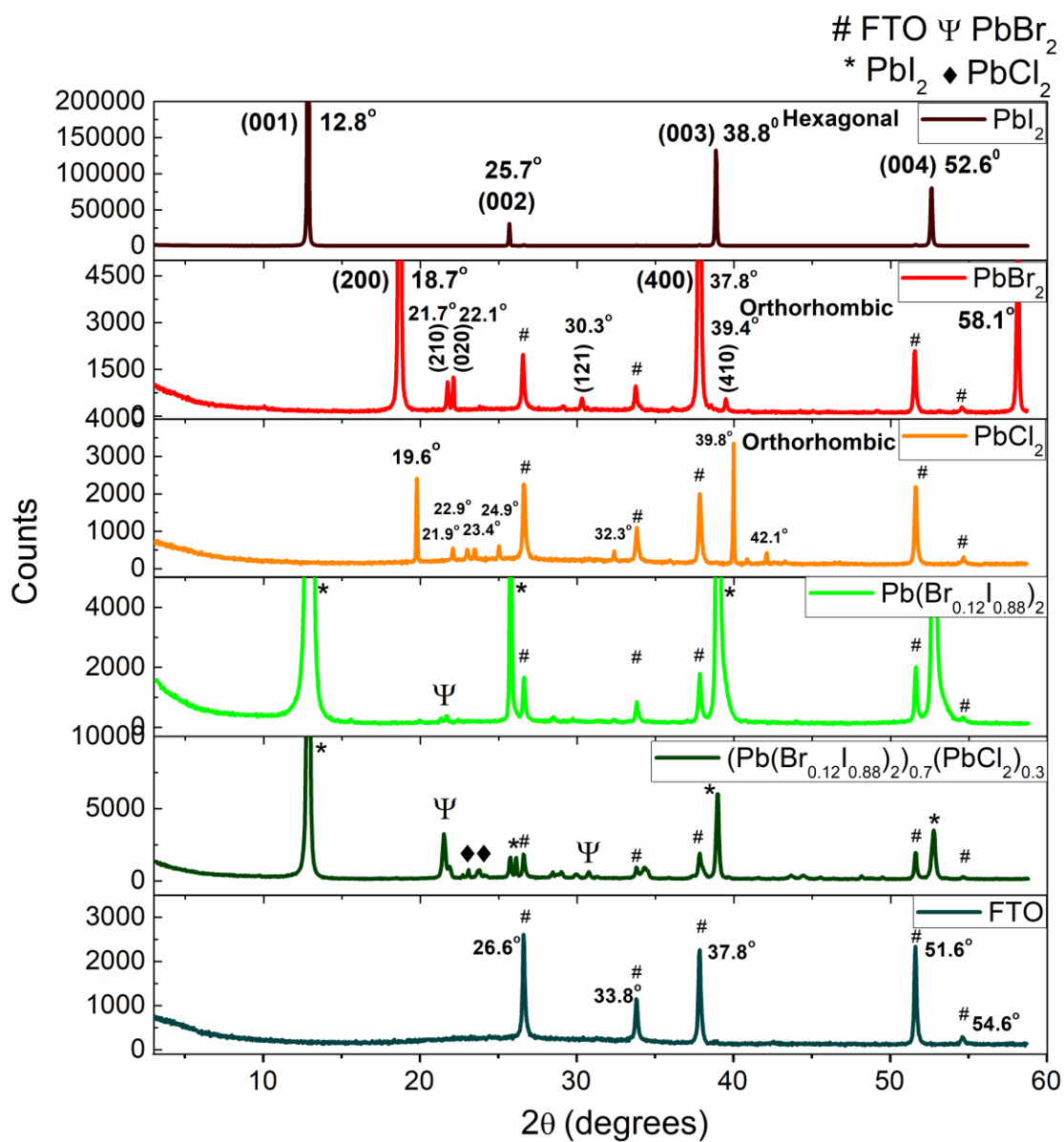
**Supplementary Figure S12: Comparison between a DMF/DMSO and a neat DMF solvent mixture for perovskite devices.** A) Images of a backlit perovskite films prepared with a DMF/DMSO and a neat DMF solvent mixture. B) PCE comparison between both methods. C) JV characteristics and stabilized efficiency of a DMF/DMSO device D) JV characteristics of a neat DMF device.



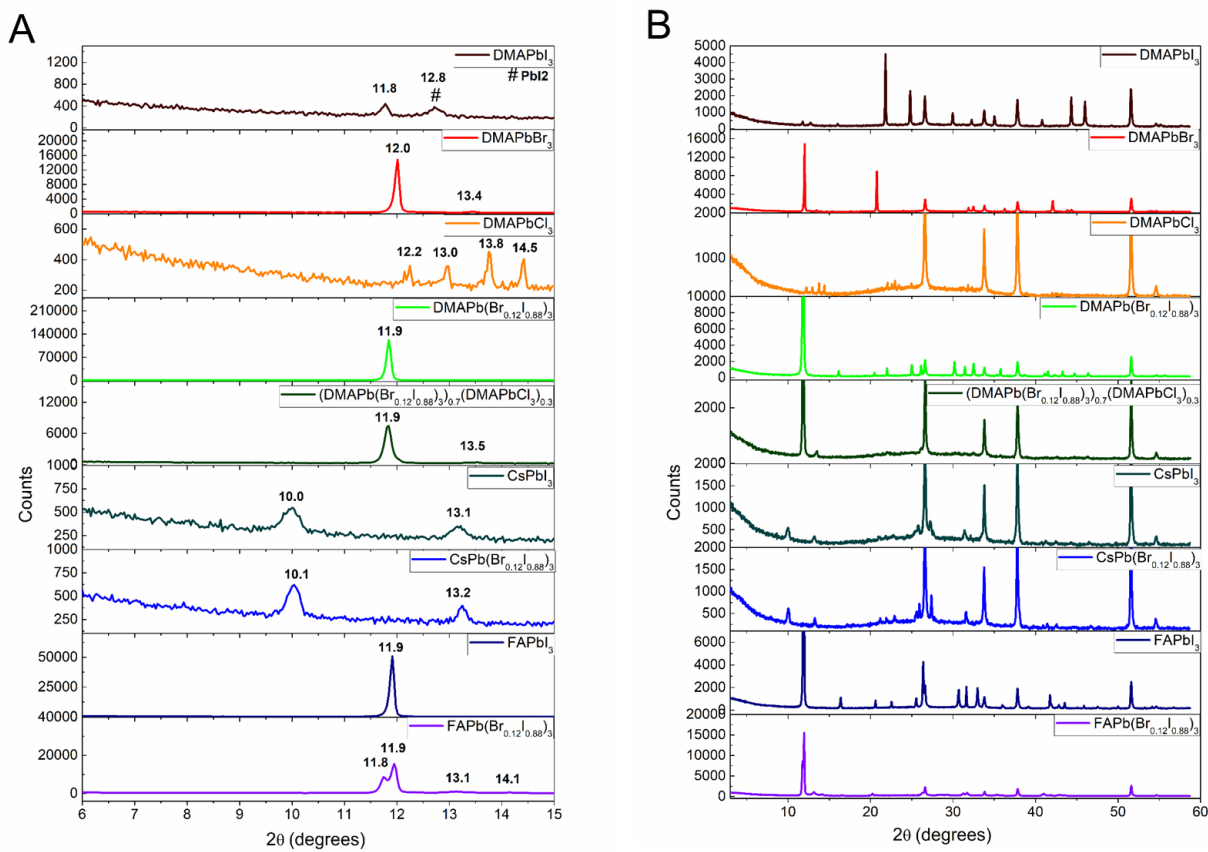
**Supplementary Figure S13: A-site excess cation of the  $\text{DMA}_x\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.2}\text{I}_{0.8})_{3+x}$  perovskite system after a 60 mins anneal at 185 ° C. a) A series of photographs b) X-Ray diffraction patterns c) Ultraviolet-visible (UV-Vis) absorbance spectra of corresponding thin films.**



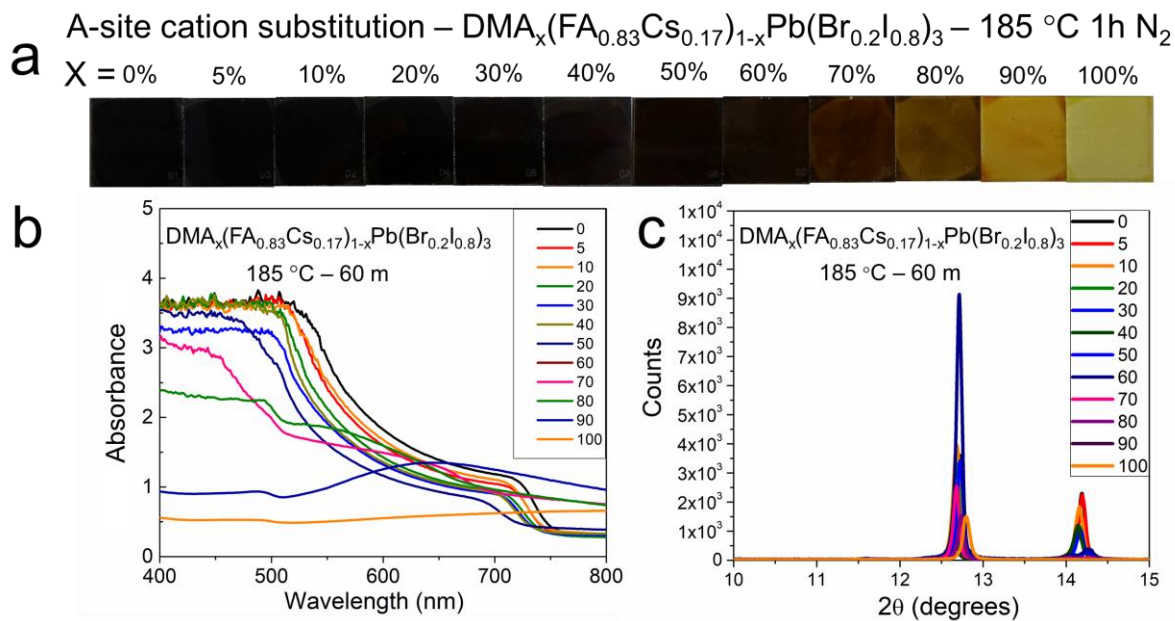
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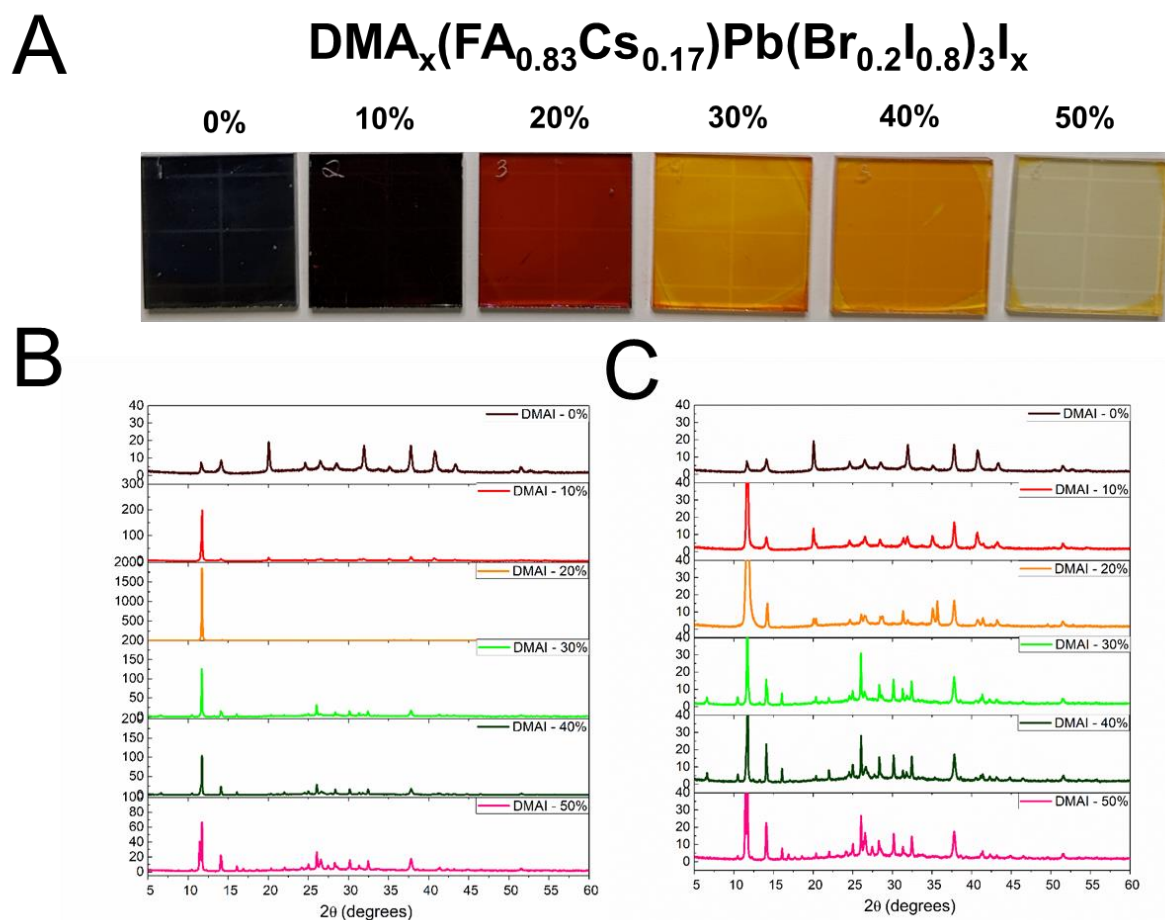
**Supplementary Figure S15: X-Ray diffraction pattern (XRD) for several  $\text{PbX}_2$  compositions formed on fluorine-doped tin oxide (FTO) coated glass substrates when annealed at 100 °C for 5 m.**



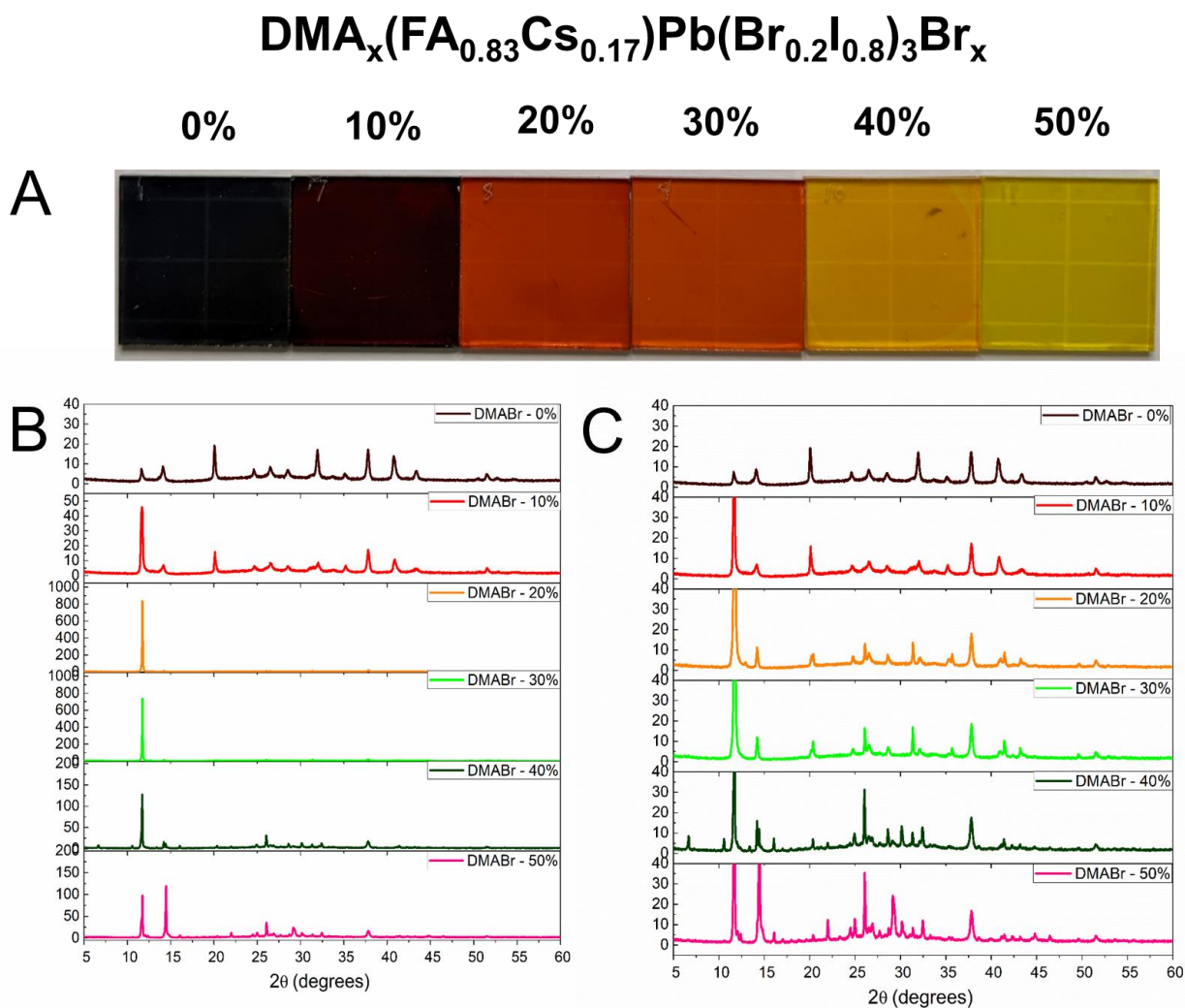
**Supplementary Figure S16: X-ray diffraction pattern (XRD) for DMAPbI<sub>3</sub>, DMAPbBr<sub>3</sub>, DMAPbCl<sub>3</sub>, DMAPb(Br<sub>0.12</sub>I<sub>0.88</sub>)<sub>3</sub>, (DMAPb(Br<sub>0.12</sub>I<sub>0.88</sub>)<sub>3</sub>)<sub>0.7</sub> DMAPbCl<sub>3</sub>)<sub>0.3</sub>, CsPbI<sub>3</sub>, CsPb(Br<sub>0.12</sub>I<sub>0.88</sub>)<sub>3</sub>, FAPbI<sub>3</sub>, FAPb(Br<sub>0.12</sub>I<sub>0.88</sub>)<sub>3</sub> compositions formed on fluorine-doped tin oxide (FTO) coated glass substrates when annealed at 100 °C for 5 m. We show the XRD for these perovskite compounds from A) 2θ 6 to 15° and B) 2θ 3 to 60°.**



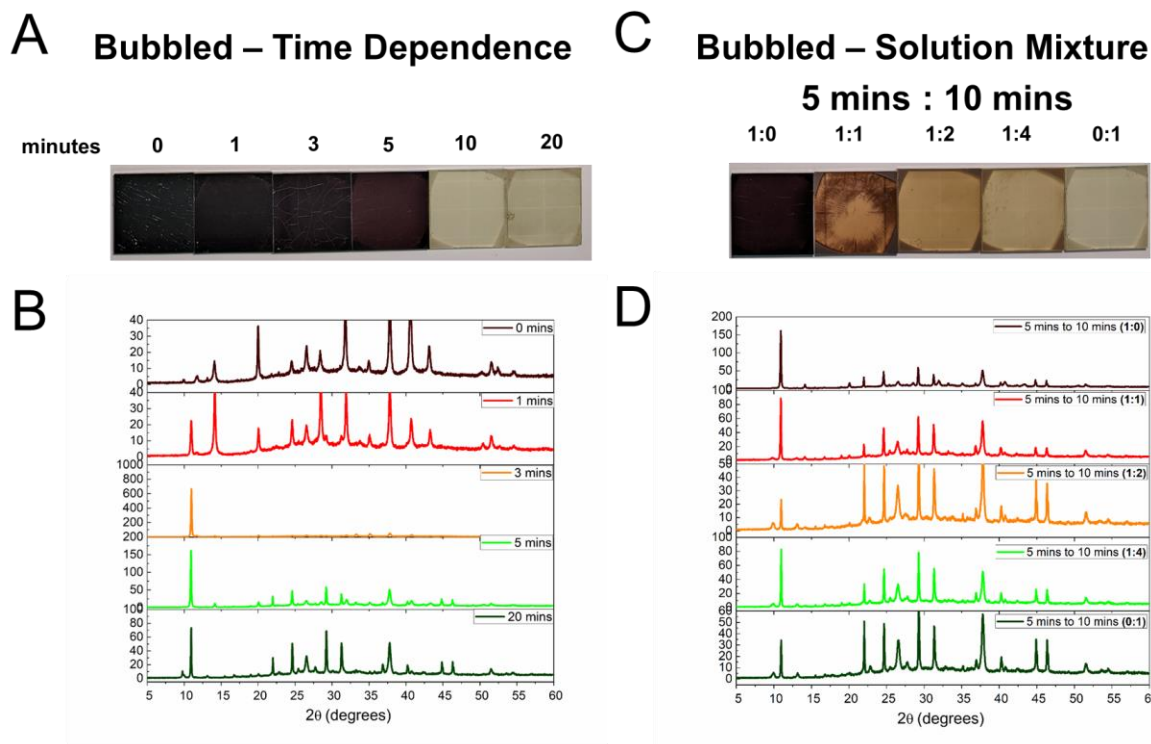
**Supplementary Figure S17: A-site cation substitution of the  $\text{DMA}_x(\text{FA}_{0.83}\text{Cs}_{0.17})_{1-x}\text{Pb}(\text{Br}_{0.2}\text{I}_{0.8})_3$  perovskite system after a 60 m anneal at 185 °C. A) A series of photographs B) X-Ray diffraction patterns C) Ultraviolet-visible (UV-Vis) absorbance spectra of corresponding thin films.**



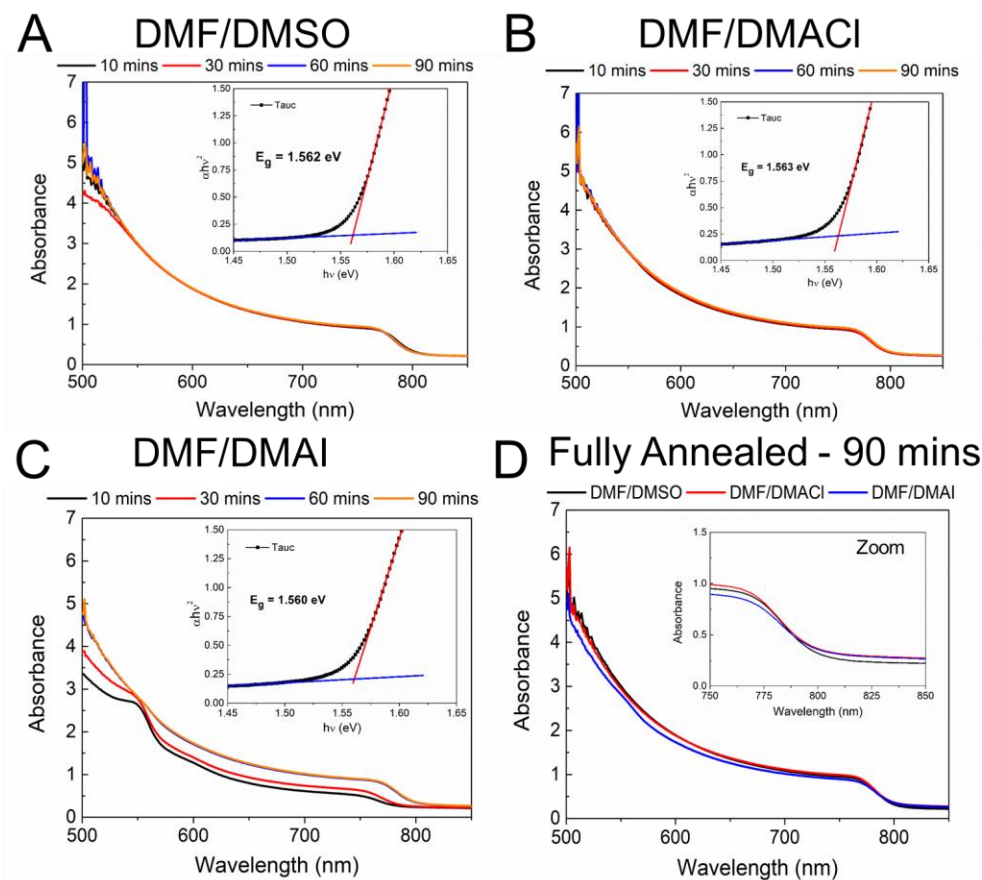
**Supplementary Figure S18: Impact of DMAI on the intermediate phases of the  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.8}\text{I}_{0.2})_3$**  A) A series of photographs of  $\text{DMA}_x\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.8}\text{I}_{0.2})_3\text{I}_x$  perovskite films spin-coated heated at 100 °C for 1m, with various amounts of DMAI additive, where percentages are expressed in excess amounts with respect to lead. B) A series of X-Ray diffraction patterns of the corresponding thin film showing the intermediate precursor phases in the form of hexagonal polytypes. C) A series of zoom-in graphs of the corresponding XRD patterns.



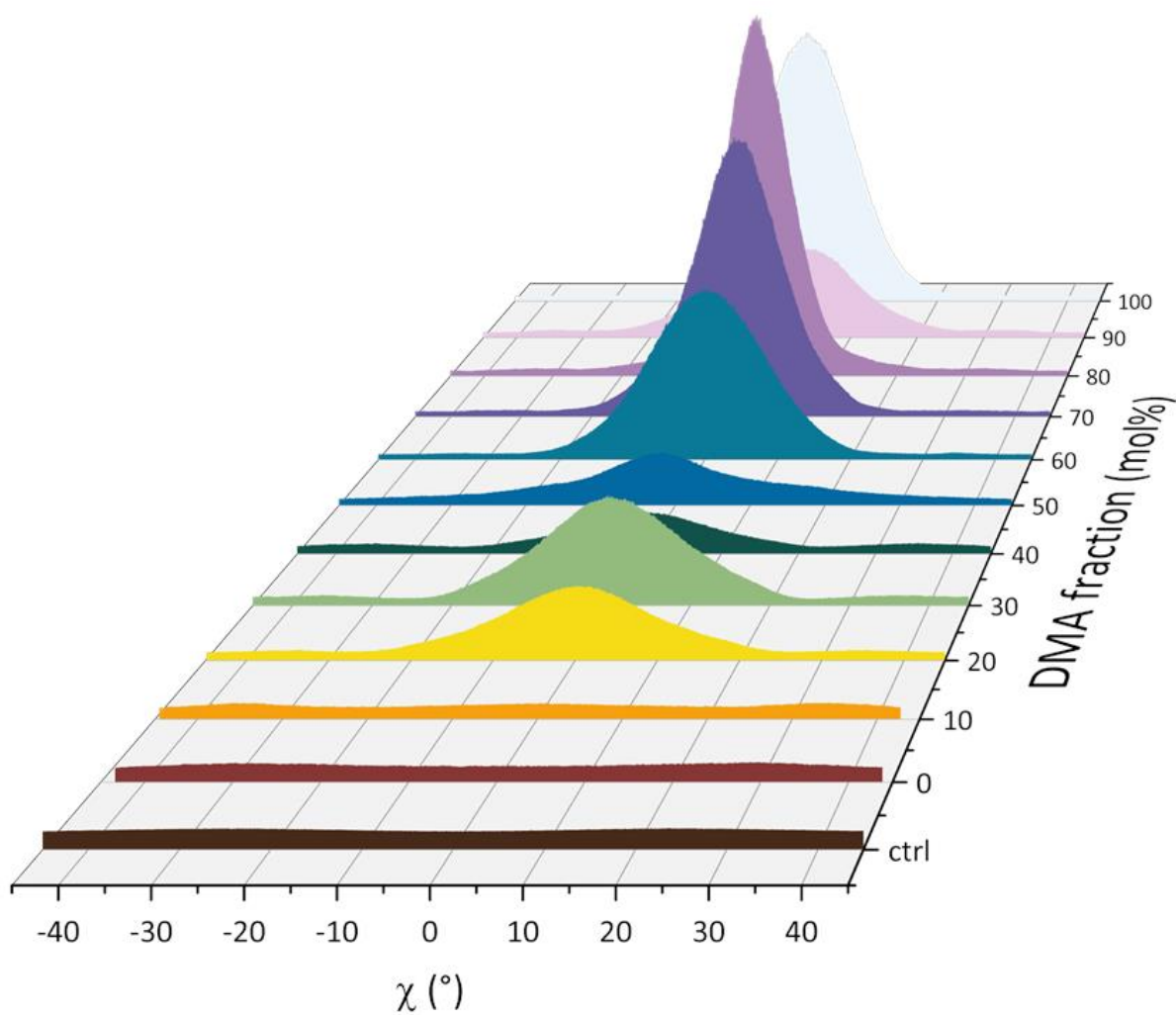
**Supplementary Figure S19: Impact of DMABr on the intermediate phases of the  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.2}\text{I}_{0.8})_3$ .** A) A series of photographs of  $\text{DMA}_x\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.2}\text{I}_{0.8})_3$  perovskite films spin-coated heated at 100 °C for 1m, with various amounts of DMABr additive, where percentages are expressed in excess amounts with respect to lead. B) A series of X-Ray diffraction patterns of the corresponding thin film showing the intermediate precursor phases in the form of hexagonal polytypes. C) A series of zoom-in graphs of the corresponding XRD patterns.



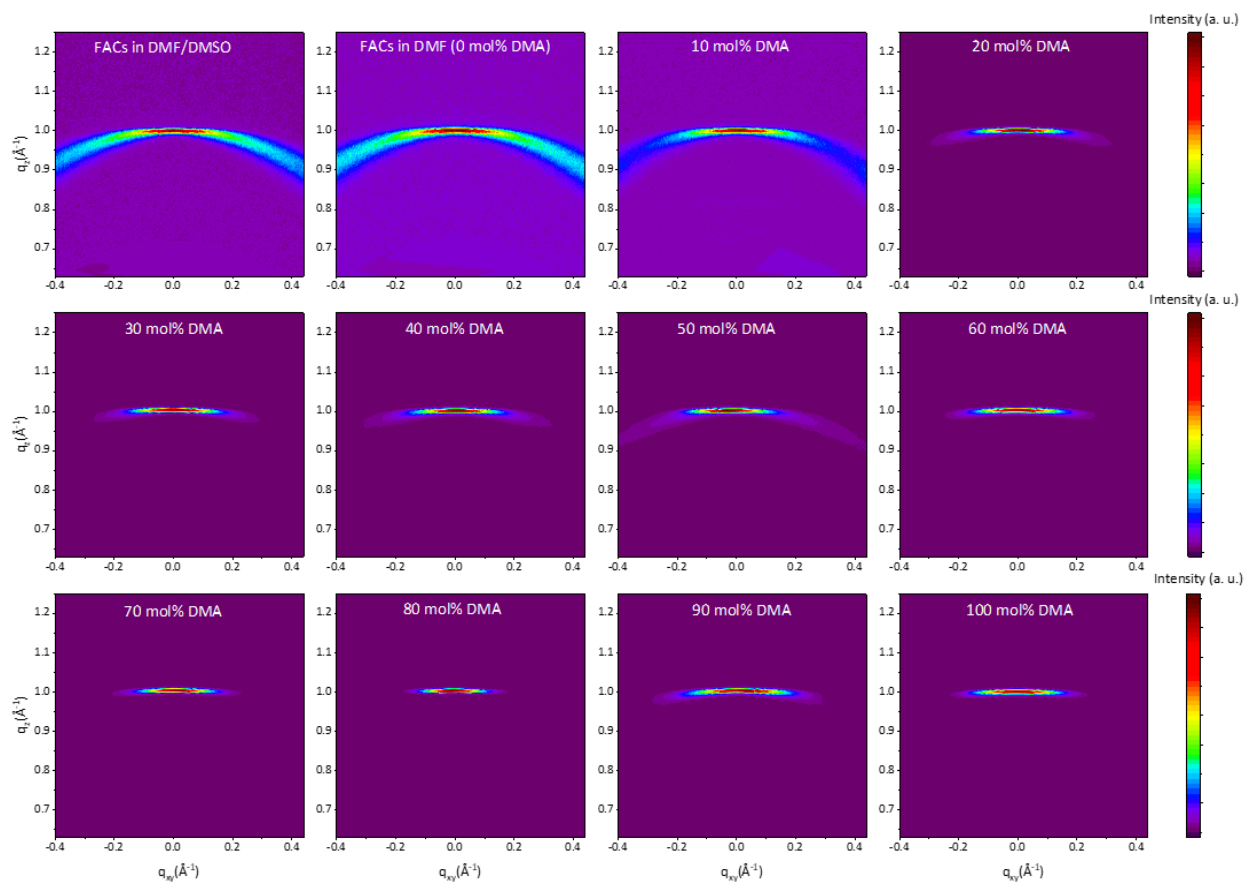
**Supplementary Figure S20: Impact of bubbling dimethylamine solution into a neat DMF perovskite precursor solution on the intermediate phases of the  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.8}\text{I}_{0.2})_3$ .** A) A series of photographs of  $\text{DMA}_x\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.8}\text{I}_{0.2})_3$  perovskite films spin-coated heated at 100 °C for 1m, with various amounts of DMA additive, where the amount of DMA is correlated to the amount of time the solution was bubbled for. B) A series of X-Ray diffraction patterns of the corresponding thin film showing the intermediate precursor phases in the form of hexagonal polytypes. C) A series of photographs of  $\text{DMA}_x\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.8}\text{I}_{0.2})_3$  perovskite films spin-coated heated at 100 °C for 1m, prepared with various perovskite precursor solutions composed of a mixture between the 5 minutes and the 10 minutes bubbled solution. D) A series of X-Ray diffraction patterns of the corresponding thin film showing the intermediate precursor phases in the form of hexagonal polytypes.



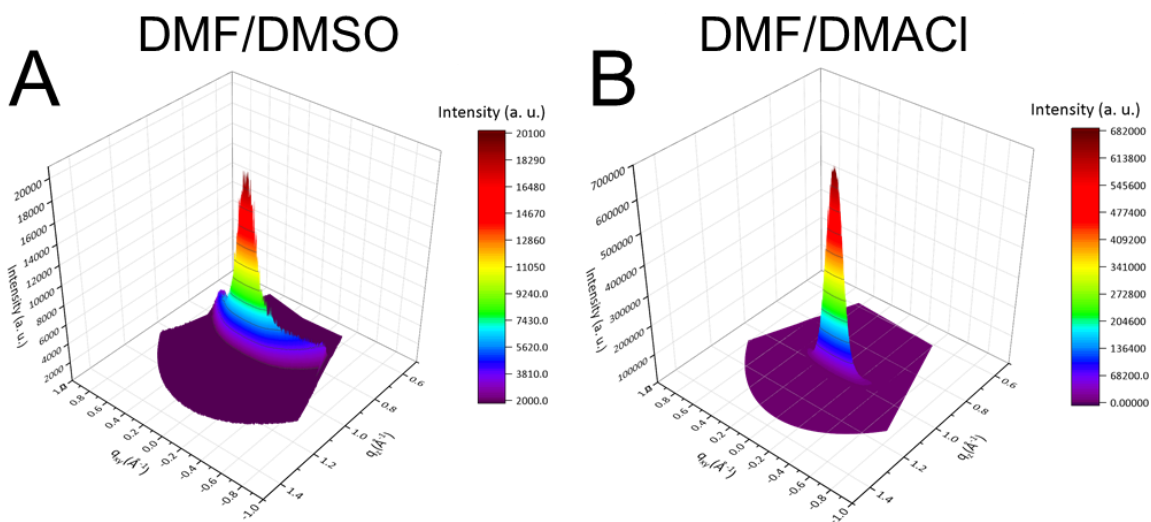
**Supplementary Figure S21: Optical band gap comparison between the perovskite films prepared with three different precursor solutions:  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{PbI}_3$  (DMF/DMSO),  $\text{DMA}_{0.3}\text{FA}_{0.83}\text{Cs}_{0.17}\text{PbI}_3\text{Cl}_{0.3}$  (DMF/DMACl),  $\text{DMA}_{0.3}\text{FA}_{0.83}\text{Cs}_{0.17}\text{PbI}_{3.3}$  (DMF/DMAI). All films were characterized throughout the annealing process after a 10 mins of annealing at 170 °C on a hotplate, and a subsequent annealing in an oven at 175 °C after 30, 60 and 90 mins. A series of Ultraviolet-visible (UV-Vis) absorbance spectra measured throughout the annealing process of a film prepared with a precursor solution composed of **A)**  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{PbI}_3$  **B)**  $\text{DMA}_{0.3}\text{FA}_{0.83}\text{Cs}_{0.17}\text{PbI}_3\text{Cl}_{0.3}$  **C)**  $\text{DMA}_{0.3}\text{FA}_{0.83}\text{Cs}_{0.17}\text{PbI}_{3.3}$  (DMF/DMAI). **D)** A UV-Vis comparison spectra of a series of fully annealed films.**



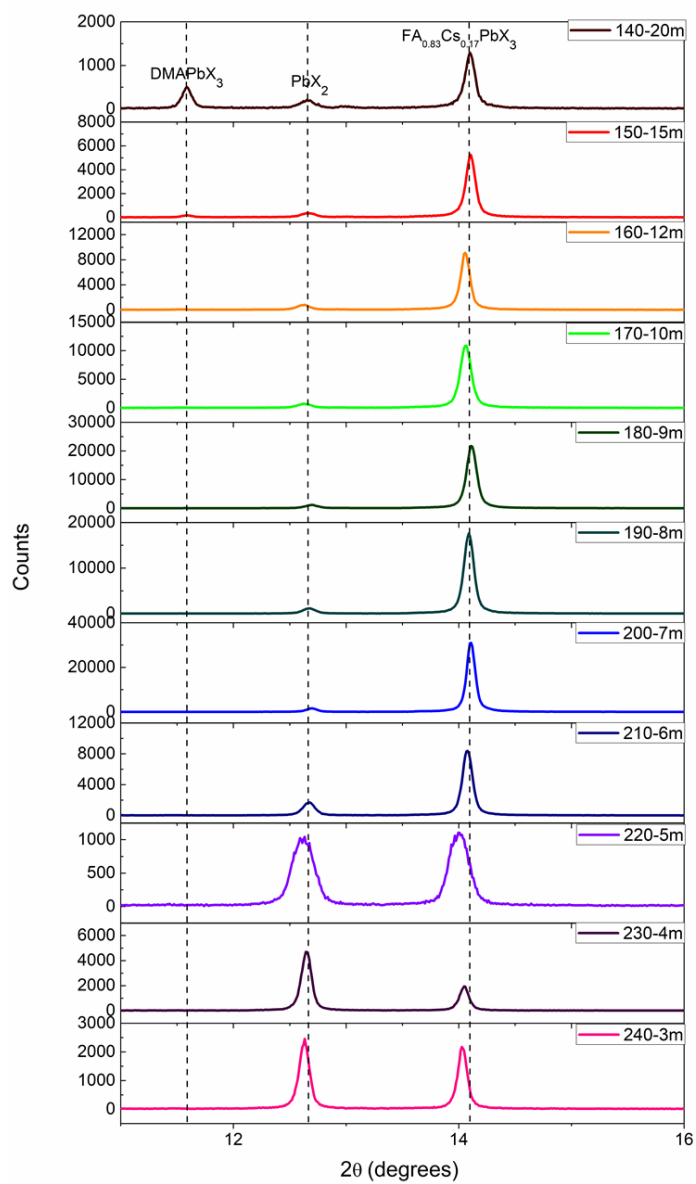
**Supplementary Figure S22: A 2D XRD beta peak analysis, showing the (100) peak intensity as a function of the azimuth angle ( $\chi$ ) for a series  $\text{DMACl}_x(\text{FA}_{0.83}\text{Cs}_{0.17})\text{Pb}(\text{I}_{0.8}\text{Br}_{0.2})_3$  perovskite film.**



**Supplementary Figure S23:** 2D XRD of the (100) peak of a  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$  perovskite film prepared using DMF/DMSO and a series of  $\text{DMA}_x\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3\text{Cl}_x$  dissolved in DMF only.



**Supplementary Figure S24:** A 3D dimensional plot of a 2D XRD beta peak analysis, showing the intensity of the (100) peak as a function of  $q_y$  and  $q_z$  for the **A)** DMF/DMSO -  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.8}\text{Br}_{0.2})_3$  and the **B)** DMF/DMACl -  $\text{DMA}_x(\text{FA}_{0.83}\text{Cs}_{0.17})\text{Pb}(\text{I}_{0.8}\text{Br}_{0.2})_3\text{Cl}_x$  perovskite film.

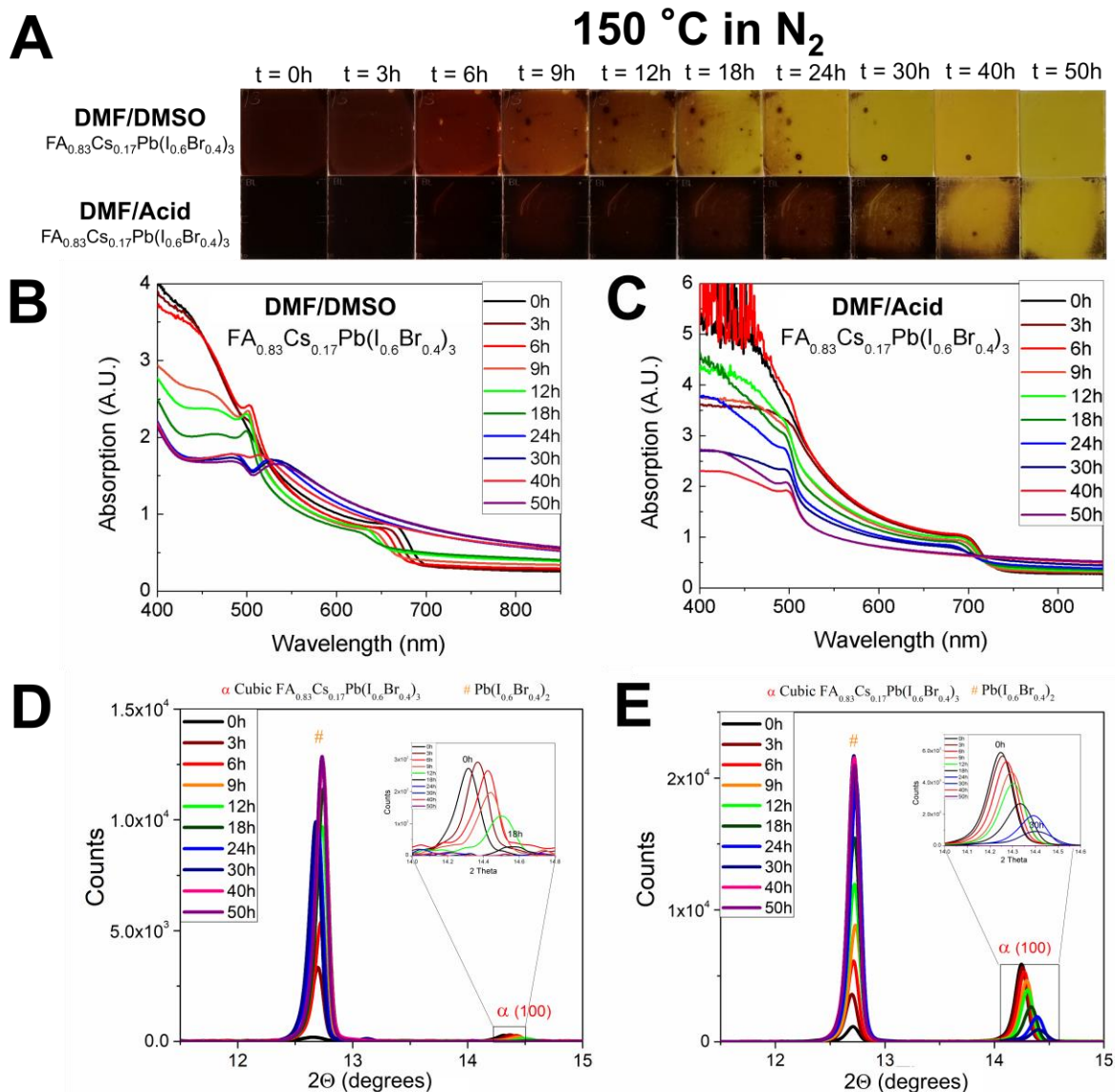


**Supplementary Figure S25: A series of  $\text{DMA}_x(\text{FA}, \text{Cs})_{1-x}\text{Pb}(\text{Br}, \text{I})_3\text{Cl}_x$  perovskite films after various annealing conditions varying time and temperature.**

We observed a similar behaviour for the wide bandgap  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$  perovskite compositions. Neat  $\text{FAPbI}_3$  or  $\text{CsPbI}_3$  perovskite compositions are prone to revert from their black perovskite phase to a yellow non-corner-sharing phase when cooled down to room temperature or exposed to moisture.<sup>[1–5]</sup> However, excess heat can also create a similar colour change, where thermal decomposition occurs when the more-volatile organic matter is removed from the crystal lattice when exposed to heat, creating a  $\text{Pb}(\text{Br}_x\text{I}_{1-x})_2$  film associated with an XRD peak located at  $2\theta \sim 12.7^\circ$ .

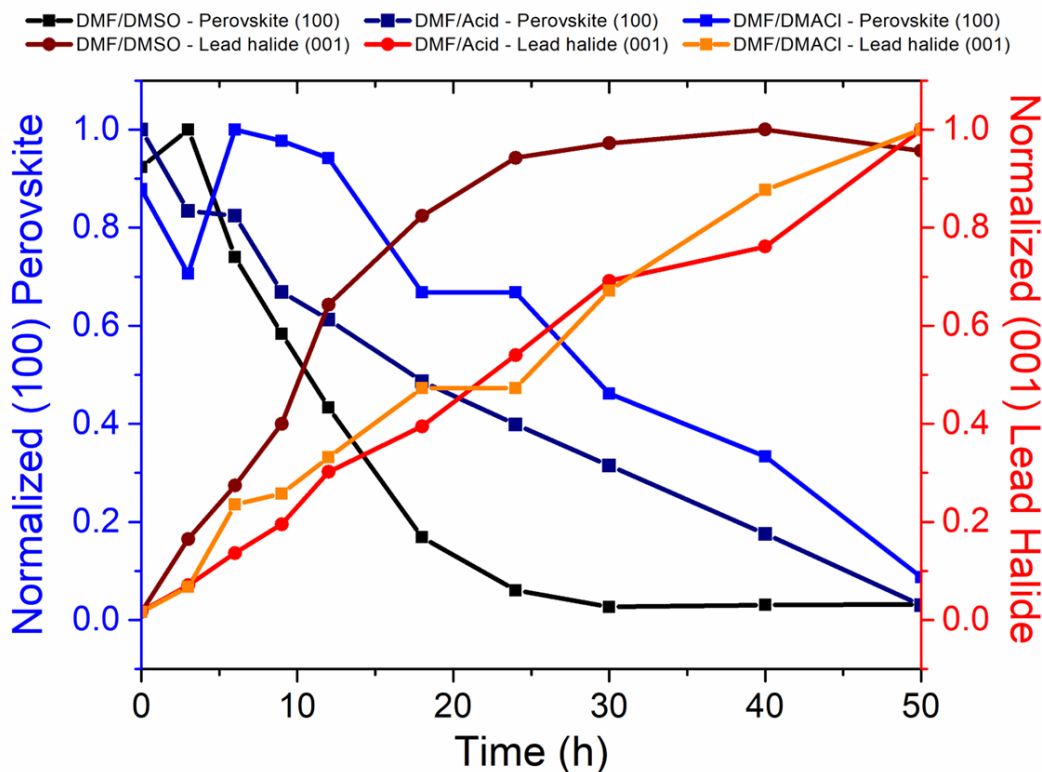
We present in **Fig. S26B-D** the UV-Vis absorption spectra, and the XRD pattern zoomed in the  $2\theta \approx 10\text{--}15^\circ$  of the corresponding films in **Fig. S26A**. In **Fig. S26B** we observe that the DMF/DMSO perovskite films show a significant shift in the absorption onset to a shorter energy wavelength within the first few hours of heating and a complete loss of the perovskite absorption onset after 24 h of heating. On the other hand, as shown in **Fig. S26C**, the DMF/acid perovskite films show a degradation rate roughly half that of the DMF/DMSO films for  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ , where we observe a disappearance of their absorption onset after 40 h. We observed a widening of the optical band gap over time and a shift in the  $14^\circ$  XRD perovskite (100) peak to larger  $2\theta$  angles. A shift of the (100) peak to larger  $2\theta$  angles indicates a contraction of the crystal lattice, caused by a compositional change of the perovskite to a higher bromide to iodide ratio. Hence, we hypothesize that the larger iodide species appear to leave the crystal structure at a faster rate than the smaller bromide halogen. From the XRD, we observe the rise of the  $\text{PbX}_2$  peak located around  $2\theta \approx 12.7^\circ$ . We plot the variations of the XRD peak intensity ratio of the  $\text{PbX}_2$  peak to the cubic (100) perovskite peak, where we also identify the slower degradation rate in the DMF/acid films.

# Thermal Stability



**Supplementary Figure S26: Thin film thermal stability.** **A)** Photographs of FA<sub>0.83</sub>Cs<sub>0.17</sub>Pb(I<sub>0.6</sub>Br<sub>0.4</sub>)<sub>3</sub> perovskite thin films when heated at 150 °C in a N<sub>2</sub> atmosphere. The top row shows films fabricated with the standard DMF/DMSO fabrication method, and the bottom row shows films fabricated with the DMF/Acid fabrication method. **B, C)** UV-Vis absorbance spectra of films of corresponding films. **D, E)** XRD pattern of corresponding films, where # and  $\alpha$  stand for the reflections originated from the PbX<sub>2</sub> (X is a mixture of I and Br) and cubic FA<sub>0.83</sub>Cs<sub>0.17</sub>Pb(I<sub>0.6</sub>Br<sub>0.4</sub>)<sub>3</sub> phase, respectively.

## 150 °C N<sub>2</sub> Thermal Degradation - Normalized XRD peak

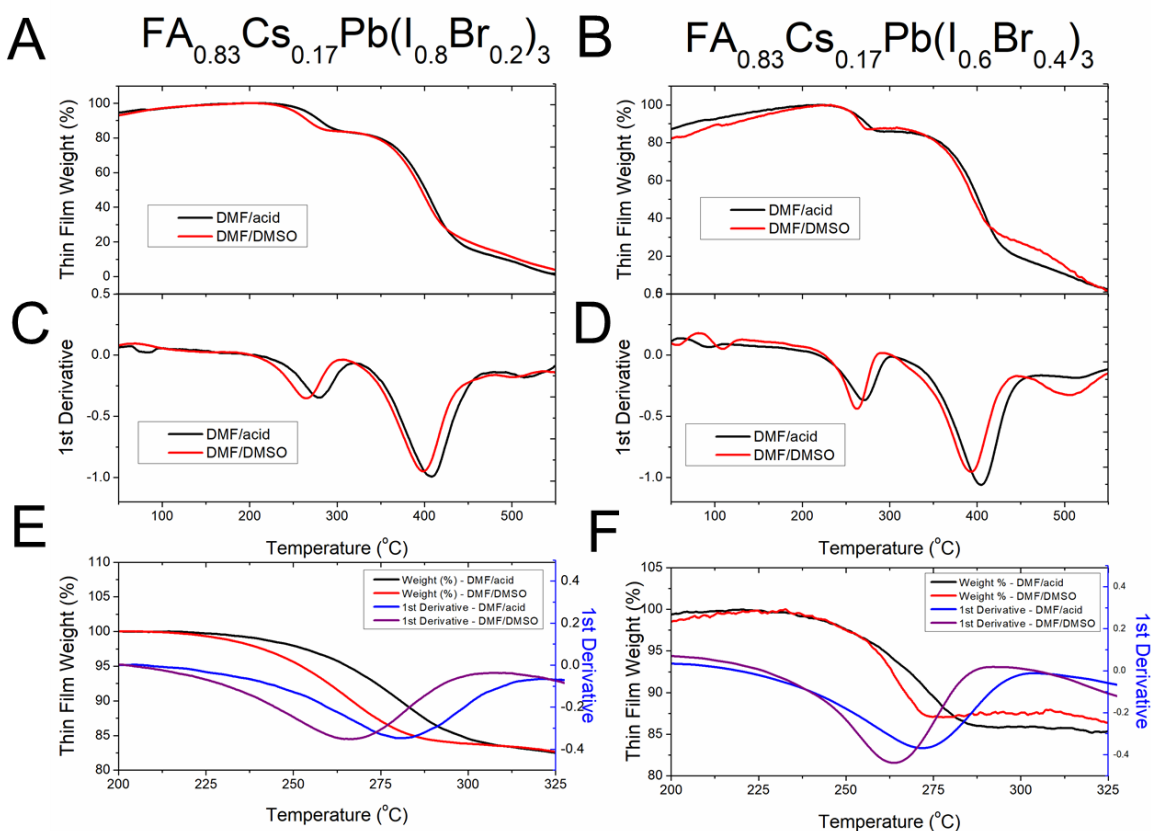


**Supplementary Figure S27: Evolution of normalised intensity ratio between lead halide and perovskite XRD peak versus thermal aging time.** All perovskite films were deposited on a FTO substrate and heated for up to 50 hours on a 150 °C hotplate in a N<sub>2</sub>-filled glovebox. The three films were prepared with three different preparation methods: DMF/DMSO, DMF/acid, DMF/DMAcI. The data for this plot is taken from Fig. 5 of the main manuscript.

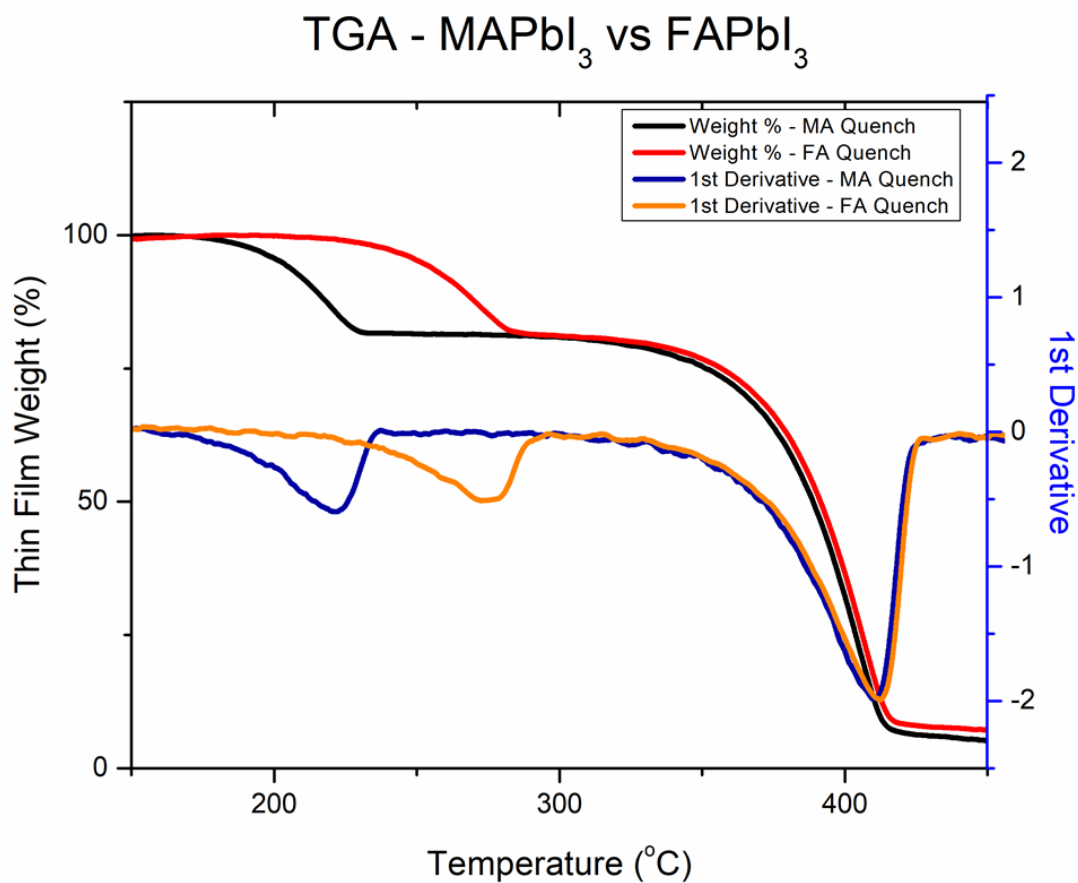
In Fig. S28, we show the TGA weight loss curves along with the 1<sup>st</sup> derivatives of the TGA heating curves for these different preparation techniques. We observe a 14 °C difference, from 265 to 279 °C, between the peaks of 1<sup>st</sup> derivative of the highly orientated DMF/DMSO and DMF/acid preparation methods for the narrower bandgap FA<sub>0.83</sub>CS<sub>0.17</sub>Pb(I<sub>0.8</sub>Br<sub>0.2</sub>)<sub>3</sub> perovskite. This difference may appear quite small; however, as shown in Fig. S28, the TGA differential for the 1<sup>st</sup> derivatives between MAPbI<sub>3</sub> and FAPbI<sub>3</sub> is 50 °C. Hence, we can expect that a 14 °C represents a significant impact in overall thermal stability, considering that the MA-based perovskite fully degrades within the first hour when heated at 150 °C in a N<sub>2</sub> atmosphere (Fig. S29). Therefore, the TGA study shows that the highly textured DMF/acid method perovskite film exhibits increased thermal stability, beyond the susceptibility to degradation in

oxygen and sunlight, in contrast to the isotropic DMF/DMSO perovskite films, which is in good agreement with our thermal stressing results of the thin films.

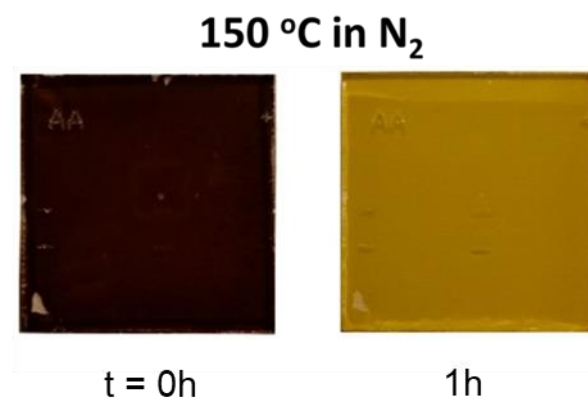
We note that TGA performed on the thin films shows a significant buoyancy effect<sup>[6,7]</sup> where the measured mass at an early time exceeds the original mass. This buoyancy phenomenon is caused by the density of the surrounding gas decreasing upon heating, which creates the appearance of the sample gaining weight. The most significant variation in air density occurs at lower temperatures, hence at the beginning of the experiment.



**Supplementary Figure S28: Thermogravimetric analysis (TGA) of formamidinium-caesium lead mixed-halide perovskite  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_x\text{I}_{1-x})_3$  thin films prepared with different preparation techniques. A) TGA heating curves. B) Corresponding first derivatives for the perovskite thin films. C) Magnification showing both heating curve and first derivatives of the temperature region where organic mass loss is prominent.**

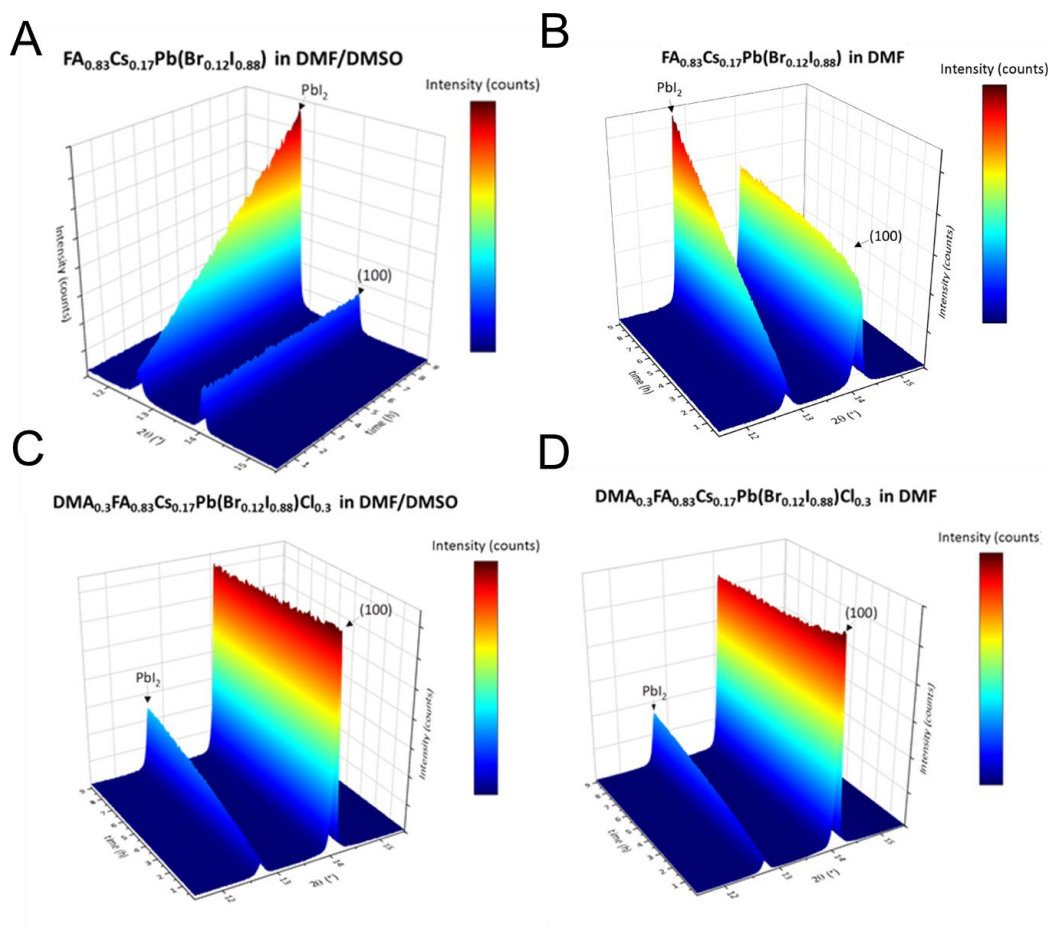


**Supplementary Figure S29: TGA data of the MAPbI<sub>3</sub> compared to the FAPbI<sub>3</sub> perovskite films.** TGA heating curves and the corresponding first derivative of the MAPbI<sub>3</sub> and FAPbI<sub>3</sub> perovskite films were prepared using the DMF/DMSO anti-solvent method.



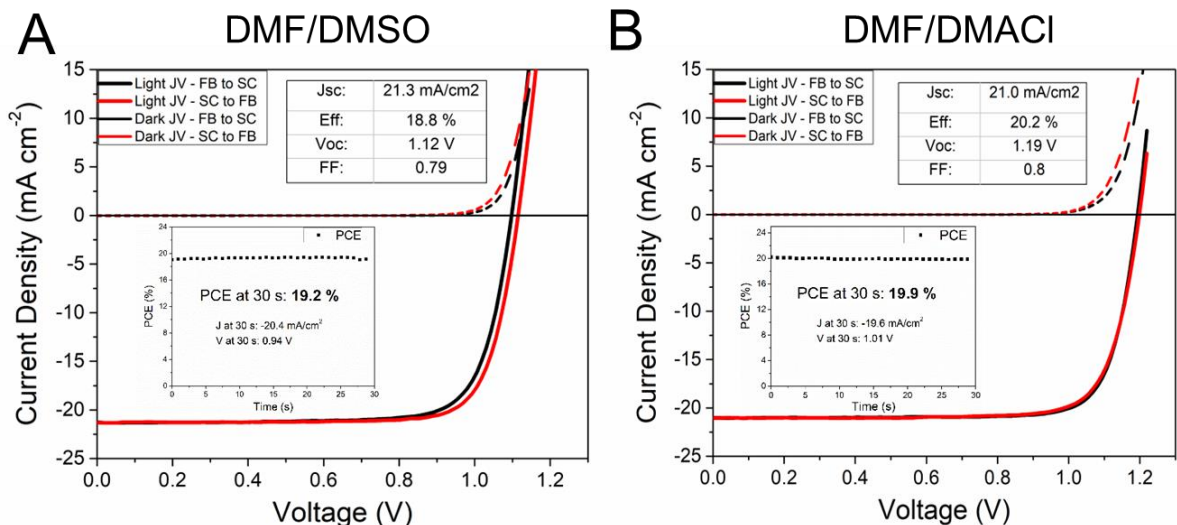
**Supplementary Figure S30: Thermal stability of a MAPb(I<sub>0.6</sub>Br<sub>0.4</sub>)<sub>3</sub> film using the DMF/DMSO anti-solvent quenching method, stressed at 150 °C in a nitrogen atmosphere. *Photographs of films measured before and after thermal stressing.***

# 130 °C Thermal Degradation – Air Atmosphere ~33% RH

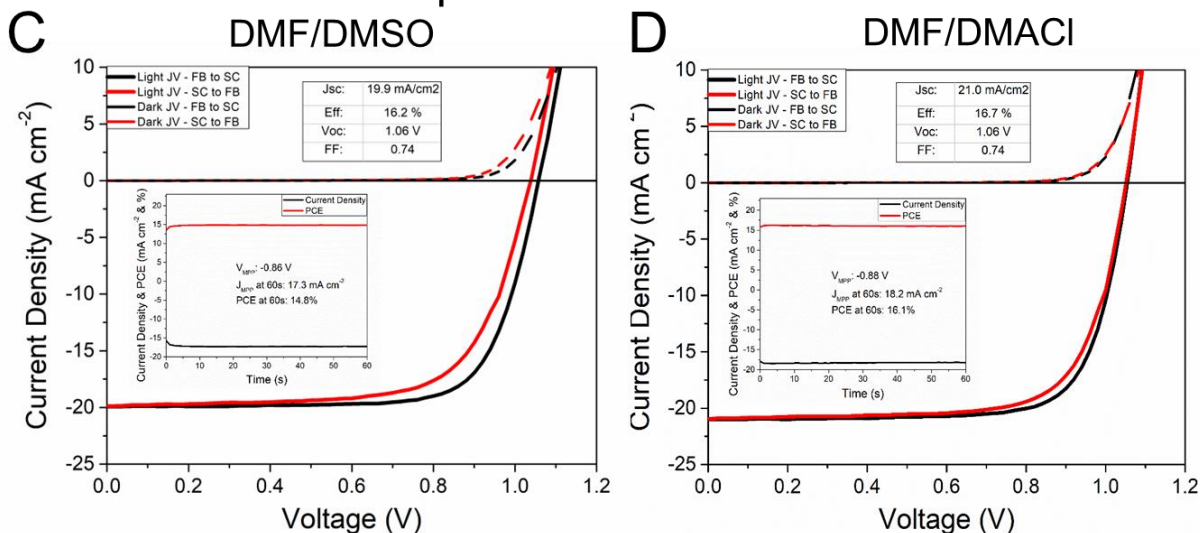


**Supplementary Figure S31: Evolution of XRD during the thermal degradation of perovskite films at 130 °C in an air atmosphere with ~ 33% relative humidity. The perovskite films were prepared using A)  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.12}\text{I}_{0.88})_3$  with a DMF/DMSO solvent mixture B)  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.12}\text{I}_{0.88})_3$  with a neat DMF C)  $\text{DMA}_{0.3}\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.12}\text{I}_{0.88})\text{Cl}_{0.3}$  with a DMF/DMSO solvent mixture D)  $\text{DMA}_{0.3}\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.12}\text{I}_{0.88})\text{Cl}_{0.3}$  with a neat DMF solvent.**

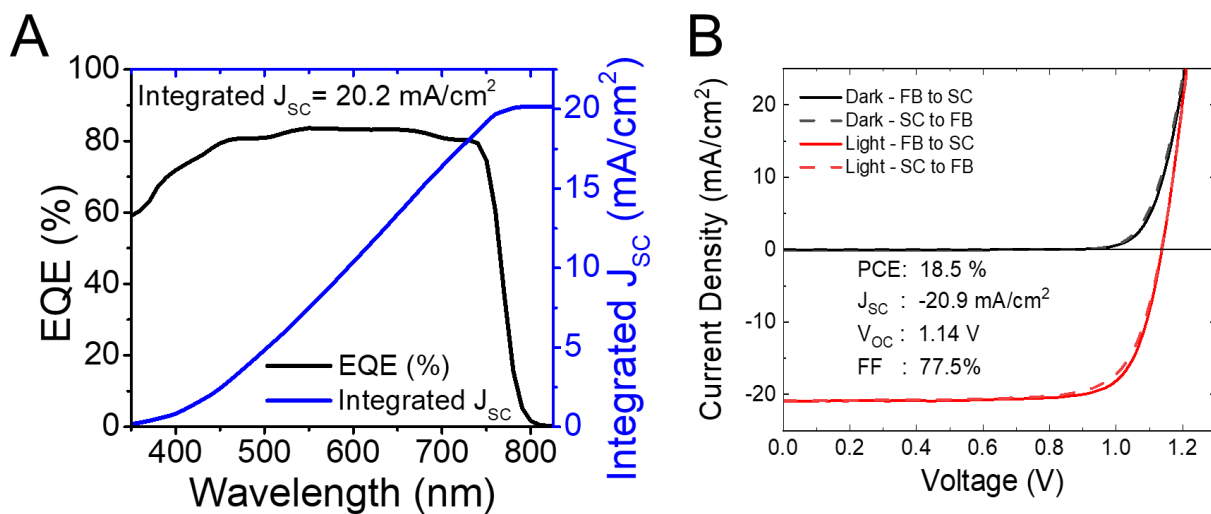
## n-i-p Architecture



## p-i-n Architecture

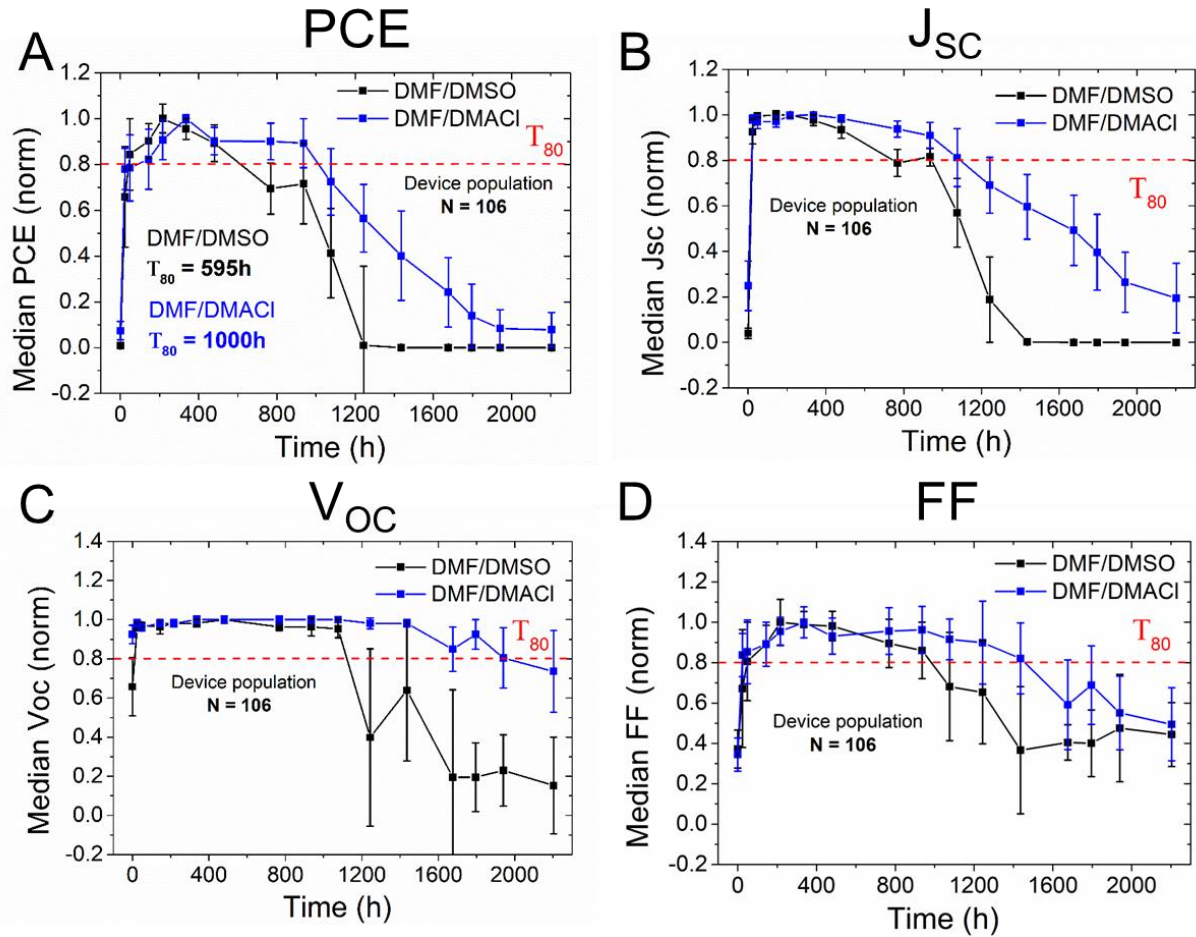


**Supplementary Figure S32: Performance comparison of champion perovskite solar cells devices prepared with DMF/DMSO or the DMF/DMACI fabrication method using a n-i-p or p-i-n architecture. A, B) J-V characteristics for the champion n-i-p device of DMF/DMSO and DMF/DMACI designs. (Inset) corresponding stabilised PCE at the maximum power point. C, D) J-V characteristics for the champion p-i-n devices of DMF/DMSO and DMF/DMACI designs, measured at its peak efficiency. (Inset) corresponding stabilised PCE and current density measured at the maximum power point.**



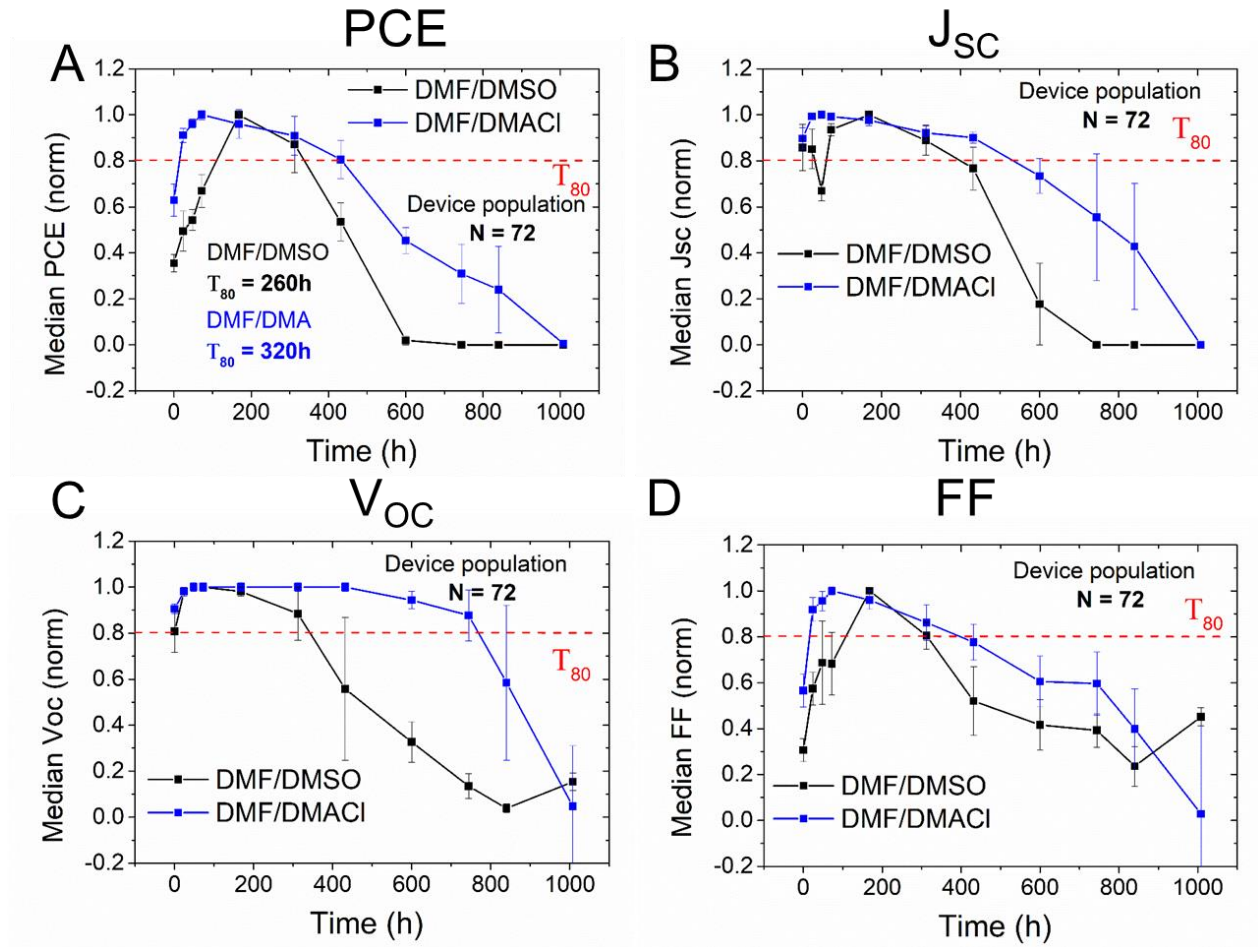
**Supplementary Figure S33: Comparison between the  $J_{sc}$  measured with the solar simulator and the integrated  $J_{sc}$  calculated with the measured EQE and the AM1.5 solar spectrum. a) An EQE measurement of a n-i-p DMF/DMAcI  $\text{DMA}_{0.3}\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{Br}_{0.12}\text{I}_{0.88})_3\text{Cl}_{0.3}$  perovskite device along with the integrated short-circuit current density assuming a AM1.5 solar spectrum. b) J-V characteristics for the corresponding device measured with the solar simulator.**

# 65 °C – Full Spectrum – Air – Encapsulated



**Supplementary Figure S34: Evolution of the JV performances between DMF/DMSO and DMF/DMACI fabrication methods under full spectrum, simulated AM 1.5, 76 mWcm<sup>-2</sup> average irradiance at  $V_{oc}$  in air without a UV filter at 65 °C, using a Suntest XLS<sup>+</sup> aging box which irradiates pulsed light. All devices are encapsulated p-i-n devices comprised of a FTO/PTAA/Al<sub>2</sub>O<sub>3</sub>NPs/perovskite/LiBr/C<sub>70</sub>/Zr(Acac)<sub>4</sub>/PEIE/Au structure. We show the JV characteristics of the A) PCE, B)  $J_{sc}$ , C)  $V_{oc}$  and D) FF. The error bars were calculated using the median absolute deviation (MAD), as a measure of statistical dispersion; 106 devices were used.**

# 85 °C – Full Spectrum – Air – Encapsulated



**Supplementary Figure S35: Evolution of the JV performances between DMF/DMSO and DMF/DMAI fabrication methods under full spectrum, simulated AM 1.5, 76 mWcm<sup>-2</sup> average irradiance at  $V_{oc}$  in air without a UV filter at 85 °C, using a Suntest XLS + aging box which irradiates pulsed light. All devices are encapsulated p-i-n devices comprised of a FTO/PTAA/Al<sub>2</sub>O<sub>3</sub>NPs/perovskite/LiBr/C<sub>70</sub>/Zr(Acac)/PEIE/Au structure. We show the JV characteristics of the A) PCE, B)  $J_{sc}$ , C)  $V_{oc}$  and D) FF. The error bars were calculated using the median absolute deviation as a measure of statistical dispersion. 72 devices were used.**

Single crystals are known to retain their crystal structure for longer periods in comparison to polycrystalline thin films when exposed to humidity.<sup>[8,9]</sup> On the other hand, the hydration process is significantly faster for thin films due to their relatively high surface-to-volume ratio and the abundance of grain boundaries and surface defects.<sup>[9]</sup> It has been previously postulated and shown that grain boundaries (or the defects present at grain boundaries) offer a higher degree of adsorption and penetration of polar

water molecules, allowing for the formation of hydrated perovskite phases.<sup>[10–12]</sup> Degradation is thought to proceed via surface defects due, for instance, to the adsorption of water or oxygen.<sup>[13]</sup> Thermal instability has also been linked to a disordered crystal structure, enhanced by lattice dislocations and defects along the surface of the grain boundaries.<sup>[9,14–16]</sup> These structural imperfections may increase the rate of decomposition by reducing the likelihood of forming a continuous lead halide plane, which can slow down, or “self-terminate” the decomposition. Hence, defect control via process or additives, as in this case, promotes a reduction in the density of surface defects, particularly those located at the grain boundaries. Thus, reducing the number of sites at which oxygen and water can adsorb to the perovskite surface and undergo chemical reactions with the ions in the perovskite is likely to lead to enhanced stability.

## Characterization

### Wide-angle X-ray scattering (WAXS) measurement:

Wide-angle X-ray scattering (WAXS) measurement was performed using the Stanford Synchrotron Radiation Lightsource (SSRL) Beamline 11–3 with an X-ray wavelength of 0.9744 Å. Two-dimensional scattering data were collected using a Rayonex MX225 detector in a grazing incidence geometry with the X-ray beam held at an incident angle of 3°. Images are calibrated using a LaB6 standard and integrated between  $10^\circ < \chi < 170^\circ$  ( $\chi$  is the polar angle) using GSAS-II.<sup>[17]</sup>

### Two-dimensional (2D) X-ray diffraction (XRD<sup>2</sup>):

2D-XRD spectra were conducted in ambient air at room temperature using a Rigaku SmartLab X-ray diffractometer with CuK $\alpha_1$  (1.54060 Å) and a HyPix-3000 2D hybrid pixel array detector, operated at 40 kV.

### Nuclear magnetic resonance (NMR):

<sup>1</sup>H-NMR spectra were recorded on a Bruker Avance III 400 MHz or 600 MHz spectrometers. For each measurement, 16 perovskite films (2.5x2.5 cm) were scratched off the substrates. The perovskite material

was then suspended in deuterated acetonitrile ( $\text{CD}_3\text{CN}$ ), and the suspension was decanted. All spectra are referenced versus residual solvent peaks with respect to  $\delta(\text{TMS}) = 0$  ppm.

**Scanning electron microscopy:** The morphology of perovskite films was investigated using a SEM (Hitachi S-4300) at an accelerating voltage of 3-5 kV.

**Solar cell characterization:** The current density–voltage (J-V) curves were measured (2400 Series SourceMeter, Keithley Instruments) under simulated AM 1.5 sunlight at approximately  $100 \text{ mWcm}^{-2}$  irradiance generated by an Abet Class AAB sun 2000 simulator, with the intensity calibrated with an NREL calibrated KG5 filtered Si reference cell. The mismatch factor was calculated to be less than 1%. The active area of the solar cell is  $0.0919 \text{ cm}^2$ , by employing an opaque mask with an aperture. The forward J–V scans were measured from forward bias (FB) to short circuit (SC), and the backward scans were from short circuit to forward bias, both at a scan rate of  $0.25 \text{ V s}^{-1}$ . A stabilization time of 5 seconds under 1 sun illumination and forward bias of 0.2V above the expected  $V_{\text{oc}}$  was done prior to scanning. All measurements were done in air.

**External quantum efficiency measurement:**

The external quantum efficiency (EQE) was measured by Fourier-transform photocurrent spectroscopy (FTPS) using each perovskite solar cell as the detector in a Bruker Vortex 80v, and an AM1.5 filtered xenon lamp (Oriel Sol 3A) as the light source. The cells were aged under open-circuit conditions under the AM1.5 spectrum, and the EQE spectra were measured periodically by filtering out above-band-gap illumination to extend the dynamic range of the measurement of the response to sub-band-gap illumination. The measurements were calibrated against the response of a certified Si reference cell (Newport).

**Thermogravimetric analysis (TGA):**

We performed thermogravimetric analysis (TGA) directly on a perovskite-coated glass substrate to preserve and study the morphology of the perovskite. A thin microscope glass coverslip was used as substrate. The choice of a low-weight substrate allowed for an acceptable signal-to-noise ratio for the TGA measurement. A TA Instruments Q500 Thermogravimetric Analyser was used for the measurements of the coatings. This instrument allows the measurement of weight change as a function of temperature/time in a controlled environment. Instrument control was performed using TA Instruments Thermal Advantage software. Subsequent data analysis was performed using TA Instruments Universal Analysis data analysis program. The sample was cut to size and placed inside a 100  $\mu\text{l}$  Platinum crucible (coated side up), and heated at a rate of  $10^\circ \text{C}$  per minute in a controlled atmosphere (Nitrogen) at a flow rate of 100 ml per minute. Precise gas flow control was maintained via a Mass Flow Controller built into

the instrument. The mass of the sample was recorded as a function of temperature during the experiment. Data has been plotted to show the relationship between weight and temperature, and also included are the first derivative profiles for the weight losses observed, which give a clear indication of the onset and range of decomposition.

#### **TOF-SIMS:**

An ION-TOF TOF-SIMS V Time of Flight SIMS (TOF-SIMS) spectrometer was utilized for depth profiling and chemical imaging of the perovskite utilizing methods outlined in detail by Harvey et.al.<sup>[18]</sup>. Analysis was completed utilizing a 3-lens 30kV BiMn primary ion gun. 3-D tomography was completed with 100nm lateral resolution using a  $\text{Bi}_3^{++}$  primary ion-beam cluster (100 ns pulse width, 0.1 pA pulsed beam current) and a 50x50  $\mu\text{m}$  area was sampled with a 1024:1024 primary beam raster. Depth Profiling was accomplished with a 1kV oxygen ion sputter beam (5-10 nA sputter current) with a raster of 150x150 microns. After completion of the SIMS measurements, the depth of the craters was determined by optical interference light microscopy in order to convert the SIMS sputter time scale to a sputter depth scale.

#### **Stability test:**

All the devices were aged under full spectrum simulated AM1.5G, 76  $\text{mW cm}^{-2}$  irradiance at  $V_{oc}$  using an Atlas SUNTEST XLS+ (1700W air-cooled Xenon lamp). The chamber temperature was set to °65 or 85 °C. The aging test is in correspondence to ISOS-L-2 aging condition. We note that the light source is pulsed at 100Hz frequency.

#### **Halide segregation analysis:**

We identify the majority phase as the bandgap of the material targeted for synthesis, while the minority phase is the low bandgap phase formed due to halide segregation, which occupies a volumetric fraction  $f$  of the film. We consider the inflection point of the majority phase EQE to be the bandgap of the majority phase ( $E_{g,majority}$ ), while the bandgap of the minority phase ( $E_{g,minority}$ ) was determined by fitting the sub-bandgap absorption to absorptance modelled via a generalized transfer matrix model.<sup>[19]</sup> We modelled the optical refractive index  $\tilde{n}$  of the halide-segregated perovskite as an effective medium for the two phases, leading to the following expressions:

$$\tilde{n}_{segregated} = \chi \cdot \tilde{n}_{minority} + (1 - \chi)\tilde{n}_{majority}$$

Where  $\tilde{n}_{segregated}$  is the refractive index of the halide-segregated perovskite,  $\tilde{n}_{minority}$  is the refractive index of the minority phase,  $\tilde{n}_{majority}$  is the refractive index of the majority phase, and  $\chi$  is the molar fraction of the film. We can then model the absorption,  $A(E)$ , as;

$$A(E) = 1 - e^{-\chi \cdot \alpha_{minority}(E) \cdot t} \approx \chi \cdot \alpha(E) \cdot t$$

Where  $\alpha_{minority}$  is the the absorption coefficient of the minority phase  $t$  is the film thickness, and  $\chi$  is the molar fraction of the film. Additional details are provided in the supplementary information with the assumptions that were made.

We specify that the refractive index of perovskites of different bandgaps is modelled by linearly shifting the extinction co-efficient of MAPbI<sub>3</sub> and then performing a Kramers-Kronig transform to obtain the refractive index, following the approach of Hoerantner et al.<sup>[20]</sup> In our previous work, we have shown that the bandgaps of mixed-halide perovskites do shift linearly in this way.<sup>[21]</sup> Since the fraction of the minority phase is low (few %), the Bruggeman EMA is, in effect, a linear combination of the two optical constants:

$$\tilde{n}_{segregated} = \chi \cdot \tilde{n}_{minority} + (1 - \chi) \tilde{n}_{majority}$$

With the Beer-Lambert approximation, the absorptance  $A$  can be written as:

$$A(E) = 1 - e^{-(\chi \cdot \alpha_{minority} + (1 - \chi) \cdot \alpha_{majority}) \cdot t}$$

Here  $\alpha$  is the absorption coefficient and  $t \sim 500 \text{ nm}$  is the film thickness. In the region where only the minority phase absorbs, we can write:

$$A(E) = 1 - e^{-\chi \cdot \alpha_{minority}(E) \cdot t} \approx \chi \cdot \alpha(E) \cdot t$$

The approximation is valid since  $e^x - 1 \approx x$  for  $x \ll 1$ . To calculate  $\chi$ , we evaluate this expression at  $E = E_{g,minority}$ .

Detailed balance calculations in the radiative limit were used to evaluate the change in open-circuit voltage upon halide-segregation.<sup>[22–24]</sup> The Urbach tails of the measured EQEs were extrapolated to 1.2 eV and above 1.76 eV. The calculation assumes that the radiative efficiency of the cell does not change upon segregation. As carrier funnelling is likely to increase the radiative efficiency, the calculated  $V_{OC}$  loss is an upper bound.

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