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supplementary Information

Sensitivity of mixed cation/halide perovskites to evaporation kinetics of DMSO at early stage

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Detailed precursor preparation

Perovskite compositions to verify six different states consist of $MAPbI_3$, $FA_{0.3}MA_{0.7}PbI_3$, $FAPbI_3$, $MA_{0.15}FA_{0.85}PbI_3$, $Cs_{0.1}FA_{0.9}PbI_3$, $FA_{0.8}MA_{0.2}Pb(I_{0.9}Br_{0.1})_3$.

All perovskite precursors were dissolved in 800 ul of DMF and 200 ul of DMSO to obtain 1.2 M with the amounts of components listed below.

$MAPbI_3$ (1.2 mmol) : 190.8 mg of MAI and 553.2 mg of PbI_2

$FA_{0.3}MA_{0.7}PbI_3$ (1.2 mmol) : 61.9 mg of FAI, 133.5 mg of MAI and 553.2 mg of PbI_2

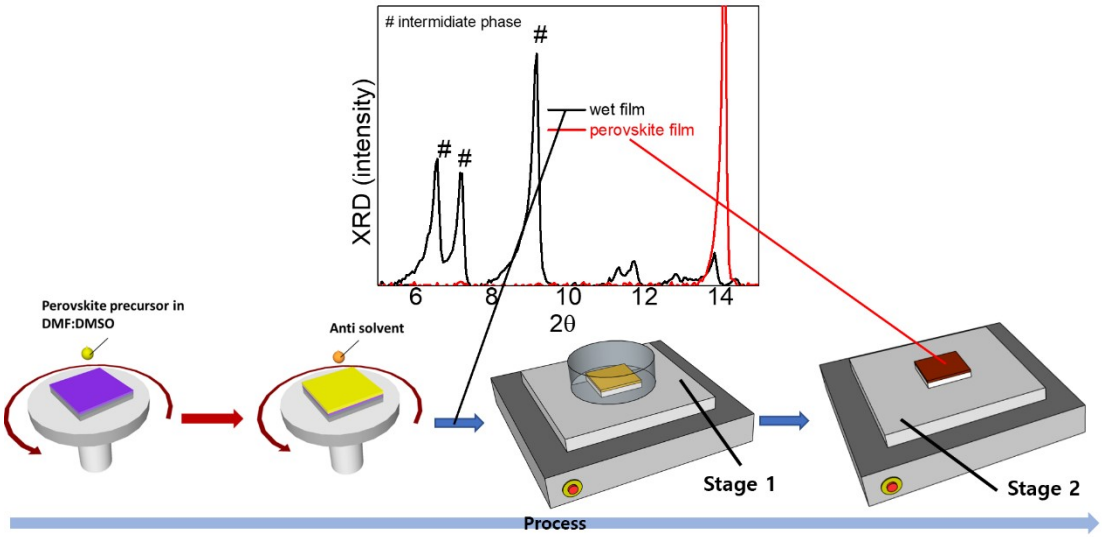
$FAPbI_3$ (1.2 mmol) : 206.4 mg of FAI and 553.2 mg of PbI_2

$MA_{0.15}FA_{0.85}PbI_3$ (1.2 mmol) : 28.6 mg of MAI, 175.4 mg of FAI and 553.2 mg of PbI_2

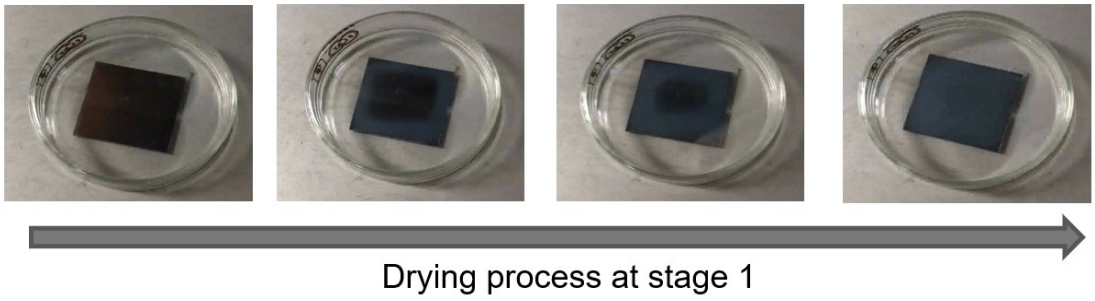
$Cs_{0.1}FA_{0.9}PbI_3$ (1.2 mmol) : 31.2 mg of CsI, 185.7 mg of FAI and 553.2 mg of PbI_2

$FA_{0.8}MA_{0.2}Pb(I_{0.9}Br_{0.1})_3$ (1.2 mmol) : 38.2 mg of MAI (0.24 mmol), 165.1 mg of FAI (0.96 mmol), 66.06 mg of $PbBr_2$ (0.18 mmol) and 470.2 mg of PbI_2 (1.02 mmol)

(a)

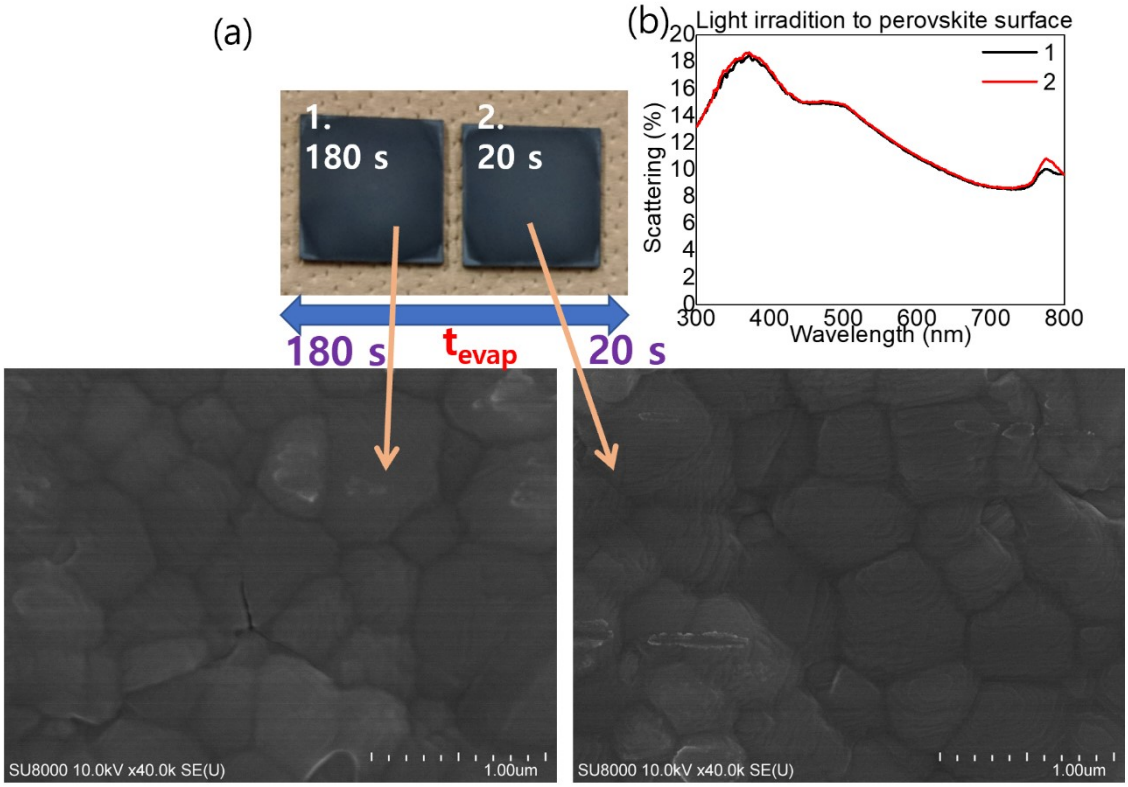


(b)



SI 1. (a) Fabrication process for perovskite films and the XRD data for the wet film and completed perovskite for $MAPbI_3$. (b) drying process at stage 1 for $FA_{0.8}MA_{0.2}Pb(I_{0.9}Br_{0.1})_3$.

In SI Fig 1b, t_{evap} is easily measured by naked eyes by observing the color change from edge to center. At early stage for $FA_{0.8}MA_{0.2}Pb(I_{0.9}Br_{0.1})_3$, the color of substrate is dark brown inside petri-dish right after the substrate was put inside petri-dish at certain temperature. The color started to change to whitish dark color from the edge. The area of whitish dark color increased by expending it to the center and whole area was turned to whitish dark color at which stage 1 was completed.

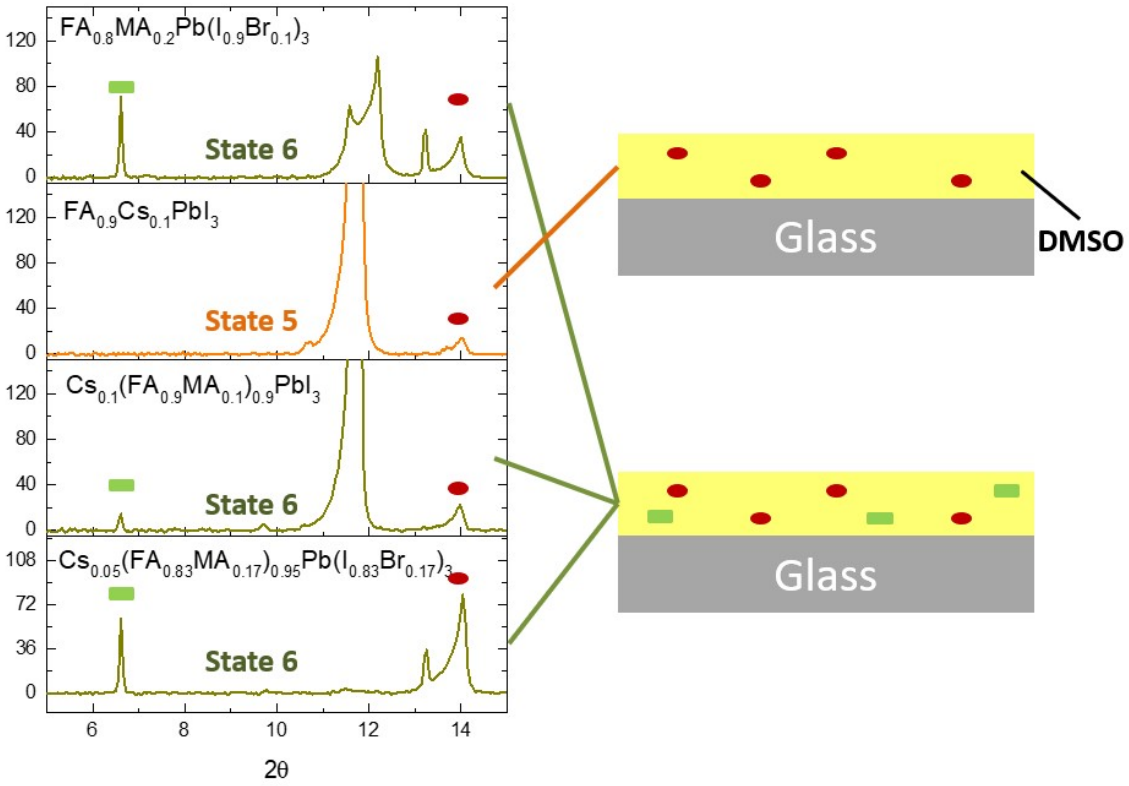


SI 2. (a) Photographs and SEM images and (b) scattering of $FAPbI_3$ with t_{evap} of 180 s and 20 s.

(a)

Perovskites	Sensitive to stage 1
$FA_{0.1}MA_{0.9}PbI_3$	X
$FA_{0.2}MA_{0.8}PbI_3$	X
$FA_{0.8}MA_{0.2}PbI_3$	X
$FA_{0.8}MA_{0.2}Pb(I_{0.9}Br_{0.1})_3$	O
$MA_{0.8}FA_{0.2}Pb(I_{0.9}Br_{0.1})_3$	X
$FAPbI_3$	X
$FA_{0.9}Cs_{0.1}PbI_3$	O
$FA_{0.9}Cs_{0.1}Pb(I_{0.83}Br_{0.17})_3$	O
$MAPbI_3$	X
$MA_{0.9}Cs_{0.1}PbI_3$	X
$Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$	O

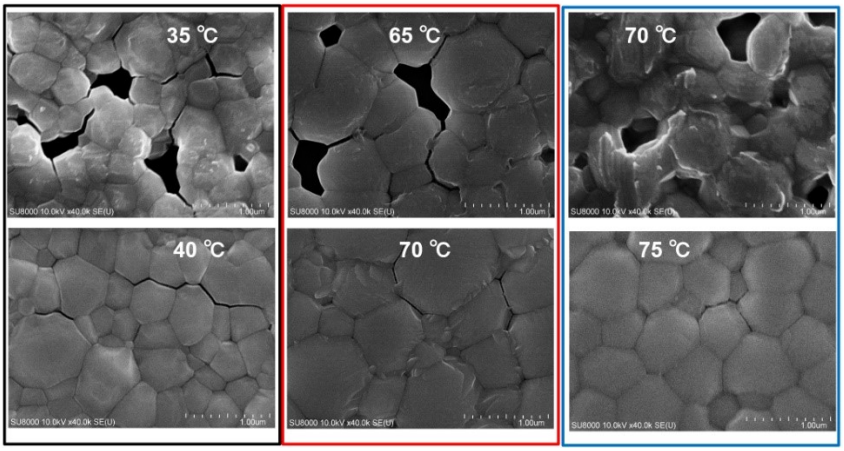
(b)



SI 3. (a) Various compositions of perovskites which show sensitivity to t_{evap} at stage 1. XRD of wet films of perovskite compositions that are sensitive to t_{evap}.

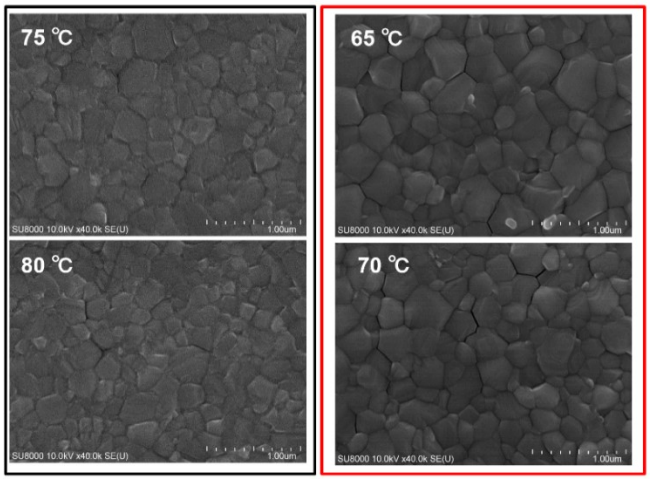
(a)

Perovskite	Threshold temp. (℃)
$Cs_{0.1}FA_{0.9}PbI_3$	30
$Rb_{0.03}Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$	60
$FA_{0.8}MA_{0.2}Pb(I_{0.9}Br_{0.1})_3$	65



(b)

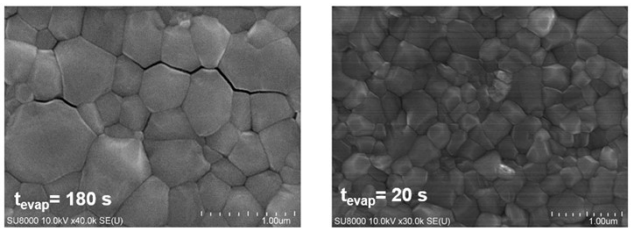
Perovskite	Threshold temp. (℃)
$MAPbI_3$	70
$Cs_{0.1}MA_{0.9}PbI_3$	65



No pin holes near threshold temp.

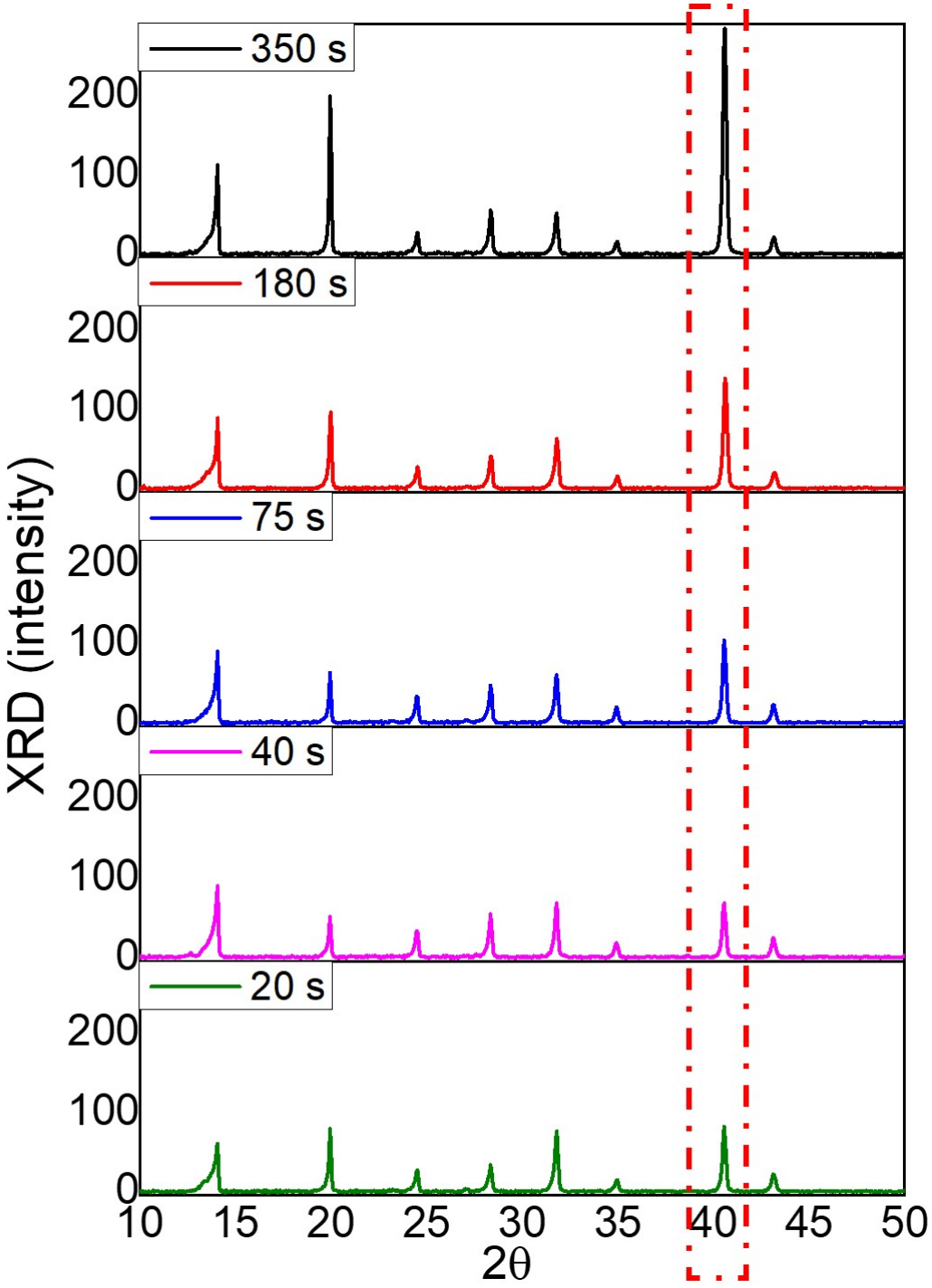
(c)

$Cs_{0.1}FA_{0.9}PbI_3$



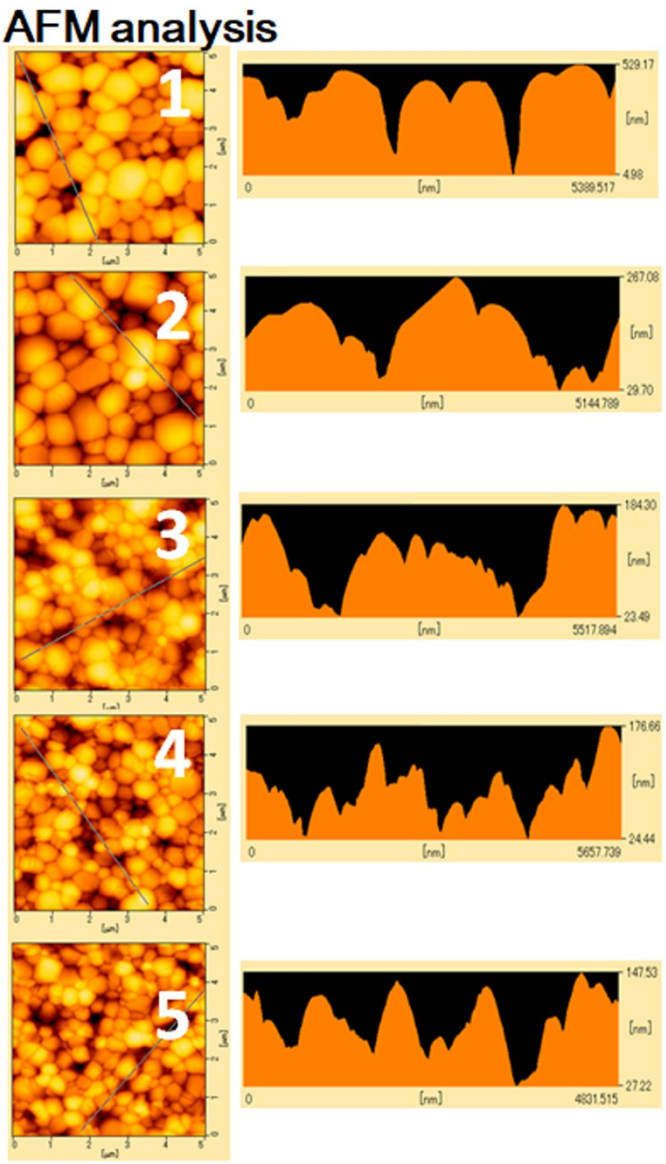
SI 4. Threshold temperature (T_{th}) at stage 1 depending on the perovskite compositions and SEM images of perovskite surface which is annealed at temperature displayed on the images at stage 1 with petri-dish followed by annealing at 150 degree for 30 mins without petri-dish at stage 2. The SEM of (a) left, middle and right images show $Cs_{0.1}FA_{0.9}PbI_3$, $Rb_{0.03}Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$, $FA_{0.8}MA_{0.2}Pb(I_{0.9}Br_{0.1})_3$ and (b) left and right image show $MAPbI_3$ and $Cs_{0.1}MA_{0.9}PbI_3$ (c) The SEM images of $Cs_{0.1}FA_{0.9}PbI_3$ with t_{evap} = 180 s and 20 s at stage 1.

Cs-doped FA-based perovskites mostly result in small grains which were also reported in many journals. In our finding, Cs-doped FA-based perovskites have low T_{th}, implying that the value of t_{evap} is very low at normal annealing conditions leading to small grain sizes. By adequately controlling t_{evap}, large grain of $Cs_{0.1}MA_{0.9}PbI_3$ could be obtained (SI Fig 4c). This is in accordance with Fig. 1a that shows grain sizes of $FA_{0.8}MA_{0.2}Pb(I_{0.9}Br_{0.1})_3$ with different t_{evap}.

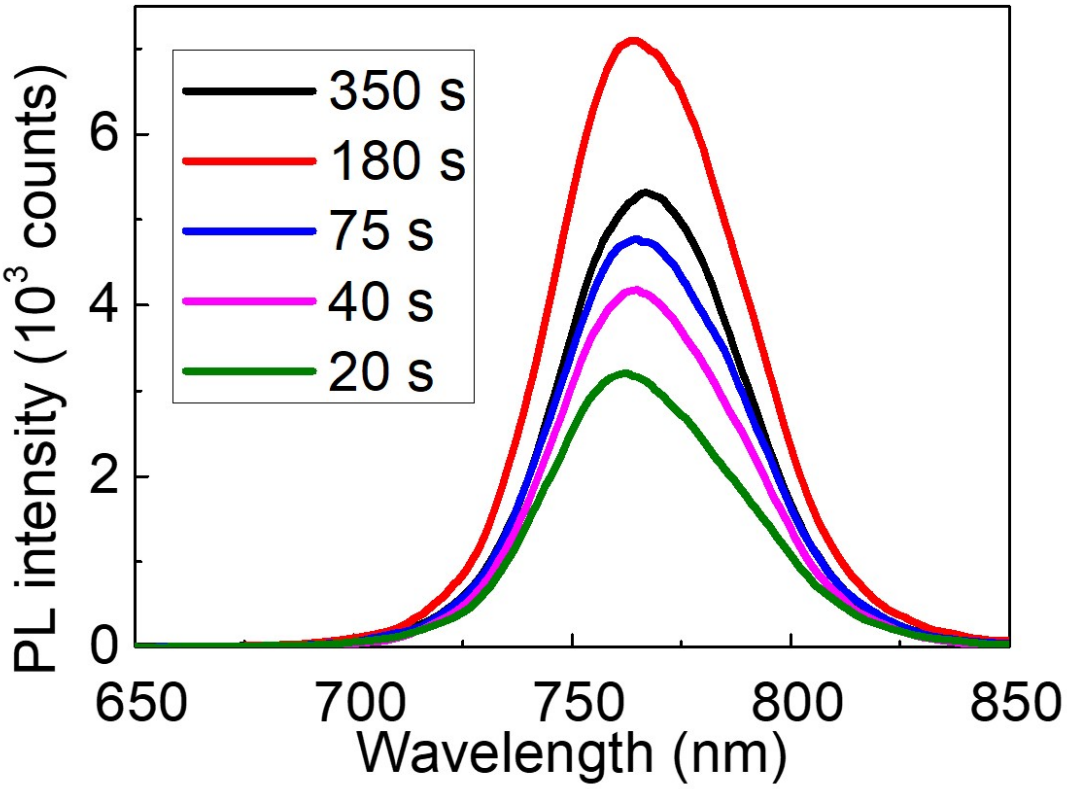


SI 5. XRD of perovskite films consisting of $(Rb_{0.03}Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.92})Pb(I_{0.83}Br_{0.17})_3$ with various t_{evap}.

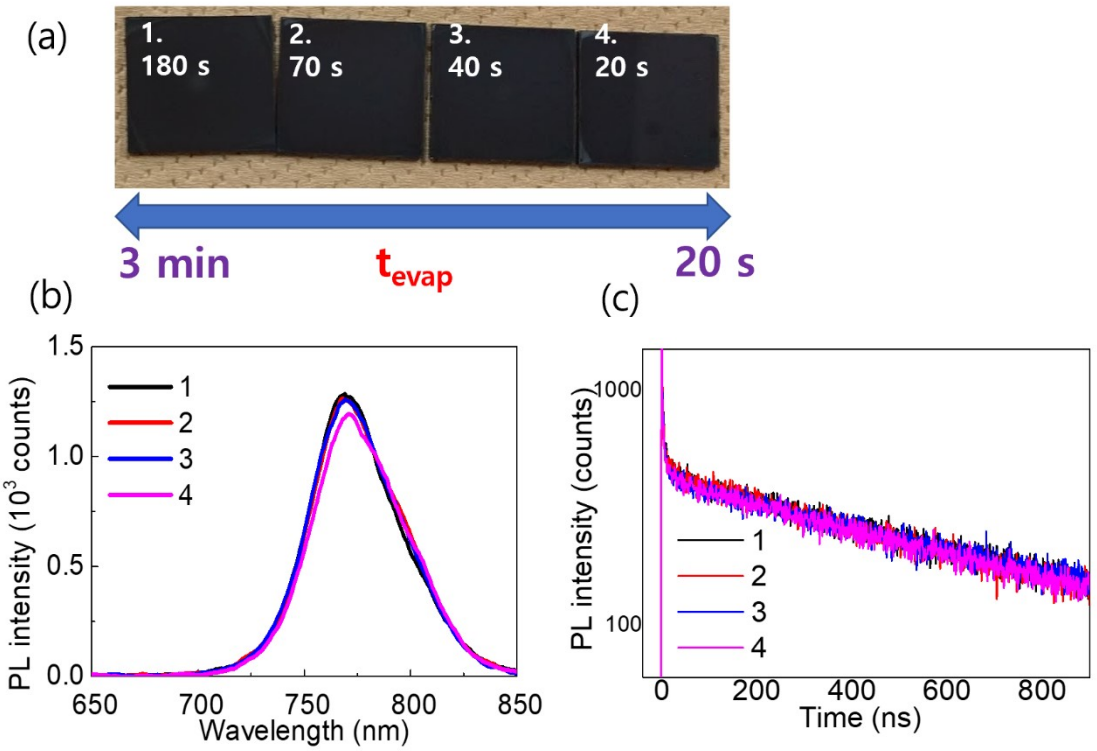
Sample	Retention time of intermediate states at stage 1
1	350 s
2	180 s
3	75 s
4	40 s
5	20 s



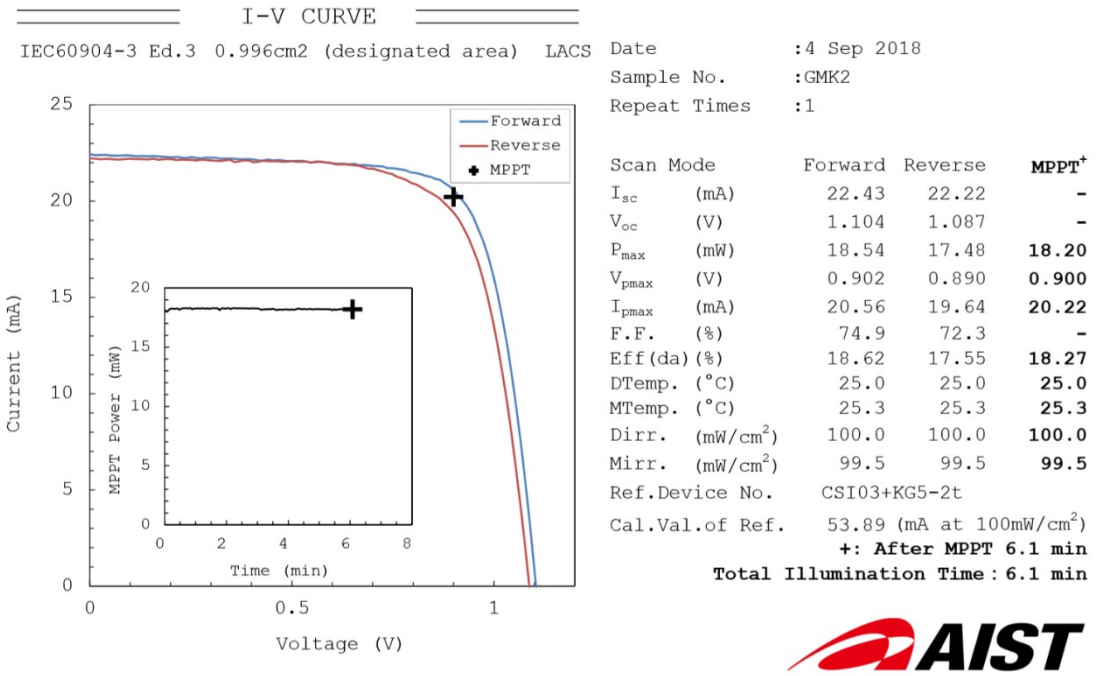
SI 6. AFM images and the height profiles of perovskite films consisting of $(Rb_{0.03}Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.92})Pb(I_{0.83}Br_{0.17})_3$ at the location designated as the line.



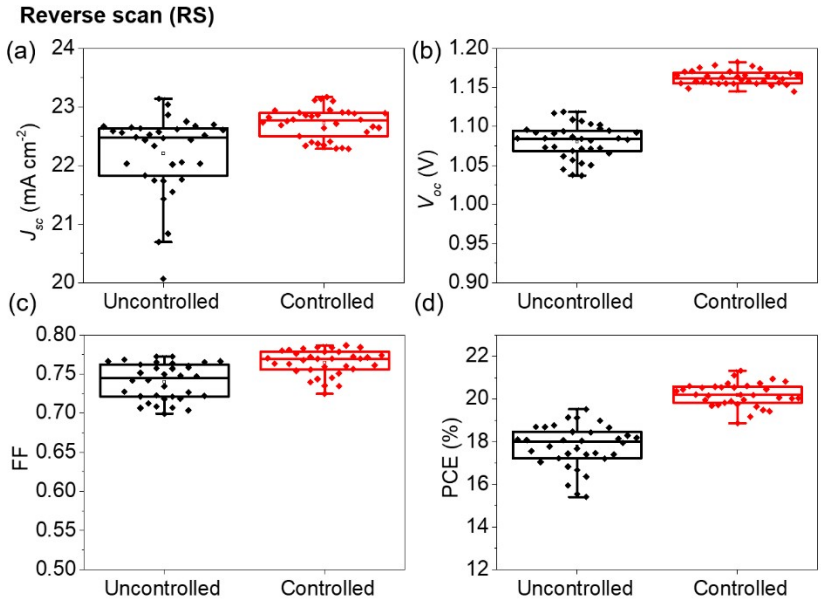
SI 7. PL intensity of perovskite films consisting of $(Rb_{0.03}Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.92})Pb(I_{0.83}Br_{0.17})_3$ with various t_{evap} (20 s to 350 s).



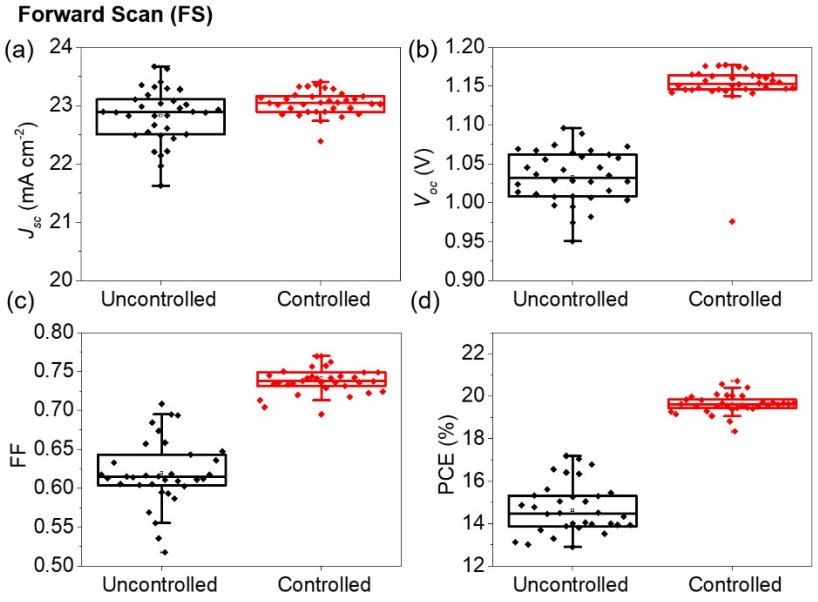
SI 8. (a) Photographs (b) PL intensity and (c) TRPL of perovskite films consisting of $MAPbI_3$ with various t_{evap}.



SI 9. Certification of large area (1 cm^2) quadrupole OIHPs with optimization from National Institute of Advanced Industrial Science and Technology (AIST) ; 18.27% of PCE was recorded from MPPT.



SI 10. Box and data overlap of a) J_{sc} (b) V_{oc} (c) FF (d) PCE for reverse scan of perovskite solar cells.



SI 11. Box and data overlap of (a) J_{sc} (b) V_{oc} (c) FF (d) PCE for forward scan of perovskite solar cells.

Perovskite solar cells having composition of $Rb_{0.03}Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.92}Pb(I_{0.83}Br_{0.17})_3$ have good reproducibility when t_{evap} (180 s) was controlled compared to unoptimized cells (without stage 1).