Supporting Information

Suppressed Halide Ion Migration in 2D Lead Halide Perovskites

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Experimental Section

Materials. Phenylethylammonium bromide (PEABr, Greatcell Solar), Phenylethylammonium bromide (PEAI, Greatcell Solar), methylammonium bromide (MABr, Greatcell Solar), methyl ammonium iodide (MAI, Greatcell Solar), lead bromide ($PbBr_2$, 99.99%, Sigma-aldrich), lead iodide (PbI_2, 99.99% with 10 mesh bead, Alfa-Aesar), dimethylformamide (DMF, anhydrous 99.8%, Sigma-Aldrich), dimethyl sulfoxide (DMSO, anhydrous 99.9%, Sigma-Aldrich), chlorobenzene (anhydrous 99.8%, Sigma-Aldrich), fluorine-doped tin oxide conducting glass (FTO, Pilkinton glass). All chemicals were used as received without additional purification.

2D Lead Halide Perovskite Films with different dimensionality (*n*). The preparation of 2D lead halide (bromide and iodide) perovskite films with tunable layer numbers of n = 10—1 follows the previously reported method in the literature.[1-3] FTO-coated glasses (2.5 cm × 2.5 cm) were used as a substrate to make 2D layered perovskite films. The FTO substrates were cleaned with soapy water and sonicated in an ethanol bath for 20 min. After that, the substrates were rinsed additionally with excess isopropanaol and dried with air-stream at ambient conditions. To remove any organic residues, the FTO substrates were further treated with plasma for 10 minutes. The FTO substrates were then immediately transferred to a N_2-filled glovebox for the deposition of lead halide films.

The 2D perovskite films were prepared in the glove box (< 10 ppm H_2O). The 2D lead bromide and iodide perovskite films were made through the same procedures except for the halide (X = Br and I) precursors employed for the synthesis. The mixed precursor solutions containing MAX, PEAX, and PbX_2 with a stoichiometric amount was used to control the dimensionality (n). The ratio of MAX:PEAX were systematically varied such as MA:PEA = 80:20 (n = 10), 66:33 (n = 6), 33:66 (n = 3—2), and 0:100 (n = 1), respectively. The mixed solutions dissolved in DMF:DMSO mixture with a 4:1 volumetric ratio were vigorously stirred for 1 hr at room temperature. The precursor solutions were then syringe- filtered through a 0.2 μm PTFE membrane filter. The 2D lead halide perovskite films were acquired through static spin-casting of 50 μL of 0.6 M PbX_2 precursor solution followed by spin-coating at 4000 rpm for 25 s with an acceleration of 1200 rpm. A 0.5 mL of chlorobenzene was rapidly injected as antisolvent after 10 seconds. After spin-casting process was completed, the perovskite films were transferred to using a hot plate and annealed at 100 °C for 5 minutes. The films were cooled down and stored inside of the glovebox until use.

Halide Ion Homogenization Experiments. The 2D lead halide (bromide and iodide) perovskite films with different layer number of n = 10—1 were physically paired each other, clamped with binder clips, and then transferred to a pre-heated hot plate with different homogenization temperature (140—23 °C). Care was taken to keep the annealing temperature of the paired 2D lead halide perovskite films at constant temperature. The clamped films were then placed on a

brass plate for direct-heating of the paired films. The temperature of the brass plate was monitored and controlled by adjusting the temperature of the hotplate. The clamped (or separated) films were periodically monitored during homogenization process. The completion of homogenization was visually inspected based upon the change of film colors and confirmed by spectroscopic measurements.

Steady State Absorption Measurements. UV-Vis absorption spectra were obtained using a Varian Cary 50 bio spectrophotometer in the wavelength of 450—800 nm for 2D lead halide perovskite films with n = 10 and 350—700 nm for 2D lead halide perovskite films with n = 1. The difference absorption spectra were acquired by subtracting the absorption spectrum at 0 min (as a reference) from the absorption spectra acquired at different annealing (or homogenization) time.

Tauc Plot Analysis in conjunction with Estimation of Bandgap energy. The absorption spectra were converted to *Tauc* plots using the equation of $(\alpha h\nu)^2$ versus $h\nu$ for the directly-allowed transitions materials. The straight line was fitted and extrapolated from the curvature onto X-axis to estimate the bandgap energy (E_g) of the perovskites during the course of homogenization at different temperature with time. Halide ion compositions were further analyzed based upon the bandgap energy of mixed lead iodide perovskite films with n = 10 determined from the *Tauc* plots (equations 1 and 2). The estimated bandgap energy (E_g) is determined to be 1.62 eV for pure 2D lead iodide film with n = 10, 2.24 eV for pure 2D lead bromide film with n = 10, and 1.93 eV for mixed 2D halide film with n = 10 (Br:I = 50:50). A simple Vegard's law with a linear interpolation is applied to approximate the halide composition.

$$\text{I composition (\%)} = [(2.24 - E_g(\text{mixed iodide film}))/(0.62)] \times 100 \qquad \text{equation (1)}$$

$$\text{Br composition (\%)} = 100 - \text{I composition (\%)} \qquad \text{equation (2)}$$

Characterizations. Top-down view, cross-sectional SEM imaging, and EDS spectra were acquired using a Magellan 400 digital field emission scanning electron microscope operated with a beam voltage of 5 kV.

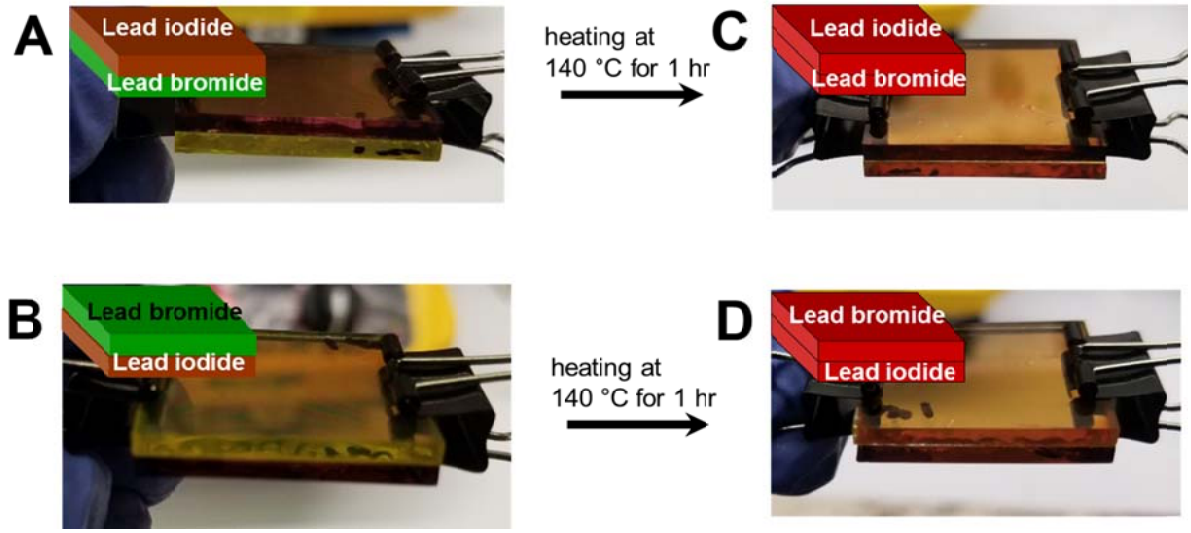


Figure S1. Digital photographs of the physically paired 2D lead halide (bromide/iodide) perovskite films clamped together with a binder clip corresponding to a layer number of n = 10 before (A,B) and after (C,D) homogenization at 140 °C for 1 hr. The 2D lead iodide slide is facing up (A,C) while 2D lead bromide slide is facing up (B,D).

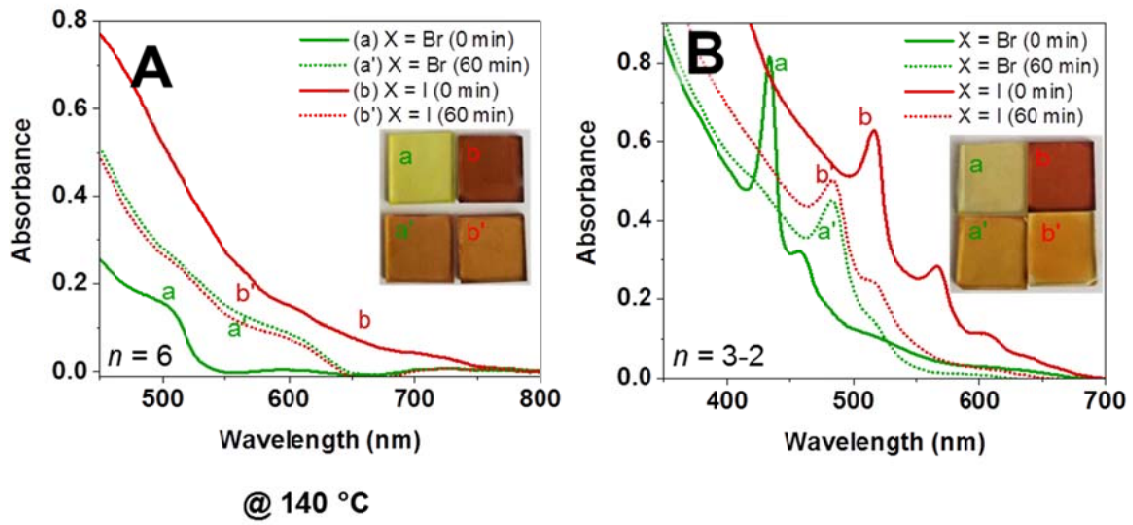


Figure S2. Absorption spectra of the two separated 2D lead halide (X = Br and I) perovskite films with different layer number of (A) n = 6 and (B) n = 3—2 before (a,b) and after (a',b') homogenization at 140 °C. The two lead halide perovskites films were clamped together and thermally treated at 140 ° C during the course of 60 minutes. Insets S2A and S2B show the digital photograph of 2D lead bromide and lead iodide films before (a,b) and after homogenization (a',b').

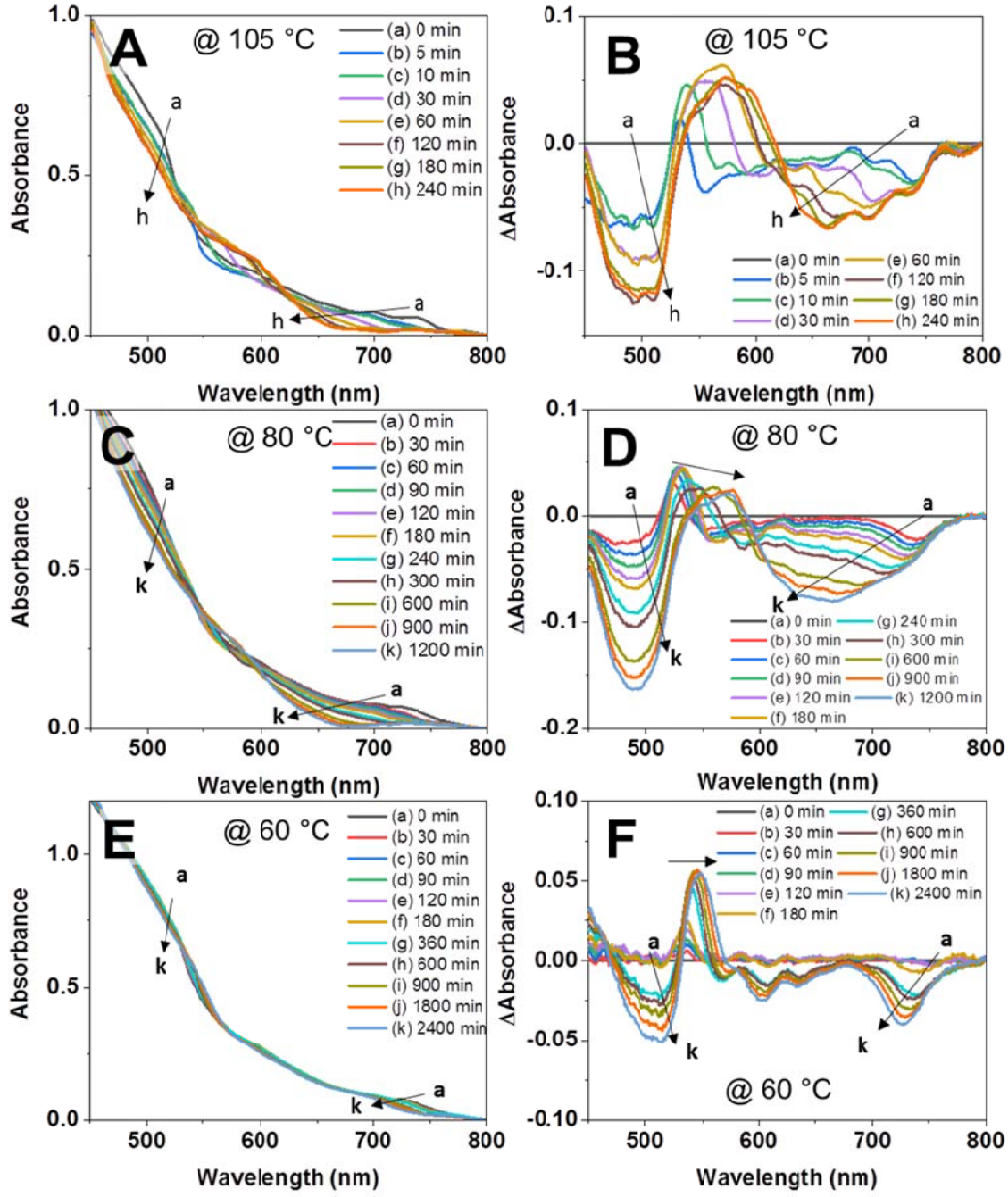


Figure S3. (A,C,E) Absorption spectra of the paired 2D lead halide (bromide/iodide) perovskite films with n = 10 recorded at different temperature of (A) 105 °C, (C) 80 °C, and (E) 60 °C as a function of homogenization time. (B,D,F) Corresponding difference absorption spectra obtained from the panel A,C,E respectively. The absorption spectrum at 0 min was served as reference to obtain the difference absorption spectra (ΔA).

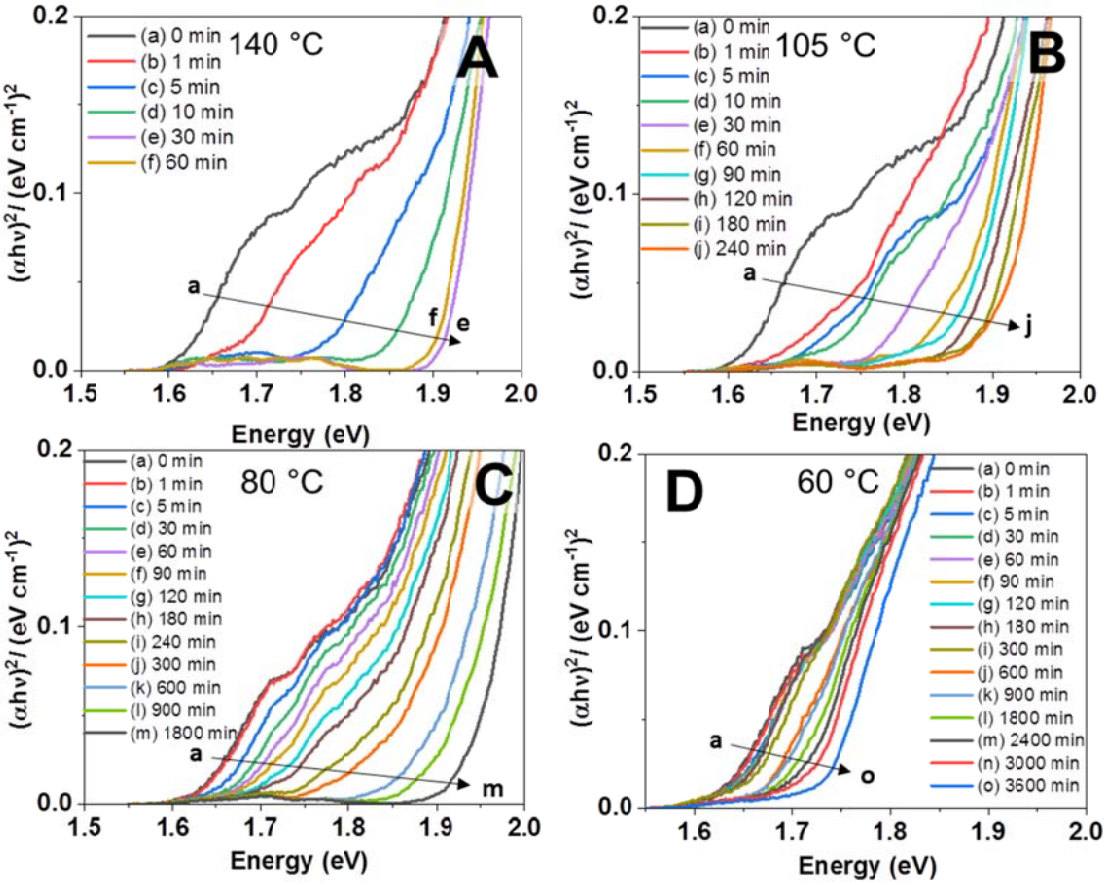
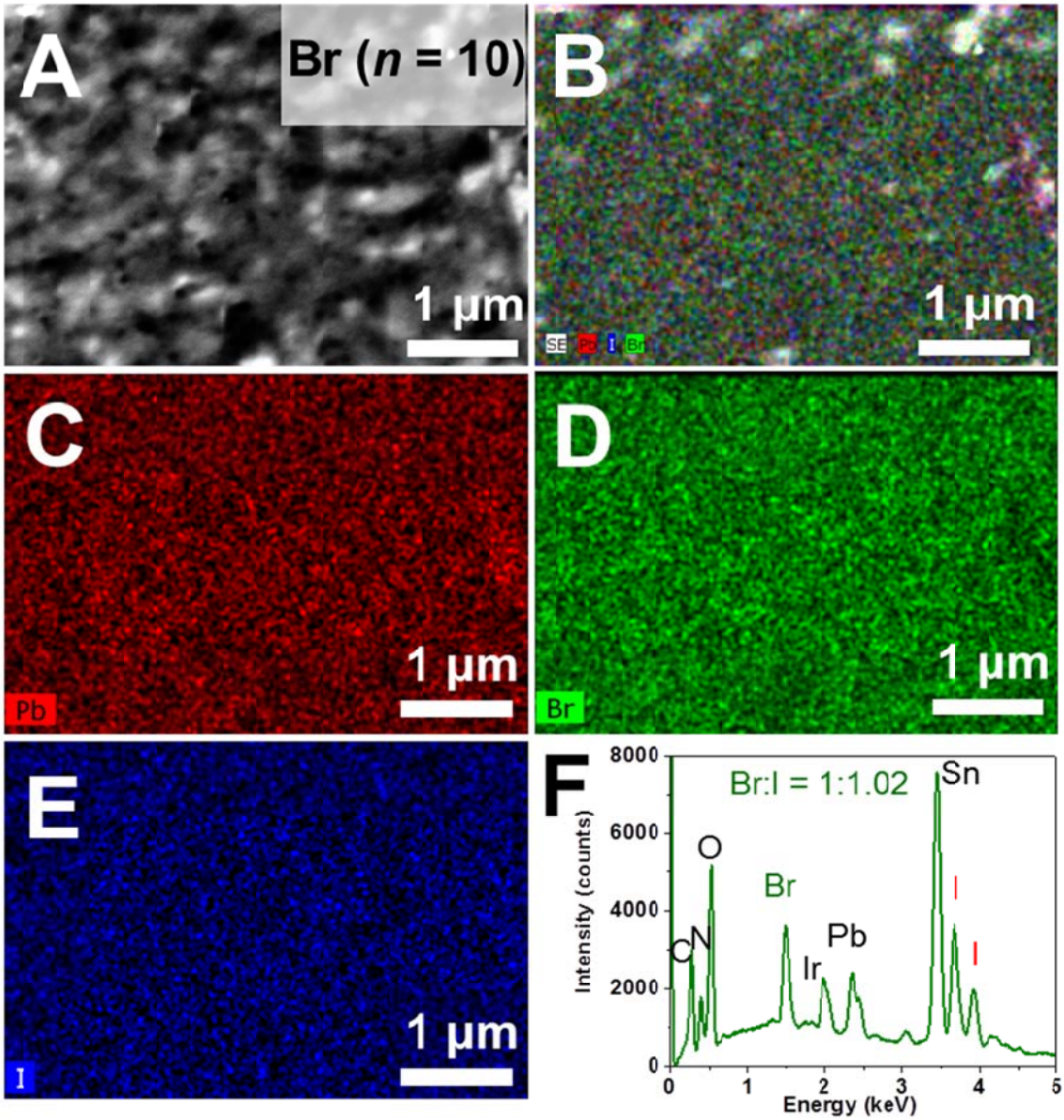


Figure S4. *Tauc* plots of the 2D lead iodide side with n = 10 from the paired 2D lead halide (bromide/iodide) perovskite films during the course of homogenization at different annealing temperature of (A) 140 °C, (B) 105 °C, (C) 80 °C, and (D) 60 °C. *Tauc* plots were converted from the absorption spectra obtained at different temperatures from 140-60 °C.


A
Br (n = 10)
1 μm
B
1 μm
SE Pb I Br
C
1 μm
Pb
D
1 μm
Br
E
1 μm
I
F
Br:I = 1:1.02
Intensity (counts)
Energy (keV)
O
Br
C
N
Ir
Pb
Sn
I
I
8000
6000
4000
2000
0
0
1
2
3
4
5

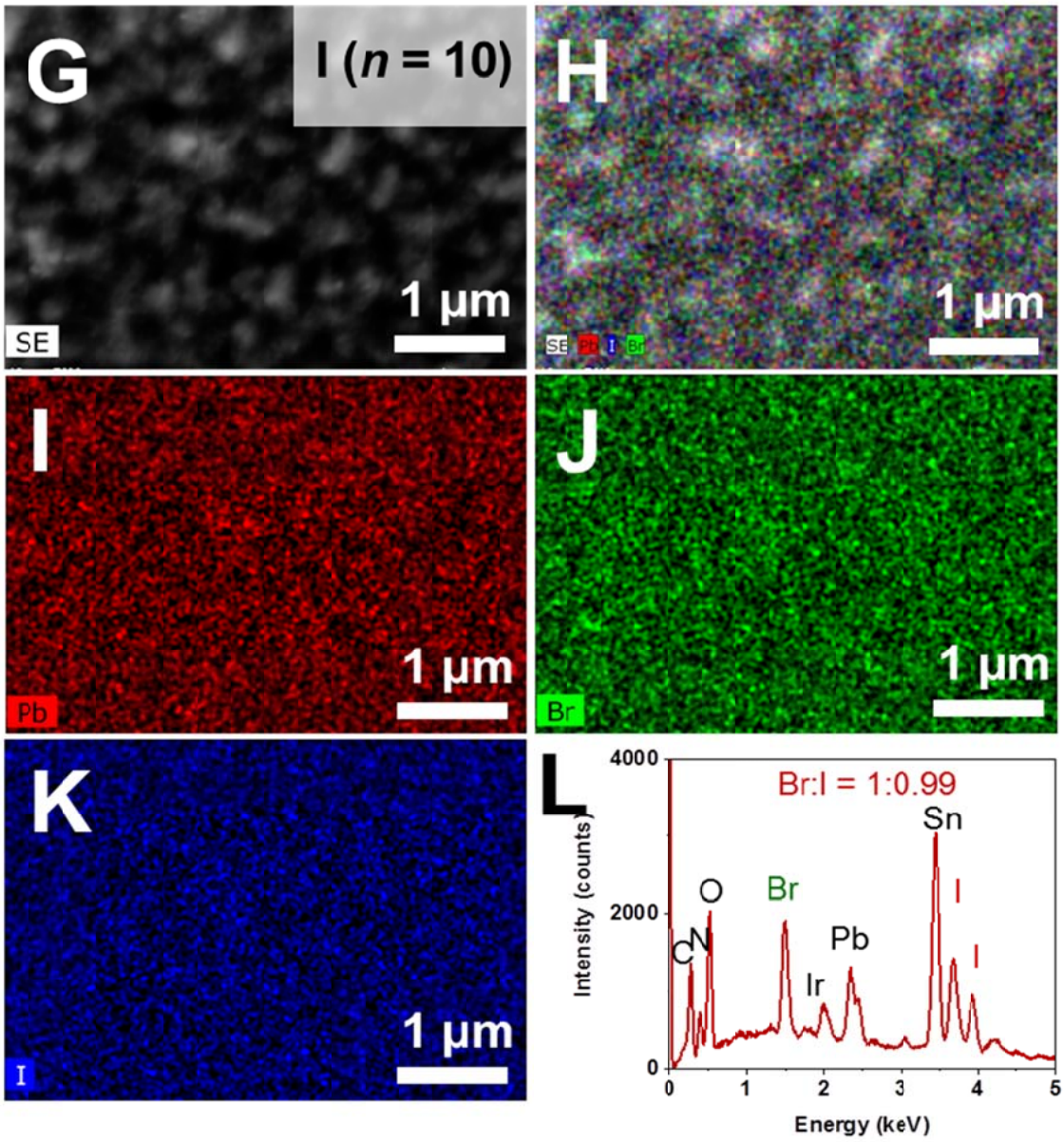


Figure S5. SEM image and EDS analysis of 2D lead bromide slide (A-F) and 2D lead iodide slide (G-L) with layer number of n = 10 following homogenization at 140 °C for 1 hr. (A,G) SEM images, (B,H) SEM images spatially overlapped with elemental mappings of Pb, Br, and I (C,I) Pb elemental mappings, (D,J) Br elemental mappings, (E,K) I elemental mappings, and (F,L) EDS spectrum for the 2D lead bromide film with n = 10 (F) and 2D lead iodide film with n = 10 (L). In the EDS spectra of F and L, Sn and Ir impurities arise from the FTO substrate and Iridium sputtering.

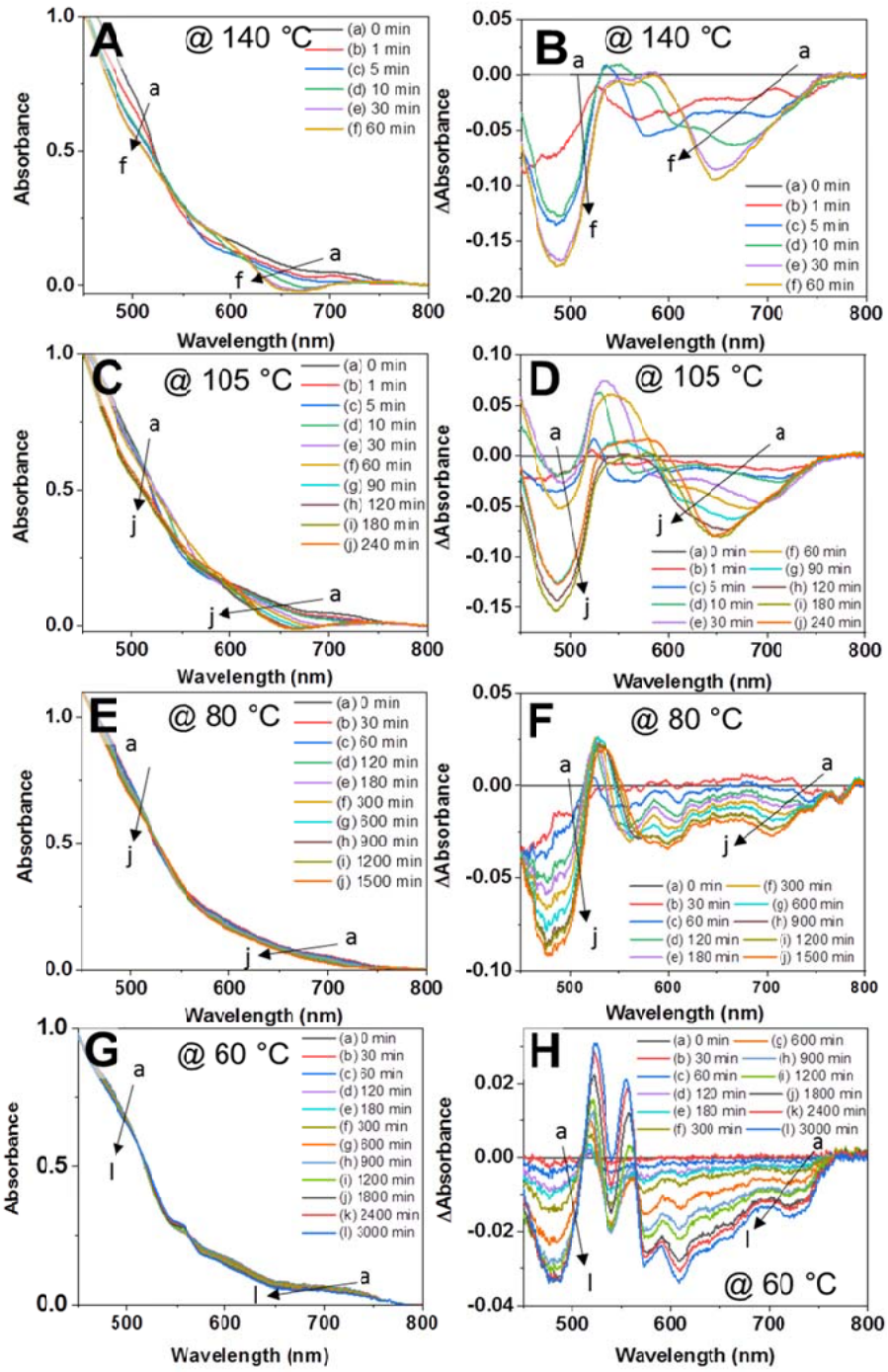


Figure S6. (A,C,E,G) Absorption spectra of the paired 2D lead halide (bromide/iodide) perovskite films with n = 6 recorded at different temperature of (A) 140 °C, (C) 105 °C, (E) 80 °C, and (G) 60 °C as a function of homogenization time. (B,D,F,H) Corresponding difference absorption spectra obtained from the panel A,C,E,G, respectively. The absorption spectrum at 0 min was served as reference to obtain the difference absorption spectra.

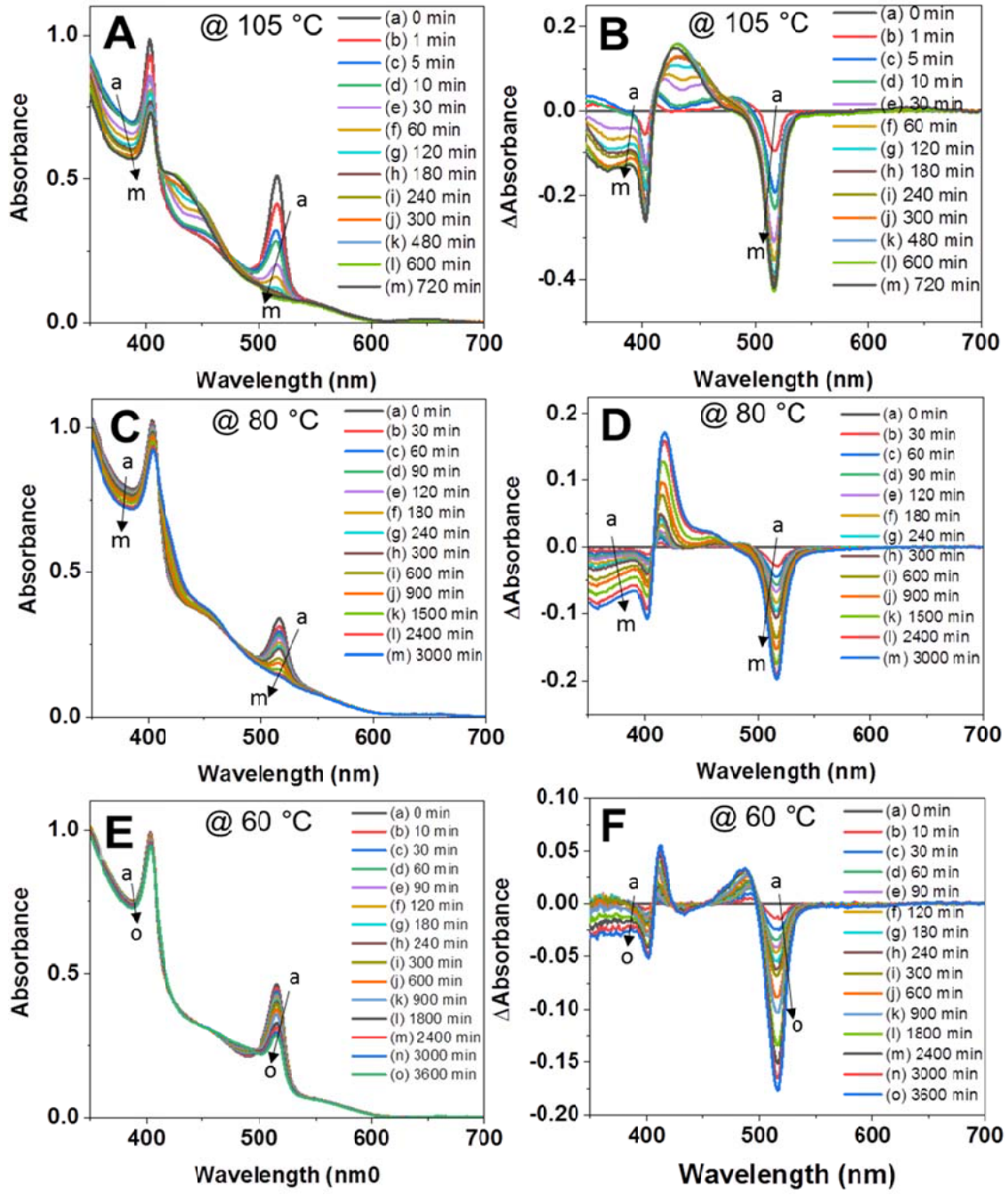


Figure S7. (A,C,E) Absorption spectra of the paired 2D lead halide (bromide/iodide) perovskite films with n = 1 recorded at different temperature of (A) 105 °C, (C) 80 °C, and (E) 60 °C as a function of homogenization time. (B,D,F) Corresponding difference absorption spectra obtained from the panel A,C,E respectively. The absorption spectrum at 0 min was served as reference to obtain the difference absorption spectra.

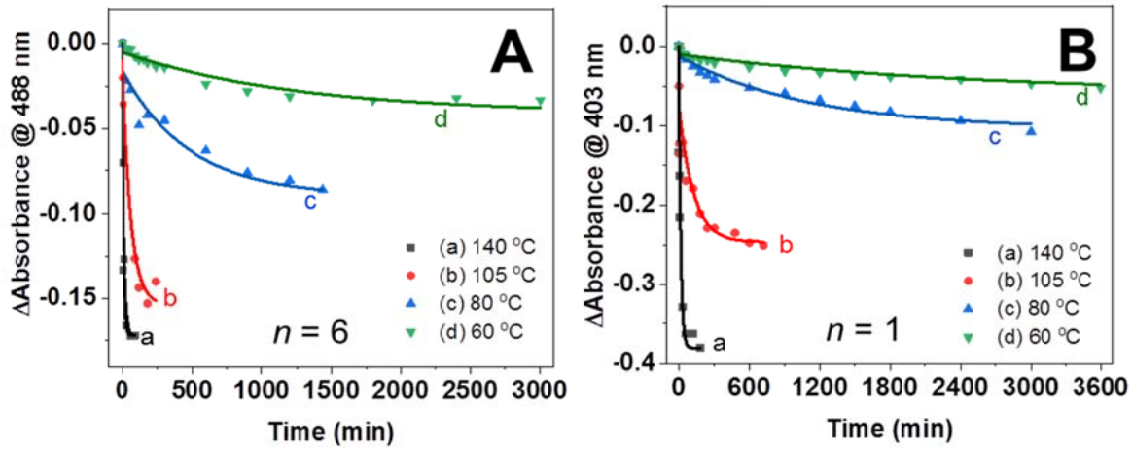


Figure S8. Changes in excitonic absorption peak of the 2D lead bromide film observed from the difference absorption spectra at 488 nm corresponding to the film of n = 6 (A) and at 403 nm corresponding to the film of n = 1 (B) during the homogenization processes at different annealing temperature of (a) 140 °C, (b) 105 °C, (C) 80 °C, (d) 60 °C, respectively.

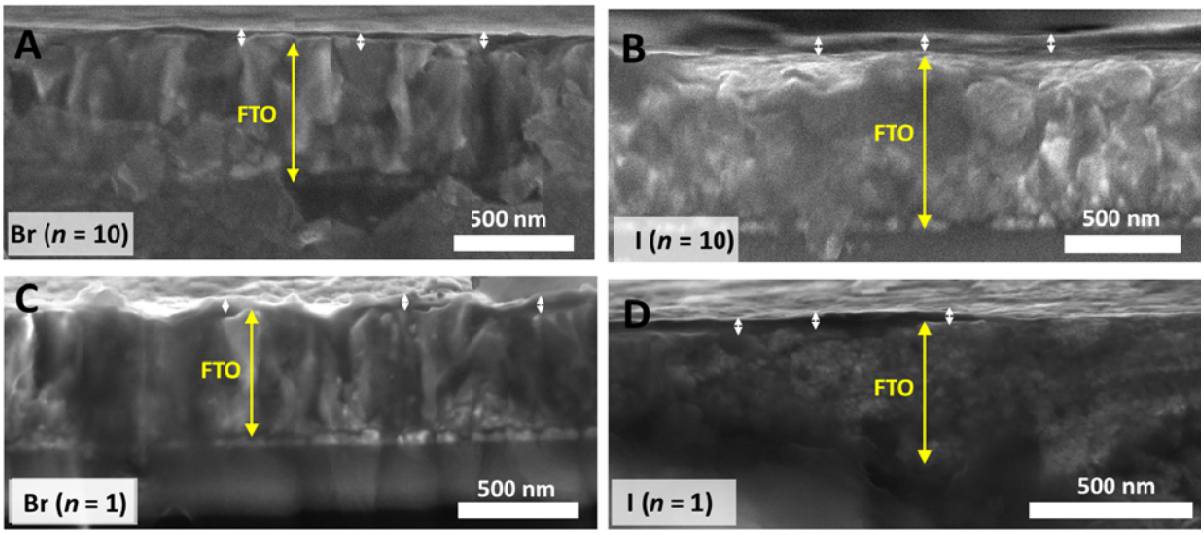


Figure S9. Cross-sectional SEM images of 2D lead halide perovskite films with (A) X = Br (n = 10), (B) X = I (n = 10), (C) X = Br (n = 1) and (d) X = I (n = 1) following homogenization at 140 °C. The average film thickness of the films is determined to be 75 ± 7 nm (A), 114 ± 9 nm (B), 90 ± 10 nm (C), and 107 ± 5 nm (D), respectively, through measuring three different points. The average thickness of entire 2D perovskite films between n = 10 and n = 1 (A-D) is approximated to be 96.5 ± 15 nm.

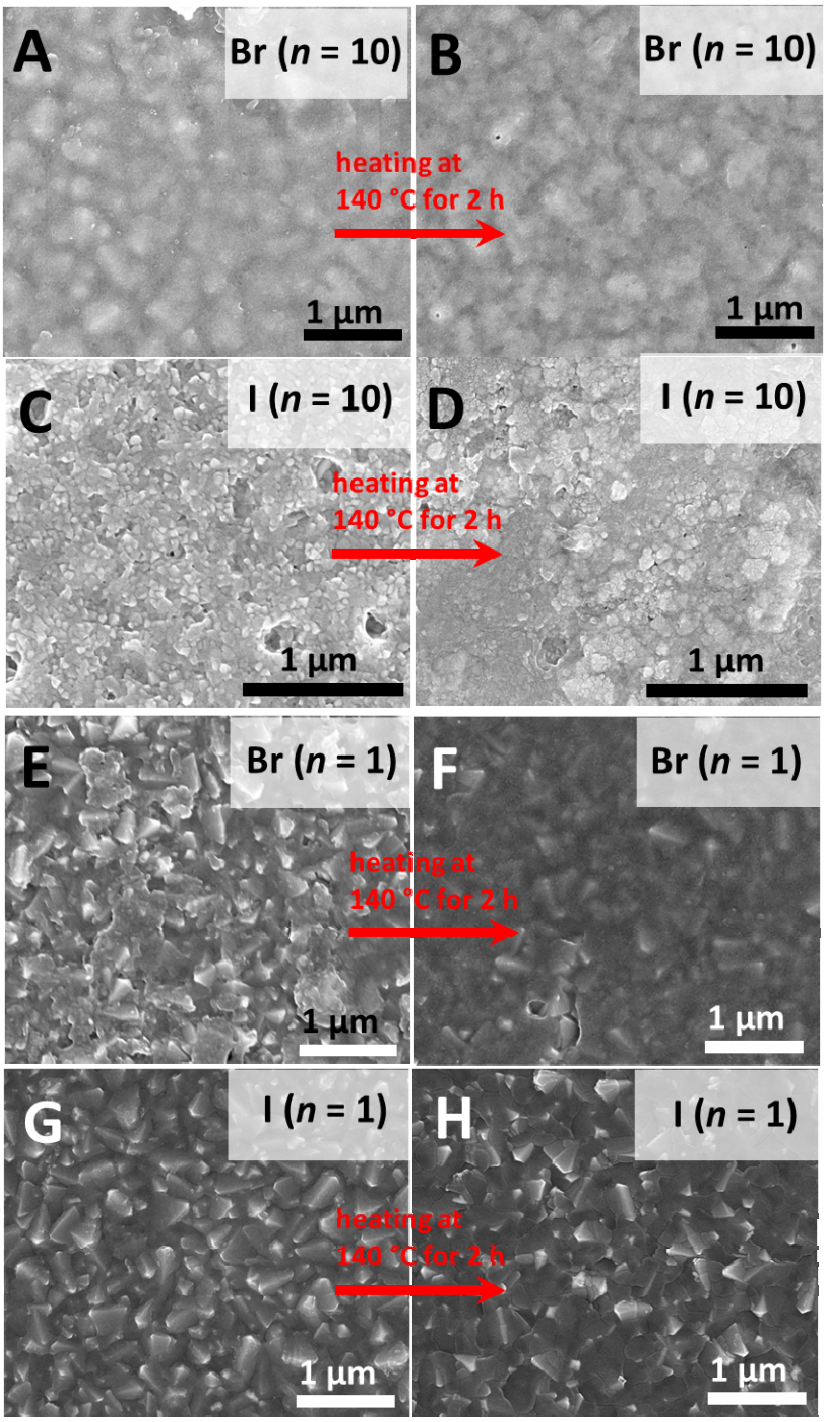


Figure S10. Top-down view SEM images before (A,C,E,G; left) and after (B,D,F,Hl right) homogenization at 140 °C for 2 hr with the 2D lead halide perovskite film of (A,B) X = Br (n = 10), (C,D) X = I (n =10), (E,F) X= Br (n = 1), and (G,H) X = I (n = 1).

References

(1) Quan, L. N.; Yuan, M.; Comin, R.; Voznyy, O.; Beauregard, E. M.; Hoogland, S.; Buin, A.; Kirmani, A. R.; Zhao, K.; Amassian, A., Ligand-stabilized reduced-dimensionality perovskites. *J. Am. Chem. Soc.* **2016,** 138, 2649-2655.
(2) Liu, J.; Leng, J.; Wu, K.; Zhang, J.; Jin, S., Observation of Internal Photoinduced Electron and Hole Separation in Hybrid Two-Dimentional Perovskite Films. *J. Am. Chem. Soc.* **2017,** 139, 1432-1435.
(3) Cho, J.; DuBose, J. T.; Kamat, P. V., Charge Carrier Recombination Dynamics of 2-D Lead Halide Perovskites. *The Journal of Physical Chemistry Letters* **2020**.