Bidirectional Halide Ion Exchange in Paired Lead Halide Perovskite Films
with Thermal Activation

Tor Elmelund¹,², Rebecca Scheidt¹, Brian Seger² and Prashant V. Kamat¹*

¹Radiation Laboratory, Department of Chemistry & Biochemistry, and
Department of Chemical & Biomolecular Engineering
University of Notre Dame, Notre Dame, Indiana 46556, USA

and

²SurfCat, Department of Physics
Technical University of Denmark
2800 Kgs. Lyngby, Denmark

*Address correspondence to pkamat@nd.edu
Experimental Section

Materials and film preparation procedures

The preparation procedure for the MAPbI$_3$ and MAPbBr$_3$ perovskite films were adapted from earlier reports.$^{1,2}$ 2.5 x 2.5 cm FTO coated glass substrates were used to resemble full solar cell device fabrication. The substrates were washed with soapy water, rinsed with DI water and placed directly into an absolute ethanol bath. The FTO slides were left to sonicate for 20 minutes before being rinsed with Isopropanol and dried with an airstream. To remove any remaining organics the substrates were plasma cleaned for 10 minutes after which a 7mm wide Kapton tape was placed at one side of the substrate to resemble full solar cell device fabrication. The substrates were then transferred to a N$_2$ filled glovebox for spin coating of perovskite films.

Two perovskite solutions (MAPbI$_3$ and MAPbBr$_3$) were prepared by dissolving all precursors in dimethylformamide, DMF (Sigma-Aldrich, anhydrous, 99.8%) and dimethyl sulfoxide DMSO (Sigma-Aldrich, anhydrous, ≥99.9%). For both MAPbI$_3$ and MAPbBr$_3$, a 0.3M solution was prepared from PbI$_2$ (Sigma-Aldrich, Ultradry, beads, −10 mesh, 99.999% trace metals basis) and MAI (Greatcell Solar) for MAPbI$_3$, while the MAPbBr$_3$ was made using PbBr$_2$ (Alfa Aesar, 98+%) and MABr (Greatcell Solar). The solutions were left to stir 1 hour at room temperature and subsequently filtered through an inorganic membrane filter (0.2 µm pore size, G8549141, Whatman) before use. The MAPbI$_3$ films were obtained using static drop casting of 50µL of MAPbI$_3$ and subsequently spin coating at 4000rpm for 25s with an acceleration of 1200 rpm. An antisolvent treatment step with diethyl-ether (Sigma-Aldrich, for HPLC, ≥99.9%, inhibitor-free) was used, with 0.5 mL being rapidly injected after 10 seconds. The films were immediately transferred to a preheated hotplate for 1 min at 65°C, and then transferred to a 100°C hotplate for 2 minutes. After annealing the films were removed from the hotplate and left to cool down before use. The MAPbBr$_3$ films were obtained using static drop casting of 50µL of MAPbBr$_3$ and subsequently spin coating at 1000rpm for 10s with an acceleration of 1200 rpm, then at 4000 rpm for 35 s with an acceleration of 1200 rpm. Here 0.1mL toluene (Sigma-Aldrich, anhydrous, 99.8%) was used for the antisolvent treatment step, and was rapidly injected after 20 seconds. The films were immediately transferred to a preheated hotplate for 10 minutes at 100°C. After annealing the films were removed from the hotplate and left to cool.
**Halide Ion Exchange of films**

The prepared MAPbI$_3$ and MAPbBr$_3$ substrates were transferred from the glovebox to a hotplate located next to the spectrophotometer (Cary 50 Bio spectrophotometer, Varian) for halide ion exchange of the films. The Kapton tape was removed, and the films were placed in contact with each other and clamped with binder clips at either end of the films. The clamped films were then placed on a brass plate with the MAPbBr$_3$ film facing downwards to allow for direct heating of the films. The temperature of the brass plate was monitored and controlled by adjusting the temperature of the hotplate.

**Characterizations and Methods used**

Steady state UV-vis absorption spectra were recorded using a Cary 50 Bio spectrophotometer (Varian). The clamped system was periodically removed from the hotplate and transferred direct to the spectrophotometer for acquiring absorption spectra and immediately transferred back to the hotplate. The absorption was used to monitor the halide ion exchange between the films.

SEM imaging was performed on a Magellan 400 digital field emission scanning electron microscope operated with a beam voltage of 2 kV.

Surface halide composition analysis was performed using X-ray Photoelectron Spectroscopy, XPS on a PHI VersaProbe II. The compositional analysis was performed using 15kV high power point.

For transient absorption measurements a Clark MR-2010 laser system (775 nm fundamental, 1 mJ/pulse, fwhm = 150 fs, 1 kHz repetition rate) was used together with a detection software from Ultrafast Systems (Helios). The white-light continuum beam is split in two beams with a 95/5 separation ratio, with the 95% beam being doubled to 387 nm to create the pulse. Using a neutral density filter together with an iris of a known diameter, the power of the pulse is kept at a power density of 8 μJ/cm$^2$. The remaining 5% portion of the white-light continuum beam is used to create the probe by directing the beam through a calcium fluoride (CAF$_2$) crystal to create a super continuum.
Supporting Results

Figure S1: Top down SEM images of homogenized films at 100 °C acquired at 600 min (A, B) for MAPbI$_{3-x}$Br$_x$ and MAPbBr$_{3-x}$Ix, respectively. (C, D) Corresponding images of films after 900 min of homogenization. All images were acquired at 100 000X magnification using 2kV acceleration voltage.
Figure S2: Cross sectional SEM image of equimolar (0.3M) planar (A) MAPbI$_3$ and (B) MAPbBr$_3$ layers deposited on 0.5 μm FTO-coated glass. The average thickness of 5 measured thicknesses across the surface were 165 ± 18 nm and 92 ± 12 nm, respectively.

Figure S3: Analyzed average MAPbI$_3$ grain size of as prepared pre homogenized film (0min) and post homogenized film (1260 minutes), showing a slight increase in average particle size. Obtained from Figure 2(A, C).
Figure S4: Tracking halide homogenization at 100 °C for directly synthesized mixed halide perovskite films with different I:Br ratios. Two films of MAPbBr$_{0.75}$I$_{2.25}$ and MAPbBr$_{2.25}$I$_{0.75}$ with absorbance spectra of films shown in (A) pre- and post-homogenization. (B) shows photographs taken of the two films pre (a,b) and post (c,d) homogenization. Figure (C, D) shows the halide composition pre (0 min) and post (1260 min) homogenization for the two films MAPbBr$_{0.75}$I$_{2.25}$ and MAPbBr$_{2.25}$I$_{0.75}$, respectively. It is evident that the initial 75/25 ratio becomes 50/50 for both films after homogenization.
Figure S5: (A, C, E, G) Steady-state absorption spectra of paired MAPbI3/MAPbBr3 perovskite films recorded at different times of homogenization at 60, 80, 120 and 140°C. (B, D, F, H) Corresponding
difference absorbance spectra obtained from the 4 different temperatures, where minute 0 spectrum is used as a reference.

Figure S6: Complementary XPS spectra of one of the two films (MAPbI3 film), with the other being shown in Figure 5. Acquired during halide homogenization at 100 °C, at 0, 600, 900 min, and 1260 min. The probed regions were (A) Pb 4f, (B) I 3d, (C) Br 3d, where fits of individual peaks are shown in red and green, the cumulative fit is shown in blue, while the original data is shown as a black scatter plot. (D) The change in halide composition of iodide and bromide during homogenization is plotted over time.
Table S1: Table showing extracted fitting parameters for the fast and slow decay processes obtained from the biexponential fittings for the kinetics shown in Figure 6E.

<table>
<thead>
<tr>
<th></th>
<th>$A_1$ (%)</th>
<th>$\tau_1$ (ps)</th>
<th>$A_2$ (%)</th>
<th>$\tau_2$ (ps)</th>
<th>$\tau_{avg}$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI$_3$</td>
<td>33.77</td>
<td>195.13</td>
<td>65.35</td>
<td>2511.32</td>
<td>1722.20</td>
</tr>
<tr>
<td>MAPbBr$_3$</td>
<td>44.50</td>
<td>164.51</td>
<td>55.47</td>
<td>1389.29</td>
<td>844.10</td>
</tr>
<tr>
<td>MAPbI$_{3-x}$Br$_x$</td>
<td>49.78</td>
<td>117.54</td>
<td>49.74</td>
<td>781.88</td>
<td>499.58</td>
</tr>
<tr>
<td>MAPbBr$_{3-x}$I$_x$</td>
<td>64.67</td>
<td>187.43</td>
<td>34.66</td>
<td>838.54</td>
<td>414.63</td>
</tr>
</tbody>
</table>

References