Supporting Information

**Photo-Effect on Ion Transport in Mixed Cation and Halide Perovskites and Implications for Photo-Demixing**

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### Table of contents

1. Experimental methods
2. Material properties
3. Analysis of d.c. polarization measurements
4. Chemical capacitance and diffusion coefficient
5. Wavelength dependence conductivity measurements
6. Toluene experiments
7. EMF of partially equilibration activity cell
8. Iodine partial pressure dependence and activation energy of FAPbI$_3$
9. Polarization experiments in anion mixtures
10. Self-trapped hole mechanism and photo de-mixing effect
1. Experimental methods

Preparation of perovskite thin-films for electrical measurements

An equimolar solution (1 M) of MAI, MABr, FAI, CsI, CsBr (Sigma Aldrich) and PbI₂, and PbBr₂ (Alfa Aesar) in DMSO was prepared and spin-coated on polished sapphire (0001) substrates, previously equipped with interdigitated Au electrodes (2 μm spacing, 100 μm length). Prior to the spin-coating step, substrates were cleaned with an O₂-plasma treatment, in order to remove organic impurities and enhance the hydrophilicity of the surface. Perovskite thin films were coated by spin-coating process at 65 rps and 150 rps for 2s and 180s on Al₂O₃ substrates, respectively. During spin-coating, a drop of chlorobenzene was used to induce rapid crystallization,\(^1\) and the sample was later annealed for 3 minutes at 100 °C. In case of CsPbI₃, we annealed the sample for 30 min at 350 °C. The thickness of films is around 200 nm. All procedures were carried out in an Ar-filled glovebox (O₂ < 0.1 and H₂O < 0.1 ppm).

D.c.-galvanostatic polarization

D.c. polarization experiments were performed by using a source meter (Keithley model 2634b) and by monitoring the voltage change. Measurements were carried out in the dark and under light illumination and by accurately controlling temperature and atmosphere over the sample (oxygen content and humidity were monitored using appropriate sensors). We varied the composition by controlling the nominal concentration of the precursors in the solution and measured the voltage via Au ion-blocking electrodes in an interdigitated arrangement. Au electrodes were considered as ideally electronically selective electrodes. As the light source, a Xenon arc lamp was used (~1 mW/cm²), and its intensity was calibrated using a power meter (Thorlabs).

Comments on the analysis of d.c polarization experiments

Our analysis of the d.c. polarization measurements is predominantly based on polarization experiments with ion blocking electrodes that we had previously successfully applied to MAPI. This technique is a standard method in solid state electrochemistry for deconvoluting ionic and electronic conductivities. Nonetheless, it relies on a variety of assumptions that need to be addressed here and certainly in great depth in future work. One of the assumptions is the absence of significant contributions from other polarization phenomena. For MAPI, we do not see a significant dependence on electrode distance, so we discard significant interfacial effects at least for its case. A second assumption is the neglect of voltage effects on the transport properties. As the voltage is small, one typically refers to linear response. Nonetheless,
variation in electron hole recombination and electronic injection processes due to ion redistribution in the sample could play a role in the changes of the measured voltage as a function of time, as these explain many of the features of halide perovskites when used in solar cell devices. Specifically, ion redistribution during the polarization experiment can induce variation in the energy barrier for electronic injection from the contacts and for electron hole recombination in the bulk and at interfaces. This can affect the measured voltage and result, depending on the situation, in an underestimation or an overestimation of the estimated ionic conductivity (see Ref. [2]). While this aspect is not expected to influence the case of experiments performed in the dark and close to equilibrium, under illumination the situation is more delicate. It cannot be concluded at the moment how far such effects are of influence in the measurements reported in this study. Especially, note that we are dealing with symmetric cells in which various effects may cancel out. This important point is not easy to address and deserves more future work.

We also point out that the frequencies are low enough to exclude significant contributions from short-range motions[3]. Finally, the de-trapping effect of polarization on the interstitial neutral defects (e.g. neutral iodine) has to be mentioned. This phenomenon has been discussed in different contexts and is important when these centers are mobile[3]. In such case the ion conductivity would be underestimated.

While the assumptions above may affect the quantitative conclusions drawn in the discussion of the data reported in this study, it is still striking that a clear difference in the effect of light is observed when comparing iodide with bromide perovskite samples. Therefore, we base our discussion in the main text on the qualitative trends illustrated by the data extracted from electrical measurements using the standard analysis.

Iodine partial pressure dependence
To control \( P(\text{I}_2) \) over the samples, argon was used as carrier gas and it was flown in a container with solid iodine chips, kept in a thermostat at a fixed temperature (always below room temperature, between \(-35^\circ\text{C}\) and \(-5^\circ\text{C}\)). The iodine partial pressure in the sample chamber was assumed to correspond to the equilibrium pressure of iodine at the thermostat temperature. Similar values are obtained by estimating \( P(\text{I}_2) \) purely from thermodynamic considerations, starting from Gibbs free energy of sublimation of solid iodine.

EMF measurement
A MAPbBr\(_3\) thin film was contacted with pellets, one that consisted of a physical mixture of Cu and CuBr and the other of Pb and PbBr\(_2\). The cell was kept under an Ar atmosphere at 60°C.
The two electrodes were connected to a high impedance source meter (Keithley model 2634b). The cell was sealed using PMMA to avoid any exchange with the external atmosphere. The light source was a LED lamp with 420 nm wavelength and 4 mW/cm$^2$ intensity.

**XRD measurements**

XRD data were obtained using a PANalytical Empyrean Series 2 (Cu Kα radiation, 40 kV, 40 mA) in grazing incidence ($\omega$=2°). X-ray diffraction patterns were acquired in an Ar filled beryllium dome.

**Toluene experiments**

MAPbBr$_3$ films were immersed in toluene in a quartz cuvette. The bromine amount lost by the sample was measured by in-situ optical absorbance as a function of time, using a $UV$-$Vis$ spectrophotometer (Cary $UV$–$Vis$ 4000 spectrometer). Illumination was achieved with a tungsten lamp that delivers approximately 1 mW/cm$^2$ light intensity over the samples.
2. Material properties

Figure S1 shows XRD patterns of mixed cation and anion perovskite thin films on Al$_2$O$_3$ substrates. The data indicate no secondary phase in the Anion mixtures, although we observe small amount of PbI$_2$ in I$_{20}$Br$_{80}$ sample. Cation mixtures (FA,MA) show no secondary phase, but FAPbI$_3$ has a certain amount of delta phase and PbI$_2$. This is due to its structural instability at low temperature (delta phase is favorable at low T). For the CsPbI$_3$, the sample was cubic-phase with dark color after preparation; however the phase partially changed to orthorhombic during XRD measurement. CsPbI$_3$ cubic-phase was stable for electrical measurements under Ar atmosphere (O$_2$ < 20 ppm).

**Figure S1.** XRD patterns of (a) MAPb(I$_{1-x}$Br$_x$)$_3$ (b) (MA$_{1-x}$FA$_x$)PbI$_3$ (c) CsPb(I,Br)$_3$ thin films on Al$_2$O$_3$ substrates.
3. **Analysis of d.c. polarization measurements**

Here we show the consistency check from the comparison of transient and steady state based on d.c. polarization curve. The observed polarization curves in the dark and under light are shown in main text. The polarization transient is in the ideal case characterized by a short time square-root time-behavior ($\sqrt{t}$) and a long-time exponential time-behavior (characterized by a time constant that is inversely proportional to the chemical diffusion coefficient). Figures below are an example of a polarization curve and time constant fitting in the dark and under light and its fitting according to the above. As shown in Figs. S2-S3 (a), (c), (e), and (g), some of the curves indicate the square root $t$ behavior for short time in the dark and under light and Figs. S2-S3 (b), (d), and (f) show long-time exponential behaviors. The time constant from the long time fitting values are in line with short time fitting values (for more details on the technique the reader is referred to the literature\textsuperscript{[4]} and references therein).
Figure S2. Stoichiometric polarization curve of FAPbI$_3$ and CsPbI$_3$ thin films in the dark and under light and fitting with short and long-time scale. While the exponential long-time fit is typically satisfactory, the short-time fit with a square-root low is less reliable.
Figure S3. Stoichiometric polarization curve of Br-based perovskite thin films in the dark and under light and fitting with short and long-time scale. While the exponential long-time fit is typically satisfactory, the short-time fit with a square-root low is less reliable.
In terms of dc polarization measurement, we expect the values of the electronic conductivity (extracted from the steady state voltage) to be accurate. However, the evaluation of the ionic conductivity from the “voltage jump” at early time scales can introduce a significant error in the evaluation of the ionic conductivity, due to the limited time resolution of the measurement. This is especially important when the sample has high ionic transference number. In order to resolve this issue, we fit the early time scale voltage response of dc polarization measurements to a function $V_{fit}(t) = A\sqrt{t} + V_0$ and extrapolate the value of $V_{fit}(t = 0) = V_0$ from the fit (see Figs. S2-S3). From the first data point measured upon application of the dc current $V(t = t_{res})$ (tres is the time resolution of the dc measurement) and $V_0$, we can evaluate the fractional error associated to the estimate of total conductivity as $\frac{\Delta V}{V} = \frac{\Delta \sigma_{tot}}{\sigma_{tot}} = \frac{V(t = t_{res}) - V_0}{V(t = t_{res})}$, and from which we estimate the error on the ionic conductivity $\frac{\Delta \sigma_{ion}}{\sigma_{ion}}$. We find that this error is negligible for measurements with low $t_{ion}$ ($\frac{\Delta \sigma_{ion}}{\sigma_{ion}} < 0.6$ for $t_{ion} < 0.9$) but can be significant for samples showing large $t_{ion}$. Therefore, in the main text, we report values of ionic conductivity that are calculated in the following ways:

i) $\sigma_{ion}$ calculated directly from total resistance the dc polarization measurement for cases where $t_{ion} < 0.9$.

For samples where $t_{ion} > 0.9$, $V(t = t_{res})$ can be small and $V_{fit}(t = 0)$ is very close to 0 V. In this case, we measure the impedance spectrum of the sample and estimate the ionic conductivity as below.

ii) $\sigma_{ion}$ was calculated using a value of $\sigma_{tot}$ extracted from the high frequency semicircle in the Nyquist plot.
4. Chemical capacitance and diffusion coefficient

The chemical diffusion coefficient can be expressed as\[ D^\delta = \frac{L^2}{\pi^2 \tau^\delta}, \]
where \( L \) is the thickness of the sample and \( \tau^\delta \) is the polarization time constant. The chemical capacitance and resistance \( C^\delta = \frac{\tau^\delta}{R^\delta} \) have been calculated from the values of the electronic and ionic conductivities and the time constants (the latter are indicated in Figs. S2-3). We found a similar diffusion coefficient in MAPbI\(_3\) and FAPbI\(_3\) both in the dark and under light illumination (see Fig. S4a). On the other hand, the diffusion coefficient of MAPbBr\(_3\) and CsPbBr\(_3\) increased by one order of magnitude under light from the dark case (see Fig. S4c). We now discuss the comparison of the chemical diffusion coefficients of MAPbI\(_3\) and MAPbBr\(_3\). First, the values of \( D^\delta \) for MAPbI\(_3\) and MAPbBr\(_3\) are similar in the dark. The value of \( D^\delta \) for MAPbI\(_3\) undergoes a slight increase under light (factor 2) while a much larger increase is observed for MAPbBr\(_3\) (factor 10). In all cases the ionic conductivity is larger or comparable with the electronic conductivity, indicating a higher ionic defect concentration than electronic carrier concentration. From our analysis we conclude that self-trapping is substantial for MAPbI\(_3\) but not for MAPbBr\(_3\).

In the following we distinguish between two types of trapping. The first one is \textit{Intrinsic self-trapping} \( h^* \rightleftharpoons h_{p^*}^* \) as the one that we expect occurring in MAPI. For this case we simply obtain

\[ \chi_p = \frac{\partial [h^*]}{\partial [h^*]} \bigg|_{Tr} = \frac{1}{K_{Tr}} = \frac{[h^*]}{[h^*]} \bigg|_{T r}, \]

where \( \chi_p \) is the differential (un) trapping factor and \( K_{Tr} \) the trapping mass action constant.

Secondly, we have to be aware of \textit{extrinsic trapping} which is particularly important when discussing the data obtained for MAPbBr\(_3\). Unlike the situation under light, where the electronic concentration in MAPbBr\(_3\) should exceed the extrinsic trap concentration, we can assume that in the dark an extrinsic trap controls the hole concentration according to \( T^+ + h^* \rightleftharpoons T^* \) where \([T^+] + [T^*] = T = \text{const.} \) at equilibrium. \( T^+ \) is the free traps and \( T^* \) the occupied traps. Such a trap maybe e.g. oxygen \( (\text{O}^+_{Br} \text{ or } \text{O}^-_{Br}) \).

The chemical diffusion coefficient \( D^\delta \) can be written as\[ D^\delta = t_v D^\delta \chi_v + t_p D^\delta \chi_p \]
\[
\frac{F^2}{RT} D^\delta = t_v \sigma_p \left( \frac{\chi_p}{c_p} + \frac{\chi_v}{c_v} \right) = t_p \sigma_v \left( \frac{\chi_p}{c_p} + \frac{\chi_v}{c_v} \right)
\]

where \( t_v \) and \( t_p \) are transference number \( (t_v \equiv \frac{\sigma_v}{\sigma}, t_p \equiv \frac{\sigma_p}{\sigma}) \), \( \chi_v \) and \( \chi_p \) denote the differential trapping factors of vacancy and hole carriers.

If \( [T^+] \gg [h^+] \), i.e. extrinsic traps dominate, this equation can also be written as \[^{[4a]}\]

\[
\frac{F^2}{RT} D^\delta = t_p \sigma_p \left( \frac{1}{[T']} + \frac{1}{[T'^\alpha]} + \frac{1}{[e_v'^\alpha]} \right)
\]

If we assume \( [T^+] \gg [T'^\alpha] \) and \( [T'] = [V^+_v] \) owing to electroneutrality, then \( D^\delta = t_p D_v \).

Under light \( [h^+] \gg T \) and \( t_v \) is still high (0.5 for experimental result) then,

\[
D^\delta = t_v \chi_p D_p
\]

for MAPbBr\(_3\) where self-trapping is small \( \chi_p \) can be set to 1; \( D^\delta \) then turns out to be indeed much higher than in the dark \( (D_p \gg D_v) \) and

\[
D^\delta \approx 0.5D_p.
\]

\( D_p \) and \( D_v \) are the individual diffusivities of hole and vacancy. For MAPI, \( \chi_p \) is rather small and \( D^\delta \) greatly depressed with respect to \( D_p \) explaining the lower \( D^\delta \). As in MAPI self-trapping can be assumed to be dominant with respect to extrinsic trapping, we obtain the same result as under illumination \( (\sim D_p/K_p) \), in agreement with the experiments. The similar results for \( D^\delta \) (MAPbI\(_3\)) at \( D^\delta \) (MAPbBr\(_3\)) in the dark must be rather coincidental and the outcome of compensation between trapping and mobility. Along the same lines: The chemical capacitance in MAPbBr\(_3\) is about one order smaller in the dark than MAPbI\(_3\), while for the chemical resistance the situation is reversed.
Figure S4. (a) Chemical diffusion coefficient ($D^\delta$), (b) chemical capacitance ($C^\delta$) and resistance ($R^\delta$) of iodide perovskites as well as (c) $D^\delta$, (d) $C^\delta$ and $R^\delta$ of bromide perovskites in the dark and under light illumination.
5. Wavelength dependence conductivity measurements

In order to confirm the influence of photon energy on our results, we performed conductivity measurement using light at different wavelengths. What we consistently found is that the effect on ion conduction only sets in if the wavelength is smaller than the critical value set by the band gap. The yellow area indicates photon energies higher than the bandgap energy for different compositions. If the photon energy is larger than the bandgap, the ionic conductivity enhancement is even larger than the white light in MAPbI₃. For MAPbBr₃, all the wavelength of light shows no enhancement of ionic conductivity, but only increase of electronic conductivity by 420 nm of light.

![Figure S5](image)

**Figure S5.** Wavelength dependence of electronic and ionic conductivities in MAPb(I,Br)₃. We used 420, 660, and 820 nm of LED lamp for light illumination with 1 mW/cm² of intensity. White light is also 1 mW/cm² of light intensity. Yellow background indicates that photon energy is higher than bandgap. Ionic conductivity of MAPbBr₃ is not strongly enhanced under all wavelength of light.
6. Toluene experiments

To gain further evidence on the difference between bromide and iodide hybrid perovskites in terms of behavior under light, we performed excorporation experiments. Specifically, we investigated the behavior of a MAPbBr$_3$ film immersed in toluene solution, which acts as a solvent for Br$_2$. We measured the absorption signal of Br$_2$ in toluene as a function of time in the dark and under light. This experiment allows us to evaluate the rate of Br$_2$ excorporation, similarly to the case of I$_2$, as shown in previous work$^6$.

First, we measured a reference absorption spectrum for a 7 mmol solution of bromine dissolved in toluene. As indicated in the insets of Fig. S6, we can obtain clear absorption signal around 400 nm, which is in line with the literature data. We then measured the optical absorption of toluene in which a MAPbBr$_3$ film was immersed. Even though Br$_2$ has a high solubility in toluene$^7$, the excorporation rate of bromine under light from the sample was very low, and much weaker than iodine. In fact, the bromine content in toluene was below our detection limit for this experiment (see Fig. S6). This can be attributed to a very small homogeneity range of MAPbBr$_3$ (cf. main text).

![Figure S6](image)

**Figure S6.** Absorbance of bromine from MAPbBr$_3$ thin films immersed in toluene (a) in the dark and (b) under light illumination. The reference bromine signal collected from Br$_2$ in toluene is shown in the inset.
7. EMF of partially equilibration activity cell

We consider a mixed Br-conductor of thickness $L$ (typically mm scale) in between to bromine partial pressures $P(\text{Br}_2)$ and $P(\text{Br}_2)$ (corresponding to the chemical potentials $\mu'$ and $\mu'' = \mu_{\text{in}} = \mu' + \frac{1}{2} RT \ln P(\text{Br}_2)$).

Figure S7. Schematic of emf measurement on MAPbBr$_3$ same as main text. We used Pb/PbBr$_2$ and Cu/CuBr pellets for the bromine partial pressures $P(\text{Br}_2)$ and $P(\text{Br}_2)$ and measured the open circuit voltage of this electrochemical cell. The partial pressure of each side is expected to be very low and the waiting time not sufficient to reach equilibrium all through the sample. The situation during the experiment may be similar to the one shown above by the $\mu^*$ profile.

If the surface reaction is sufficiently fast and the waiting time $\tau$ for the whole sample to respond to the such conditions is sufficiently large ($\tau \gg L^2/D^\delta$), then

\[
\frac{-EF}{RT} = \varepsilon = \int_{\mu'}^{\mu^*} t_{\text{ion}} d\mu
\]

such that Eq (1)

\[
\varepsilon = \tilde{t}(\mu^* - \mu')
\]

where $\varepsilon = -EF/RT$ and $\tilde{t}$ is the mean ionic transference number (here, and in the following, we drop the index “ion” for simplicity, $\tilde{t}$: effectively measured transference number). If however the waiting time is much less, such that equilibration from bulk sides only allows for equilibration within $l = \sqrt{2D^\delta \tau} < L$, then in the interior the remains a region determined by the initial partial pressure ($\mu^*$). This is realized in our case where $\mu^*$ corresponds to a high $P(\text{Br}_2)$ while $\mu'$, $\mu''$ correspond to very low $P(\text{Br}_2)$ values established by the redox couples (Pb:PbBr$_2$ or Cu:CuBr).
According to low Br-diffusivity of MAPbBr$_3$ the situation in the emf cell should be the one sketched in Fig. S7; very low Br-partial pressures (and very small values of $t'$ and $t''$ owing to n-type conduction) on both sides, but high initial Br-partial pressure in the middle. Eq(1) is still valid. Let us assume that $\mu$ increases linearly from the l.h.s value $\mu'$ (at position $x = 0$) to $\mu^*$ (at $x = 1$) and stays constant for until $1 < x < L - l$ and then decreases to $\mu''$. Without a qualitative restriction of quantity, we assumed a linear behavior in the boundary regions, i.e. $\frac{d\mu}{dt} = \text{const}$.

Accordingly, we decompose Eq. 2 into three regions:

\begin{align*}
\text{l.h.s} \Rightarrow \varepsilon_l &= \int_{\mu'}^{\mu} t_j d\mu_j \\
\text{middle} \Rightarrow \varepsilon_m &= \int_{\mu'}^{\mu^*} t_j d\mu_j = 0 \\
\text{r.h.s} \Rightarrow \varepsilon_r &= \int_{\mu^*}^{\mu''} t_j d\mu_j
\end{align*}

The middle one drops out in the balance:

\begin{align*}
t_j &= \frac{t' - t'^*}{\mu - \mu'} + \frac{t'^* - t^* \mu - \mu'}{\mu - \mu''} \\
&\quad (a_j \equiv \frac{t' - t'^*}{\mu - \mu'}, b_j \equiv \frac{t'^* - t^* \mu - \mu'}{\mu - \mu''})
\end{align*}

According to Eq(1) the emf lowers as

\begin{align*}
\varepsilon &= \int_{\mu'}^{\mu} (a_j, \mu + b_j) d\mu_j + \int_{\mu'}^{\mu^*} (a_j, \mu + b_j) d\mu_j = \frac{1}{2} a_j, \mu^2 \Big|_{\mu'}^{\mu^*} + b_j, \mu^3 \Big|_{\mu'}^{\mu^*} + \frac{1}{2} a_j, \mu^2 \Big|_{\mu''}^{\mu^*} + b_j, \mu^3 \Big|_{\mu''}^{\mu^*} \\
&= \frac{1}{2} \frac{t' - t'^*}{\mu - \mu'} (\mu^2 - \mu'^2) + \frac{t'^* - t^* \mu - \mu'}{\mu - \mu''} (\mu^2 - \mu'^2) + \frac{1}{2} \frac{t' - t'^*}{\mu - \mu'} (\mu^2 - \mu'^2) + \frac{t'^* - t^* \mu - \mu'}{\mu - \mu''} (\mu^2 - \mu'^2) \\
&\quad + \frac{1}{2} \frac{t' - t'^*}{\mu - \mu'} (\mu^2 - \mu'^2) + \frac{1}{2} \frac{t' - t'^*}{\mu - \mu'} (\mu^2 - \mu'^2) + \mu^* (t' - t') + t' (\mu' - \mu).
\end{align*}

Collecting terms we obtain

\begin{align*}
\varepsilon &= \frac{1}{2} t' (\mu' - \mu') - \frac{1}{2} \mu^* (t' - t') + \frac{1}{2} (t' \mu' - t' \mu')
\end{align*}

If we introduce the condition $\dot{t'} = t' = 0$, the result is...
\[ \varepsilon = \frac{1}{2} t' (\mu^- - \mu^{'}) \]

Combined with Eq (2), this result shows that the effectively measured transference number is 
\[ \overline{t} = \frac{1}{2} t^* \] (we refer to this value as \( \bar{t}_{ion}^{corr} \) in the main text) which satisfactorily agrees with the experiment results (see main text). The measured voltage value is hence much lower than the one expected given boundary values \( t', t'' \) and less than the one expected considering the initial value \( t^* \).

A better approximation is obtained if only \( t' \) is set to zero corresponding to \( \mu'^{<} \mu'' \). Then
\[ \varepsilon = \frac{1}{2} t'^{<} (\mu^- - \mu^{'}) - \frac{1}{2} \mu^{'^<} (t'^{<} - t^{'}) + \frac{1}{2} (t'^{<} \mu^- - t^{'^<} \mu^{'}) \] and hence \( \overline{t} \leq \frac{1}{2} t' \).
8. Iodine partial pressure dependence and activation energy of FAPbI$_3$

We performed conductivity measurements under fixed iodine partial pressure (~10$^{-6}$ bar) on cation mixtures and measured activation energy of FAPbI$_3$. The ionic conductivity is reduced on increased FA concentration. The activation energy of FAPbI$_3$ is 0.6 eV, which is higher than for MAPbI$_3$ (0.4 eV). This reflects the high migration barrier for the I-vacancy motion owing to larger cation size.

**Figure S8.** (a) Conductivity measurements as a function of iodine partial pressure and Ar as carrier gas for (MA,FA)PbI$_3$ thin films at 40°C. Ionic and electronic conductivity extracted from d.c. galvanostatic polarization. (b) Temperature dependence of electronic and ionic conductivities of FAPbI$_3$ in the dark under fixed iodine partial pressure from 40 to 70°C.
9. Polarization experiments in anion mixtures

To obtain a detailed explanation for photo de-mixing, we observed the dc-polarization conductivity variations in time for halide mixtures MAPb(I$_{1-x}$Br$_x$)$_3$ under light. The polarization experiments give reliable $\delta$ and also $D^\delta$ values if x=0 or x=1, where the changes in conductivity stabilize over a relatively short time. If however de-mixing occurs (x~0.5) then the relaxation times are increased, probably due to the morphological evolution. In that cases no true $D^\delta$-values can be extracted. The unusually long stabilization time value indicate the occurrence of de-mixing (see Fig. 5 in the main text).

Figure S9. Equilibration of total conductivity of anion mixture perovskites under light. We extracted the conductivity values from polarization measurement. The samples were kept under Ar atmosphere under light for ~20 hours during d.c. measurement. A similar equilibration time scale under illumination was observed in MAPbI$_3$ and MAPbBr$_3$. Longer equilibration times were observed upon illumination in mixture samples (for x = 0.5 we indicate the lower limit for the equilibration time constant).
10. Self-trapped hole mechanism and photo de-mixing effect

Here we discuss a straight-forward explanation of photo-enhanced ion conductivity enabled by the hole trapping mechanism. The primary step of photoexcitation is the transfer of electrons from the valence to the conduction band which in chemical terms is approximately a charge transfer of electrons from the filled I-orbitals to empty Pb-orbitals (i). The next step is the localization of thus formed neutral iodine (ii) which owing to the smaller size can be accommodated interstitially. Herein further relaxation to $I_x^2$ dumbbells or higher aggregates $I_x^{(x-1)}$ can occur (iii). In energetic terms we refer to (i) overcoming the band gap ($E_g$) (ii), losing half of the band width ($E_b$) (delocalization energy) and (iii) gaining the polarization energy ($E_r$). In alkali halides the last step is mainly attributed to $X^-_2$ molecule formation. Step (ii) involves the very narrow valence band as far as the holes are concerned, while for conduction electrons the wider width of the conduction band (together with the less favorable $E_r$) makes a self-trapping energetically unfavorable. For KI the total balance is favorable as far as hole self-trapping is concerned. Comparing KI with MAPI the major difference is the wider valence band of the perovskite. It is certainly a rough approximation to borrow the relaxation energy from KI, but this tentative approach already leads to a total self-trapping close to zero but slightly positive. A less favorable polarization energy for Br (lower polarizability, lower tendency to form higher aggregates) directly explains the much lower effects observed from MAPbBr$_3$. This simple mechanism also explains the insensitivity of the ionic conductivity effects if the cation (MA) is exchanged (FA). Moreover, the mechanism directly explains the observed reversible de-mixing of MAP(I,Br)$_3$ on illumination without resorting to elastic effects. Let us concentrate on the anions. Then the mixing process can, following Bragg and Williams, be viewed as a partial transformation of I-I and Br-Br bonds to I-Br bonds, the reaction energy $\Delta \rho \varepsilon$

$$I-I + Br-Br \leftrightarrow 2I-Br \text{ or } 2Br-I$$

$$\varepsilon_{I-I} + \varepsilon_{Br-Br} \leq 2\varepsilon_{I-Br} = 2\varepsilon_{Br-I}$$

(3)

describing the interaction between the two anions. Approximating the configurational term in the mixing free energy $F_m$ by using ideal mixing entropy and assuming a positive $\Delta \rho \varepsilon$ (repulsion), $F_m(x_{Br})$ has the double minimum form. The half of the reaction energy, i.e.
\( \Delta_{R} \varepsilon \), determines the critical temperature below which de-mixing occurs \( (T_{c} \propto \Delta_{R} \varepsilon) \). In the dark \( \Delta_{R} \varepsilon \) is obviously small such that at room temperature all mixtures are stable \( (T_{c} < \text{room temperature}) \).

On illumination, Eq. (3) refers to the excited states. The I-I pair is stabilized by the self-trapping energy weighted by the probability of forming a hole (hole concentration per I-concentration), while the effect on the Br-Br pair may be neglected. Moreover, a replacement of I in the I-I pair by a Br will destroy the energetic effect. Hence \( \Delta_{R} \varepsilon \) measures the loss of the energetic stabilization \( \left( \delta \Delta_{R} \varepsilon = \Delta_{R} \varepsilon - \frac{1}{2} w \right) \) where \( \delta \Delta_{R} \varepsilon \) is excess reaction energy under light and \( w \) regular solution interaction energy parameter of the I-I and Br-Br pairs.

In order to bring \( T_{c} \) above room temperature, a \( w \)-value on the order of 10 meV is necessary which is consistent with the above considerations. It is noteworthy that this effect also explains the disappearance of the de-mixing at grain sizes below 50 nm. The simple reason is that in the above analysis the cost of the phase boundary formed on de-mixing was neglected. For a 50 nm grain the interfacial energy is \( \frac{G^{\Sigma}}{V/V_{m}} \sim \frac{\gamma}{L} V_{m} \) (\( G^{\Sigma} \): Excess Gibbs free energy per unit area, \( V_{m} \): molar volume, \( L \): grain size, \( \gamma \): interfacial tension). Using typical values for \( \gamma \) one obtains indeed values of the order of \( w \). For the same reason, the segregation into I-rich and Br-rich phases will not stop at small cluster sizes but develop into domains greater than 50 nm. Unfortunately more precise values are not available for checking if the described effect suffices or has to be complemented by elastic effects in order to qualitatively explain the features. A question that remains is if also \( e^- \) is self-trapped in the photo-perovskites. Unlike the alkali-halides the differences in the band widths of valence and conduction band are not that different. The possibly lower ability of Pb\(^+\) or Pb\(^0\) to be stabilized by additional lead may be compensated by a stabilization through the \( I' \).

In the extreme case that both electrons and holes are strongly self-trapped the photo-excitation would then be

\[
2I_{i}^{*} + Pb_{pb}^{x} \leftrightarrow \left( Pb_{i}^{o} + 2I_{i}^{o} \right) + 2V_{i}^{*} + V_{pb}^{o}
\]
Unlike $V_{i}^{\text{r}}$, $V_{Pb}^{\text{r}}$ is comparatively immobile. Interestingly Eq. (4) is a photoexcitation reaction in which $e^-$ and $h^+$ do not explicitly occur; this would be in agreement with the large enhancement of the ionic defect concentration beyond the remaining electronic level.

Modelling by Ginsberg\cite{8} et al invokes strain effects coupled to the electronic excitation and polarization. Photostriction effects have been observed on illumination, and it may in fact be tempting to correlate it with our mechanism of self-trapping. It is well established that illumination increases the volume of the iodide by about 0.02% and the effect on the bromide is a bit less than iodide\cite{9}. Light illumination leads to either less-distorted Pb–I–Pb bonds or extension of the Pb–I bonds, which induce lattice expansion. Here it is revealing to refer to Darken’s model\cite{10} of de-mixing of a model if oversized substitutions are introduced. This leads to an overall volume effect that is characterized by the Poisson ratio of the matrix. The resulting mixture is approximated by a regular solution model characterized by an interaction parameter $v$ (Poisson’s ratio). A negligible $v$ leads to a de-mixing at $\Delta V_2 / \Delta V_1 = 3(1-v)/(1+v)$. If we identify $\Delta V_2 / \Delta V_1$ with room temperature and associate $\Delta V_2 / \Delta V_1$ with the volume effect, Darken has established for a size mismatch of 5% solubility limit of ~15%. In our case the quantitative situation is certainly different, but the qualitative effect is the same if we replace the substitution by the illumination effect. In order for the small strain effects observed in the perovskites to account for the de-mixing, the Gibbs free energy of mixing must be very small.

Certainly, the combination of strain and chemical effects is to be considered for a refined model of photo-demixing\cite{11}.

Figure S10. Schematic of self-trapping hole mechanism of iodide and bromide perovskites under dark and light conditions.
References

[1] N. J. Jeon, J. H. Noh, Y. C. Kim, W. S. Yang, S. Ryu, S. I. Seok, *Nat. Mater.*, 2014, 13, 897.
[2] D. Moia, I. Gelmetti, P. Calado, W. Fisher, M. Stringer, O. Game, Y. Hu, P. Docampo, D. Lidzey, E. Palomares, J. Nelson, P. R. F. Barnes, *Energy & Environmental Science* 2019, 12, 1296-1308.
[3] J. Maier, 2004.
[4] aJ. Maier, *Physical Chemistry of Ionic Materials: Ions and Electrons in Solids*, Wiley, 2004; bJ. Maier, in *Modern Aspects of Electrochemistry* (Eds.: C. Vayenas, R. E. White, M. E. Gamboa-Aldeco), Springer New York, New York, NY, 2007, pp. 1-138; cT. Y. Yang, G. Gregori, N. Pellet, M. Grätzel, J. Maier, *Angew Chem Int Ed Engl* 2015, 54, 7905-7910.
[5] aJ. Maier, *Journal of the American Ceramic Society* 1993, 76, 1212-1217; bJ. Maier, *Journal of the American Ceramic Society* 1993, 76, 1223-1227.
[6] G. Y. Kim, A. Senocrate, T.-Y. Yang, G. Gregori, M. Grätzel, J. Maier, *Nature Materials* 2018, 17, 445-449.
[7] A. V. Vasilyev, S. V. Lindeman, J. K. Kochi, *New Journal of Chemistry* 2002, 26, 582-592.
[8] aC. G. Bischak, A. B. Wong, E. Lin, D. T. Limmer, P. Yang, N. S. Ginsberg, *The journal of physical chemistry letters* 2018, 9, 3998-4005; bC. G. Bischak, C. L. Hetherington, H. Wu, S. Aloni, D. F. Ogletree, D. T. Limmer, N. S. Ginsberg, *Nano Letters* 2017, 17, 1028-1033.
[9] aB. Chen, T. Li, Q. Dong, E. Mosconi, J. Song, Z. Chen, Y. Deng, Y. Liu, S. Ducharme, A. Gruverman, F. D. Angelis, J. Huang, *Nature Materials* 2018, 17, 1020-1026; bT.-C. Wei, H.-P. Wang, T.-Y. Li, C.-H. Lin, Y.-H. Hsieh, Y.-H. Chu, J.-H. He, *Advanced materials* 2017, 29, 1701789; cY. Zhou, L. You, S. Wang, Z. Ku, H. Fan, D. Schmidt, A. Rusydi, L. Chang, L. Wang, P. Ren, L. Chen, G. Yuan, L. Chen, J. Wang, *Nature Communications* 2016, 7, 11193.
[10] P. H. R.W. Cahn, 1996, 1.
[11] Y. Wang et al. *in preparation.*