Ion Movement Explains Huge $V_{\text{OC}}$ Increase despite Almost Unchanged Internal Quasi-Fermi-Level Splitting in Planar Perovskite Solar Cells

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Light soaking under “1 sun” is performed on planar p–i–n perovskite solar cells with a Cs$_{0.05}$MA$_{0.10}$FA$_{0.85}$PbI$_{0.95}$Br$_{0.05}$ absorber while measuring current and voltage transients simultaneously to spectral photoluminescence (PL). From theory a tenfold increase in PL intensity is expected for every 60 mV rise in $V_{\text{OC}}$ (at 300 K). However, the solar cells investigated show a reversible $V_{\text{OC}}$ increase from as low as 0.5 up to 1.05 V during light soaking, whereas the PL intensity hardly changes. A model is developed based on mobile ions in combination with a nonideal contact. It reproduces the decoupling of the $V_{\text{OC}}$ and PL as well as the transient behavior in great detail. Using state-of-the-art materials and passivation layers shows that light soaking is still a relevant feature of high-efficiency perovskite solar cells. The ionic liquid additive 1-butyl-3-methylimidazolium tetrafluoroborate slows down the light-soaking behavior, giving an example of how ionic motion in perovskite solar cells can be influenced.

1. Introduction

With power conversion efficiencies lately reaching up to 25.5%,[1] undoubtedly the maximum achievable performance of perovskite solar cells (PSCs) is not a limiting factor for the commercialization of this technology. Apart from the scalability of such impressively efficient PSCs, stability is considered the major issue hindering their industrial readiness.[2,3] Often the stability of a PSC is not easy to determine as degradation is driven by different stress factors such as heat[4–6] and illumination[7,8] as well as exposure to oxygen and moisture.[9,10] Device performance has also been shown to depend on the device’s preconditioning, the most prominent effect being the hysteresis during current–voltage scans (JV scans).[11,12] Furthermore, there are somewhat astonishing effects such as performance losses of PSCs that seem to recover when the cells are left in the dark for a longer period of time (hours to days).[13] In other cases, cells regain efficiency within a certain time of light soaking[14–16]. All these reversible effects have been linked to ion movement. It can now be considered consensus as numerous experimental works have proven the existence of mobile ions in the perovskite absorber and/or determined their concentration.[17–19] Simultaneously, various effects of ion movement on solar cell performance have been analyzed in numerous simulation studies.[18,20–26] To distinguish irreversible degradation effects from reversible changes in performance, a detailed understanding of the processes occurring in the bulk of the absorber and at the interfaces with the electron or hole transport layer (HTL) is of utmost importance to eventually eliminate all of the phenomena that are limiting device performance and stability.

A large increase of the open-circuit voltage ($V_{\text{OC}}$) upon light soaking with a simultaneously rather constant photoluminescence (PL) intensity was first observed and explained by Wu et al.[28] In their work, a resistive barrier to majority carrier flow at the interface between the perovskite film and the charge transport layer in combination with significant interface recombination is proposed as the origin of this effect. In our work, we support this proposed mechanism by drift–diffusion simulations that reproduce the observed light-soaking effect in great detail. In addition, they also replicate the transient behavior of the devices. Detailed experimental work shows that the slow light-soaking behavior is still a relevant issue of the used state-of-the-art perovskite architectures and how it is influenced by the ionic liquid additive 1-butyl-3-methylimidazolium tetrafluoroborate (BMI$\text{BF}_4$) increasing device performance as well as device stability.

2. Results and Discussion

As the link between $V_{\text{OC}}$ and PL intensity will be used frequently in the following, it shall be presented again shortly: From standard semiconductor physics, it can be shown that the quasi-Fermi-level (QFL) splitting $\Delta E_F$ in a semiconductor is given by...
\[ \Delta E_F = E_G - k_b T \ln \left( \frac{k_e n_e n_h}{R_{rad}} \right) \]  

(1)

where \( E_G \) denotes the bandgap, \( k_b \) the Boltzmann constant, \( T \) the temperature, \( k_b \) the radiative recombination coefficient, \( N_e \) and \( N_h \) the effective density of states for the conduction and valence band, respectively, and \( R_{rad} \) the radiative recombination rate, which itself is determined by

\[ R_{rad} = k_e n_e n_h \alpha \exp \left( \frac{\Delta E_F}{k_b T} \right) = \exp \left( \frac{e V_{OC}}{k_b T} \right) \]  

(2)

with \( n_e \) and \( n_h \) the electron and hole densities, respectively, and \( e \) denoting the elementary charge. The last step assumes a solar cell with constant \( \Delta E_F \) throughout the bulk of the absorber. Then, \( \Delta E_F / e \) is externally measurable as the open-circuit voltage \( V_{OC} \). Integrated over the volume of the absorber, \( R_{rad} \) is proportional to the PL signal (neglecting reabsorption) of the solar cell and exponentially dependent on \( V_{OC} \). In this case, it can be easily calculated with Equation (1) that at 300 K a tenfold increase of \( R_{rad} \) will result in an increase of \( \Delta E_F \) of roughly 60 meV. In return, this implies that even small changes in \( V_{OC} \) will have a huge impact on the measured PL intensity if \( \Delta E_F \) is constant throughout the bulk of the absorber.

We built PSCs with a mixed-cation, mixed-halide lead-based perovskite \( \text{Cs}_0.05\text{MA}_0.10\text{FA}_0.85\text{PbI}_{0.95}\text{Br}_{0.05} \), absorber layer in planar p-i-n architecture (indium tin oxide (ITO)/[2-(3,6-dimethoxy-9H-carbazol-9-y)ethyl]phosphonic acid (Meo-2PACz)/perovskite/[6,6]-phenyl-C61-butyric acid methyl ester (PCBM)/aluminum-doped zinc oxide (AZO)/aluminum (Al); layer structure shown in Figure S1, Supporting Information, for a solar cell delivering an efficiency of 20%. This indicates that the discussed light soaking is indeed, at least to a significant fraction, caused by the radiative recombination of charge carriers that are electronically available and not, for example, by electronically disconnected islands in the perovskite absorber, which could not be influenced by charge extraction or transport layer properties.

The whole process of increasing \( V_{OC} \) is reversible by letting the solar cell rest in the dark for a longer time span (Figure S3, Supporting Information). Measuring \( JV \) curves before and after the light soaking reveals that the performance has increased drastically (Figure 1b). Importantly, the performance increase also happens during maximum power point (MPP) tracking and is shown in Figure S4, Supporting Information, for a solar cell delivering an efficiency of 20%. This shows that the discussed effect is of relevance for highly efficient PSCs in real operation conditions. Hysteresis effects occurring during \( JV \) scans are comparably small and are discussed in the Supporting Information (Figure S5, Supporting Information). The large increase of \( V_{OC} \) together with an almost unchanged PL contradicts the logarithmic dependence of \( V_{OC} \) on PL signal in Equation (2). According to this, an increase of the PL signal by more than four orders of magnitude would be expected from the increase of \( V_{OC} \) by 250 mV. To illustrate this discrepancy, Figure 1a also shows the theoretically expected PL signal calculated from the measured \( V_{OC} \) increase as well as the theoretically expected \( V_{OC} \) calculated from the PL measurement (red and black dotted lines, respectively).

Figure 1. a) Transient \( V_{OC} \) (black) and simultaneously measured PL intensity (solid red) during light soaking. \( V_{OC(t)} \) calculated from the PL measurement (black dotted), PL(t) calculated from experimental \( V_{OC} \) (red dotted), according to Equation (1). b) Upsweep \( JV \) curves before and after light soaking of the same device.
This combination of an increase in \( V_{OC} \) of 250 mV together with a PL signal that is changed by less than a factor of 2 (and even decreasing) can only be explained by a gradient of the majority charge carrier QFL toward the respective contact. Figure 2a shows a simplified representation of the QFLs of a solar cell with rather selective contacts under illumination at open-circuit conditions. The hole contact is at the left end and the electron at the right end of the device and for sake of simplicity, the conduction and valence band are drawn as flat lines. As contact refer we here to the combination of the high-conductivity electrode (metal or strongly doped metal oxide layer) and the electron or HTL. Recombination due to a poor selectivity of the contact actually occurs at the interface between the absorber and transport layer. Note that band diagrams from the drift–diffusion simulations are shown in Figure S8, Supporting Information, including the transport layers (wide-bandgap semiconductors with a thickness of 20 nm). The results of the simulations will be discussed further subsequently.

The relation between the splitting of the QFL \( \Delta E_F \) and the radiative recombination is given in Equation (1). The externally measurable \( V_{OC} \) can be taken from Figure 2 as the difference between the QFL of the valence band at the hole contact and the QFL of the conduction band at the electron contact. Radiative recombination depends exponentially on the area between the QFLs of the valence and conduction band, respectively. Note that for the solar cell with rather selective contacts (Figure 2a), some charge carriers may get lost due to surface recombination but \( \Delta E_F \) is constant throughout the bulk and therefore identical to \( eV_{OC} \) (measurable between the contacts). When at least one contact has a strongly reduced selectivity (as shown in Figure 2b), there will be a large surface recombination current toward this contact under open-circuit conditions. The corresponding loss of charge carriers reduces \( \Delta E_F \) and \( V_{OC} \) in the same manner as long as there is no significant gradient in the majority-carrier QFL close to the contact. For this reason, the situation shown in Figure 2b leads to a lower \( V_{OC} \) than in the case of Figure 2a and a significantly reduced PL signal of roughly one order of magnitude for every 60 mV decrease in \( V_{OC} \), in accordance with Equation (1). To maintain roughly the same PL intensity despite a (strongly) reduced \( V_{OC} \), the same \( \Delta E_F \) is required throughout almost the entire absorber layer together with a significant gradient of at least one of the majority carrier QFL close to its respective contact.

The QFL gradient \( \nabla E_{F,e} = \frac{eJ_{e,h}}{\sigma_{e,h}} = \frac{J_{e,h}}{\mu_{e,h} n_{e,h}} \) (3)

Therein, the electrical conductivity is the product of the elementary charge and the mobility and concentration of the corresponding charge carriers. Therefore, a stronger gradient of a QFL does not necessarily cause a larger (surface recombination) current if the conductivity is lower. As a consequence, this can lead to the case shown in Figure 2c, where the number of charge carriers getting lost due to surface recombination is comparable to Figure 2a (thus maintaining a similar QFL splitting and therefore PL intensity throughout the bulk) but still a significantly reduced \( V_{OC} \) is measured.

For organic solar cells, the low majority charge carrier conductivity in the vicinity of a nonselective contact was found to cause a very large QFL gradient, which leads to a strong decoupling of \( V_{OC} \) and PL intensity. Also, in silicon heterojunction solar cells (i.e., crystalline silicon absorber sandwiched between thin layers of amorphous silicon) this phenomenon has been observed for weakly doped (and thus low conductive) a-Si transport layers. The transient \( V_{OC} \) and PL intensity data in Figure 1 strongly indicate that such a large gradient as shown in Figure 2c must be present initially and is subsequently reduced during light soaking under open-circuit conditions. The reversibility and the timescale of the phenomenon hint toward movement of ionic species as the origin of the temporal evolution. Deng et al. discussed the way the movement of positively charged methylammonium ions and iodide vacancies can cause this behavior and termed it “light-induced self-poling” (LISP). As proposed by John et al., the timescale for halide motion should be in the microsecond range, whereas the much larger activation energies for Cs\(^+\)-, MA\(^+\)-, and FA\(^-\)-vacancy movement indicate a timescale up to minutes. As the experimental data in this study (using a CsMAFAPbIBr photoactive layer) revealed a timescale of the order of minutes for the light-soaking effect, only

![Figure 2](https://www.advancedsciencenews.com)
the monovalent cations can be made accountable for the rather slow changes observed.

In the following we will present our model with the assumption of negative mobile ion vacancies (corresponding to the negatively charged Cs\(^+\), MA\(^+\), or FA\(^+\) vacancies), positive immobile counter charges, a hole contact with reduced selectivity, and a selective electron contact. Note that by hole contact again the combination of electrode and HTL is meant. Similarly, electron contact includes the electrode and the electron transport layer (ETL) in the following. When left at 0 V in the dark, the ions arrange according to their electrochemical equilibrium between drift (due to the built-in field) and diffusion. This accumulates negative ions in front of the electron contact and leaves behind a positive space charge in the vicinity of the hole contact, as shown schematically in Figure 3, left graph (referred to as “unconditioned” in the following). The positive space charge leads to a decreased hole density near the hole contact and thereby lowers their conductivity in this region. Under illumination and open-circuit conditions, a surface recombination current will flow because of the reduced selectivity of the hole contact. For a given (surface recombination) current, the decreased hole conductivity resulting from this specific ion distribution increases the gradient of the QFL of the valence band \(E_{\text{F, h}}\) according to Equation (3) and as shown in Figure 2c. Simultaneously the ion distribution will increase the electron conductivity near the hole contact, allowing for a higher electron current to the hole contact and creating a situation that the rate of surface recombination is actually limited by the hole current, i.e., by the majority charge carriers. With ongoing light soaking, the ions will redistribute according to changes of the internal electric field due to the buildup of photovoltage and this will finally resemble the case shown in Figure 3, right graph (referred to as “conditioned” in the following). As shown further subsequently, this redistribution can also be caused by application of a forward voltage in the dark. As now the hole density in front of the hole contact is much less reduced by ions, their conductivity increases. This decreases the gradient according to Equation (3), which in turn results directly in a higher \(V_{\text{OC}}\). This increase in majority carrier conductivity would lead to a higher surface recombination current, thus lowering the PL signal. However, simultaneously the ions lower the conductivity of the minority carriers (i.e., the electrons) in the vicinity of the hole contact, rendering the surface recombination current electron limited. Depending on the exact parameters (especially the electron and hole mobilities), the changes of the conductivities can counterbalance each other, which keeps the number of carriers lost due to surface recombination and with that the PL signal rather constant. However, the surface recombination current can even increase during light soaking. This happens when the effect of the increased hole conductivity (which is the limiting factor for surface recombination in the unconditioned state) is larger than the decrease of the electron conductivity. This leads to a decreasing PL signal with a simultaneously increasing \(V_{\text{OC}}\), opposite of what would be expected from Equation (2).

This model was implemented in the semiconductor simulation tool Sentaurus Device\(^{[34]}\) to perform numerical drift–diffusion simulations as in our previous studies on organic solar cells\(^{[30,35–37]}\). The standard parameter set for the simulations is listed in Table S1, Supporting Information. In addition to electrons and holes, negative mobile ions are included. These ions are initially placed homogeneously in the perovskite layer and, to obey charge neutrality, the mobile ion density is outbalanced by the same density of immobile counter charges (positively charged, also placed homogenously). The ion movement is restricted to the perovskite layer (especially no ion flow through the contacts possible) and no ion generation or recombination mechanisms are considered. Only direct recombination is considered in the bulk. The absorber/HTL interface is made nonselective by setting the Shockley–Read–Hall (SRH)-recombination velocity to a large value at said interface, while the absorber/ETL interface is considered selective (without SRH recombination). For simplicity, the generation of electron–hole pairs was implemented to be homogeneous and restricted to the absorber layer.

To simulate the unconditioned and the conditioned state of the solar cell, the mobile ions were allowed to reach their equilibrium position at a certain starting voltage (0 V for unconditioned device, 1.1 V for the conditioned device). For the sake of simplicity, the voltage scan rate was chosen to be large enough to consider the ions frozen during the subsequent \(J V\) scan.

![Figure 3. Illustration of the ion movement during the light-soaking or forward-biasing process. The negative ions accumulate either at the electron contact (0 V in the dark, unconditioned device) or at the hole contact (light soaking under \(V_{\text{OC}}\) or forward biasing, conditioned device). \(\alpha_e\) and \(\alpha_h\) denote the electron and hole conductivity, respectively.](https://www.advancedsciencenews.com/content/2001104/suppinfo.png)
Figure 4a shows the unconditioned and conditioned JV curves for the parameter set from Table S1, Supporting Information, with different ion concentrations. Clearly, the different ion distributions (shown in Figure S6, Supporting Information) of the unconditioned and conditioned state affects $V_{OC}$ as it affects the surface recombination losses as described earlier. The $V_{OC}$ difference between the unconditioned and conditioned states increases with the ion concentration; however, above a certain ion concentration the JV curve shows features not observed in the experiments, e.g., kinking in forward direction. We found an ion concentration of $3 \times 10^{16} \text{ cm}^{-3}$ to deliver a large $V_{OC}$ difference while still obtaining a fill factor comparable to the experiments. The PL intensity of the unconditioned device at $V_{OC}$ is a factor of five higher than in the conditioned state, whereas from Equation (2) it would be expected to be more than four orders of magnitude lower. This shows that a strong decoupling of $V_{OC}$ and PL is reproduced in the simulation, corresponding very well to the experimental results. Further, Figure S8, Supporting Information, shows the band diagram at $V_{OC}$ corresponding to Figure 4a before and after light soaking at an ion concentration of $3 \times 10^{16} \text{ cm}^{-3}$. The band diagram of the unconditioned state fully validates the presence of the aforementioned QFL gradient in the valence band toward the HTL.

Note that the model is invariant upon a change of the ionic charge (from positive to negative ions) if at the same time the nonselective contact is changed as well (from hole contact to electron contact). This means the results alone cannot tell which ionic species is responsible for the effects seen in the experiments without precise knowledge about which contact comprises insufficient selectivity. However, when assuming that the mobile species are negatively charged a nonselective hole contact was needed to reproduce the experiments in good accordence, which was not possible with a nonselective electron contact (Figure S9, Supporting Information).

The model also allowed for the simulation of a transient $V_{OC}$ increase. For this, the ions were at first allowed to reach their equilibrium at 0 V. Subsequently the (optical) charge carrier generation was activated and the $V_{OC}$ increase was traced, as shown in Figure 4b for the previously used parameters. The ion diffusion coefficient at 300 K was set to $5 \times 10^{-13} \text{ cm}^2 \text{s}^{-1}$ to fit the $V_{OC}$ increase duration in the simulations to the experimental data at room temperature (cf. Figure 1a). To obtain a better fit for the first 100 s of the $V_{OC}$ increase, it is useful to assume a pre-light soaking. Without this, the device in the simulation is assumed to be in the equilibrium position for a light intensity of exactly zero, whereas realistically the sample will always be subjected to a certain background light intensity during storage or handling. For this reason, an initial background illumination corresponding to $10^{-4}$ suns was assumed and the curves shown in Figure 4 were simulated using this pre-light soaking. In the Supporting Information the difference in $V_{OC}$ increase with and without initial background illumination is shown (Figure S10, Supporting Information). It can be seen also that the transient light-induced $V_{OC}$ increase and the PL data from the experiments are consistently reproduced by our model.

As the movement of ionic species is driven by the electric field and diffusion, two postulations can be made, which in the following shall be verified by experiments: 1) When forward biasing the device in the dark, the ions should also rearrange, bringing the device into the conditioned state with a (much) higher $V_{OC}$ in a subsequent JV measurement; 2) in contrast to light soaking at open circuit conditions, light soaking the device at 0 V should not rearrange the ions and therefore also no $V_{OC}$ increase should be observed.

To show that forward biasing the solar cell (without any illumination) also causes the same changes, electroluminescence (EL) measurements were performed. Figure 5 shows the EL measurement and its effect on solar cell performance for the same device for which the light-soaking behavior is displayed in Figure 1.

In the beginning the EL intensity is below the detection limit. This in combination with a high PL (Figure 1a) is a strong indication for the presence of an initial injection barrier at the nonselective contact. Note that the fact that a forward current density of 20 mA cm$^{-2}$ can be injected at these reasonably low voltages (around 1.1 V) indicates that only one contact inhibits nonselectivity. If both contacts showed a poor selectivity, this current injection would require higher voltages. With the QFL gradient present close to the hole contact, as discussed previously, hole injection is limited by the corresponding low hole conductivity. Meanwhile, the injection of electrons at the selective electron contact is unhindered. Therefore, these electrons flow through the entire bulk of the device and recombine nonradiatively at the hole contact, allowing for a rather high (almost
electron-only) forward current in the device. However, as the applied forward bias rearranges the ions, the gradient is subsequently reduced (in the same manner as described previously for the light-soaking case under open-circuit conditions). Thus, more holes are injected at the hole contact. Now the charge carriers can recombine radiatively in the bulk, giving rise to an EL signal. It should be noted that during the forward biasing/EL experiment also no spectral changes were observed (Figure S2b, Supporting Information). Measuring the $J^V$ curve of the device directly before and after the EL measurement (Figure 5b) shows that forward biasing indeed causes similar effects as light soaking under open-circuit conditions (Figure 1b), in accordance with what was postulated previously.

It could be assumed that even at short-circuit conditions, the device will react to the illumination and get eventually into the light-soaked or conditioned state with higher $V_{OC}$ at a subsequent $JV$ scan. However, as the model postulates, the ions react to changes in the electric field. At 0 V the contacts are not recharged and thereby no change in the electric field is present for the ions to react upon. To verify this experimentally, light soaking at 0 V was performed over 2 h (Figure S7, Supporting Information). During this the short circuit current $J_{SC}$ stayed constant and a subsequent $V_{OC}$ measurement showed no increase of $V_{OC}$, in perfect agreement with the model. With these results, both postulations have been confirmed, fortifying the correctness of the assumptions made in the model.

To further analyze the behavior of the solar cells, light-soaking experiments under open-circuit conditions with simultaneous transient voltage and PL measurements as well as EL experiments were performed at different temperatures. The series of measurements started at a temperature $T = 260 \, \text{K}$, prior to which the device was kept in the dark. At each temperature, the solar cell was light-soaked under open-circuit condition for 20 min. After $V_{OC}$ light soaking, the cell was left in the dark and without bias for 10 min, after which the EL experiment was performed for 10 min. In between the subsequent measurements, the cell was left in the dark for 30 min, during which time the temperature was increased and stabilized. Consistent with the picture of ionic movement the $V_{OC}$ increase slows down for lower temperatures as the ion diffusion coefficient decreases[37] (Figure 6a). The transient temperature-dependent PL measurements (Figure 6a) show a similar trend, with a slower change in PL intensity for lower temperatures, however remaining rather constant compared to the huge changes in $V_{OC}$. To further investigate this, temperature-dependent simulations were performed for the transient $V_{OC}$ increase, which are shown in Figure S11, Supporting Information. For these simulations, it was for simply assumed that only the diffusion coefficient changes upon temperature variation. With an activation energy of 0.3 eV for the ion diffusion, the time scale changes due to temperature in the $V_{OC}$ increase can be very well remodeled. John et al. reported a value of 0.32 eV for the activation energy Cs$^+/-$ vacancy movement, well in line with the value used in the simulation. The EL measurements show again a huge increase of EL intensity following the increase in charge carrier selectivity suggested by the voltage necessary to drive the constant forward current. The temperature dependence of the EL measurement is the same as for the $V_{OC}$ light soaking, again being fully consistent with the picture of ionic movement. To demonstrate the universality of the light-soaking phenomenon, measurements were conducted on a completely different PSC architecture as well. Figure S12, Supporting Information, shows temperature-dependent $V_{OC}$ and PL measurements of a mesoporous n-i-p cell using a high-bandgap double-cation perovskite formulation. Even though the device architecture is completely different, a quite similar light-soaking behavior can be observed.

As the discussed light-soaking effect is supposedly governed by ionic movement in the perovskite layer, it is worthwhile to investigate the impact of additives to the photoactive layer. For this case, the ionic liquid BMIMBF$_4$ was used. With this additive, remarkable increases in device performance and stability have been reported by Bai et al.[38] In their study, PL-quenching experiments of samples with in-plane electrodes led to the conclusion that ion movement is drastically slowed down for samples containing the ionic liquid additive. Employed in the solar cells used for this publication, BMIMBF$_4$ increases the steady-state open-circuit voltage as well as the PL intensity, suggesting that the ionic liquid has a general passivating effect on the perovskite bulk. For the light-soaking experiments, the concentration of BMIMBF$_4$ was varied between 0.4 and 0 mol% with respect to lead atoms. Figure 7a shows the time-dependent $V_{OC}$ and PL behavior. The PL intensity increases for increasing amounts
of the additive, suggesting that the ionic liquid has a general passivating effect on the perovskite bulk. During light soaking, the time evolution of PL intensity is rather constant; in fact the PL intensity decreases over time for each sample, as has been reproduced by our numerical simulations. For the $V_{OC}$ increase, different time scales become visible, with the sample containing the highest concentration of BMIMBF$_4$ featuring the slowest $V_{OC}$ increase and gradually increasing in speed for lower concentrations. EL measurements shown in Figure 7b display the same clear trend in the time dependence. These findings support that

Figure 6. a) PL signal and $V_{OC}$ rise during light soaking at different temperatures. b) EL and voltage at a constant current of 20 mA cm$^{-2}$ for different temperatures.

Figure 7. Variation of BMIMBF$_4$ additive concentration. a) PL Intensity and $V_{OC}$ transients during light soaking. b) EL intensity and voltage during forward biasing at 20 mA cm$^{-2}$.
the ionic liquid additive slows down ion movement when its concentration in the investigated samples increases. Scanning electron microscope (SEM) images of the samples are shown in Figure S13, Supporting Information. Those images suggest that there is no significant change in perovskite crystallinity (grain boundaries, crystallite size) that could be made accountable for the change of light-soaking behavior, leading to the conclusion that the ionic liquid additive hinders ion movement rather on the molecular scale than due to a change in perovskite crystallinity.

3. Conclusion

In this work, we have presented data from mixed-cation, mixed-halide Cs$_{0.05}$MA$_{0.10}$FA$_{0.85}$Pb(I$_{0.95}$Br$_{0.05}$)$_2$ PSCs showing a $V_{OC}$ increase upon light soaking by more than 250 mV while at the same time maintaining a rather constant PL intensity. It was found that a similar $V_{OC}$ increase can also be achieved by forward biasing the devices in the dark. The combination of transient $V_{OC}$, PL, and EL data led us to the conclusion that the origin of the effect is an initially rather strong gradient in the QFL of the majority charge carriers in the vicinity of the hole contact. By conditioning the device either by light soaking under open-circuit conditions or by forward biasing in the dark, this gradient is reduced, which leads to the observed increase in $V_{OC}$. The rather constant PL intensity indicates that the rate of surface recombination hardly changes during this time.

Further, temperature-dependent light-soaking experiments were performed. The results showed the same general behavior but on significantly longer time scales at lower temperatures. This is well in accordance with ionic movement and the reduction of their diffusion coefficient with decreasing temperature. A quantitative model was developed which reproduced the experimental findings in great detail. It shows that the modified internal electric field (due to buildup of the photovoltage or due to the applied forward bias) redistributes the mobile ions. This causes a redistribution of electrons and holes, thus reducing the gradient of the majority-carrier QFL. This finally leads to an increased $V_{OC}$ and decouples the $V_{OC}$ from the PL intensity in accordance with the experimental results. This last point is especially important to consider when drawing conclusions about the external $V_{OC}$ from techniques such as PL mapping, where a so-called implied open circuit voltage ($iV_{OC}$) is determined from PL data. This study shows that a high PL intensity is a necessary but not sufficient condition for achieving a high open-circuit voltage and highlights the importance of mobile ionic species for the transient behavior of PSCs also on timescales of days.

4. Experimental Section

**Device Fabrication:** Solar cells were fabricated on prepatterned ITO glass substrates (2.5 x 2.5 cm$^2$) with the architecture shown in Figure S1, Supporting Information. The cleaned ITO glass was treated with 15 min of UV–ozone before applying the HTL.

**Hole Transport Layers:** MeO-2PACz (TCI) was dissolved in ethanol (1 mmol L$^{-1}$) and spun onto the substrate at 4000 rpm, leading to a layer thickness too thin to measure with our profilometer and not distinguishable by the SEM cross section measurements. The layer was then annealed at 100 °C for 10 min. MeO-2PACz can also be washed with ethanol in another spin-coating step to remove the excess material, ensuring a monolayer. This washing step did not bring a significant change in solar cell performance in the lab. Processing of the HTL took place in a N$_2$ atmosphere.

**Perovskite Layer:** The 1.3 m perovskite precursor solution was prepared by weighing PbI$_2$ (TCI) CsI (Sigma Aldrich), MABr, and FAI (Greatcell Materials) to a stoichiometry of Cs$_{0.05}$MA$_{0.10}$FA$_{0.85}$Pb(I$_{0.95}$Br$_{0.05}$)$_2$, adding 5% lead access with respect to the monovalent cations. The salts were dissolved at 70 °C in a mixture of dimethylformamide and dimethyl sulfoxide with the volume ratio 4:1. Different amounts (0–0.4 mmol% with respect to lead atoms) of BMIMBF$_4$ were added directly to the precursor solution.

The perovskite layer was deposited by spin coating the precursor solution at 1000 rpm for 10 s and 5000 rpm for 20 s dropping the antisolvent ethylacetate 5 s before the end of the spin-coating process. The film formation was finished by directly placing the sample onto a 100 °C hotplate and annealing for 60 min. These steps were performed in a N$_2$-filled glovebox.

**Electron Transport Layers:** After a short cooling time an ETL was applied using a 10 mg mL$^{-1}$ solution of PC$_{60}$BM in CHCl$_3$, which was dynamically spin coated at 4000 rpm. After this step, the substrates were taken out of the nitrogen atmosphere for spin coating AZO nanoparticles (Avantium N21-X) as a second ETL at 4000 rpm in air. The cells were completed by thermal evaporation of a 100 nm aluminum back electrode, defining the cell area of 0.0925 cm$^2$.

**Measurement Setup:** PL and EL measurements were performed with an Andor Shamrock 193i Czerny-Turner spectrometer. For graphs that show PL or EL intensity, the recorded spectra were integrated over the wavelength. The illumination source for PL measurements was a frequency-doubled cw Nd:YAG laser from Pegasus laser systems (Pluto, P532.400, $\lambda = 532$ nm). $J_V$ curves, as well as transient voltage measurements, were obtained with a Labview-controlled Keithley 2400 source meter. $J_V$ curves were measured in both scan directions with a scan rate of 0.14 V s$^{-1}$; from −0.1 to 1.2 V (upsweep) and subsequently from 1.2 to −0.1 V (downsweep). The Keithley source meter was also used as power supply for the EL measurements.

Temperature-dependent measurements were conducted on the same setup as the luminescence spectroscopy. Therefore, the samples were mounted to a cryostat with the temperature controller Lakeshore 331. The temperature controller stabilizes the temperature to a set value, by heating against the liquid nitrogen cooling. The nitrogen flow is spatially separated from the sample holder, which can be evacuated by a turbo pump (around 10$^{-4}$ mbar). The PL and EL measurements were conducted in the same way as described in the previous section. Electrical connection was ensured by contact pins inside the cryostat, so the cells working point could be controlled with the use of a Keithley source meter.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.
Data Availability Statement

Research data are not shared.

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