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ABSTRACT
The desirable small hysteresis in the current–voltage characteristics of perovskite solar cells is often understood as a result of small ionic concentration or mobility and low interface charging by depleted/accumulated ions. However, devices having very small apparent hysteresis at practical scan rates can exhibit strong ionic effects seen in the transient response to excitation events. We explore Cs-based double-cation perovskite solar cells showing vanishing hysteresis and nearly hour-long responses to light- and voltage-step excitation, which are tracked by the evolution of open-circuit voltage and injected current, together with electroluminescence emission, respectively. The observed responses, including the increase of electroluminescence with time, are explained by the modulation of the electric field within the perovskite by mobile ions under the condition of interface recombination of mobile charge carriers dominating overall recombination. This is further explored by a numerical model containing mobile ions, which requires that charge carriers recombine predominantly at the interfaces of the device in order to obtain transient responses comparable to the experiments. Further support for the predominance of interface recombination is experimentally obtained by steady-state photocarrier grating characterization, which yields diffusion lengths of photogenerated carriers above 1 μm, i.e., well above the 300 nm perovskite layer thickness. The numerical model further shows that within the case of dominating interface recombination, the shape of both the light- and voltage-step transient responses are strongly determined by the energy band offsets between the perovskite and the contact layers of the solar cell.

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I. INTRODUCTION
The field of photovoltaic research and optoelectronics witnessed an unprecedented emergence and advance of perovskite solar cells (PSC) and light-emitting diodes,1,2 earning a place in the debate about materials for clean energy in the near future.3 Despite the impressive energy conversion efficiencies attained so far,4 the rapidly growing knowledge base on optimum materials and preparation techniques emerged mostly empirically before attaining a solid knowledge of the critical physical mechanisms controlling the operation and degradation of PSC.5–10 This is due in part to the complexity introduced by the presence of mobile ions in the perovskite, which was only later assured to originate the undesirable hysteresis of the current/(J)/voltage/(V) curve observed in most PSC.11 Although these efforts in characterization and modeling allowed for several optimizations of PSC, yielding higher efficiencies and smaller degradation rates,12–14 the potential benefits on performance and reduced degradation of further restricting ionic motion are constantly updated.15,16 The increasing number of characterization techniques involves transient response experiments, which appear effective in unveiling the effects of ionic motion on device behavior.17–19 For instance, some PSC exhibiting very low hysteresis under practical measurement conditions reveal strong effects of ionic motion during light- or voltage-step transient response,17 where steady-state is reached in timeframes from...
Double-cation perovskite solar cells were prepared by depositing PTAA (polytriarylamine) on ITO glass substrate by drop-spin at 6000 rpm for 30 s using 0.75 mg ml$^{-1}$ toluene solvent, followed by a PFN (poly[9,9-bis(3′-[N,N-dimethylamino]propyl)-2,7-fluorene-alt-2,7-(9,9-dioctylfluorene)]) layer applied by drop-spin at 8000 rpm for 20 s using methanol as solvent and an annealing step for 10 min at 100 °C. The FACsPb(Br)$_3$ perovskite layer was then deposited by the two-steps drop-spin process described above. This was followed by a drop-spin at 4000 rpm of a PCBM (butyric acid methyl ester) layer deposited for 30 s using chloroform and an AZO (aluminum-doped zinc oxide) for 60 s (Avantama N21-X, as purchased). The final preparation step consisted in the deposition of an aluminum contact by thermal evaporation, yielding 100 nm thick Al layers.

B. Optoelectronic characterization

Current density ($J$/voltage $V$) measurements were realized under AM1.5G illumination (100 mW cm$^{-2}$) using an Abet SunLite 0.2 solar simulator and Keithley 2400 source meter. The cells were pre-conditioned with a light soaking (LS) process, where the samples are held under the solar simulator until the open-circuit voltage $V_{OC}$ reaches a stationary value within four digits precision, significantly improving the open-circuit voltage and the power output of the samples, as shown in Fig. S1 in the supplementary material. After an LS time between 30 and 180 min, depending on the sample, the cells reach a typical open-circuit voltage around 1.05 V. The $J(V)$ measurements (see Fig. S2 in the supplementary material) consisted in backward and forward voltage sweeps between −0.2 and 1.2 V with a scan rate of 100 mV/s, delivering the solar output characteristics given in Table SII in the supplementary material.

The characterization of the transient response of solar cells was carried out by recording the responses to voltage-step and light-step excitation. The light-step response consisted of recording the open-circuit voltage of solar cells, previously stored under dark conditions, by opening the shutter of the solar simulator (opening time below 100 ms). The open-circuit voltage was recorded using a six-digit digital voltmeter in 1 s intervals, with the sample held on a temperature-controlled sample holder at 25 °C. The voltage-step response consisted of recording the injected current density using a multifunction multimeter, and simultaneously, capturing the EL emission of the solar cell upon polarization with a fixed forward bias voltage, which was provided by a Keithley 2400 source meter. The EL emission from the solar cells is based on calculating the total intensity of images captured using a commercial infrared CCD camera (mvBlueFOX) in video mode. The duration of the continuous EL image capture was typically 40 min, using a frame rate of one image per second and 0.985 s of integration time. The voltage-step response was preceded by an LS as described above for the $J(V)$ characterization. After this, they are transferred to the dark environment of the EL-setup, allowing for a partial de-excitation. The recovery of this de-excitation is then tracked by the following voltage-step response. In order to avoid degradation by current injection after long biasing intervals, the bias voltage $V = 1.1$ V was chosen as low as possible, producing light emission close to the lower detection limit of the camera. The absence of degradation
was verified by checking that the open-circuit voltage before and after the measurement was identical within three significant digits.

The ambipolar diffusion length of photogenerated charge carriers was measured by the steady-state photocarrier grating method (SSPG), which has been successfully applied to CH$_3$NH$_3$PbI$_3$, as well as to hybrid perovskites. Briefly, the technique consists in intersecting two coherent light beams from a laser onto the film’s surface, with the intensity of one beam being much higher than the other beam (Fig. S4 in the supplementary material shows the experimental arrangement). Upon biasing the sample contacts, two different photocconductivity states are measured: coherent or incoherent, altering the polarization of one of the laser beams. The coherent state produces a periodic light intensity profile on the sample and, therefore, a periodic photocarrier concentration profile. Since the carriers photogenerated in the brighter semi-period smear out to the darker semi-period by diffusion, the profile. Since the carriers photogenerated in the brighter semi-period smear out to the darker semi-period by diffusion, the

\[ \beta = 1 - \frac{2 \gamma \gamma_0}{1 + \left(2 \pi L_D / \Lambda \right)^2}, \]

where \( \gamma \) and \( \gamma_0 \) are the photogeneration exponent and the grating quality factor, respectively. The ambipolar diffusion length is related to the electron and hole diffusion lengths \( L_n \) and \( L_p \) according to \( L_D^2 = L_n^{-2} + L_p^{-2} \). The factors \( \gamma \) and \( \gamma_0 \) are not required to obtain \( L_D \) when Eq. (1) is rearranged to the so-called Balberg plot according to

\[ \sqrt{2/(1 - \beta)} = \frac{1}{\sqrt{\gamma \gamma_0}} (2 \pi L_D / \Lambda)^2 + \frac{1}{\sqrt{\gamma_0}}, \]

which yields \( L_D \) from the ratio of intercept and slope of a straight line as a function of \( \Lambda^{-2} \). In the experiments, a range of \( \Lambda \) is scanned by modifying the incidence angle of the converging beams. Applying 10 V between the contacts, we obtained an electric field of 100 V/cm, which is a typical compromise between the detectivity of the current and the low field conditions. The current signals required 30 min before stabilization at a steady-state value. Apart from sufficiently low electric fields, the method requires dark conductivity to be negligible against the photocconductivity, which in our case, was verified by above ten times higher currents measured upon illumination than in the dark. Let us recall that this method is claimed to be “self-sufficient,” i.e., discrepancies between the theoretical model and actual measurements are revealed by deviation of the data from the linear behavior predicted by Eq. (2). For example, non-negligible electric field values produce a concave instead of linear dependence of the l.h.s. of Eq. (2) and \( \Lambda^{-2} \).

III. EXPERIMENTAL RESULTS

A. Voltage-step response

Figure 1 shows a typical sequence of EL images taken immediately after a voltage-step of \( V = 1.1 \) V, where the originally black and white images are enhanced by a color scale to aid scale appreciation (right bar in Fig. 1). The EL intensity increases steadily toward steady-state, which occurs beyond 1800 s after the voltage step, i.e., half an hour. After the voltage is turned off, the cells take ca. 2 h to return to the initial \( I(V) \) curves before LS, and a new LS transient delivers the same steady-state \( V_{OC} \) (see Fig. S5 in the supplementary material). By inspection of Fig. 1, we notice that the inhomogeneous emission features are maintained over the time-frame of the experiment. In order to assess this observation quantitatively, the division of EL images at different timestamps (not shown here) shows that the emission pattern does not change appreciably. This suggests that the balance between current injection and radiative recombination in different regions of the cell did not change over time. The inhomogeneity seen in the EL images has been shown to originate mainly from fluctuations in layer thickness and composition and is beyond the scope of this paper.
Tracking the injected current and total amount of emitted light by pixel integration over the EL images, we obtain the transients shown in Figs. 2(a) and 2(b), corresponding to the current density $J(t)$ [panel (a)] and total $EL(t)$ [panel (b)] recorded in five samples belonging to different substrates prepared during a single preparation batch. Despite identical preparation materials and manufacturing, the selected solar cells cover a range regarding the shape of the current/voltage characteristics, mostly in fill factor and series resistance (see Fig. S2 in the supplementary material). The noise observed in the EL curves of Fig. 2(b) originates from the relatively low emission observed at 1.1 V, which is only three to four times higher than the background noise, which is subtracted from the signal.

As opposed to $J(t)$ and $EL(t)$ transients reported in TiO$_2$-based MAPI solar cells, we observe that despite the injected current decreases, the emitted electroluminescence slightly increases with time. This behavior implies that the number of emitted photons per injected electron/hole pair, i.e., the external LED quantum efficiency, increases over time. Defining the instantaneous external quantum efficiency $Q_e(t)$ by

$$Q_e(t) = \frac{EL(t)}{J(t)},$$

we obtain the transient quantum efficiency shown in Fig. 2(c), in units of counts/mA cm$^{-2}$. Notice that all $Q_e$ curves show an increase of at least an order of magnitude during the 40 min long transient recording. The observed behavior of $Q_e(t)$ implies that radiative recombination within the cell becomes markedly stronger with time, meaning that a larger proportion of the injected charge carriers increasingly avoid defect recombination and recombine radiatively.

A possible route to understand the observed behavior becomes possible by associating the very long duration of the observed transients to the timescale required for migration by ionic species, a well-known phenomenon present in most metalorganic perovskites (see, e.g., Ref. 32 for an extensive review). As previously discussed in the context of slow transient response in perovskite solar cells, models for electrolyte dynamics provide a response time $\tau_{ion}$ that proves meaningful for ionic species migrating in perovskites, following

$$\tau_{ion} = \frac{bL_D}{2D_{ion}},$$

where $b$ is the sample thickness, $D_{ion}$ is the diffusion coefficient of ion species, with the Debye length $L_D = \sqrt{\epsilon V_T/qN_0}$ depending on the average ion concentration $N_0$, the absolute dielectric constant $\epsilon$, the thermal voltage $V_T$ and the elementary charge $q$. As an estimate, assuming that the timescale to reach steady-state in the $J(t)$ transients equals $\tau_{ion} = 2200 \text{s}$ and with an ion concentration $N_0 = 10^{18} \text{cm}^{-3}$, Eq. (4) yields a diffusion coefficient $D_{ion} \approx 4 \times 10^{-13} \text{cm}^2/\text{s}$. Such a low value suggests that ionic transport is not controlled by halide-related ions, which have a much higher diffusion coefficient. The absence of halide diffusion was recently found in iodide–bromide-based perovskites, in which the presence of bromide was attributed to suppress iodine vacancy diffusion. This is backed by first principles calculations performed by Lin et al., which show a strong increase of the activation energy of iodine upon Br incorporation to MAP (I, Br). This effect was shown to take place also in perovskites with different cations, according to impedance spectroscopy and muon relaxation measurements and simulations by Ferdani et al., where the increase of iodine activation energy was found to originate due to a local lattice distortion generated by the inclusion of Br. In this scenario, our samples are most likely controlled by $FA^+$ cation vacancies, which in Pb-based perovskites have a smaller diffusion coefficient than $MA^+$ cation vacancies, found in the range from $10^{-16}$ to $10^{-11} \text{cm}^2/\text{s}$.

Taking into account the long response time and reversibility of the EL and LS effects mentioned above, ionic diffusion is the...
mechanism that most likely controls the response time in our samples, our devices require further investigation. Qualitatively comparable dynamics have been explained in MAPI PSC in terms of the “wiggly band” model\textsuperscript{18,20} and supported by numerical simulations.\textsuperscript{17,19,23,25} Within this model, after applying the voltage step, ion species migrate from/toward interfaces, controlling the response of the energy band diagram to the external voltage and, therefore, also the injection of free charge carriers.\textsuperscript{19,40} The extremely low mobility of ionic species implies that if the contact layers have sufficient conductivity, the ionic Debye layers at the interfaces between the perovskite and the contact layers remain initially unchanged, and most of the applied potential initially drop in the interior of the perovskite layer (cf. Scheme 3 in Ref. 18). Since the interface Debye layers remain initially unchanged, injected carriers are faced with the same interface potential barriers that are found in equilibrium. Carriers that surpass the interface barriers drift along the bulk field toward the opposite electrode, reaching the opposite interface if bulk recombination is sufficiently low. As the ions move away from the Debye layers, the applied potential falls increasingly stronger at the interfaces, reducing the electric field at the interfaces, and hence, the electric field in the interior. Depending on the specific balance between bulk and interface recombination, the injected current increases or decreases, as we show below with the numerical model. Steady-state is reached when ion motion stops, resulting in a steady-state current flow composed by interface and bulk recombination.

B. Diffusion length

The measurement of diffusion lengths under steady-state conditions using SSPG seems an appropriate quantity to probe if interface recombination is likely to dominate in our cells: if the diffusion length exceeds the thickness of the cell, interface recombination will dominate the overall recombination of the cell. Figure 3 shows the results of SSPG measurements for three film samples (data points), and the model (solid lines) using Eq. (1) (main plot) and Eq. (2) (inset, Balberg plots). The linear fits in the Balberg plots yield $L_D = 1090/1290/1630$ nm for films a/b/c, respectively, with the highest statistical fit error being 12% relative (sample c). Since in the present case, the film thickness of 300 nm is markedly smaller than $L_D$, most of the carriers are capable of reaching the interfaces before recombining, leaving interface recombination as the main recombination mechanism. Similar values have been obtained in MAPI and MAPbI$_3$(Cl) films by SSPG and also other methods,\textsuperscript{15} which helped to explain the attained high solar efficiencies.

Notice that SSPG measurements are performed with carriers flowing parallel to the film’s surface, as opposed to carriers flowing perpendicular to the solar cell surface. Since our films show columnar grains that traverse the whole film thickness, carriers are forced to traverse grain boundaries in the SSPG measurements, but not in the solar cell, meaning that the diffusion length values obtained here are likely to be smaller than the diffusion lengths actually controlling solar cell operation.\textsuperscript{41} Moreover, the obtained diffusion length values obtained above neglect front/back interface recombination, and must, therefore, be interpreted as lower limit values, i.e., smaller than the actual diffusion length. However, since the films are grown on bare glass, whereas in the cells the perovskite forms over PTAA and PFN, the diffusion length of the film may differ from the values when embedded into the solar cell layer stack. Nevertheless, in the simulations to be presented in Sec. IV, we find that the scenario of dominating interface recombination is compatible with the current, electroluminescence, and open-circuit voltage transients obtained experimentally.

C. Light-step response

Figure 4 shows the light-step response of the open-circuit voltage $V_{OC}(t)$, which increases monotonously with time up to a steady-state value occurring between 30 and 180 min. The mechanism behind the long durations again points to ion migration, which now controls the spatial distribution of photogenerated carriers as follows. Initially, upon illumination, the initial bulk electric field drives electrons and holes toward both interfaces. As time evolves, ionic charges slowly screen the electric field, whereby the separation of photogenerated carriers toward the interfaces is weakened, decreasing interface recombination. If bulk recombination is considerably weaker than interface recombination, the open-circuit voltage increases with time. MAPI solar cells exhibiting very low hysteresis at typical scan rates (e.g., 100 m V/s) also were found to show $V_{OC}(t)$ transients with similar shapes\textsuperscript{17,42} and were explained by the modulation effect of migrating ions on interface recombination.\textsuperscript{15}

We noticed that the observed transient duration was found dependent on the storage time and excitation history, leading to variations in the duration of the $V_{OC}$ transients. Although this poses uncertainties to the interpretation of the transients in terms of, e.g., the characteristic time of Eq. (4), the steady-state values of $V_{OC}$ are found to be independent of excitation history. This allows connecting the voltage-step to the light-step response in steady-
state, where we find that the resulting $V_{OC}$ is higher in samples with higher electroluminescence emission. This observation points to the steady-state optoelectronic reciprocity principle, within which $V_{OC}$ and $Q_i$ obey a proportionality according to the following expression:43

$$V_{OC} = V_{OC,rad} + n_{rad} \frac{kT}{q} \ln(Q_i).$$

(5)

Here, $V_{OC,rad}$ is the open-circuit voltage attainable with radiative recombination as the only recombination mechanism, $k$ and $q$ are Boltzmann’s constant and the elementary charge, respectively, $T$ is the temperature, and $n_{rad}$ is a radiative ideality factor (see below). Pairing the steady-state values of $V_{OC}$ and $\ln(Q_i)$ from Figs. 2 and 4, we obtain Fig. 5, where the straight line is a linear regression with Eq. (5), yielding the ideality factor $n_{rad} = 1.2 \pm 0.25$. According to detailed recombination models from Müller et al., values of $n_{rad} > 1$ are possible when radiative recombination takes place through radiative transitions between bands and bandtail states (so-called Urbach states) or between bandtails entirely.44 Transmittance data of our perovskite films deposited on glass show bandtails with a characteristic energy of 30 meV (see Fig. S3 in the supplementary material), suggesting a non-negligible incidence of bandtail recombination in the studied solar cells.

**IV. SIMULATION**

Simulations of $I(V)$ curves and transient response are performed using the partial differential equation solver IonMonger, a computationally efficient, open-source code programmed by Courtier et al.,45,46 IonMonger simulates one-dimensional drift–diffusion transport and electrostatics of free carriers as well as one mobile and one fixed ionic species in multi-layered semiconducting layers. The code effectively captures the essence of the complex interaction between electronic and ionic transport in perovskites, establishing important insights into the physical mechanisms limiting solar cell operation47 and allowing the extraction of key material parameters from typical characterization methods.48 Here, rather than attempting to adjust the simulations to our experimental results rigorously, we focus on finding the key physical conditions that deliver the main features of the measured transients, preserving low hysteresis in the $I(V)$ curves at the adopted scan rate of 100 mV/s. The approach consists in exploring three simulation scenarios: (1) bulk vs interface recombination, (2) interplay between ion concentration and ionic diffusion time, and (3) the role of energy band offsets at interfaces. The key parameters for the three simulation scenarios are given in Table I, while Table SI in the supplementary material lists the remaining parameters of the model. The parameters employed at variables in each scenario are shown in boldface. In scenario 1, defect recombination parameters from Shockley–Read–Hall recombination statistics are varied through the transition times between bands and defect energy levels or pseudo-lifetimes $\tau_{np}$ for bulk defect recombination,49 while the interface recombination is varied by means of the recombination velocities $S_{ETL}$ and $S_{HTL}$ at the ETL/perovskite and perovskite/HTL interface, respectively. Scenario 2 covers the ionic parameters $N_D$ and $D_{ion}$, while scenario 3 varies the energy band offsets $\Delta E_{ETL}$ and $\Delta E_{HTL}$ at the respective interfaces (Fig. S6 in the supplementary material shows a schematic band diagram with both energy band offsets).

In the voltage-step simulations, the electroluminescence quantum efficiency is accounted for by means of the internal radiative efficiency $Q_i$, defined by

$$Q_i(t) = \frac{I_{rad}(t)}{I(t)},$$

(6)
with the radiative current density $J_{\text{rad}}(t)$ calculated by integrating the radiative recombination rate over the cell thickness $b$ according to

$$ J_{\text{rad}}(t) = qB \int_0^b n(x, t)p(x, t)dx, \quad (7) $$

where $B$ is the radiative recombination coefficient and $n$ and $p$ are the free electron and hole concentrations at each point in time and space, respectively. When observing the results obtained for $Q_e(t)$, we bear in mind the proportionality $Q_e(t) \approx p_e(t)$, where $p_e$ is the emission probability of photons to the outside of the device, which depends on several factors such as layer stack materials, geometries, rugosity, etc. Notice that since $p_e$ depends solely on optical losses, the simulated $Q_e(t)$ and measured $Q_e(t)$ transients are directly comparable regarding shape and duration, avoiding the extra complexity from an optical model.

Figure 6 shows simulation results for scenario 1, where red curves correspond to the cell dominated by interface recombination (no bulk defect recombination assumed), and black curves correspond to a cell controlled by bulk recombination (no interface recombination). Plots (a) and (b) correspond to the voltage-step response of $I$ and $Q_e$, respectively, and plot (c) shows the light-step response $V_{OC}$. The recombination parameters in each case (see Table I) were adjusted to obtain the same stationary value of $V_{OC} = 1.05$ V, agreeing with the experimental values (cf. Fig. 4).

Comparing the simulated with the measured transients from Sec. III C, we see that only the case of interface recombination is able to yield the measured trends, i.e., a monotonous increase of $V_{OC}$ in the light-step response, and a decrease of $J(t)$ with a simultaneous increase in electroluminescence in the voltage-step response, all with comparable stationary values. It is important to highlight that this agreement is reached only under the conditions $\Delta E_{\text{ETL}} < \Delta E_{\text{HTL}}$ and $S_{\text{ETL}} > S_{\text{HTL}}$, or alternatively, with both relations inverted. However, $S_{\text{ETL}} > S_{\text{HTL}}$ is the condition that agrees with recent experimental results in MAPI as well as triple-cation perovskite films obtained with the same ETL and HTL materials, where both perovskites revealed lower photoluminescence quantum yield when in contact with PCBM (ETL) than with PTAA (HTL). On a final note about scenario 1, let us mention that the initial $V_{OC} \approx 0.5$ V from the simulation is considerably higher than in our experiments (cf. Fig. 4), where $V_{OC}$ at $t=0$ ranges from 0.25 to 0.5 V. We believe that in order to solve this discrepancy, the numerical model requires the incorporation of a second mobile ionic species that strengthens the effect of ionic screening on interface recombination, further decreasing the initial $V_{OC}$ value. The features in the transients shown in Fig. 6 are directly linked to the wiggly band model: when interface recombination dominates, the initial neutralization of the bulk electric field by the voltage polarization, which allows current injection, is gradually weakened by ionic motion. This reduces the number of carriers reaching the opposite interface, consequently decreasing $I$ over time. When bulk recombination dominates, the same effect of the weakening electrical field is present; however, the (much lower) injected current increases over time. In this case, the main component of the current is due to a weaker effect which is the lowering of the interface energy barriers as the Debye layers are smeared out, letting more carriers to enter the bulk and recombine.

The large differences between the two cases studied in this scenario are also noted in the dynamic current–voltage characteristics ($J(V)$ curves shown in Fig. S7 in the supplementary material). Although having the same $V_{OC}$ and comparable hysteresis, the cell dominated by bulk recombination shows much lower performance, which originates in the very low values of the pseudo-lifetimes $\tau_n = \tau_p = 0.3$ ns required by the simulation. Such values are much smaller than lifetimes measured by, e.g., photoluminescence decay in Cs/FA-based perovskites, ranging in the several ns to $\mu$s regime. Further insight into the case of interface recombination is possible through Fig. 7, which shows the components of the total current density $J$. Here, we see that the total current (thickest red

### Table I. List of key parameters in the three investigated scenarios. The parameters that varied in each scenario are marked with bold type. See Table S1 in the supplementary material for the remaining simulation parameters and Fig. S6 in the supplementary material for a graphical definition of the energy band offsets.

<table>
<thead>
<tr>
<th>Symbols</th>
<th>Description (dimensional units)</th>
<th>Scenario 1 (Figs. 6 and 8)</th>
<th>Scenario 2 (Fig. 8)</th>
<th>Scenario 3 (Figs. 9 and 10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_n$</td>
<td>Electron pseudo-lifetime in perovskite (ns)</td>
<td>0.3</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>$\tau_p$</td>
<td>Hole pseudo-lifetime in perovskite (ns)</td>
<td>0.3</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>$S_{\text{ETL}}$</td>
<td>Electron rec. velocity at ETL interface (cm/s)</td>
<td>$10^4$</td>
<td>$10^7$</td>
<td>$10^7$</td>
</tr>
<tr>
<td>$\Delta E_{\text{ETL}}$</td>
<td>Conduction band energy offset at ETL/perovskite interface (eV)</td>
<td>0.07</td>
<td>0.07</td>
<td>0–0.3</td>
</tr>
<tr>
<td>$\Delta E_{\text{HTL}}$</td>
<td>Valence band energy offset at perovskite/HTL interface (eV)</td>
<td>0.33</td>
<td>0.33</td>
<td>0.1–0.4</td>
</tr>
<tr>
<td>$N_0$</td>
<td>Spatial average of mobile (positive) and fixed (negative) ion concentration (cm$^{-3}$)</td>
<td>$10^{18}$</td>
<td>$4.6 \times 10^{-12}$</td>
<td>$10^{18}$</td>
</tr>
<tr>
<td>$D_{\text{ion}}$</td>
<td>Room temperature ionic diffusion coefficient (cm²/s)</td>
<td>$4 \times 10^{-15}$</td>
<td>$4.5 \times 10^{-16}$</td>
<td>$4 \times 10^{-15}$</td>
</tr>
</tbody>
</table>

The values in the table are adjusted to obtain the same stationary value of $V_{OC}$. The conditions $\Delta E_{\text{ETL}} < \Delta E_{\text{HTL}}$ and $S_{\text{ETL}} > S_{\text{HTL}}$, or alternatively, with both relations inverted. However, $S_{\text{ETL}} > S_{\text{HTL}}$ is the condition that agrees with recent experimental results in MAPI as well as triple-cation perovskite films obtained with the same ETL and HTL materials, where both perovskites revealed lower photoluminescence quantum yield when in contact with PCBM (ETL) than with PTAA (HTL).
curve) is almost entirely composed by the decreasing recombination at the perovskite/HTL interface (white curve inside total current curve), with the remaining recombination current components being virtually negligible (the displacement current and the ionic currents are much lower and were excluded from the plot). Notice that although the recombination velocity at the HTL interface is much lower than at the ETL interface (cf. Table I), the component of the recombination current at the HTL interface is much higher. An inspection of the carrier concentrations at the interfaces (not shown here) shows that the lower recombination velocity at the HTL interface is overcompensated by the much higher electron concentration arriving at the perovskite/HTL interface. The difference in concentration is in turn a consequence of the lower energy offset $\Delta E_{HTL} = 0.33$ eV assumed at the ETL/perovskite interface, compared to $\Delta E_{ETL} = 0.07$ eV energy offset at the perovskite/HTL interface. The role of the energy band offsets is explored further in scenario 3. Regardless of the large difference in current components determined by the band offsets, it is worth noticing that bulk recombination (defect and radiative), as well as recombination at the ETL/perovskite interface, all increase with time. This is a consequence of the incidence of ion screening, which in the present case lowers the field driving carriers across the cell toward the opposite interface, as explained above.

Retaining the case of the solar cell controlled by interface recombination, we now enter scenario 2, where it becomes apparent that the shape of the simulated transients is highly dependent on ionic concentration $N_0$ and diffusion coefficient $D_{ion}$. Since the duration of the transients is known from the experiments, we chose not to vary $N_0$ and $D_{ion}$ independently, but inversely related through Eq. (4) with $\tau_{ion} = 35$ min, chosen as a representative value for the duration of the voltage-step measurements. The resulting range of values for $N_0$ and $D_{ion}$ is given in Table I. Figures 8(a) and 8(b) shows the simulated voltage-step response $J(t)$ and $Q_i(t)$, while Fig. 8(c) shows a light-step response of $V_{OC}$. The color code in the legend refers to the values of $N_0$ and $D_{ion}$ increasing in the direction of the arrows. By inspection, we notice that with higher ion concentration $N_0$, and all displayed quantities show a larger difference between the initial and steady-state values. Additionally, shorter times are required to reach a stationary state with higher $N_0$ values, implying that $\tau_{ion}$ is a better estimator of the transient duration in the cases with lower $N_0$.

The condition of dominating interface recombination required to reproduce the experimental trends is not sufficient in general, as opposing trends for the voltage-step response are also possible without strong bulk recombination. This becomes apparent within scenario 3, where the role of interfaces is explored in terms of the
energy band offsets at the interfaces. The values of the offsets \( \Delta E_{EETL} \) and \( \Delta E_{HTL} \) (see the range of values in Table I) are not varied independently but linked with the restriction that the built-in voltage is kept constant at the value \( V_{bi} = 1.1 \) V. We, therefore, choose a range of values for \( \Delta E_{EETL} \) and obtain \( \Delta E_{HTL} \) from
\[
V_{bi} = E_g + \Delta E_{EETL} - \Delta E_{HTL} - kT \ln\left(\frac{N_{CE} N_{VH}}{N_{DE} N_{DH}}\right),
\]
where \( E_g \) is the energy bandgap of the perovskite, \( N_{CE} \) and \( N_{VH} \) are the effective density of states in the conduction band of the ETL, and the valence band of the HTL, respectively, and \( N_{DE}/N_{DH} \) are the effective doping densities in ETL/HTL. Figures 9(a)–9(c) shows voltage-step and light-step transients simulated using various \( \Delta E_{HTL}/\Delta E_{EETL} \) combinations where, for quick reference, curves in warm(cold) colors mean \( \Delta E_{HTL} > \Delta E_{EETL} \) (warm colors), while \( \Delta E_{HTL} \leq \Delta E_{EETL} \) (cold colors) leads to opposite trends. The light-step response of \( V_{OC}(t) \) seen in Fig. 9(c) shows predominantly increasing responses, with stationary values of \( V_{OC} \) covering a wide range of 200 mV. Notice that both cases of energy offsets at the interfaces. The values of the offsets \( \Delta E_{EETL} \) and \( \Delta E_{HTL} \) (see the range of values in Table I) are not varied independently but linked with the restriction that the built-in voltage is kept constant at the value \( V_{bi} = 1.1 \) V. We, therefore, choose a range of values for \( \Delta E_{EETL} \) and obtain \( \Delta E_{HTL} \) from
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\]
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where \( E_g \) is the energy bandgap of the perovskite, \( N_{CE} \) and \( N_{VH} \) are the effective density of states in the conduction band of the ETL, and the valence band of the HTL, respectively, and \( N_{DE}/N_{DH} \) are the effective doping densities in ETL/HTL. Figures 9(a)–9(c) shows voltage-step and light-step transients simulated using various \( \Delta E_{HTL}/\Delta E_{EETL} \) combinations where, for quick reference, curves in warm(cold) colors mean \( \Delta E_{HTL} > \Delta E_{EETL} \) (warm colors), while \( \Delta E_{HTL} \leq \Delta E_{EETL} \) (cold colors) leads to opposite trends. The light-step response of \( V_{OC}(t) \) seen in Fig. 9(c) shows predominantly increasing responses, with stationary values of \( V_{OC} \) covering a wide range of 200 mV. Notice that both cases of
offset relations are able to deliver either high or low $V_{OC}$ values. This originates in the dependence of the interface carrier concentrations on the energy offsets, which determine the recombination rates. The dependence of interface recombination with the energy offsets is also evident under dark conditions in the voltage-step simulations. By inspection of Fig. 9(a), we see that the stationary value of $J$ strongly depends on the choice of band offsets. Notice that the cases with higher stationary $J$, which correspond to stronger interface recombination, correlate to the lowest values of stationary $Q$, and lowest $V_{OC}$. Figure 10 collects the steady-state $V_{OC}$ (filled symbols) shown against the offsets $\Delta E_{ETL}$ (bottom x axis) and $\Delta E_{HTL}$ (top x axis), together with the dynamic $V_{OC}$ from $J(V)$ simulations (shown in Fig. S8 in the supplementary material). Both the steady-state and the dynamic $V_{OC}$ show a coincident maximum, which occurs as the result of an optimum balance between the chosen values of recombination velocities and the majority carrier concentration at the interfaces with each choice of band offsets. In this scenario, where $S_{PETL} > S_{HTL}$ was chosen according to the higher recombination velocity known at the PCBM/perovskite interface, the maximum $V_{OC}$ takes place with $\Delta E_{ETL} > \Delta E_{HTL}$, which limits the concentration of holes that are able to recombine at the ETL interface.

V. CONCLUSIONS

We report on Cs-based double-cation perovskite solar cells with low apparent hysteresis, displaying very slow (>30 min) response to voltage-step and light-step excitation. During the voltage-step experiments, we observe an increasing electroluminescence together with a decreasing injected current density, which results in an increasing electroluminescence quantum yield. Both trends are explained as a consequence of ionic charges controlling the evolution of the electric field in the perovskite, provided interface recombination controls total recombination. The case for dominating interface recombination is further supported by steady-state photocarrier grating measurements on bare perovskite films, which result in diffusion lengths above 1 $\mu$m, markedly higher than the film thickness. The light-step response shows an increasing open-circuit voltage with steady-state values that are proportional to the steady-state electroluminescence quantum yield, connecting the dark and light response as in the optoelectronic reciprocity principle—otherwise applied to nearly ideal solar cells. Further insight into the experimental data is possible by means of a numerical model including ionic transport, which is able to reproduce the time evolution of both step responses and the slow apparent hysteresis in the case of interface recombination of charge carriers dominating over bulk recombination. The simulations show that the specific interface energy band offsets and recombination velocities ultimately determine the type of recombination current dominating the solar cell, and hence, the shape of the transient response curves.

SUPPLEMENTARY MATERIAL

See the supplementary material for supporting experimental results.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

REFERENCES
