The impact of energy alignment and interfacial recombination on the internal and external open-circuit voltage of perovskite solar cells†

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Charge transport layers (CTLs) are key components of diffusion controlled perovskite solar cells, however, they can induce additional non-radiative recombination pathways which limit the open circuit voltage (VOC) of the cell. In order to realize the full thermodynamic potential of the perovskite absorber, both the electron and hole transport layer (ETL/HTL) need to be as selective as possible. By measuring the photoluminescence yield of perovskite/CTL heterojunctions, we quantify the non-radiative interfacial recombination currents in pin- and nip-type cells including high efficiency devices (21.4%). Our study comprises a wide range of commonly used CTLs, including various hole-transporting polymers, spiro-OMeTAD, metal oxides and fullerences. We find that all studied CTLs limit the VOC by inducing an additional non-radiative recombination current that is in most cases substantially larger than the loss in the neat perovskite and that the least-selective interface sets the upper limit for the VOC of the device. Importantly, the VOC equals the internal quasi-Fermi level splitting (QFLS) in the absorber layer only in high efficiency cells, while in poor performing devices, the VOC is substantially lower than the QFLS. Using ultraviolet photoelectron spectroscopy and differential charging capacitance experiments we show that this is due to an energy level mis-alignment at the p-interface. The findings are corroborated by rigorous device simulations which outline important considerations to maximize the VOC. This work highlights that the challenge to suppress non-radiative recombination losses in perovskite cells on their way to the radiative limit lies in proper energy level alignment and in suppression of defect recombination at the interfaces.

Broader context
As perovskite solar cells continue to improve at a rapid pace, more fundamental insights into the remaining open-circuit voltage (VOC) losses are required in order to unlock power conversion efficiencies (PCEs) of ~30%. Several studies highlight that the perovskite absorber exhibits an opto-electronic quality that is comparable to GaAs in terms of external fluorescence, therefore potentially allowing PCEs close to the radiative limits. However, the high internal potential in the absorber layer can often not be directly translated into an equal potential at the metal electrodes. In this work, we reveal the reasons for the discrepancy by decoupling the main VOC losses in the bulk, perovskite/charge transport layer (CTL) interfaces and/or metal contacts for a broad range of different perovskite compositions and several, commonly used CTLs. Undoubtedly, by introducing additional non-radiative recombination centres at the interfaces, the CTLs have the most striking impact on the device VOC. Moreover, interface recombination is often exponentially increased in case of an energy level mismatch between the perovskite and the CTLs. We conclude that energy level matching is of primary importance to achieve the implied VOC of the perovskite/CTL stack, followed by suppression of defect recombination at the interfaces and in the absorber layer.

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Introduction

Huge endeavours are devoted to understanding and improving the performance of perovskite solar cells, which continue to develop at a rapid pace already outperforming other conventional thin-film technologies on small cells (<1 cm²). It is well established that further improvements will require suppression of non-radiative recombination losses to reach the full thermodynamic potential in terms of open-circuit voltage \( V_{OC} \) and fill factor \( FF \). As such, a major focus of the entire field to push the technology forward is targeted at reducing defect recombination in the perovskite bulk with numerous works highlighting the importance of grain boundaries in determining the efficiency losses. In contrast, many other studies highlight the significance of traps at the perovskite surface which is likely chemically distinct from the bulk. In many cases, performance improvements were achieved by mixing additives into the precursor solution including multiple cations and/or halides. In several studies, a slower transient photoluminescence (TRPL) decay is shown as the figure of merit to prove the suppressed trap-assisted recombination in the bulk while implying its positive impact on the overall device efficiency. Significantly fewer publications have focused on the importance of non-radiative recombination of charges across the perovskite/CTL interface. Until recently it has been challenging to pinpoint the origin of these free energy losses in complete cells, although there have been some studies with valuable insight. Methods that have been employed to study interfacial recombination in perovskite stacks include impedance spectroscopy, transient photoluminescence (TRPL) or reflection spectroscopy (TRS), transient microwave conductivity (TRMC), and transient photovoltage (TPV). Whilst these techniques exhibit in principle the required time resolution to unveil the kinetics of the interface and bulk recombination, the interpretation of these transient measurements can be very challenging. The reasons are related to the inherent fact that extraction and recombination can both reduce the emitting species in the bulk, thus causing the signal decay. Previously, a more direct approach to decouple the origin of these recombination losses at each individual interface has been introduced based on steady-state photoluminescence measurements. In particular, measurements of the emitted photoluminescence quantum yield (PLQY) on individual perovskite/transport layer junctions have been used to explain the \( V_{OC} \) through QFLS losses in the perovskite bulk and at the individual interfaces. However, the relation between the internal QFLS and the external \( V_{OC} \) remains poorly understood today, especially for different solar cells architectures with different perovskite absorbers and/or charge transport layers. For example, in a recent study, a very high external PLQY (15%) has been reported on a \( nip \) stack \( (i.e. \) an electron transport layer/perovskite/hole transport layer junction) upon grain boundary passivation using potassium iodide. Considering the provided external quantum efficiency (EQE), this high PLQY translates in an internal QFLS of \( \sim 1.26 \text{ eV} \), which is very close to the radiative limit of the given perovskite absorber layer \( (\sim 1.31 \text{ eV}) \). Yet, the \( V_{OC} \) of the optimized cells was considerably lower \( (1.17 \text{ V}) \). This suggests that interfacial recombination (which impacts the QFLS of the \( nip \) stack) is not causing the primary \( V_{OC} \) limitation and suggests that losses of \( \sim 100 \text{ mV} \) are of different nature. This raises the important question whether the external \( V_{OC} \) as measured on a complete solar cell truly represents the QFLS in the perovskite bulk and how this depends on the strength of interfacial defect recombination or the energy level alignment between the perovskite and the transport layers. Until today, the importance and impact of energy level alignment remains an important, yet heavily debated topic in perovskite solar cells. For example, several studies showed the benefit or a large impact of energy level alignment between the perovskite and the transport layers, which was however challenged in other works.

In this work, we studied the relation between the QFLS and the \( V_{OC} \) by means of absolute PL measurements in “regular” \( nip \) and “inverted” \( pin \) perovskite solar cells for a broad range of CTLs including metal oxides, conjugated polymers, small molecules, and fullerenes. First, we aimed to compare the selectivity of CTLs used for \( nip \) and \( pin \) configurations in triple cation perovskite cells; \( i.e. \) for instance \( TiO_2 \) or \( SnO_2 \) vs. PTAA underneath the perovskite or doped spiro-OMeTAD vs. \( Cs_2CO_3 \) on top. We note that in this work we define the selectivity of a CTL as its ability to maintain the QFLS of the absorber layer while providing efficient majority carrier extraction. The results suggest that when attached to the perovskite, all studied CTL cause a reduction of the QFLS with respect to the QFLS of the neat perovskite on a fused silica substrate \( (1.23 \text{ eV}) \). The results were also generalized to different perovskite absorber layers. A comparison of the QFLS obtained on CTL/perovskite \( (\text{perovskite/CTL}) \) bilayers and \( nip \) or \( pin \) stacks, suggests a simple superposition principle of non-radiative recombination currents at each individual interface. This implies that the inferior interface dominates the free energy loss in the complete cell. In efficient cells, where the QFLS matches the device \( V_{OC} \), we can further estimate the parallel recombination currents in the bulk, interfaces and/or metal contacts under \( V_{OC} \) conditions. However, in poor performing cells we find that the \( V_{OC} \) is substantially lower than the corresponding QFLS of the \( pin \) stack. Drift diffusion simulations highlight the impact of energy level offsets in causing the mismatch between the internal QFLS and the external \( V_{OC} \) which we further confirmed using photoemission spectroscopy (UPS) and transient differential charging capacitance experiments. The results underline that the primary non-radiative recombination loss channel of today’s perovskite cells is interfacial recombination at (or across) the perovskite/CTL interface and that interfacial recombination is often exponentially increased in case of an energy level offset between the perovskite and the TLs. As such, our findings highlight the importance of tailoring the energetics and kinetics at the perovskite/CTL interfaces to harvest the full potential in perovskite solar cells.

Materials

The studied CTLs in this work belong to 3 material classes, conjugated polymers, small molecules and metal oxides.
Regarding the conjugated polymers, we studied highly selective wide-band gap donors such as PolyTPD and PTAA. Poly[9,9-bis[30-([N,N-dimethyl]-N-ethylammonium)-propyl]-2,7-fluorene]-alt-2,7-[9,9-di-n-octylfluorene)] dibromide (here “PFN”) was added on top of both materials to improve the wettability. In order to draw correlations between the QFLS and the energetics of the HTL, we also investigated P3HT, as well as the highly conductive composite PEDOT:PSS. As small molecule HTL, we tested Spiro-OMeTAD which requires doping by different ionic salts and other additives. For the case of small molecule ETLs, we studied the fullerene C60 (with and without the interlayer LiF) and the solution-processable fullerene derivative PCBM. Lastly, we studied the commonly used transparent metal oxides TiO2 and SnO2. TiO2 is widely considered as an ideal electron transporting layer due to its high selectivity and high charge carrier mobility, while SnO2 is the preferred platform for planar efficient n-i-p cells. These chemical structures of the materials are shown in Fig. 1. As absorber layer we chose the so-called triple cation perovskite (CsPbI3)0.05[(FAPbI3)0.83(MAPbBr3)0.17]0.95 (see ESI, methods), while the study was later extended to other perovskite systems as discussed below.

**Comparison of CTLS for pin and nip type devices**

In order to quantify the free energy losses at the CTL/perovskite interface, we measured the absolute photoluminescence (PL) yield of perovskite/transport layer heterojunctions. The absolute PL is a direct measure of the quasi-Fermi level splitting (QFLS or \( \mu \)) in the absorber, and this approach has been recently applied to perovskite solar cells by various groups. The ratio of emitted (\( \phi_{em} \)) and absorbed photon fluxes (\( \phi_{abs} \)) defines the absolute external PL quantum yield (PLQY):

\[
\text{PLQY} = \frac{\phi_{em}}{\phi_{abs}} = \frac{J_{rad}/e}{J_G/e} = \frac{J_{rad}}{J_{rad} + J_{non-rad}}
\]

If all emission is from the direct recombination of free charges, and also every absorbed photon generates a free electron–hole pair, the PLQY equals the ratio of the radiative recombination current density (\( J_{rad} \)) and the total free charge generation current density (\( J_G \)). At \( V_{OC} \), charge extraction is zero, meaning that \( J_G \) is equal to the total recombination current (\( J_{tot} \)) of radiative and non-radiative losses (\( J_{rad} + J_{non-rad} \)). Furthermore, \( J_{non-rad} \) is equal to the sum of all non-radiative recombination pathways in the bulk (\( J_B \)), at the HTL/perovskite (\( J_{p,i} \)) and the perovskite/ETL (\( J_{n,i} \)) interface, and potentially other losses (e.g. recombination in the transport layers, or at the CTL/metal interfaces). Using the expression for the radiative recombination current density according to Shockley–Queisser and eqn (1), we can write the QFLS (\( \mu \)) as a function of the radiative efficiency

\[
J_{rad} = J_{0,rad}e^{\mu/kT} \rightarrow \mu = kT \ln \left( \frac{J_{rad}}{J_{0,rad}} \right) = kT \ln \left( \frac{\text{PLQY} \times J_G}{J_{0,rad}} \right)
\]

\[
= kT \ln \left( \frac{J_G}{J_0} \right) = kT \ln \left( \frac{J_{rad}}{J_{rad} + J_B + J_{p,i} + J_{n,i} + \ldots} \right)
\]

where \( J_{0,rad} \) is the radiative thermal equilibrium recombination current density in the dark and \( J_0 = J_{0,rad} \times \text{PLQY} \) the dark saturation current. We note, that the PLQY depends itself on external conditions such as the illumination intensity or the

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**Fig. 1** The optoelectronic quality of triple cation perovskite/CTL layer junctions. (a) Materials studied in this paper. (b) The quasi-Fermi level splitting of the studied heterojunctions with different hole and electron transporting materials and of the neat absorber layer calculated based on eqn (2) using absolute photoluminescence measurements. The absorber was spin casted from the same solution for all transport layers. The non-radiative dark saturation current is plotted on the right and was obtained from \( J_{0,rad} = J_0 - J_{rad} \) which allows comparing the strength of non-radiative recombination of different junctions.
Table 1  Optoelectronic quality of several tested perovskite–CTL layer junctions

| Film            | Absorption | PLQY | $J_{0,rad}$ [A m$^{-2}$] | QFLS [eV] |
|----------------|------------|------|-------------------------|------------|
| ITO/Pero       | 0.839      | 2.0 $\times 10^{-5}$ | $3.5 \times 10^{-16}$ | 1.060      |
| PEDOT:PSS/Pero | 0.854      | 7.5 $\times 10^{-5}$ | $9.9 \times 10^{-17}$ | 1.092      |
| P3HT/Pero      | 0.848      | 7.7 $\times 10^{-4}$ | $1.0 \times 10^{-17}$ | 1.152      |
| Pero/spiro-OMeTAD | 0.944   | 1.4 $\times 10^{-3}$ | $4.6 \times 10^{-18}$ | 1.172      |
| PTAA/PFN/Pero  | 0.852      | 5.1 $\times 10^{-3}$ | $1.3 \times 10^{-18}$ | 1.204      |
| PolyTPD/PFN/Pero | 0.851   | 7.3 $\times 10^{-4}$ | $3.2 \times 10^{-18}$ | 1.208      |
| Pero           | 0.850      | 1.4 $\times 10^{-2}$ | $4.6 \times 10^{-19}$ | 1.231      |
| SnO$_2$/Pero   | 0.854      | 5.9 $\times 10^{-3}$ | $1.5 \times 10^{-18}$ | 1.201      |
| TiO$_2$/Pero   | 0.854      | 2.1 $\times 10^{-3}$ | $3.2 \times 10^{-18}$ | 1.181      |
| Pero/PCBM      | 0.934      | 5.7 $\times 10^{-4}$ | $1.3 \times 10^{-17}$ | 1.145      |
| Pero/C$_{60}$  | 0.927      | 3.8 $\times 10^{-4}$ | $1.8 \times 10^{-17}$ | 1.137      |
| PerO/LiF/C$_{60}$ | 0.892   | 1.3 $\times 10^{-3}$ | $4.9 \times 10^{-18}$ | 1.170      |

The opto-electronic quality of several tested perovskite–CTL layer junctions is summarized in Table 1 and plotted in Fig. 1b. All internal QFLS. This originates from the fact that the non-radiative recombination pathways depend differently on the actual number of charge pairs present in the device compared to radiative recombination. Thus, in order to predict the QFLS under 1 sun and open-circuit, the PLQY needs to be measured under the same illumination conditions. Eqn (2) also shows that the QFLS depends logarithmically on the non-radiative recombination currents in the bulk, interface etc. In order to quantify the QFLS, the generated current density under illumination ($J_0$) and $J_{0,rad}$ need to be known, as well as the thermal energy (we measured a temperature of $\sim 26-28$°C on the sample under 1 sun equivalent illumination using a digital standard infrared sensor). $J_0$ and $J_{0,rad}$ are obtained from the integrated product of the external quantum efficiency (EQE) and the solar photon flux ($\phi_{sun}$) at 300 K and the black body spectrum ($\phi_{bn}$), respectively. As such, we obtained a $J_{0,rad}$ of $\sim 6.5 \times 10^{-21}$ A m$^{-2}$ ($\pm 1 \times 10^{-21}$ A m$^{-2}$) independent of the bottom CTL (ESI† Fig. S1) as it is predominantly determined by the tail absorption of the triple cation perovskite absorber layer (with Urbach energies around 15 meV). In all cases, the QFLS was measured by illuminating the films through the perovskite (or the transparent layer in case of pin or nip stacks) in order to avoid parasitic absorption of the studied CTL (see ESI† Fig. S2). The results of the PL measurements of the different transport layers are summarized in Table 1 and plotted in Fig. 1b. All results were obtained as an average of multiple fabricated films (ESI† Fig. S3) with representative PL spectra shown in ESI† Fig. S4. Details of the measurements conditions are discussed in ESI† Methods.

Fig. 1b shows that the triple cation perovskite on a fused silica substrate limits the QFLS to approximately 1.231 eV, which is $\sim 110$ meV below the radiative $V_{OC}$ limit (where the PLQY equals 1). We note that we cannot rule out that this value is limited by recombination at the fused silica/perovskite interface and also that we observe a substantially lower QFLS ($\sim 40$ meV) of the bare perovskite layer on a glass substrate (see ESI† Fig. S5). Moreover, significantly higher PLQY values above 20% were observed on methylammonium lead triiodide films where the top surface was passivated with tri-n-octylphosphine oxide (TOPO). These results highlight the high opto-electronic quality of the perovskite bulk comparable (or already better) than highly pure silicon or GaAs but also indicates substantial recombination losses at the perovskite top surface. For the HTL/perovskite junctions we also tested the influence of the underlying ITO layer, however this did not significantly influence the obtained QFLS within a small error except for samples with SnO$_2$ (see ESI† Fig. S3). Likewise, we tested the influence of the copper metal electrode on top of the C$_{60}$ in perovskite/C$_{60}$ heterojunctions and pin stacks (ESI† Fig. S6). Overall, these tests suggest that there is usually a lossless charge transfer between the CTLs and the metal electrodes. Interestingly, Fig. 1b shows that the polymers PTAA/PFN and PolyTPD/PFN performed best—even outperforming the omnipresent spiro-OMeTAD. However, it is clear that the selectivity of a TL can be different underneath or on top of the perovskite. Therefore, we do not aim to quantify the opto-electronic quality of a CTL itself but rather assess the selectivity of the CTL in a particular configuration (i.e. either on top or underneath a particular perovskite layer). Among the studied ETLs, SnO$_2$ and TiO$_2$ outperform the organic ETLs C$_{60}$ and PCBM which are usually used in pin-type cells. Therefore, this data suggests that the $p$-interface is the limiting interface for pin cells, and the $n$-interface for pin cells consistent with earlier studies. Moreover, we observe that the capping CTLs PCBM and C$_{60}$ are worse than spiro-OMeTAD. Considering that the inferior interface will dominate the final $V_{OC}$ (eqn (1) and (2)), this might be one reason for the superior performance of pin cells today. One approach to suppress non-radiative recombination at the perovskite/C$_{60}$ interface in pin cells is to insert a thin LiF interlayer as demonstrated earlier and in Table 1.

A frequently arising question is how much the perovskite morphology, which potentially varies depending on the underlying CTL, could influence the obtained QFLS and the interpretation of the results. Thus, we performed top scanning electron microscopy and AFM measurements (see ESI† Fig. S7). Interestingly, we find the largest grains on a PEDOT:PSS bottom CTL despite it being the worst among the studied transport layers. The largest grain size distribution is visible on perovskite films on TiO$_2$ while the perovskite morphology on all other substrates appears, at least qualitatively, similar where we observe relatively small grains (<10–100 nm). In addition, AFM measurements reveal rough square surface roughnesses varying from 12–27 nm, where the perovskite on PolyTPD/PFN and PTAA/PFN appears to be roughest (>20 nm) while the perovskite film on TiO$_2$ is the smoothest. We also note the similar Urbach tail of the perovskite absorber layer when processed on different CTLs (ESI† Fig. S1) which is related to the density of subgap states. This further indicates a similar opto-electronic quality of the perovskite. Considering these results, it seems unlikely that the perovskite bulk morphology can explain the changes in the non-radiative recombination loss currents which increase by orders of magnitude depending on the underlying substrate (as shown in Fig. 1b). It is also worth to note that these results do not allow distinguishing whether the critical recombination loss occurs across the perovskite/CTL interface, or at the perovskite surface next to the interface. In any case, the presence of the additional CTL triggers additional...
(non-radiative) interfacial recombination losses, which are dominating the non-radiative recombination losses.

**Comparison of the QFLS and device $V_{OC}$ and origin of free energy losses**

In the following, we aim to compare the non-radiative recombination losses at the p- and n-interfaces with the QFLS of the pin stacks and the $V_{OC}$ of the complete cells with different HTLs and (LiF)/C$_{60}$ as ETL. Fig. 2a shows that the device $V_{OC}$ (black line) generally increases with the average QFLS of the pin stack (orange line) which was taken as an average as obtained on 3–4 samples for each configuration. Importantly, for optimized cells with PolyTPD or PTAA, the $V_{OC}$ (black line) matches the QFLS of the stack (orange line) within a small error. This is also nearly identical to the QFLS of the less selective perovskite/C$_{60}$ interface (blue line). This indicates that for these particular cells, the losses determining the $V_{OC}$ occur almost entirely at the inferior interface to the perovskite while the electrodes are not causing additional $V_{OC}$ losses. On the other hand, in case of the less selective PEDOT:PSS and P3HT bottom layers, the $V_{OC}$ was found to be substantially lower than the corresponding QFLS. This will be discussed further below. The current density vs. voltage ($J$/$V$) characteristics of the corresponding cells are shown in Fig. 2b which highlight the large differences in the measured $V_{OC}$. Device statistics of individually measured stacks are shown in ESI,† Fig. S9. We note that our devices with LiF/C$_{60}$ as ETL reach efficiencies of up to 21.4% with a $V_{OC}$ of ~1.2 V (for a triple cation perovskite with a bandgap of ~1.6 eV), which is among the highest reported values for pin-type cells (ESI,† Fig. S10).

Next, we compared the PLQY with the external electroluminescence quantum efficiency (EQE$_{EL}$) as shown in Fig. 2c. Under conditions where the dark injection current equals the generation current, the EQE$_{EL}$ of PTAA and PolyTPD cells ($3 \times 10^{-4}$ for both devices) approaches the PLQY of the stack within a factor of two ($5.9 \times 10^{-4}$ for PTAA and $4.6 \times 10^{-4}$ for PolyTPD). Improving the perovskite/ETL interface by inserting LiF increases both the QFLS of the pin stack and the $V_{OC}$ to 1.17 V corresponding to a PLQY of ~$1.3 \times 10^{-4}$ and EQE$_{EL}$ of ~$8.3 \times 10^{-4}$.

However, for devices with PEDOT:PSS, the EQE$_{EL}$ (~$1.4 \times 10^{-8}$) is orders of magnitude lower than the PLQY of the stack (~$1 \times 10^{-5}$). We note that the measured EQE$_{EL}$ matches roughly the expected EQE$_{EL}$ according to Rau’s reciprocity for a $V_{OC}$ of 0.9 V as obtained from the $JV$ scan ($3.8 \times 10^{-5}$). Therefore, we conclude that the inferior interface (PEDOT:PSS/perovskite) limits the QFLS of the stack, however, there is an additional loss which affects the $V_{OC}$ but not the QFLS. This will be addressed further below. Lastly, films with P3HT lie somewhat in between PEDOT:PSS and PTAA (PolyTPD) devices. Here, both interfaces (P3HT/perovskite and perovskite/C$_{60}$) appear to be equally limiting the QFLS of the stack which also lies below the QFLS of the individual heterojunctions (bilayers). Similar to PEDOT:PSS devices, we observe a considerable mismatch between PLQY of the optical pin stack ($6.2 \times 10^{-5}$) and the EQE$_{EL}$ (~$9 \times 10^{-7}$).
We note that the measured EQEEL is again very close to the EQEEL that is expected for a P3HT device with a $V_{OC}$ of $\sim 1.0$ V ($\sim 1.8 \times 10^{-6}$).

As for the nip cells with SnO$_2$ and TiO$_2$ as the ETL, and SpiroOMeTAD as the HTL, we observe a similar trend as in our optimized pin-type cells with PTAA or PolyTPD, that is a close match between the average device $V_{OC}$ ($\sim 1.15$ V) and the average internal QFLS (1.161 eV and 1.168 eV for TiO$_2$ and SnO$_2$ based cells, respectively) under 1 sun conditions. All results obtained on nip cells are shown in ESI,† Fig. S11. Regarding the potential impact of the perovskite morphology when the samples are prepared on different hole (electron) transport layers, it is important to note that the losses in the neat material (dashed green in Fig. 2a) cannot be larger than the cumulative losses observed in the CTL/perovskite bilayers (red). Moreover, the match between the QFLS of the glass/perovskite/CTL bilayers (blue) and the pin or nip stacks (Fig. 2a and ESI,† Fig. S11) means that the recombination at the top CTL interface can consistently explain the overall $V_{OC}$ regardless, if the perovskite is deposited on glass or on the CTL (PTAA:PFN, PolyTPD:PFN, TiO$_3$, SnO$_2$). This highlights the importance of the top interface in determining the non-radiative recombination current in perovskite solar cells.

**Quantification of parallel recombination currents at $V_{OC}$**

The absolute-PL approach allows to further estimate the parallel recombination currents at $V_{OC}$. To this end, we successively quantify the non-radiative recombination currents in the neat material and the bottom and top interfaces from the PLQY of the corresponding perovskite/CTL films (eqn (1)) and knowledge of $J_{rad}$ (eqn (2)). Important to note is that the PLQY of each film needs to be known at the $V_{OC}$ or QFLS of the complete cell which requires intensity dependent PLQY measurements. Moreover, the individual recombination currents must add up to $J_{oc}$ which allows to check the consistency of the approach. This is possible in efficient cells where the QFLS in the absorber layer matches the device $eV_{OC}$ within a relatively small error ($\approx 20$ meV), but the procedure is prone to fail in cells where QFLS $> eV_{OC}$. Fig. 3a shows the obtained recombination currents for efficient pin-type and nip-type cells. Fig. 3b illustrates our optimized pin cells with LiF/C$_{60}$ as ETL at $V_{OC}$ by a bucket with holes which represent the recombination losses (see caption). We note again that the recombination current in the neat perovskite (turquoise) is obtained from a film on fused silica and therefore the loss in the neat absorber layer might be slightly different when deposited on top of a CTL. However, as we detail throughout the manuscript, changes in the perovskite morphology when deposited on different CTL cannot explain the $V_{OC}$ of the final cells, and the fact that the recombination currents add up to $J_{oc}$ suggests that this loss estimation provides a realistic description of the parallel recombination currents at $V_{OC}$.

**Understanding the QFLS across the pin (nip) junction**

The experimental results in the previous sections show that QFLS $\sim V_{OC}$ in case of good performing transport layers (PTAA and PolyTPD). This indicates that interfacial recombination in these devices lowers the QFLS throughout the whole bulk equally. However, in case of PEDOT:PSS or P3HT, the device $V_{OC}$ is lower than the QFLS in the perovskite layer. In such cases, at least one QFL bends, presumably at the interfaces or contacts, causing a further reduction in the electrochemical potential of the photogenerated charges. This bending has a much larger effect on the final $V_{OC}$ than on the average QFLS in the perovskite bulk. In order to check whether this

![Fig. 3](image_url)

**Fig. 3** (a) Bulk and interfacial non-radiative recombination currents at open-circuit as obtained on nip and pin-type cells with nearly flat quasi-Fermi levels. In pin-type cells, the non-radiative recombination current is dominated by the C$_{60}$ interface (red) – even if optimized with LiF. In nip-type cells, the recombination at the upper perovskite/spiro-interface (red) dominates the recombination loss, although the recombination at the p- and n-interface are quite similar in case of cells based on TiO$_2$. In all cases, the non-radiative recombination losses in the neat perovskite (turquoise) are smaller than at the top interface. We note the radiative recombination current density is very small, e.g. 7.8 $\mu$A cm$^{-2}$ in panel (a). (b) Illustrates a solar cell as bucket with holes where the water level represents the cells’ $V_{OC}$. The water stream from the tap corresponds to the generation current density from the sun. The holes in the bucket represent the recombination losses at $V_{OC}$ in the bulk, interfaces etc. Depending on the exact size of the holes, the water level will change so as the $V_{OC}$ of the device.
We note that the role of the $V_{OC}$ up to 80% of these devices, a considerable built-in voltage ($\Delta E_{maj}$) in these devices. Interestingly, the implementation of a majority carrier band offset at the $p$-interface causes a considerable bending of the hole quasi-Fermi level close to the interface which explains the QFLS–$V_{OC}$ mismatch (Fig. 4b). Considering that $E_{F,e}$ and $E_{F,h}$ need to extend throughout the CTLs to the metal contacts in order to produce an external $V_{OC}$, it is clear that any $\Delta E_{maj}$ will cause an exponential increase of the hole population in the HTL. This implies an exponential increase in the recombination rate. Therefore, it is expected that a finite $\Delta E_{maj}$ will lead to an equal loss in the device $V_{OC}$. In order to generalize the conditions under which the $V_{OC}$ deviates from the QFLS, we extended our simulations by studying a wide range of parameters (ESI, Table S1). We found that at least two requirements must be fulfilled in order to explain the QFLS–$V_{OC}$ mismatch:

(a) a band offset for the majority carrier of at least $\sim 0.2$ eV, and

(b) a sufficiently high recombination velocity ($> 1$ cm s$^{-1}$), otherwise $E_{F,e}$ and $E_{F,h}$ can remain flat despite the energy offset (ESI, Fig. S14). Indeed, these simulations show that the $V_{OC}$ loss scales linearly with the $\Delta E_{maj}$ offset as long as the $p$-interface is limiting. We also note that the minority carrier band offset $\Delta E_{min}$ (i.e. the LUMO of the HTL and the perovskite conduction band) is not influencing the results if $\Delta E_{min}$ is larger than 0.1 eV which is further discussed at ESI, Fig. S15. We also simulated a $p$-type stack with a PEDOT:PSS bottom layer which we simplified by a metal with a work function of 5 eV, a high surface recombination velocity for holes and an intermediate value for electrons (ESI, Table S1). For these settings we observed that $E_{F,h}$ bends up at the interface, giving rise to the experimentally observed QFLS–$V_{OC}$ mismatch of roughly 150 meV in the PEDOT cell. All results on PEDOT:PSS cells are summarized in ESI, Fig. S16. We acknowledge that these simulations only illustrate one possible scenario of the internal device energetics using a set of plausible parameters, and thus different energetic alignments or a morphological issue at the interface cannot be excluded. However, we can conclude that energy level alignment of all layers is a crucial requirement to

\[ \text{Cell with aligned transport layers} \]

\[ \text{Cell with non-aligned transport layers} \]

Table S1. Qualitative simulation parameters listed in ESI,† Table S1. Qualitatively, these simulations confirm that $E_{F,e}$ and $E_{F,h}$ are spatially flat in the perovskite bulk and extend to the corresponding electrodes which explains that $\Delta E_{maj}$ in the HTL/ETL (blue) are represented by their bandgap in between the highest occupied and lowest unoccupied molecular orbitals.
maximize the $V_{\text{OC}}$ while the defect density at the interface is also a critical parameter in determining the non-radiative recombination losses.

**Energy level alignment at the HTL/perovskite interface**

The findings in the previous sections suggest that the observed mismatch between the internal QFLS and the $V_{\text{OC}}$ in cells comprising PEDOT:PSS and P3HT is due to an energy offset at the $p$-interface. To study the energy level alignment between the perovskite and the transport layer, we first performed photoelectron yield spectroscopy measurements (PYS) on the individual layers of the solar cells (ESI,† Fig. S17). However, these measurements did not allow a reliable prediction of $\Delta E_{m\alpha j}$ which is due to the assumption of a constant vacuum level across different layers of the stack. To measure the energetic offsets between the perovskite and the transport layers with respect to the fixed Fermi level ($E_F$) of the ITO substrate, we performed UPS measurements with background illumination. Recently, it has been shown that the perovskite surface can be considerably n-doped,56 which will directly impact the location of the valence band onset with respect to $E_F$ when measuring the top surface of the perovskite film with a He beam (21.1 eV). However, when UPS is performed with an additional background light, the band bending at the surface can be flattened which then allows to access the bulk energy levels. This enabled a direct comparison between the energy levels of the transport layers and the perovskite bulk. Indeed, as shown in Fig. 5 below, by properly taking into account the surface photovoltage (SPV) effect, we found that the valence band of the perovskite is aligned with the HOMO of PTAA and PolyTPD HTLs, while P3HT and PEDOT:PSS exhibited states close to, or at the Fermi-edge. Thus, we conclude that PTAA and PolyTPD allow maintaining the high QFLS that is generated from the perovskite upon illumination which is in agreement with the drift diffusion simulations. In contrast, in case of P3HT, and even worse in case of PEDOT:PSS, carriers will lose part of their free energy once they are transferred from the perovskite to the HTL, thereby causing the additional $V_{\text{OC}}$-loss as numerically predicted and experimentally observed. A further confirmation of this picture comes from the measurement of the charge carrier density in the bulk ($n_{\text{bulk}}$) at a given $V_{\text{OC}}$ using differential charging capacitance measurements.57,58 In the case of proper energy alignment, $n_{\text{bulk}}$ would be a sole function of the $V_{\text{OC}}$, independent of the choice of the TL material. The results in ESI,† Fig. S18 show that this is not the case. Instead, for a given $V_{\text{OC}}$, $n_{\text{bulk}}$ is substantially larger for the PEDOT:PSS cell than for the P3HT and the PTAA cell with proper energy alignment. This is a direct consequence of the energy offset and the resulting difference between the QLFS and the device $V_{\text{OC}}$ (see ESI,† Fig. S18d for a schematic representation of this situation).

**Recombination losses in other perovskite systems**

In order to generalize the findings, we also studied QFLS and $V_{\text{OC}}$ losses in other currently popular perovskite materials (ESI,† Fig. S19). The results further confirm our main conclusions: (i) the perovskite bulk usually allows to reach higher $V_{\text{OC}}$ than ultimately achieved in the cell. This is confirmed in a low-gap triple

![Fig. 5 (a) Ultraviolet photoelectron (UPS) spectra of PTAA, PolyTPD, P3HT and PEDOT-PSS on ITO. The corresponding signal of the perovskite film is shown above. The perovskite surface is n-doped resulting in an apparent valence band onset of 1.35 eV. Application of a background light (with a 1 sun equivalent intensity) flattens the band bending at the surface which allows accessing the valence band onset in the perovskite bulk (0.8 eV away from the Fermi level). The spectra of PEDOT-PSS is scaled by a factor of 60 as compared to the other films. As discussed by Hwang et al.,59 a high-bandgap PSS layer is present on top of a solution processed film which weakens the photoelectron signal of states at the Fermi-edge of the underlying PEDOT-PSS bulk as shown in several publications.59,66 The deduced energy levels are plotted in (b). As predicted from the QFLS–$V_{\text{OC}}$ mismatch in these cells, in case of PTAA and PolyTPD hole transport layers, the HOMO of the HTL is aligned with respect to the perovskite valence band. However, considerable majority carrier band offsets exist in case of P3HT and PEDOT-PSS. This causes the observed QFLS–$V_{\text{OC}}$ mismatch as carriers relax to the band edges during their transport to the extracting electrode.**
cation perovskite (~1.54 eV) which is currently used in the highest efficiency solar cells,\(^1\) a hybrid vacuum/solution processed MAPbI\(_3\) (~1.6 eV)\(^6\) which is relevant for application on textured surfaces in tandem solar cells,\(^6\) a high-gap mixed perovskite with a bandgap of 1.7 eV which is the ideal bandgap for monolithic Si/perovskite tandem solar cells, as well as two-dimensional perovskites based on \(n\)-butylammonium\(^6\) – a popular system which demonstrates increased stability under thermal and environmental stress.\(^6\) However, in some cases the QFLS of the optical stack is close to the QFLS of the neat absorber layer, e.g. for a solution processed CsFAPbI\(_3\) (~1.47 eV) and MAPbI\(_3\) (~1.6 eV). (ii) In most cases, the QFLS-PL technique can well describe the \(V_{OC}\) of the final cell which allows to assess the inferior interface by comparing the QFLS of HTL/perovskite or perovskite/ETL junctions. However, in a high-bandgap (~1.7 eV) mixed perovskite system we observe again a considerable mismatch between the QFLS of the \(pin\) stack and the \(V_{OC}\). This suggests difficulties in increasing the perovskite bandgap while maintaining aligned energy levels and further demonstrates the relevance of our findings for other perovskite systems.

**Conclusions**

Using absolute PL measurements, we were able to decouple the origin of non-radiative recombination losses for cells in \(pin\) and \(nip\) configurations fabricated from different CTLs and perovskite compositions. For a triple cation perovskite system, we found that a range of commonly used CTLs induce large non-radiative recombination currents which dwarf the non-radiative losses in the neat perovskite. We identified that the most selective bottom CTLs are the polymers PTAA and PolyTPD and SnO\(_2\) which are outperforming the omnipresent TiO\(_2\) although this can vary depending on the exact preparation conditions and the absorber material. For \(pin\) cells the perovskite/C\(_{60}\) interface was found to be a major issue which induces more interfacial recombination than spiro-OMeTAD. This could be one reason for the lower performance of \(pin\)-type cells with the standard electron transporter C\(_{60}\)-type cells with the standard electron transporter C\(_{60}\). A comparison between the QFLS of perovskite/CTL bilayers, optical \(pin\)- or \(nip\)-type stacks and the \(V_{OC}\) of the complete device shows that the relevant energy losses happen at the top interface in efficient triple cation cells based on PTAA and PolyTPD, SnO\(_2\) and TiO\(_2\). In these systems, the electron/hole QFLs are expected to be spatially flat throughout the junction to the electrodes, meaning that the QFLS in the perovskite bulk equals the \(V_{OC}\) of the cells. This allows further quantification of the parallel recombination currents in the bulk and interfaces and/or metal contacts which define the \(V_{OC}\) of the complete cell. However, in cells with energetically misaligned HTLs such as PEDOT or P3HT, the \(V_{OC}\) is lower than the QFLS in the absorber layer due to an internal bending of the hole-QFL. The fundamental study was validated in high-efficiency perovskite cells in \(pin\)-configuration with PCEs up to 21.4% and through rigorous device simulations. The simulations substantiated the understanding obtained from the experimental results and highlighted the importance of a high built-in voltage and negligible majority carrier band offsets between the perovskite and the transport layers. The presence of an energy level offset at the \(p\)-contact was confirmed with UPS and differential charging capacitance measurements. In order to generalize the findings, additional perovskite systems were studied which showed that the absorber layer often allows a substantially higher \(V_{OC}\) than achieved by the cell. However, a QFLS–\(V_{OC}\) mismatch in complete devices appears also in other systems than those featuring a triple cation absorber with PEDOT:PSS and P3HT HTLs. Therefore, this work allows to conclude that energetic offsets are often harming the device \(V_{OC}\) beyond the limitation imposed by defect recombination in the absorber layer and the interfaces. This implies that proper energy level alignment is a primary consideration to harvest the full potential of the optical \(pin\) or \(nip\) stack. Only then suppression of interfacial defect recombination will allow us to reach the potential of the perovskite absorber, while suppression of defects in the perovskite bulk or at grain boundaries and photon management will be the final goal to improve this technology to its radiative limit.

**Author contributions**

M. S. planned the project, drafted the manuscript, fabricated cells and films, performed electrical measurements, developed the PL setup, measured absolute PL and performed simulations and analysed all data. P. C. developed the PL setup, measured absolute PL and data analysis, measured SEM and contributed to film fabrication and to manuscript drafting. C. M. W. provided important conceptual ideas regarding the identification of the recombination losses, cell fabrication and electrical characterization. J. A. M. performed PL measurements and performed corresponding data analysis and interpretation. J. N. performed PL measurements on cells and films and contributed to electrical measurements. S. Z. performed PESA and UV-Vis measurements and analysis of this data. D. R. fabricated cells and films, and contributed to electrical measurements. U. H. provided important conceptual ideas regarding the development of the PL setup and corresponding data analysis. Y. A. performed TPC, TPV and differential charging measurements with C. M. W. and M. S. A. R. contributed to the analysis of PL data and development of the setup. L. K. fabricated SnO\(_2\) based cells and films and performed corresponding electrical characterizations. F. Z. performed UPS measurements and interpreted corresponding data. S. A. developed SnO\(_2\) based cells and films. N. K. performed corresponding electrical characterizations. T. U. performed numerical simulations and analysed simulation results, contributed to the analysis of PL measurements and recombination losses. D. N. contributed to project planning, manuscript drafting and analysis of all electro-optical measurements. All co-authors contributed to proof reading of the manuscript.
Data availability

The data that support the plots within this paper and other findings of this study are available from the corresponding authors upon reasonable request.

Conflicts of interest

The authors declare no competing financial interests.

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