

Mismatch of Quasi-Fermi Level Splitting and V_{oc} in Perovskite Solar Cells

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Perovskite solar cells have demonstrated low non-radiative voltage losses and open-circuit voltages (V_{oc} s) that often match the internal voltage in the perovskite layer, i.e. the quasi-Fermi level splitting (QFLS). However, in many cases, the V_{oc} differs remarkably from the internal voltage, for example in devices without perfect energy alignment. In terms of recombination losses, this loss often outweighs all non-radiative recombination losses observed in photoluminescence quantum efficiency measurements by many orders of magnitude. As such, understanding this phenomenon is of great importance for further perovskite solar cell development and tackling stability issues. The classical theory developed for Si solar cells explains the QFLS- V_{oc} mismatch by considering the partial resistances/conductivities for majority and minority carriers. Here, the authors demonstrate that this generic theory applies to a variety of physical mechanisms that give rise to such a mismatch. Additionally, it is found that mobile ions can contribute to a QFLS- V_{oc} mismatch in realistic perovskite cells, and it is demonstrated that this can explain various key observations about light soaking and aging-induced V_{oc} losses. The findings in this paper shine a light on well-debated topics in the community, identify a new degradation loss, and highlight important design principles to maximize the V_{oc} for improved perovskite solar cells.

improvements year on year. By now it is expected that they will outperform the best silicon research cells. A major factor in the achievement of such high PCEs is the impressive open circuit voltages (V_{oc}), which are achievable due to low amounts of non-radiative recombination in the device.

The build-up of an internal voltage in a semiconductor is dependent on there being a population of excited electrons in the conduction band and a corresponding population of holes in the valence band. These populations of excited electrons and holes have different chemical potentials, which can be represented in a band diagram by the quasi-Fermi levels (QFL).^[2] Increasing the excited carrier population in the bands increases the difference in chemical potential between electrons and holes (and thus the QFL), which generates an internal potential (or voltage). This internal voltage in a semiconductor is often referred to as the quasi-Fermi level splitting (QFLS) divided by the elementary

charge e . One can determine the QFLS of a semiconductor via the PL quantum yield (PLQY), which is defined as the ratio of emitted to absorbed photons, through the relation; $QFLS = k_B T \ln (PLQY \times J_G / J_{0,rad})$, where J_G is the generation current

1. Introduction

Perovskite solar cells continue to impress with extremely high power conversion efficiencies^[1] (PCEs) that still make

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and $J_{0,\text{rad}}$ is the radiative current in the dark. In perovskite solar cells, the QFLS/ e (where e is the elementary charge) of devices often matches the external voltage (i.e., V_{OC}).^[3]

This strong correlation between the QFLS and V_{OC} is powerful as it allows researchers to pinpoint where voltage losses are occurring in the device by measuring the QFLS of cells, partial cell stacks, and the neat absorber layer. It has allowed researchers to determine that in most cases the QFLS is strongly limited by interface recombination in the device with interface recombination currents often being 10 to 1000-fold larger than that of the bulk.^[3–6] Disentangling the contribution of different interfaces to V_{OC} losses like this is a useful tool in the optimization of cells as one can understand whether i) the interfaces or the absorber limit the V_{OC} , and, ii) if the interfaces are limiting, which interface is the culprit.

While powerful, there are many cases where there is a mismatch between the measured QFLS and the device V_{OC} (which we refer to as QFLS- V_{OC} or Q/V mismatch henceforth interchangeably), which can bring the validity of the QFLS framework into question. Indeed, in our experience, simply using QFLS analysis of partial cell stacks when seeking V_{OC} improvements (e.g., by screening new transport layers) can lead to disappointing results when the device stack that has the highest PLQY leads to a rather low V_{OC} . This is not, however, a demonstration that the QFLS is an incorrect determination of the internal voltage of the semiconductor, but that other issues are occurring in the device, generally in or in the region near the transport layers, which cause a loss in chemical potential of the carriers on their path to the electrodes. We refer to these areas in the solar cell as the “contact regions” throughout the paper synonymous with the critical/limiting interface. Importantly, this loss in chemical potential often outweighs all non-radiative recombination losses that determine the PLQY by many orders of magnitude (Figure S1, Supporting Information). Generally, the mismatch is observed in not yet fully optimized devices.^[3,7] However, it can also occur in efficient devices, e.g. high performance all-perovskite tandem cells (Figure S2, Supporting Information) and during device aging as discussed below.

In this paper, we begin by briefly reviewing the governing mechanisms of Q/V mismatch. Although the general underlying physics of Q/V mismatch has been well described based on surface recombination at metal contacts in other solar cell technologies such as Si,^[8,9] for emerging technologies like perovskites there are a multitude of reasons that can lead to a Q/V mismatch as there are, i) a wide variety of different absorber/transport layer combinations employed, and, ii) chemical instabilities and ionic effects, which can cause local variations in absorber composition and quality. Some of the examples in perovskite cells can be well described by the principles of the model developed for Si cells, whereas other examples are better described by factors such as interface recombination and low mobility. To elaborate on this point, we demonstrate different classes of scenarios by which Q/V mismatch can occur in perovskites – especially highlighting those, which are idiosyncratic to this technology. We determine the likely contributing factors for Q/V mismatch in each case through the combination of real-world examples and simulations. This serves to provide more information to the community about reasons for deviation from expected results in the QFLS framework, especially materials parameters, which will allow a

more rational analysis of open-circuit voltage losses. Through this, the framework of analysis can become more powerful allowing further progress in understanding and improving device performance in perovskite solar cells.

2. Establishing Underlying Physics

In order to exploit the QFLS one needs to extract electrons and holes from the semiconductor to separate electrodes so that they can perform work in an electrical circuit. The quasi-Fermi levels must collapse in the metallic electrode, as the metal (or degenerately doped semiconductor such as indium tin oxide, ITO) cannot support a QFLS due to the continuum of states at the Fermi level. In an ideal scenario, the majority carriers will distribute through their contact regions without losing any of their chemical potential resulting in no Q/V mismatch (Figure 1a). However, as discussed above, Q/V mismatch can and does occur quite often in real cells. In this nonideal case, one or both of the majority carriers lose chemical potential in their respective contact regions, which manifests as a bending of their quasi-Fermi levels (Figure 1b). This begs the question as to what causes the bending of the majority QFL?

At each point in the device, the electrical current density for electrons/holes can be written as

$$J_{e/h} = J_{e/h,\text{drift}} + J_{e/h,\text{diffusion}} = -\sigma_{e/h} \frac{\nabla E_{f,e/h}}{e} \quad (1)$$

where $\sigma_{e/h}$ are the hole and electron conductivities respectively and $\nabla E_{f,e/h}$ are the gradients of the hole and electron quasi-Fermi levels respectively. Note Eq. 1 does not differentiate explicitly between drift ($J_{e,\text{drift}}$) and diffusion ($J_{e,\text{diffusion}}$) currents as both contribute to the total current density. Now we consider steady state V_{OC} conditions. Because there is no external current flowing, the total current in the device, $J = J_e + J_h$ is zero at any point between the electrodes. However, a directional charge carrier motion may still be driven by recombination (charges move from where they are photogenerated to where they recombine) represented by a recombination current density J_R . According to Equation 1, this will cause an unavoidable gradient of the electron and hole QFL. Further, because the total current is zero, $J_h = -J_e = J_R$.^[2,8]

$$\frac{\sigma_h}{\sigma_e} = -\frac{\nabla E_{f,e}}{\nabla E_{f,h}} \quad (2)$$

In other words, the gradients of the electron and hole QFL at V_{OC} are inversely proportional to the ratio of the carriers' conductivities. From his equation, it becomes clear that if most charges are generated in the perovskite bulk but most recombination occurs in the contact region, there will be an unavoidable gradient of the electron and hole QFL in the contact region and this gradient will be larger, the smaller the carrier conductivity. This is the cause of the QFLS- V_{OC} mismatch.

Later, Onno et al.^[9] used this concept to write the QFLS- V_{OC} mismatch with respect to contact resistances by considering a

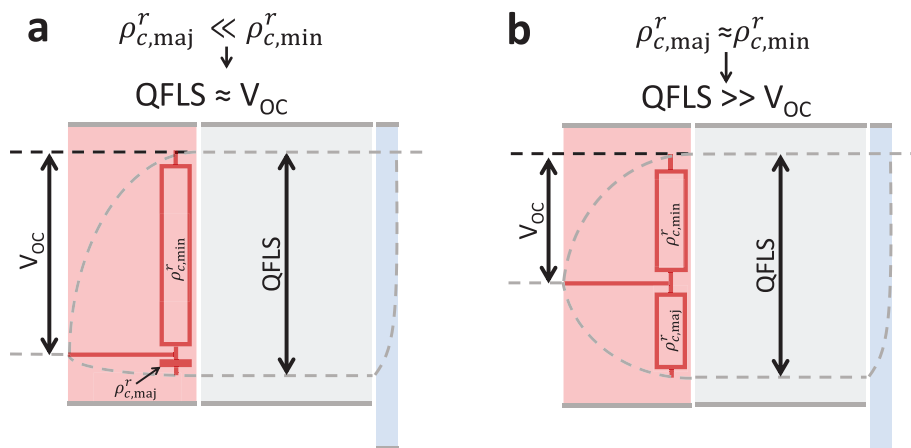


Figure 1. a) Representation of energy level alignment and the position of the quasi-Fermi levels throughout a thin film solar cell. The blue region represents a good electron transport layer, the grey region is the absorber layer, and the red region is a good hole transport layer. A voltage divider is drawn in the hole transport layer to show that a low majority carrier resistance results in a small bending of the majority QFL and therefore there is a low Q/V mismatch. b) An analogous diagram to panel a but this time the hole transport layer is unselective (i.e., the minority and majority carrier resistances are similar) which causes a large Q/V mismatch. Note, in both cases the dominant recombination is assumed to occur at the metal/hole transport layer (HTL) interface, while other scenarios are discussed in the following. Drawing adapted with permission from ref. [9].

voltage divider as shown Figure 1 (for the derivation see Note S1, Supporting Information).

$$\frac{eV_{OC}}{QFLS} = \frac{\rho_{c,min}^r}{\rho_{c,min}^r + \rho_{c,maj}^r} = S_{e,maj} \quad (3)$$

where $\rho_{c,maj}^r$ and $\rho_{c,min}^r$ are the device contact resistances for majority and minority carriers, respectively, measured in Ωcm^2 . The ratio $\rho_{c,min}^r / \rho_{c,min}^r + \rho_{c,maj}^r$ can be defined as the selectivity ($S_{e,maj}$) for majority carriers at the contact, which takes values between 0 and 1.⁹ Note that this equation only describes the mismatch at one metal electrode. We can see more schematically the implications of this equation in Figure 1, which is aided by the similarities of the equation to the voltage divider equation. In this model, photogeneration of charge establishes a QFLS in the bulk which becomes zero at the metal electrode due to infinite surface recombination. Therefore, the QFLS in the semiconductor bulk is equal to the bending of the electron QFL plus the bending of the hole QFL. On the other hand, the voltage loss due to recombination at the anode is determined by the bending of the hole QFL (of the majority carrier), only. In Figure 1a, we show a selective hole contact region (red) where $\rho_{c,maj}^r \ll \rho_{c,min}^r$, which results in a small bending of the majority QFL and a small Q/V mismatch. In many cases, for perovskite solar cells (especially for well optimized ones) the bending is smaller than the error in our determination of the QFLS, which is why we often see that the QFLS and V_{OC} match. Figure 1b shows a bad (nonselective) hole contact region, where $\rho_{c,maj}^r \approx \rho_{c,min}^r$. Here, both electrons and holes are present in the contact region, and they have similar conductivities, making the quasi-Fermi levels bend towards each other equal and $eV_{OC} = \frac{1}{2} QFLS$.

In this generic case, the Q/V mismatch can be avoided if the metal electrode Fermi level is aligned with the valence band of the perovskite which greatly increases the conductivity for majority charges in the contact region (remote doping due to charge

injection). Moreover, the Q/V mismatch can be avoided if the majority/minority carrier mobility in the contact region (TL) is sufficiently high/low (kinetic selectivity) or if there is a substantial barrier for minority carriers as in the blue electron transport layer (ETL) in Figure 1a, b, which drastically decreases the minority carrier density and concurrently their conductivity (energetic selectivity). Lastly, it is important to consider that the degree of QFL bending to the electrode depends on the recombination velocity at the (semiconductor/metal) interface (S). Only in case of an infinite recombination velocity, as considered in Figure 1, will the quasi-Fermi levels merge (Figure S3, Supporting Information). This is true for metals with a large density of states near the Fermi level and very fast thermalization of carriers (e.g., Würfel et al.^[8] gave a surface recombination velocity at the metal surface of $10^{12} \text{ cm s}^{-1}$ while Onno et al. assumed an even higher recombination velocity of $10^{20} \text{ cm s}^{-1}$). In most cases considered here, recombination will occur at the interface between the perovskite and a semiconductor, e.g. an electron- or hole-transporting layer, with a finite recombination velocity. As a result, there remains a substantial QFLS at the recombining interface and the bending of the electron- and hole QFL will be reduced, and Equation 3 is not valid anymore. In case the other contact is ideally selective, as assumed in Figure 1, this “interfacial” QFLS now determines the V_{OC} . Therefore, despite the increased complication in our solar cell, Equation 3 still holds qualitatively, because the carrier with the larger ρ_c^r will dominate the QFL bending at that contact and as such determine the Q/V mismatch. In fact, a finite recombination velocity can be taken into account in Figure 1 by adding a third resistor, presenting the recombination, in series with $\rho_{c,min}^r$ and $\rho_{c,max}^r$. The theoretical treatment of this situation is, however, beyond the scope of this paper. We also note that previous work have established analytical expressions to determine the actual surface recombination currents and their effect on the V_{OC} , e.g.^[10,11]

This simple solar cell model is very useful as it shows the origin of Q/V mismatch is due to i) high enough minority carrier

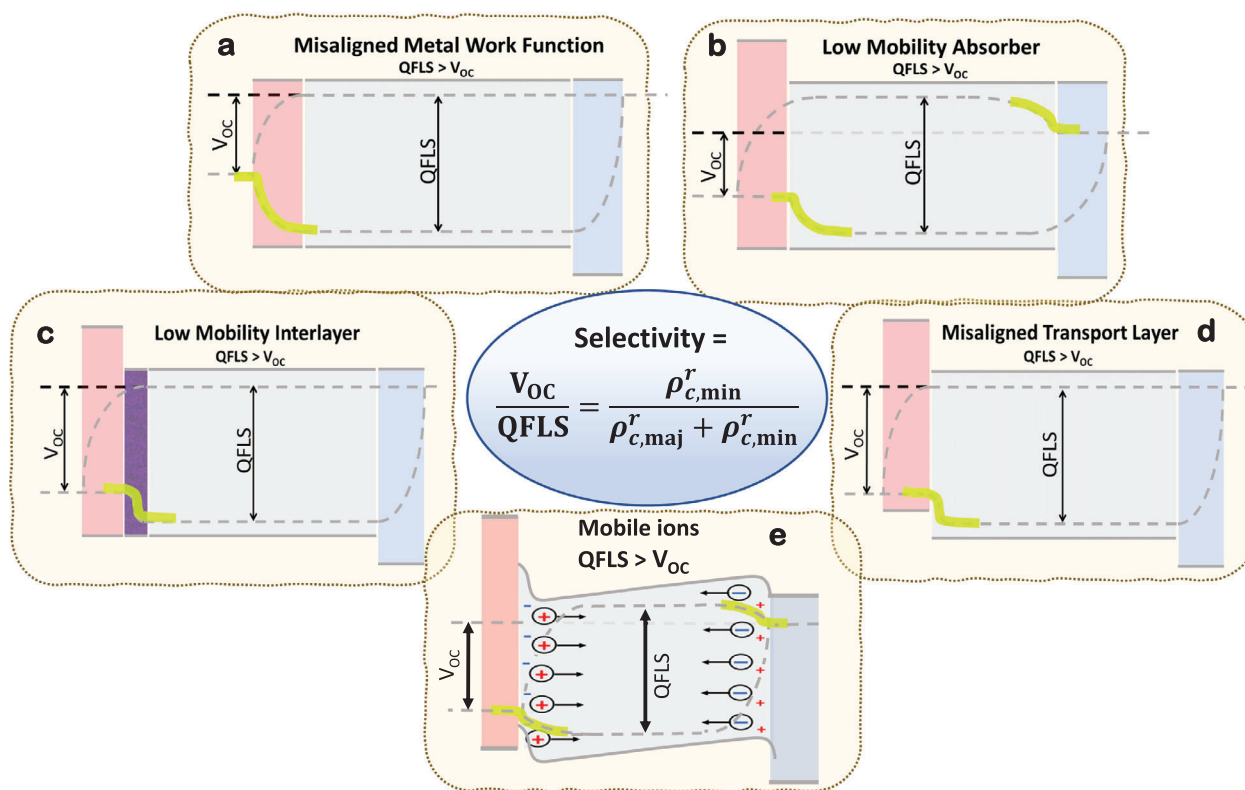


Figure 2. Scenarios where a QFLS – V_{oc} mismatch can occur in perovskite solar cells, which are; a) misaligned metal work functions; b) low mobility absorbers; c) low mobility interlayers, which can either be homo or hetero interlayers; d) misaligned transport layers and; e) energy barriers due to mobile ions.

densities at an interface and ii) fast recombination at that interface (due to a high surface recombination velocity S), however, it only considers that this recombination happens at the metal contact. In well-performing perovskite solar cells, the device structure is already very different from the model, as there are transport layers with energetic offsets for minority carriers that reduce their concentration at the metal. As perovskites have low bulk recombination, it follows that the QFLS and V_{oc} are most often limited by interface recombination at the perovskite/TL heterojunctions instead. Additionally, perovskite researchers often seek device improvements through the use of interlayers which creates additional complication to the analysis. In the remainder of this letter, we identify and experimentally demonstrate different scenarios where Q/V mismatch can occur in perovskites, which are highlighted in **Figure 2**. Through the use of simulations, we qualitatively relate them to Equation 3 and identify critical parameters that govern the Q/V mismatch.

3. Results and Discussion

3.1. Different Mechanism Resulting in A Q/V Mismatch

3.1.1. Misaligned Metal Wf

We begin with the case which is directly related to the model of Onno et al. shown in Figure 1 where a metal with a misaligned work function and the absorber are in di-

rect contact, causing a Q/V mismatch. To test this, we fabricated *pin*-type perovskite solar cells with the device structure: ITO/ $\text{Cs}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ (83-17 triple cation perovskite)/ C_{60} /bathocuproine (BCP)/Cu. In this structure, the perovskite is in direct contact with the ITO electrode that has a significant offset for majority carriers of approximately 750 meV, which can be readily measured by ultraviolet photoelectron spectroscopy (UPS) (**Figure 3a,b**). This corresponds, to a contact region without energetic selectivity (no energy barrier for electrons and holes) and without kinetic selectivity (i.e., no mobility/carrier density imbalance). Considering similar mobilities for holes and electrons in the perovskite, the resistance in the contact region for both carriers should be similar, giving a considerable Q/V mismatch. Figure 3c shows the obtained QFLS and V_{oc} we measured in these devices (mean QFLS = 1.15 eV; mean V_{oc} = 0.55 V). Therefore, we observe a Q/V mismatch and there is a bending of the QFL for holes toward the ITO which is in line with expectation. We note if the metal or transparent conductive oxide (TCO) work function is closely aligned to the perovskite valence band, the surface recombination will be inherently reduced in a very similar manner to having a well-aligned HTL (see Figure S4, Supporting Information). Indeed, HTL-free devices can be very efficient as demonstrated in ref.[12] as it depends on the exact, energy alignment.[13] Moreover, the polar character of various self assembled monolayers employed in recent literature[7,14] allows shifting the metal/TCO Wf to better align with the perovskite valence band. This was recently

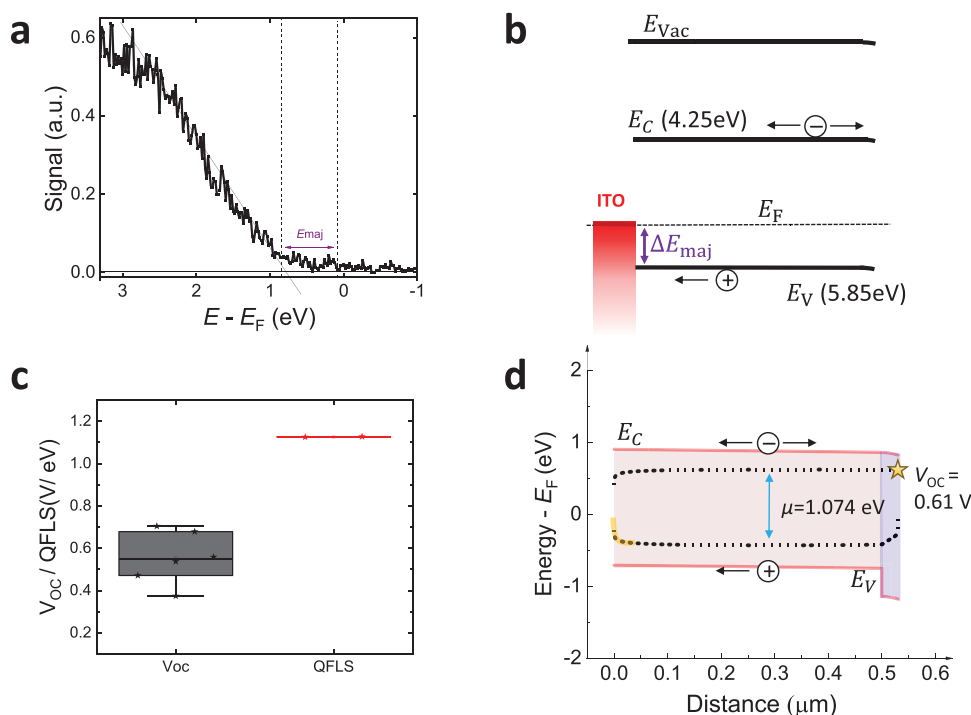


Figure 3. a) Experimentally measured valence band spectrum of an 83:17 triple cation perovskite on an ITO substrate using ultraviolet photoelectron spectroscopy (UPS). b) Deduced band diagram under near open-circuit conditions from UPS. c) the open-circuit voltage (V_{OC}) and QFLS of an ITO/83:17/C60/BCP/Cu device. d), Simulated ITO/83:17/C60/BCP/Cu device using the same measured energy offset between ITO and perovskite.

demonstrated for wide-bandgap triple cation perovskite cells (1.8 eV), where the commonly employed HTL poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) is typically misaligned with respect to the perovskite valence band.^[7] Thus, replacing PTAA with the Me-4PAC, which has a much deeper highest occupied molecular orbital (HOMO) (5.8 eV) than PTAA (5.2 eV) and also a significant dipole moment, allows to reduce the QFLS- V_{OC} mismatch thereby improving the V_{OC} .^[14]

Using the SCAPS simulation software package (full details described in the Supporting Information) we can reproduce a Q/V mismatch using the measured majority carrier offset when we use a recombination velocity $S \geq 1 \times 10^7 \text{ cm s}^{-1}$ for both carriers at the metal electrode.^[15] The simulated QFL-bending is shown in Figure 3d. In practical terms, an experimentalist may observe this in both *pin* and *nip*-type cells if there is a discontinuous transport layer on top of their transparent conductive oxide. If a strong Q/V mismatch is observed during the optimization of said TL, this could be the underlying reason.

3.1.2. Misaligned (Undoped) Transport Layers

Having confirmed that a perovskite solar cell behaves as expected in the archetypal case above we proceed to investigate cases that occur more commonly during perovskite research. An important scenario that causes a Q/V mismatch is a misaligned TL, which can become a dominant and strong loss if the offset is large. There are numerous examples where the V_{OC} loss was attributed to a misaligned TL.^[3,16,17] For example,

we showed in our previous work that *pin* cells with a structure (ITO/poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS)/Perovskite/C₆₀/BCP/Cu) had a Q/V mismatch (QFLS = 1.07 eV; V_{OC} = 0.91 V) and with a structure (ITO/poly(3-hexylthiophene) (P3HT)/Perovskite/C₆₀/BCP/Cu) had a Q/V mismatch (QFLS = 1.10 eV; V_{OC} = 1.02 V).^[3,16,17] We note that in other reports P3HT and PEDOT:PSS were found to be more efficient as it depends on the exact interfacial energy alignment, which is influenced by the processing and composition of the perovskite layer and the HTL layer.^[18,19] A misaligned TL, i) creates an injection barrier for the majority carriers back into the perovskite, and, ii) reduces the built-in field across the device.^[20] Due to the injection barrier, the majority carriers cannot equilibrate across the interface, which simultaneously reduces their population in the perovskite at the interface and increases their population in the TL (Figure 4a). Consequently, (also from increased injection from the metal) there is an increase in majority charge in the TL that attracts and increases the minority carrier population in the perovskite at the interface, which is further exacerbated by the decreased built-in field. As ρ_c^r is inversely proportional to carrier density, this decreases $\rho_{c,min}^r$ and increases $\rho_{c,maj}^r$, rendering the contact region less selective. At the same time, the increase in minority carrier density at the perovskite/HTL interface causes an exponential increase of the recombination and a direct loss in V_{OC} . This is validated as the total recombination current at a fixed voltage scales with the increase in minority carrier concentration at the interface, and increases exponentially with the band offset (Figure S5, Supporting Information). It is also important to consider that

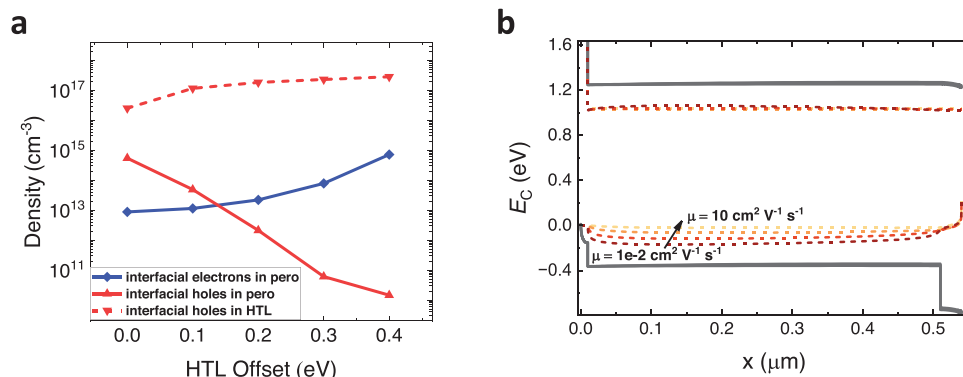


Figure 4. The effect of misaligned transport layers on Q/V mismatch. a) Interfacial carrier densities at the HTL at a fixed voltage of 0.85 V (V_{OC} of the device with the largest energy offset) with varying offset, showing a reduction in hole population coupled with an increase in electron concentration in the perovskite; b) The effect of mobility on the quasi-Fermi levels for a perovskite solar cell simulated with a 200 meV offset at the HTL.

without interfacial recombination the Q/V mismatch does not occur (Figure S6, Supporting Information).

Relating back to Equation 3, we remind the reader that the situation considered here differs from the scenario in Figure 1, where we assumed that all recombination is at the metal surface with infinite surface recombination. Here, most recombination is at the HTL/perovskite interface and the recombination velocity is finite. As argued earlier, Equation 3 still holds qualitatively and the larger is $\rho_{c,maj}^r$ relative to $\rho_{c,min}^r$, the larger is the Q/V mismatch. It is important to note that the electron and hole mobilities μ_e and μ_h are critical parameters for Q/V mismatch in all cases. This is because the bending of the quasi-Fermi levels in the device is due to a fast recombination process which outstrips the transport of carriers to the interface where the recombination is happening. Figure 4b shows the effect of varying device mobility on the quasi-Fermi levels in our standard simulation with a 200 meV offset at the HTL. We observe that as the mobility increases, the quasi Fermi level for holes flattens as the holes can more quickly diffuse to that interface and recombine. The result is that as the mobility increases, the QFLS goes down while the V_{OC} remains approximately the same, which reduces the Q/V mismatch (Figure S7, Supporting Information). This is consistent with a work by Spies et al., who previously showed the effect of charge transport on the interplay between the QFLS and the V_{OC} .^[21] In the following, the impact of mobility will be critical in the cases that follow.

3.1.3. Low Mobility Interlayers

In perovskite research, the use of interlayers at the perovskite/TL interface to improve performance is a very common strategy. These interlayers can be a number of different things including organic salts,^[22–24] metal salts,^[25–27] and insulating polymers.^[28–30] These insulating interlayers can have both a direct chemical passivation effect as well as reduce interface recombination by physically separating the perovskite from the ETL.^[6,31] In Figure 5a we show both the V_{OC} and QFLS for triple cation *pin* cells with a polymethyl methacrylate (PMMA) in between the perovskite and the C_{60} with different solution concentrations which modifies the thickness as we keep the spin

speed and acceleration the same (performance statistics Figure S8, Supporting Information).^[32] One can see that with increasing concentration, there is an initial improvement in V_{OC} which follows the QFLS. The improved V_{OC} can be attributed to a reduction of C_{60} -induced recombination due to passivation or physical separation.^[28,31] However, when we use a PMMA solution concentration of 1 mg mL⁻¹, we start to get a strong Q/V mismatch as the QFLS continues to improve but the V_{OC} starts to decrease. The results demonstrate there must be a bending of majority QFL, which can be qualitatively reproduced in the simulations by introducing a low mobility interlayer. As shown in Figure 5b, the QFLS continuously increases while the V_{OC} decreases with increasing thickness of the interlayer. Moreover, the recombination at the perovskite/interlayer was turned off but was considered at the interlayer/ C_{60} interface. Figure 5c demonstrates the simulated QFL gradient in the case of a low-mobility interlayer ($\mu_e = 10^{-4}$ cm² V⁻¹ s⁻¹) when its thickness is 20 nm. We can see in our simulations that as the layer thickness increases, the carrier densities for electrons and holes at the interlayer/ C_{60} interface become more similar (Figure 5d). As μ_e and μ_h are both 1×10^{-4} cm² V⁻¹ s⁻¹ and the conductivity is proportional to the product of the mobility and the carrier density, one can see that Equation 3 also apply here as $\rho_{c,min}^r$ and $\rho_{c,maj}^r$ become more similar. The reason for the strong QFL bending is that interface recombination quickly removes carriers and they cannot diffuse fast enough to the interface to have a flat QFL throughout the device (as alluded to above). The Q/V mismatch is further exacerbated by a raising of the QFLS in the absorber with increasing interlayer thickness due to a reduced transfer rate through the interlayer to the transport layer.

3.1.4. Low Mobility Perovskite

As we have seen with previous examples, mobility has an important role to play in Q/V mismatch for both interlayers and the HTL offset. We were therefore interested in investigating the overall mobility of the absorber in our standard cell and its effect on Q/V mismatch. Realistic values for in device perovskite mobility are ≈ 1 cm² V⁻¹ s⁻¹ when using methods that assess intergrain mobilities.^[33] This mobility is already

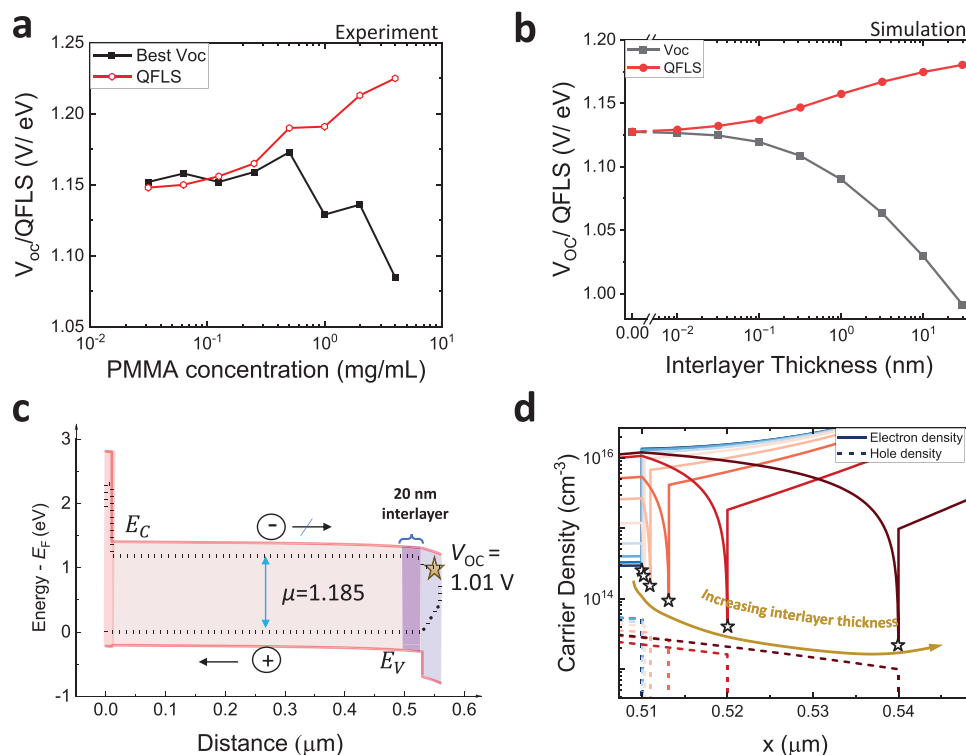


Figure 5. a) The effect of thickness (analogous to concentration) of a PMMA interlayer on the QFLS and V_{OC} . b) Simulated quasi-Fermi level splitting and V_{OC} versus thickness of the low mobility-interlayer ($\mu = 1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). c) Simulated band diagram demonstrating the effect of a low mobility interlayer on the Q/V mismatch; the majority QFL in the interlayer can be seen bending significantly reducing the external voltage. d) Electron and hole concentrations through low mobility interlayer with increasing thickness; one can see that the electron and hole concentrations become more similar at the C_{60} interface (denoted by stars in the figure) as the thickness increases.

significantly lower than that of semiconductors like GaAs and Si and can be further reduced by insulating additives in the perovskite layer. One common example of this is in 2D/3D perovskites which are of interest because of their potentially higher stability compared with 3D perovskites.^[34,35] Such perovskites have anisotropic charge transport with high in-plane mobilities and very low out-of-plane mobilities due to layers of insulating spacer cations (such as phenylethylammonium) in between the lead halide octahedra.^[36] This means that the effective mobility of such perovskites can be very low if the orientation of the lead halide planes is not perpendicular to the substrate, which requires significant synthetic effort.^[35,37] We fabricated a series of mixed 2D/3D perovskites by adding a separate 2D solution with the stoichiometry $\text{PEA}_2\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_4$ into the triple cation solution (see SI Methods) and measured their QFLS and V_{OC} (Figure 6a,b). We observe that as soon as we introduce 2% 2D perovskite into the precursor solution, we start to get a Q/V mismatch, which continues to increase up to 20% 2D perovskite where we have a Q/V mismatch of ≈ 250 mV.

In this instance, the working mechanism is likely very similar to a low-mobility interlayer. Namely, the carriers in the bulk can not diffuse fast enough to the interface, and rapid non-radiative recombination at that interface lowers the QFLS at the interface, while the bulk QFLS is high. This causes the majority and minority carrier densities (and thus their conductivities/resistivities) to become similar at the interfaces, which gives a Q/V mismatch

(Equation 3). We are able to simulate this effect and show the quasi-Fermi level bending with differing mobility in Figure 6c and the calculated QFLS and V_{OC} in Figure 6d. We measured our control, 2.5% and 10% 2D samples with the rise in photovoltage (RPV) method and saw that there is an increase in the time for the photovoltage to rise (Figure S9, Supporting Information), which indicates a decrease in mobility. This is further ratified by the qualitative similarity of simulated JV curves with our measured JV curves when we reduce the mobility in our standard simulation (Figure S10, Supporting Information). This again shows the importance of this phenomenon in perovskite solar cells as there are few technologies, which have such high performance with mobilities $\approx 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ or lower. Indeed, if the mobility of perovskites were lower and interface recombination currents were similar as they are now, the equivalence of QFLS and V_{OC} would not hold.

However, 2D layers can be highly beneficial for the V_{OC} by reducing the minority carrier concentration at the critical interface as demonstrated many times.^[38–40] To exemplify this we spin-coated phenethylammonium iodide (PEAI) on top of a $\text{Cs}_{0.05}(\text{MA}_{0.05}\text{FA}_{0.95})_{0.95}\text{Pb}(\text{I}_{0.95}\text{Br}_{0.05})_3$ “FAPI-rich” perovskite which is known to form a 2D layer on the surface.^[41–44] As shown in Figure 7a,b, this improves the performance through a higher V_{OC} although the J_{SC} is slightly reduced. We speculate that this suppresses the minority carrier concentration at the critical interface which can, for example, alleviate the losses due to an energy level mismatch between the perovskite and the C_{60}

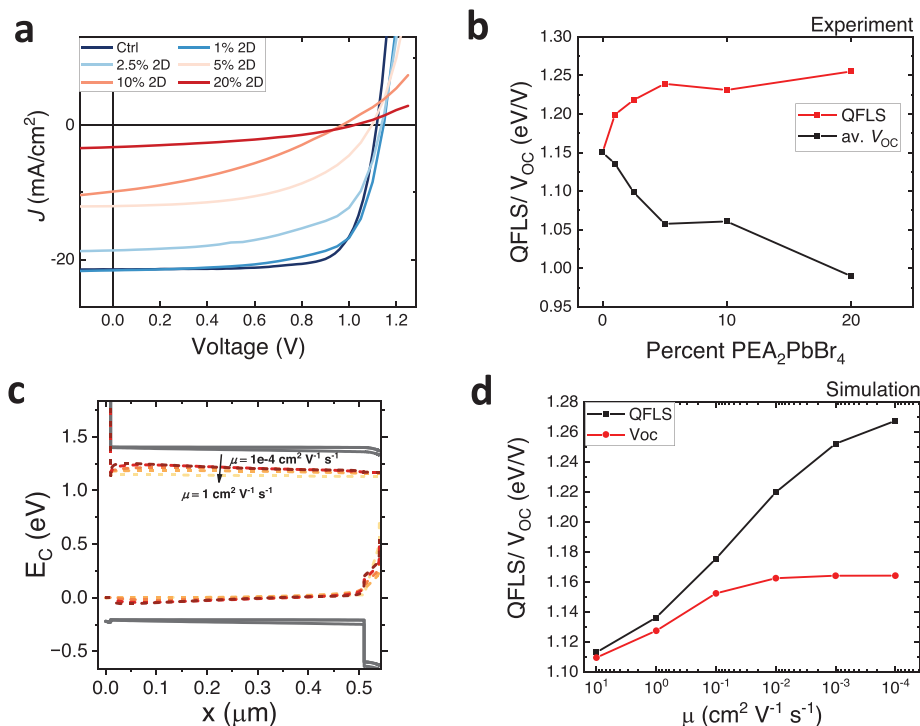


Figure 6. The effect of a low absorber mobility on Q/V mismatch. a) J/V characteristics of pin perovskite solar cells with differing amounts of 2D perovskite added to the precursor solution. b) Quasi-Fermi level splitting and open-circuit voltage (V_{oc}) of the cells with differing 2D content. c) Simulated band diagrams of *pin* perovskite solar cells with differing absorber mobilities, showing bending of the quasi-Fermi levels at the interfaces, due to interface recombination. d) Calculated QFLS and V_{oc} of *pin* perovskite solar cells with differing mobilities.

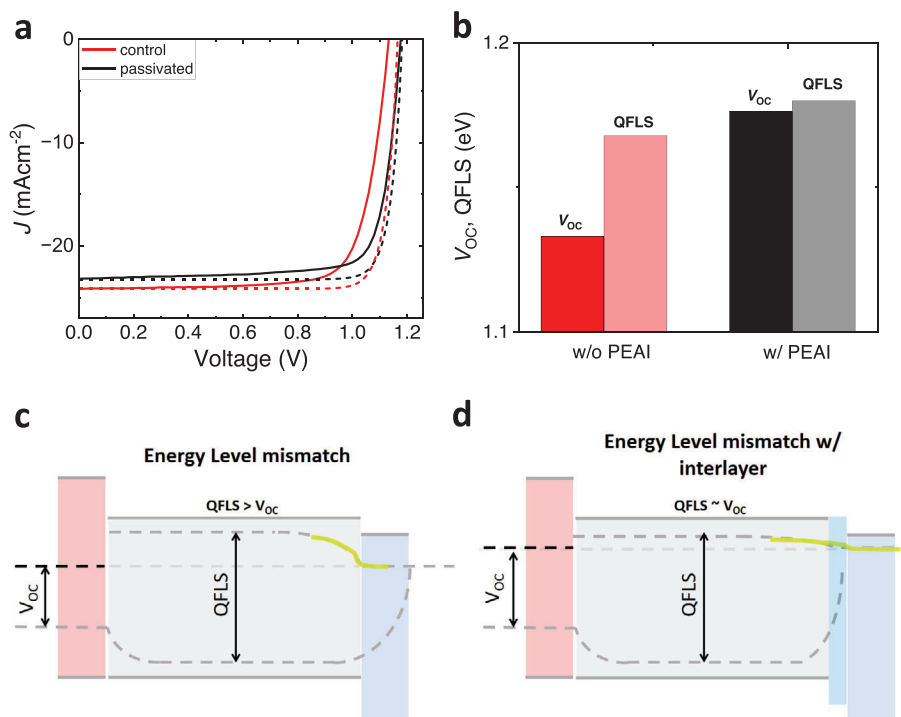


Figure 7. a,b) J/V characteristics and pseudo-J/V characteristics obtained through PL measurements of *pin*-type Cs_{0.05}(MA_{0.05}FA_{0.95})_{0.95}Pb(I_{0.95}Br_{0.05})₃ FAPI-rich perovskite solar cells with and without PEAI which likely forms a 2D perovskite on the surface. c, d) Schematic band diagrams. Considering that the as-prepared perovskite exhibits a $QFLS-V_{oc}$ mismatch, we speculate that C₆₀ layer is misaligned with respect to the perovskite.^[45] In this case, a blocking layer, such as a 2D perovskite can reduce the $QFLS-V_{oc}$ mismatch by reducing the minority carrier density at the critical interface (Equation 3).

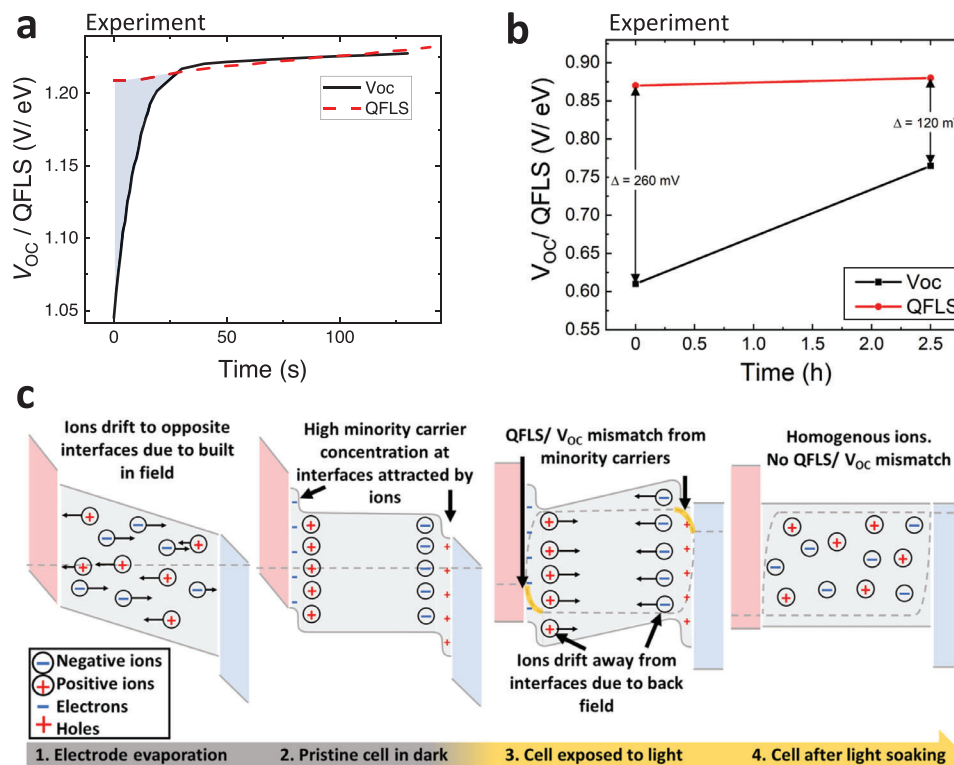


Figure 8. Light soaking effects of V_{OC} . a) Change in QFLS/ V_{OC} mismatch in triple halide perovskite device in the first 120 s of illumination. A strong mismatch is observed in the first seconds which disappears after the first 30 s. There is a small improvement in the QFLS of ≈ 20 mV over this timeframe which is outweighed by the 170 mV increase in V_{OC} . b) Change in QFLS/ V_{OC} mismatch in a pure Sn perovskite system after 2.5 h of light soaking. c) Schematic showing a general mechanism proposed by Herterich et al.^[52] for transient changes in the QFLS/ V_{OC} mismatch due to ion motion.

layer.^[45] The proposed mechanism is highlighted in Figure 7c,d. Similarly, we have previously shown for *nip*-type perovskite cells that the introduction of 2-thiophenemethylammonium bromide (2-TMABr) on top of a triple cation perovskite ((FAPbI₃)_{0.87}(MAPbBr₃)_{0.13}[(CsPbI₃)_{0.92}(CsPbI₃)_{0.08}]) forms a 2D layer, which reduces the detrimental effect of the energy offset at the perovskite/SpiroOMeDAT interface. This reduces the QFLS- V_{OC} mismatch and improves the V_{OC} and allows us to overcome the interfacial recombination losses at the *p*-interface.^[16] Moreover, perovskite salts such as PbI₂, or imidazolium bromide (ImBr) with a wide bandgap often work in a similar way as recently highlighted in ref.[7] This highlights that such V_{OC} improvements are often not the result of chemical passivation (which can be checked by comparing the PL of the neat layer with and without the additive) but rather the management of charge carriers at the interfaces and selectivity.

3.1.5. Mobile Ions

Light Soaking Effects: Transient changes in the V_{OC} , that occur in the $\approx$ s to $\approx$ hours timescale are commonly observed in perovskite solar cells.^[46–50] These either positive or negative changes are often referred to by the research community as “light soaking” effects. As there is a strong correlation between V_{OC} and QFLS, a reasonable hypothesis would be that the PLQY of the device increases with light soak-

ing which correspondingly increases the V_{OC} . However, we have observed light-soaking effects in our lab where the V_{OC} improves by over 100 meV (sometimes 500 meV).^[51] If this was due to an improvement in QFLS, it would require the PLQY to improve several orders of magnitude, which is not observed.

Intrigued by this phenomenon we studied a 1.69 eV triple halide (TH) perovskite, where ≈ 60 s was required for the V_{OC} to stabilise and it increased by ≈ 170 mV in this timeframe (Figure 8a). When we compare this to the QFLS of a pristine TH perovskite cell, we find that, while the QFLS does increase by ≈ 20 mV in the same timeframe it does not account for the total V_{OC} improvement. We believe that this phenomenon must also occur in many other perovskite systems, which will confuse QFLS analysis of stacks and complete devices. We further observed this in Sn perovskite cells where a 260 mV initial QFLS/ V_{OC} mismatch decreased to 120 mV after 2.5 h of light soaking (Figure 8b). This supports the common occurrence of this phenomenon in quite different perovskite systems. Indeed, Herterich et al.^[52] recently reported a similar light-soaking effect in *pin* triple cation cells. Using a drift-diffusion model of their solar cell, they were able to well reproduce a strong Q/V mismatch by incorporating mobile ions which they believed to be A-site cation vacancies due to their comparatively small diffusion coefficient. Their model shows that changes in space charge due to the motion of mobile ions (because of the changing field in the device upon illumination) cause strong changes in $\rho_{c,maj}^r$ and $\rho_{c,min}^r$

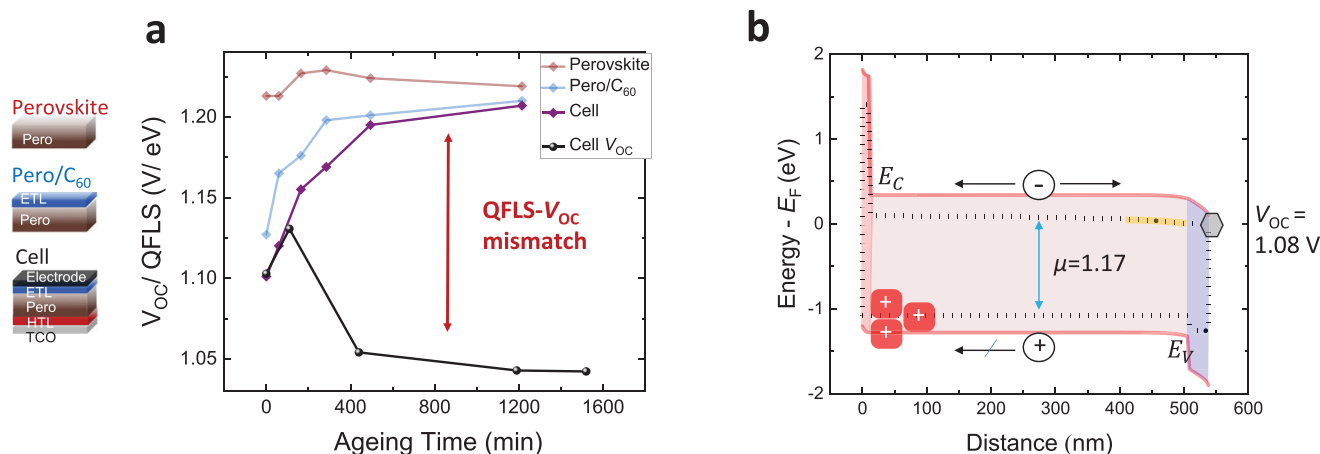


Figure 9. a) Quasi-Fermi level splitting (QFLS) of encapsulated partial and complete cell stacks and the open-circuit voltage (V_{OC}) of a cell as a function of illumination time with a 1 sun equivalent intensity demonstrating a mismatch between both quantities with longer illumination. b) Simulated band diagram demonstrating the effect of a large mobile cation density (halide vacancies) of 10^{17} cm^{-3} on the Q/V mismatch. The simulations show that the halide vacancies accumulate at the hole selective contact (red squares), which increases the hole density throughout the bulk and at the electron selective contact, while the electron population is increased close to the HTL and reduced close to the ETL. This can explain the reduced electron selectivity and observed Q/V mismatch close to the ETL.

thus causing this transient voltage loss. The change is due to an induced doping caused by carrier accumulation where the (opposite) ionic charge resides. We have illustrated and further clarified the proposed mechanism in a symmetrical case where both positive and negative ions are mobile in Figure 8c. This important and interesting effect of changes in local conductivity from mobile ion motion may govern the transient open-circuit voltage and overall efficiency of many devices. Further investigation into state-of-the-art devices as to their ionic distributions and densities should be carried out to see whether it is limiting their performance.

Device Degradation: Another key observation where the Q/V mismatch plays a crucial role is device degradation. To investigate the Q/V mismatch as a function of aging we illuminated our control device under constant 1 sun equivalent illumination under open-circuit conditions and we measured the QFLS and V_{OC} in regular intervals (Figure 9a). We can clearly observe that a Q/V mismatch starts to develop after ≈ 200 min. Figure 8a also highlights the QFLS of the corresponding partial cell stacks of the device. Similar losses also occur also in a methyl ammonium lead iodide (MAPbI₃) and a Cs_{0.15}FA_{0.85}Pb(I_{0.75}Br_{0.25})₃ (CsFA) double cation perovskite we studied (Figure S11, Supporting Information), pointing to a general aging-induced degradation loss. Although, we do not exclude alternative interpretations at this point, we can reproduce the data with an increased mobile ion density upon aging which could be driven towards the interfaces by a residual internal field under V_{OC} conditions in the control device. As shown in Figure 9b, when we add a mobile cation density of 10^{17} cm^{-3} into the simulation corresponding to more halide vacancies in the aged device, we observe an increased Q/V mismatch in the region close to the electron selective interface. Careful analysis reveals that the hole density is increased throughout the bulk and at the perovskite/ETL interface as the cations hinder the extraction of photogenerated holes. In addition, the electron density is increased at the HTL/perovskite interface and depleted at the perovskite/ETL interface as they are attracted by the cations (Figure S12, Supporting Information). Therefore, the resistivities

$\rho_{c,maj}^r$ and $\rho_{c,min}^r$ become more similar, which reduces the selectivity (Equation 3) and causes the observed bending of the electron QFL towards the interface to the electron selective transport layer. Overall, we can conclude that, in contrast to light soaking, where a preexisting accumulation of slow ions may be present at the interface that can slowly dissipate throughout the bulk under illumination and V_{OC} , the reverse process, i.e., more accumulation of mobile ions at the interface is also possible, in particular in aged devices.

4. Conclusion

Although perovskite solar cells can reach low V_{OC} losses, not-yet-optimized devices or aged devices suffer from a large reduction of the external voltage with respect to the internal voltage in the absorber layer. In this work, we reinvestigate the origin of the Q/V mismatch based on established knowledge which considers the partial resistance to majority and minority carriers in close proximity to a contact. Here, we expand the theory to a range of different real-world scenarios with completely different device structures that lead to such Q/V mismatch. These primary examples were i) a *misaligned metal work function*, ii) a *misaligned transport layer*, iii) a *low-mobility interlayer*, iv) a *low mobility absorber*, and v) the *effect of mobile ions*. Using a combination of experimental techniques with numerical simulations we are able to confirm that the underlying physical reason for these scenarios is always a fast non-radiative recombination process in the contact region (next to the metal contact or the charge transport layer) outstripping the diffusion of carriers to the interface. Through the understanding gained we are able to show that the key interface for such a loss varies depending on the exact structure used. We also highlighted that 2D layers and other wide-bandgap perovskite salts can reduce the Q/V mismatch by reducing the minority carrier density at the interface, which can substantially improve the V_{OC} . We then show that the discussed

scenarios are highly relevant to a large range of key phenomena in perovskite cells related to mobile ions, such as light soaking and device aging which demonstrate a remarkable time dependence of the QFLS- V_{OC} mismatch. The findings in this paper shine a light on well-debated topics in the community with respect to the importance of mobile ions, the energy alignment, the built-in field, light soaking, and the effects of device-aging and highlight important design principles for improved perovskite solar cells by matching the external with the internal voltage.

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

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

mobile ions, non-radiative recombination, perovskite photovoltaics, quasi-fermi level splitting, solar cells

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