Pathways towards 30% efficient perovskite solar cells

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Abstract

Perovskite semiconductors have demonstrated outstanding external luminescence quantum yields, therefore potentially allowing power conversion efficiencies (PCE) close to the thermodynamic limits. However, the precise conditions that are required to advance to an efficiency regime above monocrystalline silicon cells are not well understood. In this work, we establish a simulation model that well describes efficient p-i-n type perovskite solar cells (PCE~20%) and a range of different experiments helping to quantify the efficiency-limiting processes in state-of-the-art devices. Based on these results, we studied the role of important device and material parameters with a particular focus on chemical doping, carrier mobilities, energy level alignment and the built-in potential (V_BI) across all stack layers. We demonstrate that an efficiency regime of 30% can be unlocked by optimizing the built-in potential across the perovskite layer by using either highly doped (10¹⁹ cm⁻³) thick transport layers (TLs) or ultrathin undoped TLs, e.g. self-assembled monolayers. Importantly, we only consider parameters that have been already demonstrated in recent literature, that is a bulk lifetime of 10 µs, interfacial recombination velocities of 100 cm/s, a perovskite bandgap (E_gap) of 1.47 eV and an EQE of 95%. A maximum efficiency of 31% is obtained for a bandgap of 1.4 eV using doped TLs. The results of this paper promise continuous PCE improvements until perovskites may become the most efficient single-junction solar cell technology in the near future.

Introduction

Over the last 10 years perovskite solar cells have triggered an enormous research interest and with power conversion efficiencies of 25.2%¹ they are close to the efficiencies of monocrystalline silicon solar cells (26.7%).²³ As such, perovskites provide an exciting opportunity to approach the ultimate efficiency limitations of single junction perovskite solar cell as predicted by Shockley and Queisser⁴ due to their exceptional optical and material properties. An optimal semiconductor for solar cell applications must basically fulfill three requirements, that is (i) a high absorption coefficient, in particular strong absorption at the band edge, (ii) long charge carrier diffusion lengths to efficiently collect charges in several hundred nm thick films and (iii) a high photoluminescence quantum yield.
(PLQY). Despite the impressive efficiencies there are many other key considerations that need to be addressed prior to a successful commercialization of the technology, such as the environmental stability the toxicity of the lead, and scalability of the fabrication processes. Notwithstanding these points, in order to improve the efficiencies of state-of-the-art perovskite cells further it is imperative to supress all non-radiative recombination to an absolute minimum. This is particularly the case for the perovskite/transport layer (TL) interfaces but also in the perovskite absorber itself. This task requires a deep understanding of defect chemistry and device physics. Very encouraging in this regards are recent studies which highlighted exceptional external PL efficiencies (PLQY) in several perovskite compositions. For example Braly et al. demonstrated an external fluorescence yield of 20% with a charge carrier bulk lifetime (τ_bulk) of approximately 8 μs on even the most standard perovskite absorber which was passivated with TOPO. Even higher PLQYs were demonstrated Abdi-Jalebi et al. on a neat, unpassivated mixed perovskite film (66%) however, no lifetimes were specified. It is also clear, that when it comes to complete cells, a key consideration is the non-radiative loss at the interfaces. A suitable approach to quantify the non-radiative recombination loss at the interface is based on absolute photoluminescence. In fact, many recent record cells, now commonly report quantum efficiencies of several % which underline the exceptional opto-electronic quality of the whole device stack. Important parameters that define the non-radiative recombination loss at the interfaces are the interface recombination velocity (S) and the energy offsets between the TLs and the perovskite. In very high efficiency systems, S can be reduced to be on the order of 10 cm/s although this parameter is not routinely quantified in the literature and further research must be done to clearly disentangle the interfacial charge transfer and recombination based on kinetic measurements, such as transient PL.

Another key consideration to improve the efficiency of single junction cells is to lower the bandgap (E_gap) to the optimum value in the Shockley-Queisser model (e.g. ~1.34 eV). Commonly used perovskites such as methylammonium lead iodide (MAPI) and formamidinium lead iodide (FAPi) do allow some flexibility in modifying the bandgap within a range of 1.6 eV to 1.47 eV, while CsPbBr3 allows to increase the bandgap further to 2.4 eV which is an important consideration for tandem solar cell applications. Notably, both MAPI and FAPI perovskite cells allow achieving PCEs above 20%. Moreover, the introduction of tin-based perovskites enables a further reduction of the bandgap to approximately 1.1-1.2 eV (MAPb0.5Sn0.5I3). The incorporation of small amounts of Sn as a cation allows reducing the bandgap to the optimum bandgap in the S.Q. model (1.3-1.4 eV) and PCEs above 21% have been reported for cells based on a 1.22 eV perovskite bandgap in 2019. Unfortunately, tin perovskite brings other problems due to the high probably of oxidation from Sn2+ to Sn4+. Other key parameters include the donor and acceptor density (τ_dop) in the TLs (i.e. doping), the charge carrier mobilities (µ), as well as the kinetics and density of mobile ions which can cause recombination losses or screen the internal field and are causing hysteresis. Important parameters include the built-in field across the device (V_Bi) and the energy alignment between the perovskite and the charge TLs (ΔE_maj). It is fair to say that until today the impact of most of these parameters remains heavily debated in the community and there exist many conflicting findings in the literature with regard to these parameters. For example, some literature reports suggest that the energy alignment does not play an important role for the device performance, which is in contrast to other studies where the V_OC correlated to ΔE_maj. Other examples include the chemical doping with several reports linking doping to enhanced losses in V_OC or quasi-Fermi level splitting (QFLS), although in many inorganic solar cell technologies doping is a key factor in preventing minority carrier recombination at the metal contacts.
In this work, we aim to understand the most promising and simple optimization strategies in order to allow perovskites to reach and surpass the efficiency of monocrystalline silicon and even GaAs (29.1%). To this end we have optimized previously validated device simulations based on the well-established drift-diffusion simulator SCAPS\textsuperscript{57,58} by fitting the simulations to a number of different experimental results. Based on a set of standard simulation parameters that describe a typical \textit{p-i-n} type cell, we have varied most accessible parameters to understand their relative importance within the limits of the simulation model. Following this screening, we focused on several critical parameters, such as \( n_{dop}, \mu, V_{BI}, E_{maj}, E_{gap}, S, \tau_{bulk} \) and the device absorption. Starting from the standard simulation, we find that maximizing the carrier mobilities (in all layers) may only lead to small efficiency improvements (\( \sim 1\% \)) by allowing fill factors of up to 85%. This is in contrast to chemical doping of the transport layers which allows exceeding FFs of 85%, and to reach \( V_{OC} \) close to the radiative limits with PCEs of 24% for the standard cell configuration with doped TLs (\( n_{dop} = 10^{19} \text{ cm}^{-3} \)). We explain the huge benefit of doped TLs through an effective increase of the \( V_{BI} \) across the absorber layer which repels minority carriers from the interfaces, thereby reducing interfacial recombination losses. Related to this, we show that a high dielectric constant in the neat material would lead to a decrease in fill factor due to a decrease in the \( V_{BI} \) across the absorber layer. These considerations imply the importance to maximize the \( V_{BI} \) across the perovskite and also imply the benefit of a small ion density to prevent a screening of the internal field (<< electrode charge/volume \( \sim 10^{16} \text{ cm}^{-3} \)). Assuming a donor/acceptor carrier concentration in the TLs of \( 10^{19} \text{ cm}^{-3} \), we demonstrate that 30% efficient perovskite solar cells are within reach by only using parameters that have already been demonstrated in recent literature, i.e. a bandgap of approximately 1.47 eV, a bulk carrier lifetime of 10 \( \mu \text{s} \), an interfacial recombination velocity of 10 cm/s and an EQE of 95% throughout the spectrum. While a PCE of 30% may also be reached using ultrathin (=10nm), undoped TLs; the use of doped TL enables generally higher PCEs and relaxes several strict requirements to advance to such an efficiency regime.

Results

In the first part of the study, we optimized our device simulation parameters by fitting several experimental results. First, standard simulation parameters were established to describe our reference cells with the following architecture: ITO/PTAA/PFN-Br/perovskite/C\textsubscript{60}/BCP/Cu.\textsuperscript{25,59} These cells exhibit on average a \( V_{OC} \) of approximately 1.13 V, a fill factor of 79% and a short-circuit current density of 21.5 mA cm\textsuperscript{-2} with an average external quantum efficiency (EQE) of close to 88% between 400 nm to 750 nm (\textit{Supplementary Figure S1}) which results in a PCE of \( \sim 19.2\% \).\textsuperscript{18} We note these \textit{p-i-n} type cells exhibit initially essentially no hysteresis at different scan speeds (\textit{Supplementary Figure S2}) which will be discussed further below. Using TRPL measurements, we previously obtained an interface recombination velocity of \( S = 2000 \text{ cm/s} \) at Pero/ETL interface and \( S = 200 \text{ cm/s} \) at the HTL/perovskite interface, as well as a bulk lifetime \( \tau_{bulk} \) of 500 ns. A fit of the standard simulations to experimental \( JV \)-curves is shown in \textit{Figure 1a} while the simulation parameters are shown in \textit{Supplementary Table S1}. We note, that we used a bandgap-dependent bimolecular recombination coefficient \( (k_2) \) as detailed in \textit{Supporting Note 1}. Knowing the radiative recombination current density in the dark and the effective density of states \( N_C = N_V = 2.2 \times 10^{18} \text{ cm}^{-3} \),\textsuperscript{21} \( k_2 \) can be readily obtained (e.g. for a bandgap of 1.63 eV, we obtain a \( k_2 = 3 \times 10^{-11} \text{ cm}^{-2}/\text{s} \)).\textsuperscript{60,61} We note, that this represents the external \( k_2 \) which is impacted by photon recycling inside the bulk.\textsuperscript{5,62-65} Therefore, by using the external \( k_2 \), we effectively consider the effect of photon recycling in our simulations. Importantly, using the bandgap-dependent \( k_2 \) and no parasitic losses, we can well reproduce the Shockley-Queisser efficiency vs. bandgap (\textit{Supplementary Figure S3}) with a maximum PCE of 33.77% at a bandgap of 1.36 eV.\textsuperscript{27} Note, the precise value of \( k_2 \) has no impact under a 1 sun illumination for cells which are
limited by SRH recombination in the bulk or at the interfaces (such as the standard cell). Moreover, it is interesting to note that reported Auger recombination coefficients \((10^{-28} \text{ cm}^3/\text{s}^6)\) reduce the maximum obtainable PCE in our simulations by only 0.03% and are therefore not a limiting factor. The simulated parallel recombination currents in the perovskite layer, interface and/or metal contacts are shown in Figure 1b which well describe the experimentally obtained recombination currents (Figure 1c). The latter were obtained by measuring the QFLS of individual perovskite/transport layer films of the cell as reported in a previous publication.\(^{47}\) Notably, at \(V_{\text{OC}}\), interfacial recombination outweighs the recombination in the neat material by more than 1 order of magnitude. Moreover, the simulations reproduce the ideality factor of the standard cells of approximately 1.35 across a broad range of light intensities (Figure 1d).\(^{66}\) Based on these settings, several recent experimental results were fitted by changing only one parameter depending on the particular experiment. These experiments include cells with reduced interface recombination at the perovskite/ETL interface upon adding LiF (Figure 1e),\(^{18}\) cells with different hole transport layers resulting in different \(V_{\text{OC}}\)s (Figure 1f),\(^{47}\) as well as cells with different PTAA layer thicknesses resulting in different fill factors (Figure 1g).\(^{42,67}\) Overall, Figure 1 demonstrates that the standard simulations can well reproduce these experimental results while also produce the quantified recombination currents in the bulk and the interfaces by taking into account the measured interface and bulk lifetimes. Starting from this simulation set, we aim to find the most promising ways to improve the PCE of perovskite solar cells. A large set of simulations was performed to check most parameters accessible in SCAPS which is an open-source software.\(^{57,58}\)

Figure 1. (a) Numerically simulated and experimental light and dark JV curves of p-i-n type cells based on PTAA/PFN-Br/triple cation perovskite/C\textsubscript{60}. The interface recombination velocities and bulk lifetime were obtained from transient PL (TRPL) measurements.\(^{18}\) (b) Simulated voltage dependent radiative and non-radiative recombination currents in the neat perovskite and at both interfaces compared to the generation current. Interfacial recombination reduces the possible open-circuit voltage which is roughly 10\times larger than Shockley-Read-Hall recombination in the neat material. (c) This is consistent with experimentally measured recombination currents under open-circuit conditions using steady-state PL measurements.\(^{47}\) (d) The simulation parameter set also reproduces the ideality factor (\(n_{\text{id}} \sim \)...
1.35) of the standard cells. The standard simulation settings allow to fit several experimental results by changing a single parameter depending on the particular experiment. (e) Inserting LiF between the perovskite and C₆₀ leads to concurrent increase of the transient PL (TRPL) lifetime and device V_OC. The TRPL results suggest that S decreases 1 order of magnitude upon application of LiF which allows to reproduce the experimentally observed V_OC gain of 35 mV. (f) Cells with different HTLs and varying majority carrier band offsets as obtained from UPS measurements. Implementing energy offsets at the p-interface for the cells with a PEDOT:PSS and P3HT hole transport layer allows to reproduce the experimental JV-curves. (g) Cells with changing PTAA thickness. The mobility in the PTAA layer has a significant impact on the device fill factor consistent with previous work. We conclude that the absolute performance gains due to mobility optimizations are rather small.

**Mobility and Doping:** A generic approach to optimize the performance of a solar cell is to maximize the carrier mobility to improve the charge-extraction efficiency. To this end, we first varied the majority carrier mobility in the HTL and ETL simultaneously (Figure 2a) as well as both carrier types in the perovskite layer (Supplementary Figure S4a,b). Figure 2a shows that only small FF improvements (1%) are possible by increasing the mobility in the TLs. We note that this improvement comes from the hole mobility in the HTL because the PTAA layer mobility is significantly lower than the C₆₀ mobility (Supplementary Figure S4 c-f). In contrast, improvements in the perovskite mobility (10x) allow improving the fill factor to 85% as shown in Supplementary Figure 4a,b. However, further improvements are not feasible due to the limitations imposed by non-radiative recombination consistent with a previous study. We conclude that the absolute performance gains due to mobility optimizations are rather small.

![Figure 2](image-url)

*Figure 2.* (a) Numerically simulated current density vs. voltage characteristics of p-i-n type perovskite solar cells by simultaneously increasing the e⁻ and h⁺ mobility (μ_e⁻, μ_h⁺) in the transport layers (TLs) which allows only small efficiency improvements (< 1%). (b) By contrast, increasing the donor/acceptor doping density in the TLs significantly increases the fill factor (FF) and V_OC of the cell. (c) and (d) show the resulting band diagrams of a cell with doped and undoped TLs (10¹⁹ cm⁻³), respectively. Doping increases the effective driving field across the active layer which repels minority carriers from the...
interfacial recombination (which is that the charge extraction may not be limited by the perovskite layer but rather by the TLs, and also because interfacial recombination (which also impacts the FF) would be considerably enhanced if the \( V_{BI} \) is lower across the perovskite layer). The higher carrier density in the doped TL does not speed up the SRH recombination, therefore, it is critical for the electronic properties of the device performance.\(^{23,47-49,51}\) Figure 2a shows that a high built-in voltage above 1.2 \( V \) is required in the undoped cell with a band gap of 1.62 \( eV \) in order to efficiently extract the carriers and minimize fill factor losses. We find that \( V_{BI} \) below 1.0 \( V \) would not allow reproducing our high FFs of close to 80\% even if the carrier mobilities are significantly increased (Supplementary Figure S8). Note, that we assumed \( V_{BI} = 1.2 \ V \) in the standard settings. However, we acknowledge that we do not know its precise value neither its origin considering the almost equal workfunction of ITO and Cu.\(^{47}\) A large \( V_{BI} \) may indicate a considerable modification of the metal workfunctions in the presence of thin organic layers and/or the perovskite layer.\(^{68,69}\) It is also interesting to note that a high \( V_{BI} \) is even required if the diffusion length in the perovskite layer (\( L_d \)) exceeds the film thickness (\( d \)).\(^{70-72}\) The reason is that the charge extraction may not be limited by the perovskite layer but rather by the TLs, and also because interfacial recombination (which also impacts the FF) would be considerably enhanced if the \( V_{BI} \) is lower across the perovskite layer. Therefore, it is not enough that the built-in field drops only across the transport layers while having flat bands across the perovskite – an often drawn picture in the community. Consequently, as shown in Supplementary Figure S9, increasing the dielectric constant of the perovskite active layer is actually detrimental for the FF as it decreases the field-drop across the perovskite layer. From another perspective, this also implies that in order to
approach the radiative efficiency limit, the perovskite must be as clean and as free of ions as possible to prevent screening the built-in field across the perovskite which will be the case if the ion density is significantly lower than the electrode charge/volume ($<< \text{CU/V} = 1 \times 10^{16} \text{ cm}^{-3}$).\textsuperscript{43-45} Considering the small hysteresis in our standard cells (Supplementary Figure S2), we assume that ions do not significantly screen the built-in field in these cells; or at least that in the future, the ion density can be reduced to values 1-2 orders of magnitude below $\text{CU/V}$ at which we except a negligible impact on the device performance.

With respect to the dependence on the $V_{\text{BI}}$, a similar picture appears to be the case for the cell with doped TLs ($n_{\text{dop}}=10^{19} \text{ cm}^{-3}$ which is 10% of the effective DOS), although the cell is more tolerant to a lower $V_{\text{BI}}$ with above 0.8 V being sufficient to avoid considerable PCE and FF losses. This is also shown in Supplementary Figure S10 for cells with and without doped TLs for different $V_{\text{BI}}$ and $E_{\text{maj}}$ values. In fact, we believe that in reality no metal workfunction mismatch may be required in case of strongly doped TLs, because carriers could tunnel through the TL to the electrode which is challenging to implement numerically. Therefore, we believe that the observed PCE drop in Figure 3a at $V_{\text{BI}}$ below 0.8 V may be incorrect. As to the impact of the energetic alignment, Figure 3b shows that the energy levels of the transport layers need to be matched with respect to the energetics of the perovskite layers and any downhill energetic offset for electrons (uphill for holes) would cause substantial $V_{\text{OC}}$ and PCE losses regardless whether the TLs are doped or not. Considering our previous study where we observed a match between the internal QFLS and the device $V_{\text{OC}}$,\textsuperscript{47} we expect that the alignment in our standard cells is well optimized. We note that any energetic offset will cause an equal loss in device $V_{\text{OC}}$ as long as the interface between the perovskite and the misaligned TL is limiting the performance of the cell (and not another interface or the bulk).

**Figure 3.** (a) The impact of the built-in field ($V_{\text{BI}}$, here defined as the work function difference of the contact metals) and (b) the energy alignment between the perovskite and the transport layers (TLs) on the JV-characteristics and performance parameters of cells with doped and undoped TLs. In (b), the $V_{\text{BI}}$ was kept constant (1.2 V). In the case of intrinsic TLs, increasing the $V_{\text{BI}}$ from 1.2 V (standard cell) to 1.6 V allows to improve the FF close the non-radiative FF limit of 83.5%. Interestingly, doped TLs are more tolerant with respect to the $V_{\text{BI}}$. Considerable losses appear below 0.8 V, however, we attribute this to a limitation of the simulation model as discussed in the main text. In contrast, the energy level mismatch between the perovskite and the transport layers has a large impact on the device $V_{\text{OC}}$ regardless of the doping of the TLs.

**Suppressed Recombination:** Having analysed the impact of the charge-carrier mobility, doping and the energetics on the device performance, we now focus our attention on suppressing the defect recombination in the bulk of the material and at the interfaces.\textsuperscript{21} In the following we demonstrate the
impact of $S$ and $\tau_{\text{bulk}}$ as a function of the perovskite bandgap. **Figure 4a** shows the PCE of the standard cell as a function of the perovskite bandgap (red line). Interestingly, lowering the bandgap (from currently 1.6 eV to the optimum of 1.34 eV\textsuperscript{27}) does not lead to significant performance gains (from 19.2\% to 20.4\%) due to the limitations imposed by the interfaces and the recombination in the bulk. We note that we kept the injection barriers between the contact metals and the TLs at 0.2 eV (as used in the standard simulations) and the energy levels of the transport layers well aligned, as otherwise the PCE drops rapidly for higher and lower bandgaps (see **Supplementary Figure S11**). This also indicates difficulties in maintaining the perovskite performance when increasing the perovskite bandgap when the energy levels of the TLs do not move in accordance with the energetics of the perovskite absorber (see **Supplementary Figure S12**). Although this may actually not be the limiting mechanism (considering a possible phase segregation, see ref\textsuperscript{33}), it could be relevant when aiming for high performance tandem cells where a perovskite bandgap of 1.7 eV would be better than a typical gap of 1.6 eV.\textsuperscript{24} **Figure 4a** also shows that switching off bulk recombination (blue) does not improve the PCE across the bandgap as it is the interface recombination that governs the PCE. Improvements up to a PCE of 23.8\% are, however, possible if interface recombination is switched off completely (green); and close to 27\% when both $S$ and $\tau_{\text{bulk}}$ are switched off simultaneously (orange, "bimolecular only"). Interesting is also that the simulated PCE vs. $E_{\text{gap}}$ curves get steeper in case of suppressed recombination, i.e. going from a gap of 1.6 eV to 1.4 eV pays of much more. Considering now optimized, yet already demonstrated recombination parameters, e.g. $S = 10 \text{ cm/s}$\textsuperscript{20-22} (at both interfaces) and $\tau_{\text{bulk}} = 10 \mu\text{s}$\textsuperscript{44} (light blue) allows reaching efficiencies of 25.3\% which is above the situation without interfacial recombination. In the following we tried to maximize the PCE using undoped TLs. First, we note that all simulations so far were performed by using an absorption model for a direct semiconductor which matches the experimentally measured absorption coefficient, $\alpha$ and reproduces the short-circuit current in our standard cells with an average EQE slightly below 88\% (Supplementary Figure S1). By further increasing the light-in-coupling and thus the EQE to 95\% above the bandgap while simultaneously enhancing the carrier mobilities in all layers by a factor of 10 and also reducing the injection barriers from the metals to the TLs from 0.2 eV to 0.1 eV (i.e. increasing the $Y_{\text{BI}}$), we obtain a maximum efficiency of 29.4\% at a bandgap of 1.36 – 1.4 eV. To check whether such high EQEs are reasonable in our devices, we also performed transfer-matrix simulations\textsuperscript{75,76} (see **Supplementary Figure S13** and corresponding discussion) which predict an average above-gap EQE slightly below 95\% resulting in a $J_{\text{SC}}$ that is $\sim 1$ mA cm\textsuperscript{-2} lower than the current obtained with SCAPS for the record cell marked with an open star in **Figure 4a**. Nevertheless, we note that EQE spectra with approximately 95\% have been demonstrated in record perovskite devices (23.48\% certified),\textsuperscript{77} which is clearly a key aspect to reach the 30\% PCE milestone.

In **Figure 4b**, we checked the impact of TL doping (using again $10^{19}$ cm\textsuperscript{-3} for both TLs) which further enhanced the PCE to 28.7\% (dashed dotted light blue line in **Figure 4b**). As a comparison the red lines show the corresponding PCE improvement vs. $E_{\text{gap}}$ upon TL doping in the standard cells. We also checked under which conditions, in particular, for which energetic offsets and interface recombination velocities such high power conversion efficiencies may be maintained. **Figure 4c, d** and **e** shows the PCE as a function of $S$ and $E_{\text{maj}}$ at both interfaces for our standard cells, as well as the optimized cells with undoped and doped TLs, respectively. Interestingly, **Figure 4e** shows that PCEs of $\sim$30\% may be maintained in case of doped TLs even with interface recombination velocities of 1000 cm/s if the majority carrier band offsets are small ($E_{\text{maj}}$ between -0.1 eV and 0 eV). However, higher values and positive energy offsets lead to rapid efficiency losses. We note that an analogous plot of PCE vs. $S$ and the bulk lifetime is shown in **Supplementary Figure S14**.
Figure 4. (a) Numerically simulated power conversion efficiency (PCE) versus perovskite bandgap ($E_{\text{gap}}$) considering aligned perovskite/transport layer energy levels for different scenarios. Starting from the standard settings plotted in red ($S = 2000$ cm/s at the perovskite/ETL interface and bulk lifetime of 500 ns); (blue) in absence of bulk recombination; (green) in absence of interfacial recombination; (orange) in absence of interface and bulk recombination (bimolecular recombination only); (light blue) using optimized, yet plausible recombination parameters ($S = 10$ cm/s at both interfaces and a bulk-lifetime, $\tau_{\text{bulk}}$, of 10 $\mu$s). The magenta curve depicts an optimized cell with undoped TLs with optimized bulk and interface recombination, increased EQE (95% above gap), increased mobilities in all TLs by a factor of 10 and reduced injection barriers from the metal to the TLs (from 0.2 eV to 0.1 eV) resulting in a PCE of 29.4% at an optimum gap. (b) shows the impact of TL doping ($10^{19}$ cm$^{-3}$) for the standard cell in red (solid line without doping, dashed dotted line with doping), the cell with optimized recombination parameters in light blue (solid line without doping, dashed dotted line with doping), as well as for the cell with optimized recombination and light in-coupling and EQE of 95% (solid magenta line). The black curve shows the PCE vs. bandgap according to the Shockley-Queisser model. (c-e) PCE vs. $S$ and majority carrier bandoffsets at both interfaces for the standard cell and the optimized cells with undoped and doped TLs, respectively. Note, a positive offset is defined as energy offset towards midgap, while a negative offset means an energy barrier for electrons and holes.

Based on the bandgap-dependent analysis in Figure 4, we propose two different cell architectures employing doped and undoped TLs, which could be realized experimentally to reach the 30% PCE milestone. For the first cell shown in Figure 5a,b, we take advantage of the fact that doping allows increasing the TL thickness without compromising the device performance (assuming that the parasitic absorption of the TL and the dopant is minimal). This is an important consideration from the manufacturing perspective and will help to protect the perovskite from moisture and oxygen ingress. Here, we assumed a bandgap of 3.5 eV for the bottom TL which is comparable to the bandgaps of TiO$_2$ (3.3 eV) or SnO$_2$ (3.6 eV). Using 100 nm thick TLs, realistic interface recombination velocities of 100 cm/s, bulk lifetimes of 10 $\mu$s (shown in ref. [14]) and doped TLs ($n_{\text{dop}} = 10^{19}$ cm$^{-3}$), we can simulate a
PCE of 30% even for a bandgap of 1.47 eV (i.e. the bandgap of FAPI).\textsuperscript{32} Importantly, 2 nm thick interlayers were implemented between the perovskite and the doped TLs to avoid a direct contact between the perovskite and the doped TLs. We note that the TL thickness can be increased up to 400 nm without compromising the PCE (Supplementary Figure S15). Notwithstanding these points, we acknowledge that realizing a stable doping experimentally without greatly enhancing $S$, which may in reality overcompensate the potential benefits (Figure 4e) will remain a critical experimental challenge. The second cell shown in Figure 5c,d, is based on a 1 nm-thick self-assembled monolayer as bottom TL. It was recently shown\textsuperscript{79,80} that a self-assembled monolayer (SAM) can replace and even outperform the omnipresent PTAA layer in p-i-n type cells with negligible recombination at the bottom interface. Using, a SAM at the bottom and a thin TL at the top (20 nm) and the same setting as discussed above for the optimized cell in Figure 4a, allows reaching 30% as well; however, we emphasise that this is strictly limited by the thickness of the layer. For example, implementing two 100 nm thick TLs reduces the PCE to 27%, which is due to the increased interface loss when lowering the $V_{BI}$ across the perovskite. Nevertheless, we also note that the SAM may be beneficial in terms of parasitic absorption compared to the cell with doped TLs.

Figure 5. (a) Numerically simulated current density vs. voltage (JV) characteristics of p-i-n type cells with comparatively thick, doped TLs ($10^{19}$ cm$^{-3}$) and a bandgap of 1.47 eV, interface recombination velocities ($S$) of 100 cm/s and a bulk lifetime of 10 µs and a power conversion efficiency (PCE) of ~30%. The doped TL maximize the field across the perovskite which enhances the PCE despite significant $S$ values. We note, 2 nm-thick protection layers were inserted between the doped TLs and the perovskite. (b) The resulting parallel recombination currents as a function of applied voltage demonstrating a
photoluminescence (or electroluminescence) quantum yield (PLQY) of ~45% at open-circuit. (c) Numerically simulated JV characteristics and parallel recombination currents (d) of perovskite cells with a 1 nm-thick self-assembled monolayer at the bottom as alternative strategy to reach 30% using undoped TLs. Despite the comparatively low recombination velocity (S=10 cm/s), the field-drop across the 20 nm thick top TL renders the cell vulnerable to interfacial recombination as illustrated by the lower PLQY in the panel (d). Therefore, when aiming to avoid doping, such high PCEs may only be reached in case of ultrathin TLs when keeping the S at a realistic value (S > 1 cm/s).

Conclusions

In summary, in this work we explored possible optimization strategies to advance the PCEs of perovskite solar cells beyond those of monocrystalline silicon (>26%) and GaAs cells (>29%). To this end we established a standard simulation to describe our reference (standard) p-i-n type cells with an efficiency of close to 20% which are based on a triple cation perovskite and PTAA/PFN-Br and C60 as HTL and ETL, respectively. We then checked a wide range of simulation parameters and discussed the importance of $\mu$, $n_{dop}$, $V_{BI}$, $E_{maj}$, $E_{gap}$, $S$, $\tau_{bulk}$ as key parameters in defining the cells’ performance. Starting from the standard cells, we showed that optimization of the mobilities of the TL and the perovskite layer will allow reaching a FF of ~85%, which however corresponds to a marginal PCE improvement (~1% absolute). Instead, we propose to dope the transport layers, which enables drastic FF and $V_{OC}$ gains. We attributed this result to an effective increase in the $V_{BI}$ across the perovskite layer which drives minority carriers away from the interfaces. We further discussed the need of a high built-in field across all stack layers including the absorber layer and we found that TL doping relaxes the need of electrodes with large work function offsets. In contrast, energy level matching between the perovskite and the TL remains a necessity to avoid PCE losses irrespective of the TL doping. We then modelled the PCE as a function of the perovskite bandgap for cells with suppressed defect recombination in the bulk and/or the interface. In combination with doping, we identified that recombination parameters that have already been demonstrated in recent literature ($\tau_{bulk} = 10 \mu$s and $S = 10$ cm/s) would allow PCEs of up to 31% for a perovskite with a bandgap of 1.4 eV, if an average above-gap EQE of 95% can be realized. Based on these findings we numerically demonstrated 30% efficient perovskite cells with comparatively thick (a few hundred nm), strongly doped TLs by implementing a perovskite layer with realistic interface recombination velocities ($S = 100$ cm/s) and a bandgap of 1.47 eV. Alternatively, cells with ultrathin TLs (e.g. by implementing a self-assembled monolayers at the bottom contact) may allow to reach the 30% milestone as well, if the $V_{BI}$ across the perovskite layer can be maximized to suppress the critical interface recombination. Despite this option, doped TLs allow to relax several strict requirements to achieve a PCE of 30% as the cell performance is largely independent on the TL thickness, mobility but also more tolerant with respect to the defect density at the interface (S) and workfunction offset of the metal electrodes. Considering the results of this work, we expect that single junction perovskite solar cells will become the most efficient single-junction solar technology in the near future.

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Supporting Information

Pathways towards 30% efficient perovskite solar cells

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Supplementary Figure S1. Experimental External Quantum Efficiency of the standard cells and numerically simulated EQEs using SCAPS and on optimal transfer matrix simulations providing an integrated $J_{SC}$ of roughly 21.5 mAcm$^{-2}$. 
Supplementary Figure S2. JV-scans of the standard cell measured in forward and reverse direction at different scan rates demonstrating a negligible hysteresis within the studied time-range.

Supplementary Figure S3. A comparison between the analytic Shockley-Queisser model (assuming a perfect rear reflector) and numerical simulations assuming only radiate recombination losses using a bandgap-dependent $k_2$ as described below in Supplementary Note 1.
### Supplementary Table S1. SCAPS simulation parameters for the standard cells.

| Parameter                                                                 | Symbol     | Value      | Unit       |
|---------------------------------------------------------------------------|------------|------------|------------|
| Majority carrier band offset between perovskite and C<sub>60</sub>       | \( \Delta \varepsilon_{\text{maj,c}} \) | 0          | eV         |
| Majority carrier band offset between perovskite and PTAA                 | \( \Delta \varepsilon_{\text{maj,v}} \) | 0          | eV         |
| Lifetime in perovskite                                                   | \( \tau_{\text{pero}} \) | 500        | ns         |
| Lifetime in PTAA                                                         | \( \tau_p \) | 1          | ns         |
| Lifetime in C<sub>60</sub>                                                | \( \tau_n \) | 1          | ns         |
| Ionized acceptors in PTAA                                                | \( N_{A,P}^- \) | 0          | cm<sup>-3</sup> |
| Ionized donors in C<sub>60</sub>                                         | \( N_{D,n}^+ \) | 0          | cm<sup>-3</sup> |
| Intrinsic carrier density in perovskite                                  | \( N_i \) | \( 1 \times 10^{13} \) | cm<sup>-3</sup> |
| Minority carrier recombination velocity from perovskite to PTAA          | \( S_{\text{min,n}} \) | 200        | cm/s       |
| Minority carrier recombination velocity from perovskite to C<sub>60</sub>| \( S_{\text{min,p}} \) | 2000       | cm/s       |
| Majority carrier recombination velocity from perovskite to PTAA          | \( S_{\text{maj,n}} \) | \( 1 \times 10^7 \) | cm/s       |
| Majority carrier recombination velocity from perovskite to C<sub>60</sub>| \( S_{\text{maj,p}} \) | \( 1 \times 10^7 \) | cm/s       |
| Majority and Minority carrier velocity at front metal contact (ITO)      | \( S_{\text{met}} \) | \( 1 \times 10^7 \) | cm/s       |
| Thickness of PTAA                                                        | \( d_{\text{PTAA}} \) | 10         | nm         |
| Thickness of perovskite                                                  | \( d_{\text{pero}} \) | 500        | nm         |
| Thickness of C<sub>60</sub>                                               | \( d_{\text{C60}} \) | 30         | nm         |
| Offset between metal and PTAA                                            | \( \Delta \varepsilon_{\text{F,metal--p}} \) | 0.2        | eV         |
| Offset between metal and C<sub>60</sub>                                  | \( \Delta \varepsilon_{\text{F,metal--n}} \) | 0.2        | eV         |
| Device built-in voltage                                                  | \( V_BI \) | 1.2        | V          |
| Bandgap PTAA                                                             | \( E_G,\text{PTAA} \) | 3.0        | eV         |
| Electron affinity PTAA                                                   | \( E_{A,\text{PTAA}} \) | 2.5        | eV         |
| Bandgap perovskite                                                       | \( E_G,\text{pero} \) | 1.6        | eV         |
| Electron affinity perovskite                                             | \( E_{A,\text{pero}} \) | 3.9        | eV         |
| Electron affinity C<sub>60</sub>                                         | \( E_{A,C60} \) | 3.9        | eV         |
| Bandgap C<sub>60</sub>                                                    | \( E_G,C60 \) | 2.0        | eV         |
| Electron mobility in C<sub>60</sub>                                      | \( \mu_{n,\text{PTAA}} \) | \( 1 \times 10^{-2} \) | cm<sup>2</sup>/Vs |
| Hole mobility in PTAA                                                    | \( \mu_{p,\text{PTAA}} \) | \( 1.5 \times 10^{4} \) | cm<sup>2</sup>/Vs |
| Electron mobility in perovskite                                          | \( \mu_{n,\text{pero}} \) | 1          | cm<sup>2</sup>/Vs |
| Hole mobility in perovskite                                               | \( \mu_{p,\text{pero}} \) | 1          | cm<sup>2</sup>/Vs |
| Relative dielectric constant PTAA                                         | \( \epsilon_{\text{PTAA}} \) | 3.5        |            |
| Relative dielectric constant perovskite                                   | \( \epsilon_{\text{pero}} \) | 22         |            |
| Relative dielectric constant C<sub>60</sub>                             | \( \epsilon_{\text{C60}} \) | 5.0        |            |
| Effective electron density of states in HTL                              | \( N_{C/V,\text{PTAA}} \) | \( 1 \times 10^{20} \) | cm<sup>3</sup> |
| Effective electron density of states in C<sub>60</sub>                   | \( N_{C/V,C60} \) | \( 1 \times 10^{20} \) | cm<sup>3</sup> |
| Effective electron density of states in perovskite                        | \( N_{C/V,\text{pero}} \) | \( 2.2 \times 10^{18} \) | cm<sup>3</sup> |

**Remarks:** We note that we do not claim that every individual parameter is perfectly consistent with existing literature, however, we consider them as plausible. Many parameters were obtained from our own optical and electro-optical transient measurements, such as the recombination rate constants and lifetimes in the perovskite layer, interfacial recombination velocities, carrier mobilities in the transport layers, energy levels and density of states in the perovskite. The absorption coefficient (\( \alpha \ [1/cm] \)) of
the perovskite layer in the simulations was matched to the experimentally measured absorption coefficient, in particular at the bandedge which has a significant impact on the EQE and short-circuit current. We further implemented an Urbach tail of 15 meV consistent with experimental data.

Supplementary Note 1.

We obtain the external bimolecular recombination rate constant $k_2$ from the radiative recombination current density in the dark ($J_{0,\text{rad}}$) and knowledge of the effective density of states $N_C = N_V = 2.2 \times 10^{18}$ cm$^{-3}$ (ref.21) which corresponds to an effective electron mass $m_e^*$ of 0.2.

$$J_{0,\text{rad}} = e d k_2 n_i^2 = edk_2N_CN_V\exp(-E_G/k_BT), \tag{eq. S1}$$

where $e$ is the elementary charge, $d$ is the film thickness, $E_G$ the bandgap and $k_B T$ the thermal energy. Note, $J_{0,\text{rad}}$ is obtained from integrating the EQE and black body spectrum ($\phi_{BB}$)

$$J_{0,\text{rad}} = \int_0^{\infty} \text{EQE} \ast \phi_{BB} \, dE \tag{eq. S2}$$

Considering that $\phi_{BB} \propto E_G^2 \exp(-E_G/k_BT)$ and $J_{0,\text{rad}} \propto \exp(-E_G/k_BT)$ shows that $k_2$ must depend on the bandgap itself. For a bandgap of 1.63 eV and $d = 500$ nm, we obtain an external $k_2$ of $3 \times 10^{-11}$ cm$^3$/s which is similar to previously specified values ref.21,60,61

**Supplementary Figure S4.** Numerically simulated current density vs. voltage characteristics of p-i-n type perovskite solar cells by varying the e$^-$ and h$^+$ mobility ($\mu_{e^-}$, $\mu_{h^+}$) in the perovskite layer (a) and resulting power conversion efficiency (PCE) vs. perovskite mobility (b); $\mu_{h^+}$ in the HTL (c) and resulting PCE vs. HTL mobility (d), $\mu_{e^-}$ in the ETL (e) and resulting PCE vs. ETL mobility (f).
Supplementary Figure S5. (a) A comparison of the parallel interfacial recombination currents for a simulated standard cell with and without doped TLs. The main effect of the doping is the suppression of the interfacial recombination current (red) which is significantly lower than in the reference cell (e.g. \( \sim 25x \) at an applied voltage of 1.0 V). (b) compares the JV-curves of cells with and without doped TLs to a cell with no \( V_{BI} \) drop across the TLs (red). This is achieved by including a high relative dielectric constant (e.g. \( \epsilon_r = 1000 \)) in the TL. Further optimizing the TL mobilities (100x higher compared to the reference cell) shows that the transport limitations are negligible (orange line). Further maximizing the \( V_{BI} \) to 1.6 eV (blue) can closely describe the cell with doped TLs (where the small differences dependent on the exact value of \( \epsilon_r \)). This comparison shows that the effective increase of the \( V_{BI} \) across the perovskite absorber layer due to the doping of the TLs is the primary reason for the performance improvement.

Supplementary Figure S6. Simulated JV characteristics of p-i-n type perovskite solar cells by varying the acceptor concentration in the hole transport layer (TL) (a) and the donor concentration in the electron TL (b). Considering that perovskite/ETL interface is limiting the performance, doping the HTL does allow performance improvements. In contrast significant improvements are achieved upon doping of the ETL until the HTL/perovskite interface and or the bulk limit the cells performance.
Supplementary Figure S7. A doped interlayer (here implemented between the perovskite and the ETL) gives the same PCE as a doped ETL.

Supplementary Figure S8. Heat maps of fill factor (a) and PCE (b) vs. built-in voltage and electron and hole mobility in the perovskite layer ($\mu_e$ and $\mu_h$) for the standard cell. In order to reproduce the high experimental fill factor (of ~80%), a considerable $V_{BI}$ of above 1.1 V is required regardless of the perovskite mobility because it is the interface recombination that deteriorates the FF in case of low driving voltages.
Supplementary Figure S9. Numerically simulated JV-curves (a) and fill factors (b) as a function of the dielectric constant ($\varepsilon_r$). Increasing $\varepsilon_r$ flattens the $V_{BI}$ in the perovskite layer as shown (c) and (d). The continuous reduction of the FF in panel (b) with increasing dielectric constant in the perovskite layer regardless of mobility in the perovskite highlights that a considerable $V_{BI}$ in the perovskite is crucial to maximize the FF. Even if the perovskite electron and hole mobility is as high as 50 cm$^2$/V/s, a (nearly) flat $V_{BI}$ in the perovskite layer (here implemented by using a hypothetical $\varepsilon_r$ of 1000) would not allow to reproduce the high fill factors obtained experimentally (almost 80%) as a result of the increased interface recombination in this scenario. Note, that a perovskite mobility of 1 cm$^2$/V/s better describes our experimental results when using an $\varepsilon_r$ of ~25. From this perspective, decreasing $\varepsilon_r$ in the perovskite layer may be actually beneficial for the performance, however, we do not propose this as a viable optimization strategy because the exciton dissociation will suffer at too low $\varepsilon_r$. Nevertheless, this allows to conclude that it will be highly beneficial to make the perovskite “clean” of ions such that the built-in field (in this work defined by the workfunction difference) of the electrodes can drop across all layers and is not screened across the perovskite layer.
Supplementary Figure S10. (a) Heat maps of PCE vs. built-in voltage and majority offset ($E_{maj}$) at both ETL and HTL for the standard cell with undoped transport layers (a) and for the same cell with doped TLs (b). Doped TLs allow more tolerance with respect to the electrode workfunction difference (defined as the $V_{BI}$ in the work) but not with respect to $E_{maj}$.

Supplementary Figure S11. The graphs shows a drop in PCE if the energy levels of the TLs and the workfunctions of the contact metals are kept as used in the standard simulations (“unaligned”).
Supplementary Figure S12. Alignment of the energy level of the transport layers with respect to the perovskite is an important consideration for increased bandgap perovskites. If only the bandgap is increased but the transport layer energetics is not changed than the $V_{OC}$ cannot be improved.

Supplementary Figure S13. (a) Transfer Matrix simulations of the optimized cells with a bandgap of 1.4 eV. Limitations on the $J_{SC}$ are only imposed by the reflections from the glass and the parasitic absorption in ITO and PTAA while the parasitic absorption of the thin PTAA layer and other layers are minimal (less than 1% average EQE loss in PTAA). However there is a relatively large reflection loss due to the comparatively high $n$ of the perovskite layer and the glass which can be, however, minimized by using an antireflection coating (~4% gain). Leaving only reflection from the perovskite, we obtain an EQE that is on average slightly below 95% above the gap which leads to $J_{SC}$ loss of roughly ~1 mAcm$^{-2}$ as compared to the $J_{SC}$ obtained with SCAPS in the record cell (marked with an open circle in Figure 4a) at a bandgap of 1.4 eV. (b) shows the $n$ and $k$ values of the perovskite layer used for the simulations.
Supplementary Figure S14. (a) Heat maps of PCE vs. interface recombination velocity \((S)\) (at both perovskite/transport layer interfaces) and bulk carrier lifetime \((\tau_{\text{bulk}})\) for the standard cell and (a) for the high efficiency system with a perovskite bandgap of 1.4 eV and doped TLs (b).

Supplementary Figure S15. The power conversion efficiency vs. the thickness of both transport layers with donor/acceptor concentrations of \(10^{19} \text{ cm}^{-3}\). The thickness of the TLs can be increased up to 400 nm without significant PCE losses which allows maintaining a PCE of approximately 30%.