Interface Optimization via Fullerene Blends Enables Open-Circuit Voltages of 1.35 V in CH$_3$NH$_3$Pb(I$_{0.8}$Br$_{0.2}$)$_3$ Solar Cells

Zhifa Liu, Johanna Siekmann,* Benjamin Klingebiel, Uwe Rau, and Thomas Kirchartz*

Nonradiative recombination processes are the biggest hindrance to approaching the radiative limit of the open-circuit voltage for wide bandgap perovskite solar cells. In addition to high bulk quality, good interfaces and good energy level alignment for majority carriers at charge transport layer-absorber interfaces are crucial to minimize nonradiative recombination pathways. By tuning the lowest-unoccupied molecular-orbital of electron transport layers via the use of different fullerenes and fullerene blends, open-circuit voltages exceeding 1.35 V in CH$_3$NH$_3$Pb(I$_{0.8}$Br$_{0.2}$)$_3$ device are demonstrated. Further optimization of mobility in binary fullerenes electron transport layers can boost the power conversion efficiency as high as 18.9%. It is noted in particular that the $V_{oc}$ fill factor product is >1.096 V, which is the highest value reported for halide perovskites with this bandgap.

1. Introduction

One of the main reasons why halide perovskite solar cells have attracted so much interest over the past years is their ability to generate high open-circuit voltages relative to their respective bandgaps.[1,2] Using simple solution-based processing, open-circuit voltages within ~60 mV of the radiative limit have been experimentally realized in solar cells with efficiencies exceeding 20%.[3–7] Approaching the radiative limit that closely requires nonradiative recombination processes to be very slow compared to most other semiconductors. This requirement of slow recombination must be valid in the bulk of the material[8] but also at grain boundaries and at interfaces to charge-transport layers. The fact that recombination can be extremely slow even when charge-transport layers are attached to the absorber layer[4,9–12]

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mobility\textsuperscript{44,45} and has previously led to a generally worse electronic properties in organic polymer:fullerene solar cells\textsuperscript{46–49}. Therefore, it is currently unclear how to design the electron transport material for perovskite absorbers with a wider range of bandgaps.

Figure 1a shows the $V_{\text{oc}}$ versus the bandgap of a variety of perovskite solar cells. The colored lines represent the external luminescence quantum efficiency $Q_{\text{e, lum}}$ that the solar cells need to have to fulfill the relation\textsuperscript{50}

$$q (V_{\text{ac}} - V_{\text{oc}}) = q \Delta V_{\text{oc}} = -kT \ln (Q_{\text{e, lum}})$$

(1)

with $V_{\text{ac}}$ the radiative open-circuit voltage, $q$ the elementary charge, $k$ the Boltzmann constant, and $T$ the cell temperature. The bandgaps were all calculated by the inflection point of the external quantum efficiency to enable better comparison between the data points\textsuperscript{51,52}. The most notable achievements among wide bandgap perovskites are cells based on compositions such as $\text{Cs}_0.05\text{FA}_0.95\text{Pb}(\text{I}_{0.7}\text{Br}_{0.3})_3$,\textsuperscript{15} $\text{Cs}_0.05(\text{FA}_0.95\text{MA}_0.05\text{Pb}(\text{I}_{0.75}\text{Br}_{0.25})_3$,\textsuperscript{53} $\text{Cs}_0.17\text{FA}_{0.83}\text{Pb}(_{0.6}\text{Br}_{0.4})_3$,\textsuperscript{54} and $\text{CsPb}(\text{I}_{0.75}\text{Br}_{0.25})_3$.\textsuperscript{55} The bandgaps vary from 1.69\textsuperscript{53} to 1.845 eV\textsuperscript{55} with efficiencies up to 20.1\%, at a bandgap of 1.69 eV and a $V_{\text{oc}} = 1.21$ V\textsuperscript{53}. The $V_{\text{oc}}$ fill factor (FF) product, a proxy for the voltage at the maximum power point, plotted as a function of $E_g$ for the same devices is shown in Figure 1b. The device by Zhang et al.\textsuperscript{55} shows a high $V_{\text{oc}}$ and high $V_{\text{oc}}$ FF product, but a large voltage loss $\Delta V_{\text{oc}}$. By applying Equation (1) we can estimate the external luminescence quantum efficiency of the solar cell\textsuperscript{55} to be $Q_{\text{e, lum}} = 0.25\%$. It is important to stress that due to additional recombination at interfaces to charge transfer layers, the calculated $Q_{\text{e, lum}}$ of the devices is much smaller than the external luminescence quantum efficiency of well passivated perovskite films, exceeding $Q_{\text{e, lum}} = 35\%$\textsuperscript{8,56}.

In contrast to Zhang et al.\textsuperscript{15,55} the champion device that is reported in this work (blue star) shows low voltage losses leading to high luminescence quantum efficiency $Q_{\text{e, lum}} = 5\%$ which is comparable with low bandgap devices like Jiang et al.\textsuperscript{11} (violet) and Liu et al.\textsuperscript{4} (red star) (see Figure 1a). Furthermore, the champion device shows a high $V_{\text{oc}}$ FF product exceeding 1.09 V (see Figure 1b). The corresponding solar cell is based on a methylammonium lead iodide-bromide absorber prepared using lead-acetate ($\text{Pb(CH}_3\text{COO})_2$), methylammonium iodide (MAI), and methylammonium bromide (MABr) as precursors. This absorber layer is combined with poly(triaryl amine) (PTAA) as a hole transport layer (HTL) and different combinations of fullerenes with varied LUMO as electron transport layers (ETLs). We test three different fullerenes, namely, PCBM, CMC ($\text{C}_{60}$-fused N-methylpyrroloidine-m-C$_{12}$-phenyl),\textsuperscript{57,58} and ICBA and all binary combinations of these as ETLs. ICBA is known to have a roughly 200 meV\textsuperscript{59} lower electron affinity as compared to PCBM and has therefore previously been used in higher bandgap perovskites.\textsuperscript{38} CMC is also a monoaduct fullerene but with a longer side chain and has been reported to have a slightly higher electron affinity (40 meV) than PCBM.\textsuperscript{58} While we find high open-circuit voltages $>1.29$ V for all of these ETLs, substantial differences in all device parameters are still observed. We find that the best efficiencies up to 18.9\% and open-circuit voltages up to 1.35 V are possible using a combination of CMC and ICBA to form a binary layer.

2. Results

2.1. Device Performance

For optimizing wide bandgap CH$_3$NH$_3$Pb(I$_{0.8}$Br$_{0.2}$)$_3$ layers grown on PTAA for highest possible open-circuit voltage, lead acetate-based perovskite precursors were chosen because they have been shown\textsuperscript{4,60} to yield smooth, low defect-density perovskite layers which enable the highest reported $V_{\text{oc}}$ for perovskite layers with a bandgap around 1.6 eV. In order to increase the bandgap of the perovskite layer, we doped 20% MABr into CH$_3$NH$_3$PbI$_3$ (MAPI) layer to produce perovskite absorber layers with a wide bandgap of 1.72 eV. For bulk passivation, previous studies have shown that addition of MAI into the perovskite precursor solution can lead to passivation of grain boundaries and substantially increased photoluminescence lifetimes.\textsuperscript{44} Furthermore, studies on MAPI-based solar cells have shown that excess MAI results in a smaller electron affinity at the surface of MAPI, which led to better energy alignment and...
likely an increased built-in voltage in finished devices. Our study shows a continuous improvement in open-circuit voltages when the excess concentration of MAI is increased from 1.67 to 3.33 mol% in CH3NH3Pb(I0.8Br0.2)3 precursor solution. It is important to mention that all our cells show an increase in Voc if measured again two days after the first measurement (Figure S5, Supporting Information). Our best cell shows a Voc = 1.35 V measured on day four after production. Cells measured after 4 days lose mostly in Jsc as pure PCBM. The Jsc—the bar gives the median, and the point is the mean value. The Jsc is highest for the cells with PCBM and decreases by 3.4%, and for ICBA is even higher than the measured Jsc due to current loss during activation (Figure S9, Supporting Information).

2.2. Electron Transport Layer Variations

In order to achieve the high Voc, we varied the type of fullerenes used as ETL. In the following we want to show the impact of different fullerenes and their blends on the characteristic values of the cells. Figure 3a,c shows the illuminated JV-curves of the best devices, all reaching Voc > 1.29 V. The statistical data in Figure 3b gives a brief overview of the impact of different ETLs on the cell performance, divided in (from left to right, top to bottom) Voc, FF, and η for the pure fullerenes and blends. The box contains 50% of the data points, the antenna shows minimum and maximum value, the bar gives the median, and the point is the mean value. The Jsc is highest for the cells with PCBM and decreases by mixing with CMC or ICBA. While the cells with pure CMC and ICBA have lower Jsc, the CMC:ICBA blend shows a similar high Jsc as pure PCBM. The Voc shows the opposite trend. PCBM and its blends reach Voc > 1.33 V while CMC, ICBA, and their blend increase the Voc up to 1.35 V. With regard to Jsc and Voc CMC and ICBA behave similar, but looking at the FF we notice a reduced performance for ICBA and PCBM:ICBA blend. Surprisingly, the blend of CMC and ICBA results in an increase of FF compared to both pure materials, the difference between the mean fill factor for CMC, ΔFF = 3.4%, and for ICBA is even ΔFF = 12.4%. Thus, the Voc FF product is highest for CMC:ICBA and—combined with the good Jsc—this ETL leads to the highest efficiency η = 18.9%.

Figure 2. a) Schematic of the device stack. The electron transport layer (ETL) varies between different fullerene derivates and combination of those b) structures of PCBM, CMC, and ICBA. c) Illuminated current–voltage curves of the best device measured four days after production. d) External quantum efficiency η of a device on the same sample as our champion cell (Figure S11, Supporting Information). The external quantum efficiency is corrected by the reflection of the cover glass of the sample holder. The integrated Jsc = 18.2 mA cm−2 in is by 1 mA cm2 higher than the measured Jsc due to current loss during activation (Figure S9, Supporting Information).
The other devices reach efficiencies of ≈17% with the exception of the ICBA-based device, where the poor FF leads to a low efficiency of η < 16%.

Thus, to summarize the findings from Figure 3, we find that the relatively high electron affinity of PCBM indeed leads to the lowest open-circuit voltages in the series, verifying the need for looking into alternative electron transport layer materials. The substitution of PCBM by ICBA enables higher open-circuit voltages thereby verifying the assumption that the energy level alignment at the perovskite–PCBM interface leaves room for improvement.[52] The cells based on ICBA, however, also show a drastically reduced FF consistent with the observed charge transport problems of fullerene multiaffects encountered in the past in the context of polymer:fullerene solar cells.[47,48] The apparent solution for this dilemma is found to be the use of the fullerene monoaduct CMC blended in 1:1 ratio with either PCBM or—with even higher efficiencies—ICBA. Thus, the use of binary blends of different fullerenes allows combining their advantages rather than being limited by the shortcomings of the respective molecules. This is an observation that has also previously been made in the context of organic solar cells, where ternary blends using, e.g., two different acceptor molecules combined with one donor have efficiencies that exceed those of the binary blends.[67–69]

### 2.3. Loss Analysis

In the following, we will briefly study the key loss mechanisms in our solar cells by comparing the performance indicators $J_{sc}$, $V_{oc}$, FF, and efficiency to the values of a cell with the same bandgap in the Shockley–Queisser model. We use the methodology that has been introduced by Guillermo et al.[50] and Krückemeier et al.[52]

In Figure 4a the power density of our champion device is shown as a function of voltage (blue) and is compared with the power density of a cell with the same bandgap (1.72 eV) with an ideal FF (red), ideal $V_{oc}$ and ideal FF (green) and finally the power density–voltage curve of the cell in the Shockley–Queisser model (yellow). Figure 4a emphasizes that we optimized the cells for high $V_{oc}$ and high FF. Thus, the difference between ideal $J_{sc}$ and measured $J_{sc}$ is the highest but can be explained by the low absorber thickness of 280 nm that gives the best electronic quality and highest open-circuit voltages.

Figure 4c shows the ratio of different losses for our champion device with a 1:1 blend of CMC and ICBA and 5 other fullerenes or fullerene blends as ETL. The percentage of SQ efficiency is plotted on a logarithmic axis, i.e., the relative size of the boxes is independent of their position in the total loss bar. The normalized efficiency can be written as

$$\eta_{rad} = \frac{J_{sc}V_{oc}FF_{rad}}{J_{sc}V_{oc}FF_{ed}}$$

Note that the FF depends on the $V_{oc}$. Hence, the loss in FF is divided in the loss in maximum fill factor that is due to the loss in $V_{oc}$, i.e., $FF_{ed}(V_{oc}^{rad})/FF_{ed}(V_{oc}^{m})$ (blue Figure 4c), and the loss in fill factor that is due to the series resistance and the ideality factor $FF_{rad}/FF_{ed}(V_{oc}^{m})$ (red Figure 4c). Regardless of the fullerene, the photocurrent loss $J_{sc}/FF_{ed}$ (yellow Figure 4c) is the highest loss, which can be partly explained by the small thickness (280 nm) of the absorber layer and no additional light management. All cells show a small loss in calculated FF due to a small difference in
The resistive loss in $F_F$ varies for the different ETL. In case of ICBA ($F_F^{\text{real}}/F_F^{\text{ideal}}$) is particularly high suggesting a reduced conductivity of the ICBA layer. The loss in $V_{oc}$ can be divided in the difference between the actual absorption coefficient and the assumed step function in SQ (blue Figure 4c) and nonradiative loss (green Figure 4c). The perovskite and thus the bandgap and shape of the external quantum efficiency spectrum in the region close to the bandgap is not severely affected and hence the ratio $V_{oc}^{\text{rad}}/V_{oc}^{\text{SQ}}$ is nearly the same for all cells. The ratio $V_{oc}^{\text{real}}/V_{oc}^{\text{rad}}$ is highest for cells which contain PCBM in the ETL and lowest for cells with either ICBA, CMC or ICBA:CMC as ETL. Our champion device based on the CMC:ICBA blend ETL shows a moderate normalized efficiency $\eta_{\text{rad}}/\eta_{\text{SQ}} = 0.66$, but our nonradiative $V_{oc}$ loss is comparable with high efficiency devices based on much lower bandgaps, e.g., Jiang et al.[3] Figure 4d illustrates the exceptionally low voltage losses of our solar cells compared to the voltage losses in other wide bandgap perovskite devices that typically exceed those of lower bandgap perovskites.[15,33,71,72]

2.4. Interfacial Recombination

The most obvious finding from our previous analysis of device data is the observation of high open-circuit voltages and low nonradiative recombination losses. This implies that our process yields a high-quality bulk material which only shows minimal losses due to interface recombination. Interface recombination is affected both by the energy-level alignment[73–75] at the interface between absorber and both charge transport layers and by its kinetics that are typically expressed in terms of surface- or interface-recombination velocities.[76]

Here, we will first study the kinetics of recombination using transient photoluminescence measurements and subsequently the energy-level alignment of the different fullerenes by a combination of ultraviolet photoelectron spectroscopy (UPS) and photothermal deflection spectroscopy (PDS).

2.4.1. Recombination Kinetics

We measured transient photoluminescence with time-correlated single-photon counting on half cells without the BCP and silver contact with the decays being shown in Figure 5a and b. This was done to reduce the impact of capacitive effects that would be expected from electrode charging and discharging in complete devices.[77] In order to analyze the data, we calculate the differential decay time by first fitting the Tt-PL decays and then differentiating the fits using

$$\tau_{\text{diff, HLI}} = -2 \left( \frac{\ln(\phi)}{dt} \right)^{-1}$$

where $\phi$ is the luminescence. The factor of 2 originates from the assumption of high-level injection (HLI), i.e., $\phi \propto n^2$.[78]

Figure 4. Analysis of losses. a) Power density $P$ of the best cell (blue) compared to the ideal cell in different steps of ideality, ideal fill factor (red), Shockley–Queisser $V_{oc}$ (green), and complete SQ model (yellow). The biggest improvement could be achieved by increasing $J_{sc}$. b) The radiative limit $V_{oc}^{\text{rad}} = 1.42$ V is calculated from the product of photovoltaic quantum efficiency and black body spectrum as described, e.g., by Rau.[50] The photovoltaic quantum efficiency is extended by fitting an Urbach tail of $E_U = 16$ meV to the measured quantum efficiency $\Phi_{\text{phot}}$ as explained by Krückemeier et al.[52] Because the $V_{oc}^{\text{rad}}$ should be independent of the ETL, we show the data from the cell with the CMC:ICBA blend as ETL. c) The percentage of Shockley–Queisser efficiency for cells with different ETLs separated in current loss ($J_{sc}$), fill factor losses ($F_F^{\text{real}}/F_F^{\text{ideal}}$, $F_F^{\text{ideal}}(V_{oc}^{\text{rad}})/F_F(V_{oc}^{\text{rad}})$), and radiative and nonradiative voltage loss ($V_{oc}^{\text{rad}}/V_{oc}^{\text{SQ}}$, $V_{oc}^{\text{rad}}/V_{oc}^{\text{real}}$). d) Percentage of Shockley–Queisser efficiency for perovskite cells with different bandgaps.
where \( n \) is the charge-carrier concentration. The resulting differential decay times are plotted as a function of the quasi Fermi-level splitting \( \Delta E_{F} \) which is proportional to \( \ln(\phi) \) as computed in Equation (S5) of the Supporting Information. Note that early times after the pulse correspond to high \( \Delta E_{F} \) and late times to low \( \Delta E_{F} \). The differential decay times as shown in Figure 5c,d. show a rapidly decreasing decay time toward high quasi Fermi-level splitting (short times), and a small decrease at intermediate values of \( \Delta E_{F} \). At smaller values of \( \Delta E_{F} \) (long times) the decay times differ for the different fullerenes. Decay times for CMC:ICBA (green) and PCBM:ICBA (gold) nearly saturate in a slightly sloped plateau, PCBM (gray) and ICBA (lilac) continue decreasing but with a smaller slope, PCBM:CMC (red) saturates after a steep rise and CMC (blue) increases fast. It should be mentioned that the steady-state PL shows a peak shift (Figure S13, Supporting Information) for PCBM:CMC, which could be the reason for the difference to the other mixed fullerenes. The peak shift could be related to phase segregation during the activation of the sample.\(^{[24,25]}\) The decays are generally comparably slow as those measured on similar MAPI samples as presented, e.g., by Liu et al.\(^{[4]}\) and Haddad et al.\(^{[76]}\)

The first regime of the decay time versus \( \Delta E_{F} \) plot (short times) can be affected by charge extraction to the charge transport layers and the ITO electrode as well as by radiative and Auger recombination, leading to relatively short decay times.\(^{[78,79]}\) The intermediate and late regime should be dominated by either bulk or interface recombination with an approximately constant lifetime, i.e., some type of defect-assisted SRH process.\(^{[80]}\) In contrast to the other fullerenes and blends the differential decay time of CMC increases even further toward lower values of \( \Delta E_{F} \) (long times), representing the flat parts of the TR-PL decays shown in Figure 5a. These regimes are representative of the part of the original data with the lowest signal-to-noise ratio, where the TR-PL data approaches its background (noise) level. For the other ETLs, we cut off the regime with lowest signal-to-noise ratio as described in Figure S16 of the Supporting Information. In addition, the long-time regime can be affected by slow processes such as capacitive discharges of electrodes or contact layers that reinject charge into the perovskite absorber.\(^{[77,80]}\) Therefore, we conclude that the region most representative of the information of interest, namely, all types of SRH recombination, is the flat or intermediate region. If we analyze the data of the 1:1 blend of CMC and ICBA at the point

![Figure 5: Normalized transient photoluminescence \( \phi \) of glass/ITO/PTAA/perovskite/ETL samples with pure and b) mixed fullerenes measured with time correlated single-photon counting (TCSPC). In order to analyze the data, we fit two exponential functions to the normalized data (darker lines). c,d) We computed the differential decay time \( \tau_{\text{diff},\text{HLI}} \) by using Equation (3) and plotted the result versus Fermi-level splitting \( \Delta E_{F} \). Samples using an ETL made from a (1:1) blend of CMC and ICBA show the highest lifetime of \( \tau > 1 \mu s \). e,f) Surface-recombination velocity \( S \) computed with Equation (3) for bulk lifetime \( \tau_{\text{bulk}} = 10 \mu s \) (dotted line), 5 \( \mu s \) (dashed line), and 1 \( \mu s \) (solid line).]
where the derivative of the differential decay time has a minimum, we obtain differential decay times of $\tau_{\text{diff,HIL}} = 0.75 \mu$s at $\Delta E_i = 1.46 \text{ eV}$. As described in Section S5.2 of the Supporting Information, we can estimate surface-recombination velocities from these decay times via

$$S(\Delta E_i) = 2d \left( \frac{1}{\tau_{\text{diff,HIL}}} - \frac{1}{\tau_{\text{bulk}}} \right)$$

and obtain values ranging from $S = 17$ up to $67 \text{ cm s}^{-1}$. We vary the assumed bulk recombination time from $\tau_{\text{bulk}} = 1$, 5, and $10 \mu$s\textsuperscript{[56]} and use a thickness $d = 280 \text{ nm}$ (Figure 5e,f). Especially for ICBA and CMC:ICBA, a bulk lifetime $\tau_{\text{bulk}} < 1 \mu$s would be inconsistent with the long differential decay times, which therefore implies that the value for $S$ computed from Equation (4) becomes extremely low or even negative. In the latter case, the assumed bulk lifetime must be unphysical and a longer lifetime has to be assumed. The values of the surface-recombination velocity presented here are slightly higher than what was previously estimated for the PTAA/MAPI interface\textsuperscript{[46]} based on Tr-PL measurements but slightly lower than previous estimates\textsuperscript{[76,79]} for recombination at the MAPI/PCBM interface. The surface-recombination velocity of PCBM in the assumed bulk lifetime range is nearly one order of magnitude higher than $S$ for CMC:ICBA. Furthermore the combination of PCBM and CMC results in a similarly high $S$ while the ICBA in PCBM:ICBA seems to compensate the PCBM. Note that the effect of the variation of the bulk lifetime is particularly important for cases, where the differential decay time is rather long. Thus, for ICBA and CMC:ICBA, there is a substantial variation in the estimated value of $S$ with $\tau_{\text{bulk}}$, while for the other ETLs, there are only minor variations.

### 2.4.2. Energy Level Alignment and $V_{\text{oc}}$ Losses

In addition to surface quality the energy alignment between perovskite and CTL limits the $V_{\text{oc}}$.\textsuperscript{[10,76]} Large offsets, e.g., in the conduction band at the absorber–ETL interface would lead to an interfacial bandgap at this interface that is substantially lower than the bulk bandgap. If recombination is efficient via the interface (i.e., electrons in the ETL can efficiently recombine with holes in the perovskite), the interface may strongly deteriorate the $V_{\text{oc}}$.\textsuperscript{[82]} Therefore, characterization of energy levels is crucial for a complete understanding of interfacial recombination in a solar cell. Typically, UPS is used to measure the work function $\Phi$ and the valence-band edge $E_V$ at the surface of the samples. Given that we are interested in the LUMO positions of our ETLs, we have to combine UPS data with data from optical spectroscopy to obtain the bandgap and thereby the electron affinity $\chi$.

We derived the work function and the valence-band edge with UPS measurements as shown in Figure S19 of the Supporting Information for all fullerenes and blends on glass/ITO/PTAA/perovskite/ETL stacks. We activated the half cells before the UPS measurement by illumination under a white LED lamp as described in the Supporting Information. Figure 6a illustrates the difference between the ionization energy $E_i = E_{\text{vac}} - E_V$ of PCBM and the other fullerenes. We determined a smaller $E_i$ for ICBA of 160 meV, which is in good agreement with the offset (200 meV) measured by Faist et al.\textsuperscript{[59]} The relevant quantity for band alignment with the perovskite is however the electron affinity as it determines electron extraction and recombination of electrons in the ETL with holes in the perovskite. However, fullerenes do not show a clear absorption onset that could be used to determine the bandgap but feature a weakly absorbing absorption feature at around 1.75 eV and then a slow rise.

![Figure 6](https://example.com/image.png)

**Figure 6.** a) Schematic band diagram of PCBM compared to the other ETLs. b) Bandgap difference $\Delta E_i$ between PCBM and the other ETL materials, measured with PDS and total transmittance and reflectance spectroscopy. c) Ionization energy $E_i = E_{\text{vac}} - E_V$ relative to the ionization energy of PCBM. The work function $\Phi$ and the valence-band energy relative to the Fermi-level energy $E_F = 0$ eV were derived from UPS measurements. d) Difference between electron affinity of PCBM and the other ETLs. The electron affinity was computed with the PDS measurements and UPS measurements and the median $V_{\text{oc}}$ with the error bar representing the datapoints within 1.5 x IQR (Figure S12, Supporting Information).
until strong absorption is visible in the blue and UV parts of the spectrum. This has led to substantial variations of electron affinities determined by combining UPS and absorption spectroscopy in literature.\textsuperscript{[45,58,81–84]} In order to circumvent this challenge, we again only compare relative changes in bandgap that we determine from PDS measurements analyzed at three different constant absorption coefficients $\alpha = 1 \times 10^3 \text{cm}^{-1}$, $\alpha = 5 \times 10^3 \text{cm}^{-1}$, and $\alpha = 1 \times 10^4 \text{cm}^{-1}$. The arithmetic means of the three optical bandgap differences with respect to PCBM are shown in Figure 6b. We observe that the optical bandgap of CMC is $\approx 40 \text{meV}$ bigger than the bandgap of PCBM while the other fullerenes show slightly lower bandgaps than PCBM.

Figure 6d shows the relative position of the LUMO of the different ETLs compared to PCBM determined from the values in Figure 6b,c and the median $V_{oc}$ from the solar cell characterization. The error bars of $V_{oc}$ represent the datapoints within $1.5 \times$ IQR (interquartile range), where the IQR represents the region of 50% of the data points (Figure S10, Supporting Information). PCBM and PCBM:CMC share the same electron affinity, while the other blends and fullerene layers have a lower electron affinity. The LUMO of ICBA is closest to vacuum, fitting to the high $V_{oc}$. However, the correlation between $V_{oc}$ and $\Delta \chi$ is not distinct enough to solely explain the high $V_{oc}$. Instead, we propose that the combination of the optimization of the energy level alignment and slight improvements in the interface passivation suggested by the Tr-PL decays and the experimental uncertainties in measuring energy level alignment with accuracies of a tens of mV.

### 2.5. Fill Factor Losses

As observed in Figure 4c,d, the fill factor losses are still substantial and even at fill factors $\approx 80\%$ generally exceed the losses in $V_{oc}$ in the cells discussed here. The same is true for most high efficiency perovskite solar cells reported in literature and stands out relative to more mature technologies such as Si or GaAs where these losses are substantially lower.\textsuperscript{[52]} These losses partly originate from the high ideality factors observed even in high efficiency perovskite solar cells\textsuperscript{[13,85]} and from the resistive losses induced by the relative low conductivity and low permittivity of the organic charge transport layers.\textsuperscript{[86]} In the following, we will therefore study the general distribution of FF losses in more detail and analyze in particular resistive losses due to low mobilities in the ETLs via space-charge-limited current (SCLC) measurements.

#### 2.5.1. Analysis of Current–Voltage Curves

In order to distinguish between resistive contributions to the fill factor loss and those based on an ideality factor $n_{id}$ higher than one, we use a simple method to determine the series resistance $R_s$ by comparing illuminated and dark $JV$-curve in the 4th quadrant.\textsuperscript{[87,88]} When neglecting the parallel resistance and assuming the superposition principle\textsuperscript{[89,90]}, holds, the diode equation

$$J_i = J_0 \times \left( \exp \left( \frac{q(V_i - J_i R_i)}{n_{id} k T} \right) - 1 \right) - J_{sc}$$  \hspace{1cm} (5)

with $k$ the Boltzmann constant and $T$ the cell temperature and $J_0 = J_{sc} \times \exp \left( - \frac{V_{oc}}{k T} \right)$ describes the $JV$-curve of a solar cells. In the dark the diode equation is reduced to

$$J_d = J_0 \times \left( \exp \left( \frac{qV_d}{n_{id} k T} \right) - 1 \right)$$  \hspace{1cm} (6)

where the $JV$-curve is independent of light induced effects. The $J_{sc}/V_{oc}$ curve, i.e., $J_{sc}$ and $V_{oc}$ measured at different illumination intensities is independent of $R_s$

$$J_{sc} = J_0 \times \left( \exp \left( \frac{qV_{sc}}{n_{id} k T} \right) - 1 \right)$$  \hspace{1cm} (7)

since the current is zero at $V_{oc}$. Figure 7a shows the illuminated $JV$ curve (blue) the dark $JV$ curve shifted by $J_{sc}$ (yellow), the $J_{sc}/V_{oc}$ curve shifted by $J_{sc}$ (red) and the ideal $JV$ curve (green), i.e., $R_s = 0 \Omega \text{cm}^2$ and $n_{id} = 1$ for a PCBM cell. For equal current densities $J$, the difference between illuminated $JV$ curve and dark $JV$ curve divided by $J_{sc}$ leads to the series resistance\textsuperscript{[87]}

$$R_s = (V_d - V_i)/(J_d - J_i) = (V_d - V_i)/J_{sc}$$  \hspace{1cm} (8)

as long as the series resistance is independent of illumination intensities (Figure 7c). The mean series resistance for the PCBM cell is $R_s = 5.4 \Omega \text{cm}^2$ in a voltage range of $V_d = 1.24$ to 1.36 V (being very similar for forward and reverse scan) and increases toward lower voltage due to the increased internal resistance of the semiconducting layers making up the device.\textsuperscript{[87]} Note that the series resistance can as well be calculated by the difference between illuminated $JV$ curve and $J_{sc}/V_{oc}$ curve, dark $JV$ curve, and $J_{sc}/V_{oc}$ curve,\textsuperscript{[87]} respectively. The latter two approaches are however more prone to hysteresis effects as discussed in more detail in Section S7.2 of the Supporting Information. According to Green’s equation for the fill factor\textsuperscript{[92]} it depends not only on the series resistance but also on the ideality factor $n_{id}$. Therefore, we determine the ideality factor by calculating the slope of the short-circuit current plotted against the open-circuit voltage at different illumination intensities (Figure 7b; Figure S26, Supporting Information). The ideality factor for PCBM is in the range of roughly $n_{id} = 1.7$ to 1.9 for the reverse scan direction and even higher in the forward scan. In Figure 7d we plotted the power density versus voltage for the different $JV$ curves in a similar manner to Figure 4a. The maximum of the power density curve gives us the efficiency of our solar cell. The difference between illuminated and $J_{sc}/V_{oc}$ curve reveals the fill factor loss $\Delta FF_{s} = FF_{sc,V_{oc}} - FF_s = 3.7\%$ due to the series resistance in the cell. The difference between $J_{sc}/V_{oc}$ curve and ideal power density curve gives us the loss due to nonideal diode behavior, i.e., an ideality factor $n_{id} > 1$.\textsuperscript{[93]} The fill factor loss due to nonideal diode behavior is slightly larger than the loss due to $R_s$

$$\Delta FF_{s} = FF_{sc} - FF_{sc,V_{oc}} = 5.9\%$$ (see Table 1).
2.5.2. Space-Charge-Limited Current Measurements

The observation of improved FF for the binary ETLs compared to pure fullerene ETLs as shown in Figure 3d, suggests that the choice of fullerene or fullerene blend affects the conductivity of the ETL which in turn could modulate the resistive losses caused by the ETL. Hence, we studied the difference in electron mobility $\mu$ across the different ETLs using SCLC measurements. Therefore, we constructed electron only devices, similar to the cell stack. As shown in Figure 8a, we used ZnO nanoparticles and the standard BCP/Ag contact also used in the solar cells as electron injecting and extracting contact for the electron-only devices. In SCLC measurements, the current should follow the Mott–Gurney law\(^{(94)}\)

$$ J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d} $$ \tag{9} 

where $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_r = 3$ is the assumed relative permittivity, and $d$ is the thickness of the fullerenes and fullerene blends if certain conditions are met. These conditions include most notably the absence of diffusion—an assumption that is typically violated if there are either charged defects or asymmetric injection barriers present in the device. In order to distinguish between both effects, we measured the dark JV curve from $-4$ to $4$ V with the difference between forward and reverse bias being indeed substantial (see Figure S21, Supporting Information).\(^{(95,96)}\) To minimize the influence of diffusion on the data, we use the curve obtained by injecting electrons at the BCP/Ag electrode and extracting them at the ZnO electrode and limit ourselves to voltages $V > 1$ V.

Figure 8a shows a double-logarithmic representation of this part of the data shown as $J \times d^2$ versus voltage showing a transition from a region affected by diffusion to a region that is approximately following the Mott–Gurney law for higher measurements, the current should follow the Mott–Gurney law\(^{(94)}\)

$$ J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d} $$ \tag{9} 

where $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_r = 3$ is the assumed relative permittivity, and $d$ is the thickness of the fullerenes and fullerene blends if certain conditions are met. These conditions include most notably the absence of diffusion—an assumption that is typically violated if there are either charged defects or asymmetric injection barriers present in the device. In order to distinguish between both effects, we measured the dark JV curve from $-4$ to $4$ V with the difference between forward and reverse bias being indeed substantial (see Figure S21, Supporting Information).\(^{(95,96)}\) To minimize the influence of diffusion on the data, we use the curve obtained by injecting electrons at the BCP/Ag electrode and extracting them at the ZnO electrode and limit ourselves to voltages $V > 1$ V.

Table 1. $J_{sc}$, $V_{oc}$, FF, and $\eta$ for a solar cell based on an PCBM ETL compared to FF and $\eta$ from an ideal JV curve with the same $J_{sc}$ and $V_{oc}$ but $R_s = 0$ and $n_{id} = 1$ and a curve with zero series resistance (but nonideal $n_{id}$), derived from the measurement of the $J_{sc}/V_{oc}$ curves shown in Figure 8a,b.

| Material | $J_{sc}$ [mA cm$^{-2}$] | $V_{oc}$ [V] | FF [%] | $P_{FF,sc}$ [%] | $P_{FF,oc}$ [%] | $\eta$ [%] | $\eta_{id}$ [%] | $\Delta FF_{sc}$ [%] | $\Delta FF_{oc}$ [%] |
|----------|-----------------|------------|--------|-----------------|----------------|---------|--------------|----------------|----------------|
| PCBM     | 16.4            | 1.30       | 81.1   | 84.8            | 90.7           | 17.3    | 18.1        | 19.4           | 3.7            | 5.9            |
FF represents the datapoints within 1.5 IQR (Figure S12, Supporting Information). With AAA sun simulator on day four. The error bar for the mobility represents the uncertainty in thickness due to surface roughness. The error bar of injecting materials. b) Electron mobility from ASA simulation (see the Supporting Information) plotted against the median FF of all cells measured. The Mott–Gurney law (Equation (4)) Inset: schematic of the electron-only device stack using BCP/Ag und ZnO as the electron transporting layers combined with a better understanding of ideality-factor losses. The latter losses may be reduced by either further approaching the radiative limit for example by better surface quality or by moving the most recombination active parts of the device into low level injection.

3. Conclusion

Reaching high open-circuit voltage is one of the main challenges for wide bandgap perovskite solar cells. Using CH$_3$NH$_3$Pb(I$_{0.8}$Br$_{0.2}$)$_3$ with a bandgap of $E_g = 1.72$ eV and a blend of CMC:ICBA as electron transport layer we managed to fabricate solar cells with a high $V_{oc} = 1.35$ eV leading to a nonradiative loss of only $\Delta V_{oc} = 70$ mV without compromising in $FF = 81.2\%$. Using transient photoluminescence spectroscopy and a combination of ultraviolet photoelectron spectroscopy and photothermal deflection spectroscopy, we were able to assign the high $V_{oc}$ to low interfacial recombination and partly improved energy alignment. In addition, we studied the losses in fill factor, which are substantial given that representing $FF$ in the SQ model is nearly 91% for a $V_{oc}$ of 1.35 V. By using a comparison of measured current–voltage curves and suns-$V_{oc}$ measurements, we find that the $FF$ losses are distributed approximately equally between losses due to the ideality factor $n_q > 1$ and due to resistive losses. The resistive losses most likely originate from the finite conductivity of the charge transport layers. Space-charge-limited current measurements show that the electron mobility in the ETL materials varies for all fullerenes and fullerene blends, showing a monotonic correlation between $FF$ and electron mobility that holds for all samples but one. This suggests that further pathways toward higher efficiencies can be based on higher conductivities and mobilities in the electron transport layers combined with a better understanding of ideality-factor losses. The latter losses may be reduced by either further approaching the radiative limit for example by better surface quality or by moving the most recombination active parts of the device into low level injection.

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

fullerene blends, high open-circuit voltage, low nonradiative recombination, perovskites solar cells, wide bandgaps

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