Supplementary Information

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

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Supplementary Methods

Absolute Photoluminescence Measurements: Excitation for the PL imaging measurements was performed with a 445 nm CW laser (Insaneware) through an optical fibre into an integrating sphere. The intensity of the laser was adjusted to a 1 sun equivalent intensity by illuminating a 1 cm²-size perovskite solar cell under short-circuit and matching the current density to the J_{SC} under the sun simulator (22.0 mA/cm² at 100 mWcm⁻², or 1.375x10²¹ photons m⁻²s⁻¹). A second optical fiber was used from the output of the integrating sphere to an Andor SR393i-B spectrometer equipped with a silicon CCD camera (DU420A-BR-DD, iDus). The system was calibrated by using a calibrated halogen lamp with specified spectral irradiance, which was shone into to integrating sphere. A spectral correction factor was established to match the spectral output of the detector to the calibrated spectral irradiance of the lamp. The spectral photon density was obtained from the corrected detector signal (spectral irradiance) by division through the photon energy (hf), and the photon numbers of the excitation and emission obtained from numerical integration using Matlab. In a last step, three fluorescent test samples with high specified PLQY (~70%) supplied from Hamamatsu Photonics where measured where the specified value could be accurately reproduced within a small relative error of less than 5%. *Measurement conditions:* All films and cells were prepared fresh and immediately encapsulated in a glovebox after preparation with the exception of films and cells with spiro-OMeTAD which require oxygen doping for enabling sufficient transport capability in the device (non-oxgygen treated spiro-OMeTAD cells exhibited FFs below 20 % with negligible photovoltaic performance). Thus, films and cells with spiro-OMeTAD were treated in atmosphere overnight at 25% relative humidity, and subsequently encapsulated before the PL measurements. The PL of the samples was readily recorded after mounting the sample after an exposure between 10-20 s to the laser light. Thus, the PLQY is obtained on timescales relevant to the $V_{\rm OC}$ measurements on the cells. We note that all absolute PL measurements were performed on films with the same HTL, ETL and perovskite thicknesses as used in the operational solar cells. The absorption of the samples was considered in the PLQY calculation and was approximately 85% for cells illuminated through the top encapsulation glass, and ~93% through the bottom glass.

Electroluminescence: Absolute EL was measured with a calibrated Si photodetector (Newport) connected to a Keithley 485 pico Ampere meter. The detector (with an active area of $\sim 2 \text{ cm}^2$) was placed directly in front of the device (< 0.5 cm) and the total photon flux was evaluated considering the emission spectrum of the solar cell and the external quantum efficiency of the detector (around 86 % in the relevant spectral regime). A slight underestimation of the EQE_{EL} ($\approx 1.25\times$) cannot be excluded at present as some photons from the solar cells may escaped to the side and were not detected. A forward bias was applied to the cell using a Keithley 2400 source-meter and the injected current was monitored. Measurements were conducted with a home written LabVIEW routine. Typically, the voltage was increased in steps of 20 mV and the current stabilized for typical 1s at each step. No relevant changes in the EQE_{EL} were observed for different stabilization times.

Device Fabrication: Pre-patterned $2.5 \times 2.5 \text{ cm}^2 15 \Omega/\text{sq}$. ITO (Automatic Research, Germany), glass or fused silica substrates were cleaned with acetone, 3% Hellmanex solution, DI-water and *iso*-propanol, by sonication for 10min in each solution. After a microwave plasma treatment (4 min., 200W), the samples were transferred to an N₂-filled glovebox (except PEDOT:PSS which was spincoated in air) where different CTLs were spincoated from solution.

Bottom selective contacts: (HTLs or ETLs): PEDOT:PSS (Heraeus Celivious 4083) was spincoated at 2000 r.p.m. for 40s (acceleration 2000 r.p.m/s) and subsequently annealed at 150 °C for 15 minutes; P3HT (Sigma Aldrich, Mn~27 000) was spincoated from a 3 mg/mL DCB solution at 3000 r.p.m for 30s (acceleration 3000 r.p.m/s) and subsequently annealed 100 °C for 10 minutes. P3HT films were also oxygen plasma treated for 5 s to ensure sufficient wetting of the perovskite as discussed in a previous work.¹ PolyTPD (Ossila) was spincoated from a 1.5 mg/mL DCB solution at 6000 r.p.m for 30 s (acceleration 2000 r.p.m/s) and subsequently annealed 100 °C for 10 minutes. PTAA (Sigma Aldrich) was spincoated was spincoated from a 1.5 mg/mL Toluene solution at 6000 r.p.m for 30 s (acceleration 2000 r.p.m/s) and subsequently annealed 100 °C for 10 minutes. For PTAA and PolyTPD coated samples, a 60 µL solution of PFN-P2 (0.5 mg/mL in methanol) was added onto the spinning substrate at 5000 rpm for 20 s resulting in a film with a thickness below the detection limit of our AFM (< 5 nm). For compact/mesoporous TiO₂ samples, first a nippon Sheet Glass 10 Ω /sq was cleaned by sonication in 2% Hellmanex water solution for 30 minutes. After rinsing with deionised water and ethanol, the substrates were further cleaned with UV ozone treatment for 15 min. Then, 30 nm TiO₂ compact layer was deposited on FTO via spray pyrolysis at 450°C from a precursor solution of titanium diisopropoxide bis(acetylacetonate) in anhydrous ethanol. After the spraying, the substrates were left at 450°C for 45 min and left to cool down to room temperature. Then, a mesoporous TiO₂ layer was deposited by spin coating for 20 s at 4000 rpm with a ramp of 2000 rpm s-1, using 30 nm particle paste (Dyesol 30 NR-D) diluted in ethanol to achieve 150-200 nm thick layer. After the spin coating, the substrates were immediately dried at 100°C for 10 min and then sintered again at 450°C for 30 min under dry air flow. Before processing the perovskite layer TiO2 coated films were microwave plasma treatment (4 min., 200W). Compact SnO₂ films were fabricated by using a Tin(IV) oxide nanoparticle dispersion diluted 1:7 vol. with DI-H2O and filtered through 0.45 µm PVDF filter prior to spin coating on the substrate at 2000 rpm (acceleration 2000 r.p.m/s) for 30 s. After 20 minutes of annealing at 150 °C, the spin coating procedure was repeated and the samples were annealed again for 30 more minutes. Before processing the perovskite layer TiO2 coated films were microwave plasma treatment (4 min., 200W).

Perovskite Layer: The triple cation perovskite solution was prepared by mixing two 1.3 M FAPbI₃ and MAPbBr₃ perovskite solutions in DMF:DMSO (4:1) in a ratio of 83:17 which we call "MAFA" solution. The 1.3 M FAPbI₃ solution was thereby prepared by dissolving FAI (722 mg) and PbI₂ (2130 mg) in 2.8 mL DMF and 0.7 mL DMSO (note there is a 10% excess of PbI₂). The 1.3 M MAPbBr₃ solution was made by dissolving MABr (470 mg) and PbBr₂ (1696 mg) in 2.8 mL DMF and 0.7 mL DMSO (note there is a 10% excess of PbI₂). The 1.3 M MAPbBr₃ solution was made by dissolving MABr (470 mg) and PbBr₂ (1696 mg) in 2.8 mL DMF and 0.7 mL DMSO (note there is a 10% excess of PbBr₂). Lastly, 40 μ L of a 1.2M CsI solution in DMSO (389 mg CsI in 1 mL DMSO) was mixed with 960 μ L of the MAFA solution resulting in a final perovskite stoichiometry of (CsPbI₃)_{0.05}[(FAPbI₃)_{0.05}(MAPbBr₃)_{0.17}]_{0.95} in solution. The perovskite film was deposited by spin-coating at 4000 r.p.m (acceleration 1300 rpm/s) for 35 seconds; 10 Seconds after the start of the spinning process, the spinning substrate was washed with 300 μ L EA for approximately 1 second (the antisolvent was placed in the centre of the film). The perovskite film was then annealed at 100 °C for 1 hr on a preheated hotplate.

Top selective contacts: (HTLs or ETLs): SpiroOMeDAT was spincoated from a *spiro-OMeTAD* (Merck) solution in chlorobenzene (70 mM) at 4000 rpm for 20 s (acceleration 4000 rpm/s). Spiro-OMeTAD was doped with bis(trifluoromethylsulfonyl)imide lithium salt (Li-TFSI, Sigma-Aldrich), tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) tris(bis(trifluoromethylsulfonyl)imide) (FK209, Dynamo) and 4-tert-Butylpyridine (tBP, Sigma-Aldrich). The molar ratio of additives for spiro-OMeTAD was: 0.5, 0.03 and 3.3 for Li-TFSI, FK209 and tBP respectively. PC₆₁BM (Solenne BV) was spincoated from a 30 mg/mL DCB solution at 6000 rpm (acceleration 2000 r.p.m/s) for 30 s and the resulting Perovksite/PCBM film further annealed at 100 °C for 30 minutes. For C₆₀ (Creaphys) and LiF ETLs, the perovskite films were transferred to an evaporation chamber where 30 nm of C₆₀ (1 nm of LiF) were deposited at 0.1 Å/s (0.03 Å/s) under vacuum (p = 10^{-7} mbar).

Metal contacts: *pin*-type devices were completed by transferring the samples to an evaporation chamber where 8 nm BCP (Sigma-Aldrich) at 0.2 A/s and 100 nm copper (Sigma-Aldrich) at 0.6 Å/s were deposited under vacuum ($p = 10^{-7}$ mbar). *nip*-type devices were completed by transferring the samples to an evaporation chamber where 100 nm gold (0.7 Å/s) were deposited under vacuum ($p = 10^{-7}$ mbar). *nip*-cells were oxgygen doped overnight at 20% relative humidity prior to device and PL measurements.

Current density-voltage characteristics: *JV*-curves were obtained in a 2-wire source-sense configuration with a Keithley 2400. An Oriel class AAA Xenon lamp-based sun simulator was used for illumination providing approximately 100 mW cm⁻² of AM1.5G irradiation and the intensity was monitored simultaneously with a Si photodiode. The exact illumination intensity was used for efficiency calculations, and the simulator was calibrated with a KG5 filtered silicon solar cell (certified by Fraunhofer ISE). The temperature of the cell was fixed to 25 °C and a voltage ramp of 67 mV/s was used. A spectral mismatch calculation was performed based on the spectral irradiance of the solar simulator, the EQE of the reference silicon solar cell and 3 typical EQEs of our cells. This resulted in 3 mismatch factors of M = 0.9949, 0.9996 and 0.9976. Given the very small deviation from unity the measured J_{SC} was not corrected by the factor 1/M. All EQEs presented in this work were measured by ISE-Fraunhofer.

Scanning Electron Spectroscopy: SEM images were acquired with a Zeiss Ultra Plus SEM.

Photoemission Spectroscopy Measurements: Photoemission experiments were performed at an ultrahigh vacuum (UHV) system consisting of sample preparation and analysis chambers (both at base pressure: 1×10^{-10} mbar) as well as a load lock (base pressure: 1×10^{-6} mbar). All of the samples were transferred to the UHV chamber using a transfer rod under rough vacuum (1×10^{-3} mbar). Ultraviolet photoemission spectroscopy (UPS) was performed using a helium discharge lamp (21.22 eV) with a filter to reduce the photoflux and to block visible light from the source hitting the sample. All spectra were recorded at room temperature and normal emission using a hemispherical Specs Phoibos 100 analyzer, and the overall energy resolution was 140 meV.

Transient Photocurrent (TPC)/Photovoltage (TPV) and differential charging: Photovoltage transients were recorded with an oscilloscope (Agilent 81150A) at different external load resistance (R_{Load}) of 1 M Ω (TPV) and 50 Ω (transient photocurrent). A constant background illumination was provided by a white LED which was continuously increased ranging from 10⁻³ equivalent suns to approximately 3 suns. Each measured data point corresponds to a different illumination intensity. A Q-switched neodymium-doped yttrium aluminium garnet (Nd:YAG) laser (NT242, EKSPLA)) with a pulse length of 5 ns, a repetition rate of 10 Hz and excitation wavelength of 532 nm was used to generate the charge carriers, while neutral optical density (OD) filters were used to attenuate the power output. The laser fluence was kept low to ensure a small perturbation on top of the constant background current (generating a maximum voltage deflection of 20 mV at 1 M Ω without background illumination). In order to obtain the carrier lifetime (τ) from TPV, the photovoltage was fitted with a monoexponential decay at each laser fluence. au plotted versus the obtained V_{oc} at the given intensity. At low intensities, the effects of external circuit are visible with an RC-time of ~1ms. The differential capacitance was obtained by integrating the TPV signals to obtain ΔQ , while the ΔV was obtained from the maximum photovoltage of the TPV transients at each intensity. The differential capacitance is obtained from $C_{DC} = \Delta Q / \Delta V$ and plotted versus the V_{OC} . The geometrical capacitance (C_{geo}) is visible at low intensities or V_{OCS} and accumulated charge in the active layer at higher V_{OCS} . The accumulated charge carrier density in the bulk is obtained by integrating $n_{\text{bulk}} = \frac{1}{eAd} \int_0^V (C_{\text{DC}} - C_{\text{geo}}) \, dV$ and also plotted versus the V_{OC} at each intensity. **SCAPS simulations:** Simulation parameters and further details are discussed at **Supplementary Table S1**. SCAPS is an open-source code and can be obtained from https://users.elis.ugent.be/ELISgroups/solar/projects/scaps upon the conditions requested by the developers Marc Burgelman et al.



Supplementary Figure S1. External Quantum Efficiency (EQE) spectra, the product of the black body (ϕ_{BB}) spectrum and the EQE, and the integral of $\phi_{BB} * EQE$. The graphs shows that $J_{0,rad}$ is very similar for all system (6.5 $\pm 1 \times 10^{-21}$ A/m²) independent of the bottom charge transport layer. This also suggests that the optoelectronic quality of the perovskite layer is not significantly altered due to the different HTL underneath.



Supplementary Figure S2. Quasi-Fermi level splitting of various perovskite films illuminated through the perovskite (blue circles) or the charge transport layer (red symbols) using a 445 nm CW laser. In case of the neat perovskite film, the red symbol corresponds to a measurement through the bottom glass substrate. We note that the 445 nm laser is absorbed within a narrow window in the perovskite layer (<150 nm penetration depth) according to optical transfer matrix simulations which are also shown in **Supplementary Figure S12**. The graph shows that illuminating through the electron transport layers (ETLs) C₆₀, PCBM causes a significantly lower QFLS (up to 30 meV) compared to illumination through the perovskite, which is attributed to substantial parasitic absorption in the ETL at this wavelength. A smaller difference in the QFLS depending on the illumination side was observed for the other transport layers.



Supplementary Figure S3. The obtained quasi-Fermi level splitting of perovskite films including the studied hole and electron transporting materials and the neat absorber layer. Each data point corresponds to a different sample film. For each film an area of 1 cm² was illuminated and the average QFLS plotted. We also studied films on glass and glass/ITO substrates (glass/FTO in case of TiO2) which are more relevant for actual devices. The values obtained on glass/ITO (glass/FTO) are plotted in red (films on glass in blue). We note small differences between these two substrates indicating small losses between the HTL and the metal electrode in some cases. The lines show the mean values and the boxes the standard deviations.



Supplementary Figure S4. Representative PL spectra of the bare perovskite film and perovskite films with different electron and hole transport layers.



Supplementary Figure S5. The QFLS of triple cation perovskite films on glass and fused slilica shows that the latter substrate causes less non-radiative recombination losses, which indicates some recombination is occurring at the glass/perovskite interface. The lines show the mean values and the boxes the standard deviations.



Supplementary Figure S6. The PL emitted from glass/ITO/PEDOT/pero/C60 and glass/ITO/PTAA/PFN/pero/C60 stacks with and without the copper electrode. No significant difference in the emission is observed in the presence of copper which is attributed to the fact that all samples are placed on a reflective sample holder in the Ulbricht sphere where the PL experiment was performed. Thus, emission that is emitted to the bottom sample holder is likely reflected back, similar to light that is emitted to the copper electrode which might explain the small impact of the copper electrode.



Supplementary Figure S7. Scanning electron microscopy (SEM) top sectional images of perovskite films fabricated on different underlying charge transport layers reveal differences in the perovskite morphology. Remarkably, are the substantially larger grains on PEDOT hole transport layers (despite their low radiative efficiency) and the broad distribution of different grain sizes on TiO₂ films. Relatively small grains are observed on PolyTPD:PFN, ITO, P3HT and PTAA:PFN bottoms layers. Overall, no clear correlation between the perovskite morphology and the photovoltaic performance can be deduced from these SEM results.



Supplementary Figure S8. Atomic Force Microscopy (AFM) top sectional measurements on perovskite films fabricated on different underlying charge transport layers reveal differences in the root mean square roughness (RMS) for each layer. Interestingly, the most efficient films in terms of photoluminescence exhibit a slightly rougher surface compared to the others, while films on TiO₂ were the smoothest.



Supplementary Figure S9. Device statistics of 6 mm²-size perovskite solar cells (with standard configuration ITO/HTL/perovskite/C60/BCP/Cu) showing the impact of the hole transport layer on the solar cell parameters. The average V_{OC} values are plotted in Figure 2. The cells plotted on the right in each panel were fabricated using and additional LiF layer (~1 nm) between the perovskite and C₆₀ which allowed efficiencies above 20%. The lines show the mean values and the boxes the standard deviations.



Supplementary Figure S10. *JV*-characteristics of one of our most efficient cells fabricated at low temperatures (100 °C) using the standard Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pbl_{0.83}Br_{0.17} triple cation perovskite absorber with a bandgap of approximately 1.6 eV, with PTAA/PFN and LiF/C60 as hole-and electron selective CTLs. The inset shows the stabilized efficiency evolution of the cell and the external quantum efficiency spectrum. The integrated product of the EQE and the solar spectrum (21.5 mAcm⁻²) closely matches the measured short-circuit current density under the solar simulator (21.8 mAcm⁻²).



Supplementary Figure S11. Quasi-Fermi level splitting of the individual perovskite/transport layer films as well as the average device V_{OC} of *nip* cells based on (**a**, **b**) TiO2 and (**c**, **d**) SnO₂ confirming that substantial interfacial non-radiative recombination losses lower the QFLS of the perovskite (1.23 eV) to 1.16-1.17 eV in the stack. For both cell types, the non-radiative recombination losses at the perovskite/spiroOMeTAD junction appear to limit the QFLS of the complete stack. For TiO₂ cells, 2 substrates with 4 pixels (30 mm²) in total were fabricated of which the *JV*-curves are shown in panel (**b**) with efficiencies of around 19%. For SnO₂ cells, 2 substrates with 12 pixels in total (16 mm²) were fabricated of which the *JV*-curves are shown in panel (**b**) with efficiencies are shown in panel (**d**) with efficiencies up to 18% (max).



Supplementary Figure S12. V_{OC} vs. short-circuit current for two different laser wavelengths (445 nm and 638 nm) on *pin*-type devices with (**a**) PTAA:PFN and (**b**) PEDOT as hole transport layer, while C₆₀ was used as electron transport layer in both cases. The graph demonstrates that the V_{OC} is essentially independent on the initial carrier generation profile over several orders of magnitude in laser intensity (or short-circuit current). (**c**) and (**d**) show the corresponding *E*-field intensity in the two devices which was simulated based on optical transfer matrix simulations using an open source code developed by McGehee et al. which was adapted from ref.^{2,3}

Supplementary rune St. Sent S Simulation parameters for the Simulations Shown in Figure S

Parameter	Symbol	Value	Unit
Majority carrier band offset between perovskite and C_{60}^{*}	$\Delta E_{\mathrm{maj,c}}$	0	eV
Majority carrier band offset between perovskite and PTAA*	$\Delta E_{maj,v}$	0	eV
Majority carrier band offset between perovskite and PEDOT*	$\Delta E_{maj,v}$	0.5	eV
lifetime in perovskite*	$ au_{ m pero}$	1000	ns
lifetime in PTAA	$ au_p$	1	ns
lifetime in C ₆₀	$ au_n$	1	ns
Ionized acceptors in PTAA*	$N_{A,p}^{-}$	1x10 ⁵	cm⁻³
Ionized donors in C ₆₀ *	$N_{\mathrm{D},n}^+$	1x10 ⁵	cm⁻³
Intrinsic carrier density in perovskite	Ni	1x10 ¹⁰	cm⁻³
Minority carrier recombination velocity from perovskite to PTAA*	S_n	200	cm/s
Minority carrier recombination velocity from perovskite to PEDOT*	S_n	200	cm/s
Majority carrier recombination velocity from perovskite to PEDOT*	\overline{S}_p	1x10 ⁷	cm/s
Minority carrier recombination velocity from perovskite to C_{60}^{st}	S_p	1000	cm/s
Thickness of PTAA*	$d_{ m PTAA}$	10	nm
Thickness of perovskite*	$d_{ m pero}$	400	nm
Thickness of C ₆₀ *	$d_{ m C60}$	30	nm
Offset between metal and PTAA*	$\Delta E_{\mathrm{F,metal}-p}$	0.2	eV
Offset between metal and C_{60}^*	$\Delta E_{\mathrm{F,metal}-n}$	0.2	eV
Device built-in voltage*	$V_{\rm BI}$	1.2	V
Electron affinity PTAA*	$E_{A,PTAA}$	2.7	eV
Bandgap PTAA*	$E_{\rm G,PTAA}$	2.8	eV
Workfunction PEDOT*	$E_{\rm PEDOT}$	5.0	eV
Bandgap perovskite	$E_{\rm G,pero}$	1.6	eV
Electron affinity perovskite*	$E_{A,pero}$	3.9	eV
Bandgap perovskite	$E_{\rm G,pero}$	1.6	eV
Electron affinity C ₆₀ *	$E_{\rm A,C60}$	4.2	eV
Bandgap C ₆₀ *	$E_{\rm G,C60}$	1.8	eV
Electron mobility in C ₆₀ *	$\mu_{n,\mathrm{PTAA}}$	1x10 ⁻²	cm²/Vs
Hole mobility in PTAA*	$\mu_{p,\mathrm{PTAA}}$	1x10 ⁻⁴	cm²/Vs
Electron mobility in perovskite*	$\mu_{n, { m pero}}$	10	cm²/Vs
Hole mobility in perovskite*	$\mu_{p, { m pero}}$	10	cm²/Vs
relative dielectric constant PTAA	ϵ_{PTAA}	3.5	
relative dielectric constant perovskite*	$\epsilon_{ m pero}$	22	
relative dielectric constant C ₆₀	$\epsilon_{ ext{C60}}$	4.2	
Effective electron density of states in HTL	N _{C/V,PTAA}	1x10 ²⁰	cm⁻³
Effective electron density of states in C ₆₀	<i>N</i> _{C/V,C60}	1x10 ²⁰	cm⁻³
Effective electron density of states in perovskite	N _{C/V,pero}	3.1x10 ¹⁸	cm⁻³

Remarks: We note that we do not claim that every individual parameter is perfectly consistent with existing literature, however, we consider them as plausible. Importantly, all parameters marked with a star were varied as part of a much larger set of device simulations in order to understand the interplay between these parameters as good as possible. In particular, the impact of the majority (ΔE_{maj}) and minority carrier (ΔE_{min}) band offsets are discussed in the main text. The impact of strongly doped (1x10¹⁸/cm³) and essentially undoped (1x10⁵/cm³) charge transport layers was tested with an insignificant influence on the here presented results. The role of the

carrier mobilities of the charge transport layers was tested with an insignificant influence on the here presented results. The interface recombination velocities and bulk lifetimes were varied as discussed here and in a previous work.⁴ The impact of the transport layer thickness was tested. The built-in voltage is given by the workfunction difference of the electrodes, and its influence was tested. The interface recombination velocities in the metal contacts were set to 1×10^7 cm/s for both majority and minority carriers, while PEDOT was treated similar to a contact metal, however, with asymmetric minority and majority recombination velocities. The QFLS was calculated as an average of the emission from the perovskite, that is QFLS_{avg} = ln $\left(\int_{0}^{d_{pero}} \exp(QFLS(x)) dx\right)$.



Supplementary Figure S13. Simulated *JV*-curves for different built-in voltages (V_{BI}) across the device. The V_{BI} is given by the workfunction difference of the electrodes and is limited by the perovskite bandgap of 1.6 eV. The V_{BI} was varied by equally reducing the energetic offsets between and the perovskite valence/conduction bands and the workfunctions of the metals at the bottom and top contact, respectively. The results suggest that a considerable V_{BI} of \approx 1V is required in order to efficiently extract the charges and reproduce experimental *JV*-curves.



Supplementary Figure S14. Device simulations of V_{OC} and average quasi-Fermi level splitting (QFLS) on PTAA/perovskite/C60 stacks for different interface recombination velocities of electrons at the HTL/perovskite interface (S_n) to reveal the origin of a mismatched QFLS and device V_{OC} . The simulations predict such a mismatch in case of a majority carrier band offset (E_{maj}) between the perovskite valence band and the highest occupied molecular orbital of PTAA if the interface recombination velocities are above 1 cm/s. Notably, based on these simulations we expect no QFLS- V_{OC} mismatch in absence of a band offset regardless of the interface recombination velocity. The simulated V_{OC} for the most realistic scenario with $S_n = 300$ cm/s (green curve) at the HTL/perovskite interface shows that that even small majority carrier band offsets larger than >0.1 eV are already inconsistent with the experimentally measured V_{OC} 's of ~1.14 V in the PTAA/PFN/perovskite/C₆₀ device. We also note that for low interface recombination velocities $S_n \sim 1$ cm/s, the simulated QFLS and V_{OC} are limited by the interface recombination velocity S_p at the perovskite/ETL interface which was set to 1000 cm/s for these simulations. Voltages above 1.26 V can be achieved in the limit of negligible recombination at both interfaces (< 1 cm/s).



Supplementary Figure S15. Simulated open-circuit voltage versus minority carrier band offset (E_{min}) demonstrating that even smallest ΔE_{min} values of only 0.1 eV are in principle sufficient to prevent substantial charge recombination at the wrong interfaces. The primary reason for this result is that rapid recombination at the HTL/perovskite junction (which was set here to 200 cm/s) prevents minority carriers from entering the wrong CTL. The inset illustrates the energy bands for two device simulations where ΔE_{min} was increased from -0.1 eV to 1.4 eV demonstrating the nearly identical QFLS in the bulk (QFLS and energy bands are superimposed). The simulated electron and hole quasi-Fermi levels are shown by black lines and blue dots for ΔE_{min} energy offsets of 0.1 eV and 1.4 eV, respectively. Also shown are the conduction and valence bands in red, the device V_{OC} and average quasi-Fermi level splitting (QFLS). We acknowledge that these simulations represent an ideal scenario where we only varied the position of the LUMO level of the HTL, however in reality such small minority carriers which could, for example, cause much higher recombination velocities (*S*). Thus, while we can say that even small energetic offsets are sufficient to prevent minority carriers from entering the wrong contact, we cannot exclude that in reality such small offsets would cause much larger recombination losses by affecting other important parameters.



Supplementary Figure S16. (*a*) The simulated quasi-Fermi level splitting (QFLS, black dotted lines) of a PEDOT:PSS/perovskite/C₆₀ stack shows a bending of the hole QFL towards the p-interface. The simulations can well reproduce the experimentally observed QFLS-V_{oc} mismatch of ~150 meV. The perovskite absorber layer and C₆₀ are represented by their unoccupied states in orange and blue, respectively. Occupied states are drawn for PEDOT:PSS in striped red. (*b*) The drift diffusion simulations can also closely predict the experimentally obtained ideality factor (n_{1D}) of the perovskite cell with PEDOT:PSS as HTL. (*c*) Cross sectional scanning electron microscopy (SEM) images of a PTAA:PFN/perovskite and (*d*) PEDOT:PSS/perovskite film reveal a quite rough PEDOT:PSS layer. Therefore, a morphological problem cannot be excluded at the p-interface in case of PEDOT:PSS despite the good match between the simulations and the experimental data (V_{oc} , QFLS and n_{1D}).



Supplementary Figure S17. The ionization potentials (IPs) of the materials shown in the main text measured with photoelectron yield spectroscopy in air. The optical bandgaps were estimated from Tauc plots based on UV-Vis measurements. The IPs of C_{60} , TiO₂, and SnO₂ were outside the measurement range of the spectrometer (< -6.5 eV), therefore IPs previously determined from ultraviolet photon electron spectroscopy are plotted ref.⁵ It is important to note that the plotted energy levels are only relevant for each film in isolation and by no means represent the true energetics in the complete solar cell stack where junctions form and the vacuum level is not constant across all interfaces.



Supplementary Figure S18. (a) Transient Photovoltage (TPV) experiments on *pin*-type triple cation perovskite solar cells based on P3HT and PTAA. Lifetimes of the excess charge carriers are plotted as a function of the steady-state V_{OC} in the devices. The shorter lifetime at a given V_{OC} is consistent with the increased interfacial recombination in the P3HT cell as compared to PTAA cell. (b) To further prove the observed mismatch between the QFLS and the V_{OC} in case of PEDOT:PSS and P3HT containing devices, we performed differential charging capacitance measurements $C_{DC} = \Delta Q / \Delta V$, where the differential charge (ΔQ) was obtained from transient photocurrent (TPC) extraction and the differential voltage (ΔV) from TPV upon a small laser perturbation.^{6,7} The graph clearly displays two regions, where at low V_{OCS} the capacitance is given by the geometric capacitance while the sudden rise of the differential capacitance at higher V_{OCS} is caused by the accumulation of charge in the active layer (chemical capacitance). (c) The carrier density as obtained from the integration of the voltage dependent chemical capacitance in (b) shows that, for a given V_{OC} , the charge density in the device is substantially larger for the PEDOT:PSS cell than for the P3HT cell and the PTAA cell. This suggests that there is a substantial mismatch between the internal QFLS and the external Voc. (d) A schematic illustration showing why a mismatch between the QFLS and the V_{OC} leads to more charge in the device than expected from the device



Supplementary Figure S19. Quasi-Fermi level splitting (QFLS) of different perovskite systems with and without attached transport layers, *n-i-p* and *p-i-n* stacks and corresponding device V_{OC} . The different perovskite systems include (**a**) methyl ammonium and bromide-free $C_{S0.05}FA_{0.95}PbI_3$ with power conversion efficiencies of up to 20%, (**b**) low-gap triple cation perovskite $C_{S0.05}(FA_{0.95}MA_{0.05})_{0.95}Pb(I_{0.95}Br_{0.05})_3$ as used in today's record *n-i-p* cells,⁸ (**c**) hybrid vacuum/solution processed MAPI⁹ which is relevant for application on textured substrates for Si/perovskite tandem applications,¹⁰ (**d**) a simple one-step solution processed MAPI, (**e**) Pb-acetate based MAPI with exceptional V_{OC} s of 1.26 V (published in ref.¹¹), (**f**) high-gap mixed perovskite $C_{S0.15}FA_{0.85}Pb(I_{0.75}Br_{0.25})_3$ with optimal bandgap for monolithic Si/perovskite tandem cells,¹² (**g**) and two-dimensional perovskite solar cells

based on BA₂MA_{n-1}Pb_nI_{3n+1} (n=2-4) (published in ref.¹³). In most systems the absorber layer allows to reach substantially higher open-circuit voltages than achieved in the cells, but not in all systems. For example, in lowgap CsFAPI and our solution processed MAPI, the V_{oc} of the cell is close (20 – 30 meV) to the QFLS of the perovskite. Substantial V_{oc} improvements trough interfacial optimizations seem however feasible for low-gap triple cation perovskite (b), hybrid vacuum processed perovskite (c), high-gap mixed perovskite (f) and 2D perovskite (g). In the high-bandgap perovskite system (f), we observe again a considerable mismatch between the QFLS of the *pin*-stack and the V_{oc} (~120 mV). As discussed in this paper, such a mismatch can be explained by an energetic misalignment between the perovskite and the transport layers. This highlights the difficulties in increasing the perovskite bandgap while maintaining the energy level alignment and demonstrates the relevance of the findings for other perovskite systems. In the 2D systems, the application of the HTL was found to passivate the bottom surface while the perovskite/C₆₀ is limiting also here the V_{oc} of the final cells.

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