Article:

Abdi-Jalebi, M., Andaji-Garmaroudi, Z., Cacovich, S. et al. (2018) Maximizing and stabilizing luminescence from halide perovskites with potassium passivation. Nature, 555. pp. 497-501. ISSN: 0028-0836

https://doi.org/10.1038/nature25989

Maximising and Stabilising Luminescence from Halide Perovskites with Potassium Passivation

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Metal halide perovskites are attracting tremendous interest for a variety of high-performance optoelectronic applications[1]. The ability to continuously tune the perovskite bandgap by tweaking the chemical compositions opens up new applications for perovskites as coloured emitters, in building-integrated photovoltaics, and as components of tandem photovoltaics to further increase the power conversion efficiency[2–4]. Nevertheless, parasitic non-radiative losses are still limiting performance, with luminescence yields in state-of-the-art perovskite solar cells still far from 100% under standard solar illumination conditions[5–7]. Furthermore, in mixed halide perovskite systems designed for continuous bandgap tunability (bandgaps ~1.7-1.9 eV)[2], photo-induced ion segregation leads to bandgap instabilities[8,9]. Here, we substantially mitigate both non-radiative losses and photo-induced ion migration in perovskite films and interfaces by decorating the surfaces and grain boundaries with passivating potassium-halide layers. We demonstrate external photo-luminescence quantum yields of 66%, translating to internal yields exceeding 95%. The high luminescence yields are achieved while maintaining high mobilities over 40 cm^{2}V^{-1}s^{-1}, giving the elusive combination of both high luminescence and excellent charge transport[10]. We find that the external luminescence yield when interfaced with electrodes in a solar cell device stack, a quantity that must be maximised to approach the efficiency limits, remains as high as 15%, indicating very clean interfaces. We also demonstrate the inhibition of transient photo-induced ion migration processes across a wide range of mixed halide perovskite bandgaps that otherwise show bandgap instabilities. We validate these results in full operating solar cells, highlighting the importance of maximising and stabilising luminescence in device structures. Our work represents a critical breakthrough in the construction of tunable metal halide perovskite films and interfaces that can approach the efficiency limits in both tandem solar cells, coloured LEDs and other optoelectronic applications.

We fabricated a series of passivated triple-cation perovskite thin films on glass[11] ($Cs_{0.06}FA_{0.79}MA_{0.15}Pb(I_{0.85}Br_{0.15})_3$, where MA = methylammonium, CH_3NH_3; FA = formamidinium, $CH_3(NH_2)_2$, by diluting the precursor solution with potassium iodide (KI) solution. We herein denote the perovskite as $(Cs,FA,MA)Pb(I_{0.85}Br_{0.15})_3$ and the passivated samples with $x = [K]/([A]+[K])$ and A = (Cs,FA,MA), where x represents the fraction of K out of the A-site cations in the precursor solution. We note that the standard triple-cation precursor solution recipe ($x = 0$) has a slight halide deficiency but introducing KI leads to samples with a small excess of halide, along with very slight changes to the I/Br ratio (Extended Data Figure 1). The films have uniformly packed grains each of size ~200-400 nm (Extended Data Figure 1). Absorption and photoluminescence measurements reveal a reduction in the optical bandgap of the perovskite film with increasing KI addition, consistent with the additives selectively interacting with the bromide (Extended Data Figure 2).

For a solar cell or light-emitting diode to approach its efficiency limit, all recombination should be radiative and luminescence maximised[12]. In state-of-the-art perovskite films, there are still substantial non-radiative losses originating from charge-carrier trap states present in the perovskite layer[13]. The origin of the trap states is still unclear, but they may be associated with ionic defects such as halide vacancies[14,15]. In Figure 1a, we show the external photoluminescence quantum efficiency (PLQE) of the $(Cs,FA,MA)Pb(I_{0.85}Br_{0.15})_3$ perovskite films with increasing K content measured at excitation densities equivalent to solar illumination. The PLQE shows a significant jump from the 8% ($x = 0$) to 41% ($x = 0.05$) reaching a remarkably high PLQE of 66% for $x = 0.40$. By accounting for photon recycling and light-out-coupling effects[16], these values translate to an internal PLQE exceeding 95% for the passivated compositions (Figure 1a). Furthermore, the PLQE does not change significantly with excitation power for the passivated samples, unlike the $x = 0$ sample in which the PLQE increases with intensity due to a filling of the high density of trap states[17] (Extended Data Figure

2). These results are also reflected in micro-PL measurements (Extended Data Figure 3). Time-resolved PL (TRPL) measurements (Figure 1b) show the removal of the fast non-radiative decay component with passivation, leading to radiative bimolecular recombination (Extended Data Figure 4).

We use time-resolved microwave conductivity (TRMC) to assess the impact of the passivation on charge transport in the $(Cs,FA,MA)Pb(I_{0.85}Br_{0.15})_3$ perovskite thin films (Extended Data Figure 5)[10,18]. In Figure 1c, we show the maximum photo-conductance (charge mobility) for each of the K contents. We find that the carrier mobility remains mostly constant at a large value of ~42 $cm^2V^{-1}s^{-1}$ for perovskite with $x = 0$ and $x = 0.1$, before dropping for higher K content to ~30 $cm^2V^{-1}s^{-1}$ ($x = 0.4$), which could be an effect of decreasing grain sizes for $x > 0.2$[19] (see Methods). These results are consistent with lower trap densities[13] for the passivated samples, with the elimination of almost all non-radiative channels and retention of excellent charge transport up to $x = 0.1$.

In Figure 2a, we show the PLQE from $(Cs,FA,MA)Pb(I_{0.85}Br_{0.15})_3$ thin films as a function of time under continuous illumination with intensity equivalent to 1-sun. We find a substantial but slow transient rise for the reference film ($x = 0$) associated with photo-induced halide migration[20]. In contrast, the high values of PLQE for the passivated films are stable under continuous illumination, suggesting that the photo-induced migration processes are substantially inhibited. To further investigate the latter claim, we add KI to precursor solutions with higher fractions of Br, which typically show substantial PL shifts due to photo-induced halide segregation and subsequent emission from low-bandgap iodide-rich components[8]. We show that the PL spectral output of passivated films $(Cs,FA,MA)Pb(I_{0.4}Br_{0.6})_3$ is remarkably stable at the optimal bandgap for perovskite/silicon tandems (1.75 eV)[2] under 1-sun illumination (Figure 2c). In contrast, the sample without passivation shows substantial red-shifts and bandgap changes over time (Figure 2b). In Figure 2d, we show that this photo-stability is also seen across bromide fractions covering the range of idealised wide bandgaps for perovskite-perovskite tandems (1.7-1.9 eV)[2], albeit with slightly reduced stability at the highest bromide fractions (Extended Data Figure 4). We also find that the critical bandgaps for tandems can even be stabilised at low passivation levels (x = 0.1, Figure 2d). This is the first report showing such exceptional stability in mixed halide compositions across a wide range of bandgaps under solar illumination in ambient conditions[3].

We now investigate the chemical composition of the $(Cs,FA,MA)Pb(I_{0.85}Br_{0.15})_3$ perovskite thin films, performing scanning transmission electron microscopy-energy dispersive X-ray spectroscopy (STEM-EDX). In Figure 3a, we show a cross sectional view of a lamella of the $x = 0.2$ composition. From the STEM-EDX elemental analysis, we observe a potassium-rich phase at the grain boundaries of the perovskite as well as the interface with the substrate (Extended Data Figure 6). Analysis of the dataset using a Non-negative Matrix Factorisation (NMF) algorithm[21] highlights the presence of two compositional phases present in the specimen, reported as Factor 1 and Factor 2 in Figure 3b-c. Factor 1 shows characteristic EDX features, including Br L_α, Pb M_α, I L_α lines (Figure 3d), which can be associated with the perovskite phase, while Factor 2 is rich in bromine and potassium (Figure 3e) and interestingly, particularly prominent at the grain boundaries and top and bottom surfaces of the perovskite film. This is likely related to a new crystalline phase observed in Grazing-Incidence Wide-Angle X-Ray Scattering (GIWAXS) experiments (Extended Data Figure 7). These results are also consistent with Hard X-ray Photoelectron Spectroscopy (HAXPES) measurements, which reveal a decrease in K moving from the film surface into the bulk (Extended Data Figure 8). These results collectively indicate the formation of potassium halide (particularly Br-rich) passivation layers decorating the surfaces, with the potassium not incorporating into the perovskite lattice. We note that this is in contrast to other works reporting the addition of small monovalent cation to the perovskite including Na, Rb or K, which propose incorporation of these components into the lattice[5,22–25], though a recent report shows that Rb does not incorporate and suggests the same for K[26].

In Figure 3f, we summarise our interpretation of the results. Here, we are introducing excess iodide through the KI source into the perovskite precursor solutions, which compensates for any halide vacancies. The excess halides fill these vacancies, thereby passivating the non-radiative recombination pathways, leading to exceptionally high luminescence efficiencies. The excess halides are immobilised in the form of benign potassium-rich halide-sequestering species at the grain boundaries and surfaces, thereby inhibiting halide migration and suppressing any additional non-radiative decay arising from interstitial halides. At K content beyond $x = 0.1$, these non-perovskite species are too large and perturb charge transport. This suggests there is an optimal K content at $x \sim 0.1$, which is a compromise between high radiative efficiency and retention of high charge carrier mobility. Finally, we propose that potassium selectively depletes Br from the perovskite crystal structure, which is consistent with an increased lattice parameter, red-shifting band-edge, and decreasing Br/I ratio in the bulk with K addition (Extended Data Figures 2 and 8). We note that these observations and enhanced properties are not achieved in the absence of Br (Extended Data Figure 2). The addition of small fractions of bromide to the perovskite precursor solutions has been shown to improve perovskite film formation[27]. However, bromide-rich perovskites typically have increased trap states and inferior charge carrier mobility compared to their iodide-based counterparts[28]. Here we exploit the beneficial properties of bromide in the grain formation process while suppressing the formation of Br-induced defect states in the bulk of the crystal.

At open-circuit in a solar cell, external luminescence should be maximised[12], and we must minimise any additional non-radiative losses upon introduction of device electrodes. In Figure 4a and d, we show the time-resolved PL decays and PLQE, respectively, for the $(Cs,FA,MA)Pb(I_{0.85}Br_{0.15})_3$ perovskite with and without potassium passivation when deposited on a standard n-type mesoporous TiO_2 electron-accepting contact (see Extended Data Figure 9 for other excitation intensities). We find that charge-carrier recombination in the presence of the electrode is slower and more radiative (higher integrated TRPL intensity) in the presence of potassium, with the PLQE dropping by a factor of only 1.7 (to 27.1%) compared to a drop of factor 6.7 (to 3.0%) without passivation. In Figure 4b, we show the time-resolved PL decays for the perovskite containing a top layer of a standard p-type Spiro-OMeTAD hole-accepting contact. We again find that the passivation leads to slower charge carrier recombination and a less significant drop in PLQE upon introduction of the electrode (Fig. 4d), with a drop of factor 4.5 to 10.4% compared to a drop by factor 38 to 0.5% without passivation. Finally, we show the time-resolved PL decays for the full device stack (i.e. both electrodes) in Figure 4c, clearly showing the slower recombination and vastly reduced PLQE drop with the potassium sample. The external PLQE of the full stack is retained at 14.5% with the passivating interlayers (a reduction of factor 3.2 upon addition of the electrodes), an order of magnitude higher than the 1.2% of the control stack (reduction of factor 17). These results show that the potassium interlayers not only improve the optoelectronic properties of the neat material, but also lead to vastly improved interfaces with device electrodes.

To validate our findings, we construct full solar cells using the device architecture fluorinated-tin oxide (FTO) / compact-TiO_2 (~30 nm) / thin-mesoporous TiO_2 (~200 nm) / perovskite (~500 nm) / Spiro-OMeTAD (~150 nm) / Au (80 nm). In Figure 5a, we show the forward and reverse current-voltage (J-V) curves of champion devices containing the $(Cs,FA,MA)Pb(I_{0.85}Br_{0.15})_3$ absorbers with $x = 0$ and $x = 0.1$ under full simulated sunlight, with the extracted parameters given in Table 1 (see Extended Data Figure 10 and 11 and Table 1 for other K compositions, dark J-V curves, and device statistics). We find that the device efficiency increases from 17.3% ($x = 0$) to 21.5% ($x = 0.1$) with passivation, with the elimination of hysteresis in the latter case consistent with an inhibition of ion migration[1,20]. This is also consistent with a rapid rise to a stabilised power efficiency of 21.3%, compared to a slower rise to just 17.2% for the control (Fig. 5a inset). We see an increase in open-circuit voltage (V_{oc}) with passivation from 1.05 V ($x = 0$) to 1.17 V ($x = 0.1$) (Figure 5c), with the calculated V_{oc} difference from the increase in PLQE of the device stacks from 1.2 to 14.5% (Figure 4d) matching within error the difference in the V_{oc} distributions from the device statistics. The V_{oc} loss from the radiative limit is only 0.11 V and is one of the lowest losses reported in a perovskite solar cell to date[5]. We also see an increase in the short-circuit current (J_{SC}) with K addition up to $x = 0.1$ (Figure 5c), consistent with the increased carrier mobility and lifetime[29]. The optimal device performance at $x = 0.1$ therefore validates the compromise between radiative efficiency and carrier mobility. We conducted preliminary stability tests and found a negligible drop in shelf-life performanceover a month, and that the devices retain over 80% of their initial performance after 300 hours of continued operation at maximum power (Extended Data Figure 10). We show device results for larger bandgap $(Cs,FA,MA)Pb(I_{0.4}Br_{0.6})_3$ absorbers (Fig. 5d and 5f), attaining a PCE of 17.9% with minimal hysteresis for the $x = 0.1$ composition and stabilised power output of 17.1% (see Table 1 and Extended Data Figure 11 for device statistics). This is one of the highest efficiencies to date for a large bandgap (1.78 eV) perovskite ideally suited for tandem applications[3].

These results are particularly remarkable for two key reasons. First, the perovskite films and interfaces are surprisingly tolerant to passivating additives. Here, we have introduced additives at high enough loading to passivate surfaces and stabilise luminescence across a range of bandgaps without compromising charge transport or extraction. This tolerance is in contrast to conventional semiconductors such as GaAs, which require more complicated passivation approaches such as controlled growth on lattice-matched substrates[30]. Second, these results directly show the importance of obtaining high, stable external luminescence yields in full device stacks containing luminescent absorbers capable of recycling photons[12,31]. The internal luminescence yields approaching 100%, along with small loss in external luminescence yield in the full device stack, shows that perovskites can sustain the necessary photon gas to achieve voltage losses low enough to rival GaAs. We note that the perovskite compositions and passivating interlayers shown in this work lead to far greater luminescence and broader stability enhancements than reported previously for Rb or K[5,23–26]. Further work will be required to explore the limits of the K-based passivation including its efficacy on different perovskite compositions, deposition methods and contacts, and how it could be ultimately exploited (or even mimicked with other halide-sequestering species) to eliminate interfacial non-radiative losses and ionic migration. The combination of high radiative efficiency, excellent charge transport and truly photo-stable bandgaps makes these passivation approaches an extremely promising route to take perovskite devices to their efficiency limits across a range of bandgaps.

Acknowledgments M.A.J. thanks Nava Technology Limited and Nyak Technology Limited for their funding and technical support. This project has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) under REA grant agreement number PIOF-GA-2013-622630, the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement No 756962), and the Royal Society and Tata Group (UF150033). The authors thank the Engineering and Physical Sciences Research Council (EPSRC) for support. XMaS is a mid-range facility at the ESRF synchrotron supported by the EPSRC and we are grateful to the XMaS beamline team staff for their support. The authors thank Diamond Light Source for access to beamline I09 and staff member Tien -Lin Lee as well as Ute B. Cappel for assistance during the HAXPES measurements. S.C., C.D and G.D. acknowledge funding from ERC under grant number 25961976 PHOTO EM and financial support from the EU under grant number 77 312483 ESTEEM2. M. A. thanks the president of the UAE's Distinguished Student Scholarship Program (DSS), granted by the Ministry of Presidential Affairs. HR and BP acknowledge support from the Swedish research council (2014-6019) and the Swedish foundation for strategic research. E.M.H and T.J.S. were supported by the Netherlands Organization for Scientific Research (NWO) under the Echo grant number: 712.014.007.

Author Contributions M.A.J. and S.D.S. conceived and planned the experiments with additional input from R.H.F. M.A.J. fabricated all samples and devices and performed and analysed the photo-luminescence quantum efficiency (PLQE), PL stability, time-resolved PL, absorption, photothermal deflection spectroscopy (PDS), scanning electron microscopy (SEM) and device characterisation measurements. M.A.J., Z.A.J. and C.A. performed and analysed the confocal PL maps. S.C, G.D. and C.D performed and analysed the scanning transmission electron microscopy-energy dispersive X-ray spectroscopy (STEM-EDX) measurements. M.A. and S.L performed the Grazing-Incidence Wide- Angle X- Ray Scattering (GIWAXS) experiments and analysed the data. E.M.H. and T.J.S. performed the time-resolved microwave conductivity (TRMC) measurements and analysed the data. M.A.J., B.P. and H.R. performed and analysed Hard X-ray Photoelectron Spectroscopy (HAXPES) measurements. M.A.J. and E.P.B. performed XRD measurements and J.M.R. calculated the internal PLQE and assisted with TRPL measurement and analysis. M.A.J. and A.J.P. carried out the device stability tests. M.A.J. and S.D.S. took the lead in drafting the manuscript and compiled the figures. All authors discussed the results and provided feedback on the manuscript.

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Main Figure Legends and Tables

Figure 1. Increased radiative efficiency and charge carrier mobility through passivation. (a) PLQE of passivated perovskite thin films with increasing fraction of potassium measured under illumination with a 532-nm laser at an excitation intensity equivalent to ~1 sun (~60 mW.cm^{-2}) after 300 seconds of illumination. (b) Time-resolved PL decays of the films with excitation at 407 nm and pulse fluence of 0.5 μJ.cm^{-2} (excitation density ~10^{16} cm^{-3}). (c) Maximum photo-conductance for each of the K contents extracted from TRMC measurements with an excitation density of ~10^{14} cm^{-3} (Extended Data Figure 7).

Figure 2. Stabilised PLQE and inhibition of photo-induced ion migration. (a) PLQE for $(Cs,FA,MA)Pb(I_{0.85}Br_{0.15})_3$ films illuminated over time with a 532-nm laser at an excitation intensity equivalent to ~1 sun (~60 mW.cm^{-2}) in ambient atmosphere. PL from $(Cs,FA,MA)Pb(I_{1-y}Br_y)_3$ with $y = 0.6$ (b) without passivation ($x = 0$) compared to the (c) passivated sample ($x = 0.4$), illuminated continuously in ambient conditions with the same conditions as (a). (d) The PL from the passivated ($x = 0.4$) compositions with $y = 0.4$, x = 0.4 (peak at 1.70 eV), $y = 0.6$, $x = 0.1$ (1.78 eV) and $y = 1$, $x = 0.4$ (1.89 eV), measured over time under the same conditions.

Figure 3. Cross-section chemical characterisation. (a) HAADF STEM cross sectional image of a $(Cs,FA,MA)Pb(I_{0.85}Br_{0.15})_3$ passivated perovskite thin film ($x = 0.20$). NMF decomposition results in (b) factor 1 associated to the perovskite layer and in (c) factor 2 indicating the presence of a K and Br rich phase. The profiles for (d) factor 1 and (e) factor 2. (f) Schematic of a film cross-section showing halide vacancy management with excess halide, where the

surplus halide is immobilised through complexing with potassium into benign compounds at the grain boundaries and surfaces.

Figure 4. Luminescence properties of the perovskite when interfaced with solar cell device contacts. Time-resolved PL decays of encapsulated $(Cs,FA,MA)Pb(I_{0.85}Br_{0.15})_3$ films ($x = 0$ and $x = 0.1$) with excitation at 407 nm and pulse fluence of 0.05 μJ.cm^{-2} (1.5×10^{15} cm^{-3} , equivalent to ~5 sun) when the perovskite is interfaced with (a) an n-type electron-collecting electrode (compact-TiO_2/thin-mesoporous TiO_2), (b) a p-type hole-collecting electrode (Spiro-OMeTAD), and (c) both electrodes in a full device stack. (d) External PLQE measurements of the perovskite in each configuration measured under illumination with a 532-nm laser at an excitation intensity equivalent to ~1 sun (~60 mW.cm^{-2}). See Extended Data Figure 12 for other intensities.

Figure 5. Enhanced solar cell power conversion efficiency. (a) Forward (open symbols) and reverse (closed symbols) J-V curves of champion solar cells with $(Cs,MA,FA)Pb(I_{0.85}Br_{0.15})_3$ absorbers without ($x = 0$) and with ($x = 0.1$) passivation, measured under full simulated solar illumination conditions (AM1.5, 100 mW.cm^{-2}). Inset: Stabilised power output under the same conditions. (b) Open-circuit voltage (V_{oc}) and (c) short-circuit current (J_{SC}) as functions of potassium fraction x, with error bars representing the standard deviation across 10 devices for each composition. (d) J-V curves of champion solar cells with $(Cs,MA,FA)Pb(I_{0.4}Br_{0.6})_3$ absorbers without ($x = 0$) and with ($x = 0.1$) potassium passivation. External quantum efficiencies (EQE) and integrated short-circuit current for the (e) $(Cs,MA,FA)Pb(I_{0.85}Br_{0.15})_3$ and (f) $(Cs,MA,FA)Pb(I_{0.4}Br_{0.6})_3$ devices.

Table 1. Champion photovoltaic device parameters. The bandgaps are extracted from the EQE onsets, and the V_{oc} loss is the difference between the bandgap radiative limit V_{oc} and measured V_{oc}.

Potassium fraction, *x*	**Bandgap [eV]**	**J_{sc} [mA.cm^{-2}]**	**V_{oc} [V]**	**Fill factor**	**PCE [%]**	**V_{oc} loss [V]**
$(Cs,MA,FA)Pb(I_{0.85}Br_{0.15})_3$						
0.0	1.59	22.6	1.05	0.73	17.3	0.26
0.1	1.56	23.2	1.17	0.79	**21.5**	**0.11**
$(Cs,MA,FA)Pb(I_{0.4}Br_{0.6})_3$						
0.0	1.83	15.3	1.12	0.72	12.3	0.42
0.1	1.78	17.9	1.23	0.79	**17.5**	**0.27**

Methods

Film and device fabrication. All the organic cation salts were purchased form Dyesol; the Pb compounds from TCI and CsI and KI from Alfa Aesar. Spiro-OMeTAD was purchased from Borun Chemicals and used as received. Unless otherwise stated, all other materials were purchased from Sigma-Aldrich.

The triple-cation-based perovskite $Cs_{0.06}FA_{0.79}MA_{0.15}Pb(I_{0.85}Br_{0.15})_3$ was prepared by dissolving PbI_2 (1.2 M), FAI (1.11 M), MABr (0.21 M) and $PbBr_2$ (0.21 M) in a mixture of anhydrous DMF:DMSO (4:1, volume ratios) followed by addition of 5 volume percent from CsI stock solution (1.5 M in DMSO). The potassium iodide was first dissolved in a mixed solution of DMF/DMSO 4:1 (v:v) to make a stock solution of 1.5 M. We then added the KI solution into the triple cation perovskite solution in different volume ratios. We then spin-coated the perovskite solutions using a two-step program at 2000 and 6000 rpm for 10 and 40 seconds, respectively, and dripping 150 µL of chlorobenzene after 30 seconds. We then annealed the films at 100°C for 1 hour. All the film preparations were performed in a nitrogen-filled glove box. The devices were fabricated following the same procedures for substrate preparation as well as deposition of both electron and hole transport layers (i.e. TiO_2, Spiro-OMeTAD) as in our previous work[32].

Scanning Electron Microscopy. The surface morphology of the films was examined using an FESEM (Merlin). An electron beam accelerated to 3 kV was used with an in-lens detector.

Steady-state absorption and photoluminescence characterisation. Absorption spectra were recorded with a Perkin-Elmer Lambda 1050 spectrophotometer equipped with an integrating sphere to account for reflected and transmitted light. Photo-thermal deflection spectroscopy (PDS) measurements were acquired on a custom-built setup by monitoring the deflection of a fixed wavelength (670 nm) laser probe beam following absorption of each monochromatic pump wavelength by a thin film immersed in an inert liquid FC-72 Fluorinert (3M Company).

Photoluminescence quantum yield measurements were taken by mounting perovskite films or encapsulated device stacks in an integrating sphere and photoexciting with a 532-nm continuous-wave laser. The laser and the emission signals were measured and quantified using a calibrated Andor iDus DU490A InGaAs detector for the determination of PL quantum efficiency. The external PLQE was calculated as per de Mello et al[33] and the internal PLQE subsequently determined using the methods by Richter et al[16].

The absorption and photoluminescence (PL) (Extended Data Figure 2a and b) spectra reveal a reduction in the optical bandgap of the perovskite film with increasing KI. The PL peaks at 770 nm for $x = 0$ and red-shifts to 807 nm for $x = 0.4$. From Hard X-ray Photoelectron Spectroscopy (HAXPES) measurements, we find that increasing amounts of KI have no effect in the valence band (VB) edge, suggesting that the conduction band (CB) must decrease (Extended Data Figure 2b, inset). We note that this is in contrast to the case of the bandgap tunability achieved through directly changing mixed halide fractions, where the VB was shown to change but the CB remained almost fixed[34]. Measurements on similar perovskite systems without Br did not show such a strong red-shift upon adding K (Extended Data Figure 2fg,h) suggesting that the additives are selectively interacting with the bromide. These results highlight the combination of K-additives and mixed halides as levers for selectively tuning the bandgap and conduction band. We also note that the samples show a small fraction (<1% of material) with a low bandgap component (Extended Data Figure 2c) but the emission is predominantly from the slightly higher energy component. It is currently unclear why the luminescence is not dominated by the low gap component but it is possible that these low-concentration, low-bandgap components are electronically isolated from the remaining material, for example being surrounded by potassium-rich passivating material. We also note that the decrease in PLQE for $x = 0.6$ could be due to the much smaller grain size at these high passivation levels (Extended Data Figure 1). Finally, we note that the absorptance changes due to thickness changes with KI addition over the ranges for our devices ($x = 0 - 0.2$) are negligible and thus are not a significant cause of the observed enhancements in device performance.

Confocal PL maps. PL maps were collected using a WITec alpha 300 s setup. The excitation source was 405 nm cw laser (Coherent CUBE), chopped using a Stanford Research SR 540 chopping unit at frequency of 840 Hz. The light was coupled though an optical fiber to the microscope and focused using 100x Nikon lens (NA = 0.7). The sample was positioned on a X-Y piezo stage of the microscope. The PL signal was collected in reflection mode with the same 100x objective and detected using a spectrometer fitted with a CCD detector. A low-pass filter with a cut-off wavelength of 435 nm was fitted before the CCD detector to block the excitation component of transmitted light (405nm).

The confocal PL intensity maps are shown in Extended Data Figure 3a-d from perovskite films with $x = 0 - 0.4$, with the intensity distributions shown in Extended Data Figure 3i. For example, we observe a broad distribution of emission intensity peaking at 2×10^4 counts for $x = 0.20$ compared to a narrower distribution but with a maximum at only 5×10^3 counts for the reference film ($x = 0$). Although the intensity distribution is broader for the $x = 0.2$ sample, the lowest counts for this sample are as high in number as the highest counts for the reference. We find that the absolute emission intensity increases continuously with increasing content of potassium (Extended Data Figure 3i), peaking at an order of magnitude enhancement at $x = 0.40$, consistent with the PLQE data in Fig. 1a. We also show the centre-of-mass PL wavelength maps for the same perovskite films in Extended Data Figure 3e-h, along with the corresponding histograms in Extended Data Figure 3j. This further confirms the red-shifting of the microscale PL upon addition of K, consistent with the absorption and bulk PL data. Interestingly, we find a statistically-significant correlation between the PL wavelength and the intensity for each local site (i.e. the most emissive sites are the most red-shifted, see Extended Data Figure 3k). This is consistent with the bulk absorption and PL data, where the PL intensity increases and red-shifts with increasing K content.

Time-resolved photoluminescence. Time-resolved photoluminescence measurements were acquired with a gated intensified CCD camera system (Andor iStar DH740 CCI-010) connected to a grating spectrometer (Andor SR303i). Excitation was performed with femtosecond laser pulses which were generated in a homebuilt setup by second harmonic generation (SHG) in a BBO crystal from the fundamental output (pulse energy 1.55 eV, pulse length 80 fs) of a Ti:Sapphire laser system (Spectra Physics Solstice). Temporal resolution of the PL emission was obtained by measuring the PL from the sample by stepping the iCCD gate delay relative to the pump pulse. The gate width was 20 ns.

For the unpassivated control film ($x = 0$), there is a significant initial non-radiative component (Figure 1b). With increasing passivation, this component is gradually removed with a peak 'lifetime' occurring at $x = 0.1$. In this regime, the recombination is still somewhat trap-limited for this excitation density (i.e. the carrier density does not exceed the trap density to fill all traps). As the passivation increases further, the trap density is further reduced and now the density of excited carriers is above the trap density and recombination is radiative and bimolecular. In this regime, the recombination follows a power law and the lifetime is 'faster' with decreasing trap density (increasing passivation, i.e. $x = 0.2$ to 0.4). We note that the total area under the non-normalized curves in each case matches the increasing PLQE trend.

Time-resolved microwave conductivity (TRMC) measurements. The TRMC technique monitors the change in reflected microwave power by the loaded microwave cavity upon pulsed laser excitation. The photo-conductance (ΔG) of the perovskite films was deduced from the collected laser-induced change in normalized microwave power ($\Delta P/P$) by $-K\Delta(t)=\Delta P(t)/P$, where K is the sensitivity factor. The yield of generated free charges φ and mobility $\Sigma\mu=(\mu_e+\mu_h)$ were obtained by: $\varphi\Sigma\mu=\Delta G/(I_0\beta eF_A)$, where, I_0 is the number of photons per pulse per unit area, β is a geometry constant of the microwave cell, e is the elementary charge, and F_A is the fraction of light absorbed by the sample at the excitation wavelength of 600 nm.

In Extended Data Figure 5, we show the ΔG as a function of time after pulsed excitation at 600 nm for different fractions of K acquired at different fluences. The TRMC signal depicts a fast rise, originating from the formation of mobile charges, followed by decays attributed to charge recombination or immobilization of charge carriers through the traps. In Fig. 1c, we show that at least up to $x = 0.1$, the charge transport remains unperturbed with addition of K. That is, in view of the low electric field strength of the microwaves (100 V/cm), the charges are not effectively displaced by this field but instead the charges are perturbed in their diffusional motion. As a result, the distance R crossed by the charges is limited by the charge carrier diffusion coefficient and half the oscillation period ν (8.5 GHz), which amounts to:

$$R = \sqrt{\mu(k_B T/e)\tfrac{1}{2}\upsilon^{-1}} = \sqrt{42 \times 0.0259 \times 0.5 \times (8.5 \times 10^9)^{-1}} = 8.0 \times 10^{-6}\ \text{cm} = 80\ \text{nm}$$

As shown in Extended Data Figure 1, the grain sizes are ~ 200-400 nm and independent of the K concentration up to $x = 0.1$. Thus, for $x < 0.1$, the grains are larger than the probing length (80 nm) of the measurement and the TRMC mobility as probed will not be affected by their size. However, smaller grain sizes are observed for $x > 0.2$, which is most likely the reason for the lower mobilities at higher x values[19].

Furthermore, we show the resulting half lifetimes $\tau_{1/2}$ (time taken to decay half of the initial value) for the different samples in Extended Data Figure 5f across a range of excitation fluences. At low fluence, one of the carriers is trapped, leading to a long-lived signal from the untrapped carrier, which recombines following monomolecular kinetics[13,35]. At higher fluence in which the traps are filled, the recombination is bimolecular. We find that charge-carrier recombination is substantially slower for the $x = 0.1$ composition compared to the $x = 0$

reference, with the low-fluence monomolecular lifetime increasing from 1 μs ($x = 0$) to 1.5 μs ($x = 0.1$).

Scanning Transmission Electron Microscopy-Energy Dispersive X-ray Spectroscopy (STEM-EDX). A FEI Helios Nanolab dual beam Focus Ion Beam/ Field Emission Gun - Scanning Electron Microscope (FIB/FEGSEM) was employed to prepare a lamella for STEM imaging and analysis. To preserve the perovskite film during specimen preparation, capping layers of Spiro-OMeTAD and platinum were deposited. All imaging was carried out in STEM-HAADF (High Angle Annular Dark Field) mode. STEM/EDX data were acquired in FEI Tecnai Osiris TEM equipped with a high brightness Schottky X-FEG gun and a Super-X EDX system composed by four silicon drift detectors, each approximately 30 mm^2 in area and placed symmetrically around the optic axis to achieve a collection solid angle of 0.9 sr. Spectrum images were acquired with a probe current of 0.7 nA, an acceleration voltage of 200 kV, a spatial sampling of 10 nm/pixel and 100 ms/pixel dwell time. Data were acquired with Tecnai Imaging and Analysis (TIA) and analysed with Hyperspy.

In Extended Data Figure 6b-e, we report a cross-section STEM/EDX measurement for a control perovskite thin film (i.e. $x = 0$). We treated the EDX dataset with the NMF algorithm, which led to the identification of two main components in the thin film. Factor 1 is representative of the perovskite layer, while factor 2 can be associated to a Br- and Pb- rich phase. This second component shows higher intensity in correspondence of the thin film interfaces with the Spiro-OMeTAD protective capping layer and with the silicon substrate. In contrast to the passivated perovskite film ($x = 0.20$, Fig. 3), we do not observe the presence of surface decoration at the grain boundaries.

X-ray diffraction. XRD was performed using a Bruker X-ray D8 Advance diffractometer with Cu K$\alpha_{1,2}$ radiation ($\lambda = 1.541$ Å). Spectra were collected with an angular range of $5 < 2\theta < 60$ ° and $\Delta\theta = 0.01227$ ° over 10 minutes. Measurements were made on as prepared films. A Le Bail analysis was carried out on film measurements using the Bruker Topas software. Chebyshev polynomials were used to fit the background and the peak shape modelled with a pseudo-Voigt function.

Grazing Incidence Wide Angle X-Ray Scattering (GIWAXS). GIWAXS measurements were performed on the XMaS Facility at the ESRF synchrotron. A fixed-exit, water-cooled, double crystal Si(111) monochromator, placed at 25 m from the source was used to monochromatize the X-ray beam coming from a bending magnet (E_c = 9.8 keV). The X-ray energy was tuned to 10 keV (1.2398 Å) and a Rh-coated toroidal mirror was used to focus the monochromatic beam horizontally and vertically. The beam flux was ~5×10^{10} photons s^{-1} at the sample position. The original beam spot size was 500 (horizontal) × 400 (vertical) μm^2 at the sample position. We employed a set of motorized slits (Huber, Germany) immediately before the sample to have a better-defined footprint in the vertical direction. The final beam spot size with slits was 300 (horizontal) × 115 (vertical) μm^2. The beam footprint extended 300 μm horizontally and throughout the perovskite films. The samples were scanned at an out-of-plane incident angle of ~0.3°.

As shown in Extended Data Figure 7a ($x = 0$) and d ($x = 0.2$), the GIWAXS diffraction patterns collected at an incident angle of 0.3° show the main perovskite diffraction ring at q=1 $Å^{-1}$. A PbI_2 peak can be detected at q=0.9 $Å^{-1}$ for the reference film, which originates from a small fraction of excess lead iodide in the reference precursor solution. In Extended Data Figure 7f and g, we plot the line profiles azimuthally-integrated over the entire image for perovskite films with $x = 0 – 0.4$. The PbI_2 peak diminishes with higher potassium content and disappears at $x = 0.2$. Furthermore, we observe a new diffraction peak at q = 0.7 $Å^{-1}$ that appears for $x \geq 0.10$ and can be assigned to a non-perovskite K-rich crystalline phase which grows with increasing K. We also observe the growth of new peaks with increasing K content in laboratory XRD results (highlighted by * in Extended Data Figure 2d). We cannot currently unambiguously assign these peaks, for example to KBr or KI, which points to this phase (or phases) having more complicated chemical compositions (such as KBr_xI_{1-x}, K_2PbI_4 or K_2PbBr_4 [24]) and crystallinities. However, given the observations in the STEM-EDX experiments (Figure 3), we expect that at least one of the phases present is rich in K and Br and is likely to be the halide-sequestering species proposed in our model. Identifying the precise composition of these sequestering species should be the subject of exciting future work in the community.

Hard X-ray Photoelectron Spectroscopy. Photoelectron spectroscopy measurements were performed at the Diamond light Source using the beamline I09 (Oxfordshire, UK). Both soft (758 eV) and hard X-rays (2200 and 6600 eV) were used to illuminate our sample providing information from different probing depth. The soft X-ray energy was selected through a plane grating monochromator while a double-crystal monochromator (DCM) was used in the hard X-ray section. 2200 and 6600 eV correspond to the 1st and 3rd order light when the DCM is set at 2200 eV using a Si(111) crystal. A EW4000 photoelectron analyzer (VG Scienta, Uppsala, Sweden) was used to record the spectra with an analyzer slit open to 0.2 mm. No charge neutralization was used and the binding energy scale was calibrated by setting the Au 4f core level of a gold reference sample to 84.0 eV. The quantification tables and intensity ratios were calculated from the experimental results after correction by the photoionization cross-section for each element at their specific photon energy, using database values.

The overview spectra of the perovskite thin films shows all the core levels peaks corresponding to the elements forming the perovskite material, including Cs. The high-resolution spectra of the core level peaks further confirms the quality of the perovskite films as there is only a single Pb 4f component at 138.6 eV without any metallic lead feature[36] (Extended Data Figure 8). In Extended Data Figure 8, we summarise a quantitative analysis of the potassium content in perovskite films with $x = 0 - 0.2$ at different photon energies of 758, 2200 and 6600 eV, which corresponds to moving from probing the surface (~2-4 nm) to probing further into the bulk

(~20 nm). We observe that the concentration of K decreases when moving from the surface into the bulk for each of the K compositions. Interestingly, we note that the Cs content rises moving into the bulk concomitant with the decrease in K, suggesting that the K pushes the Cs further into the bulk (Extended Data Figure 8d). Furthermore, the I/Pb ratio increases at higher K content (Extended Data Figure 8e), particularly at the surface, consistent with the addition of excess I from the KI source and in agreement with a previous report showing a higher concentration of iodide at the surface[36]. Finally, the Br/I ratio decreases at higher K content particularly deeper in the film (probed with the higher photon energies), consistent with the K more selectively drawing out the Br from the lattice (Extended Data Figure 8f). These results suggest that K is predominantly at the surfaces and the addition of KI also leads to excess halides on the surfaces with a more selective interaction with bromides.

Solar cell characterisation. Current–voltage characteristics were recorded by applying an external potential bias to the cell while recording the generated photocurrent with a digital source meter (Keithley Model 2400). The light source was a 450 - W xenon lamp (Oriel) equipped with a Schott-K113 Tempax sunlight filter (Praezisions Glas & OptikGmbH) to match the emission spectrum of the lamp to the AM1.5G standard. Before each measurement, the exact light intensity was determined using a calibrated Si reference diode equipped with an infrared cut-off filter (KG-3, Schott). EQE spectra were recorded as a function of wavelength under a constant white light bias of approximately 5mW.cm^{-2} supplied by an array of white light emitting diodes. The excitation beam coming from a 300 W xenon lamp (ILCTechnology) was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd) and chopped at approximately 2 Hz. The signal was recorded using a Model SR830 DSP Lock-In Amplifier (Stanford Research Systems). All measurements were conducted using a non-reflective metal aperture of 0.105 cm^2 to define the active area of the device and avoid light scattering through the sides.

For stability measurements, the solar cells were transferred to a sealable device holder under nitrogen-glovebox conditions. During testing the device holder was continuously purged with dry nitrogen, pre-filtered (SGT Super Clean) to minimize residual oxygen, moisture and hydrocarbon content. A Newport solar simulator with equivalent AM 1.5 G 1-sun output was used to illuminate the entire device substrate; short wavelengths were filtered using a 435 nm long pass filter (Thor Labs FGL435). Ageing under these conditions resulted in a chamber ambient temperature of approximately 40˚C, as measured by a thermistor next to the solar cell device, which was reached within 30 minutes of the experiment commencing. Photocurrent characteristics were recorded by holding close to the maximum power point voltage (as ascertained from an initial J-V curve) using a Keithley 2636 SMU and a custom-written LabView VI code. Devices were stored in a nitrogen-filled glove box in the dark between shelf-life measurements.

Data availability. The data supporting the findings of this study are available in the paper, within the Extended Data items, and at https://www.repository.cam.ac.uk/handle/XXXXX.

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Extended Data Legends

Extended Data Figure 1. Stoichiometries of the precursor solutions, and thickness measurements and scanning electron microscope images of the (Cs,FA,MA)Pb($I_{0.85}Br_{0.15}$)$_3$ films. The calculated values for (a) [K]/([K]+[A]) as a function of KI volume ratio added to the (Cs,FA,MA)Pb($I_{0.85}Br_{0.15}$)$_3$ perovskite precursor solution, (b) halide (X) to lead ratio ([X]/[Pb]) for different fraction of potassium in perovskite films based on stoichiometric calculations, (c) Thickness of the films deposited on c-TiO2/m-TiO2. (d) The calculated ratios between different elements. Note that X represents halides (i.e. sum of iodide and bromide). (e-j) Scanning electron micrograph of (Cs,FA,MA)Pb($I_{0.85}Br_{0.15}$)$_3$ perovskite thin films with potassium fraction ranging from $x = 0.0$ to $x = 0.6$. The coloured insets show higher magnification images.

Extended Data Figure 2. Absorption, photoluminescence and X-Ray diffraction characteristics of the (Cs,FA,MA)Pb($I_{0.85}Br_{0.15}$)$_3$ (Br-containing) and (Cs,FA,MA)PbI_3 (pure-iodide) films. Results for (a-e) Br-containing (Cs,FA,MA)($I_{0.85}Br_{0.15}$)$_3$, and (f-j) (Cs,FA,MA)PbI_3 perovskite films. (a) Normalised UV-vis absorption and (b) photoluminescence (PL, 532-nm CW excitation) of the (Cs,FA,MA)($I_{0.85}Br_{0.15}$)$_3$ perovskite films with different K content (x). Inset: schematic of the change in conduction band with increasing x. (c) The absorption spectra of (Cs,FA,MA)Pb($I_{0.85}Br_{0.15}$)$_3$ perovskite thin films with different potassium fractions measured by photo-thermal deflection spectroscopy (PDS), showing a decreased sub-gap density of states with potassium passivation. (d) X-Ray Diffraction (XRD) data of the (Cs,FA,MA)Pb($I_{0.85}Br_{0.15}$)$_3$ thin films, with new peaks arising from increasing K labelled with a *. (e) Calculated lattice parameters using a Le Bail analysis as a function of K fraction on the XRD data. (f) PLQE as a function of excitation power measured by a 532-nm CW laser for (Cs,FA,MA)Pb($I_{0.85}Br_{0.15}$)$_3$ perovskite thin films in ambient atmosphere. (g) Normalized UV-vis absorption, (h) photoluminescence (PL, 532-nm CW excitation) and (i) Photo-thermal deflection spectroscopy (PDS) absorption spectra of the (Cs,FA,MA)PbI_3 perovskite films with different K content. (j) Calculated lattice parameters as a function of K, determined using a Le Bail analysis on X-Ray Diffraction data, for the (Cs,FA,MA)PbI_3 perovskite thin films (black square) compared to (Cs,FA,MA)($I_{0.85}Br_{0.15}$)$_3$ (red circles). (k) PLQE of different passivated perovskite thin films with and without bromide measured under illumination with a 532-nm laser at an excitation intensity equivalent to ~1 sun (~60 mW.cm^{-2}) in ambient air.

Extended Data Figure 3. Confocal photoluminescence maps of passivated (Cs,FA,MA)Pb($I_{0.85}Br_{0.15}$)$_3$ films. Confocal PL intensity map with 405-nm excitation measured in ambient atmosphere for (Cs,FA,MA)Pb($I_{0.85}Br_{0.15}$)$_3$ perovskite thin films with (a) $x = 0.0$, (b) $x = 0.10$, (c) $x = 0.20$ and (d) $x = 0.40$. Centre-of-mass PL wavelength of the films for (e) $x = 0.0$, (f) $x = 0.10$, (g) $x = 0.20$ and (h) $x = 0.40$. Histograms of the (i) absolute PL intensities and (j) PL wavelength extracted from the respective maps for $x = 0 – 0.40$. (k) Correlation between the local PL intensity and mean wavelength for $x = 0.20$.

Extended Data Figure 4. Time-resolved PL measurements and photo-stability of passivated ($Cs_{0.05}FA_{0.78}MA_{0.17}$)Pb($I_{1-y}Br_y$)$_3$ films. (a-d) Intensity dependent time-resolved PL decays of the (Cs,MA,FA)Pb($I_{0.85}Br_{0.15}$)$_3$ perovskite films with different fraction of potassium. The pulse fluences of the 407-nm excitation are quoted on the panels. PL from ($Cs_{0.05}FA_{0.78}MA_{0.17}$)Pb($I_{1-y}Br_y$)$_3$ films with (e,f) $y = 0.4$ passivated ($x = 0.4$, e) and unpassivated ($x = 0$, f), (g,h) $y = 0.8$ passivated ($x = 0.4$, g) and unpassivated ($x = 0$, h), (i,j) $y = 1$ passivated ($x = 0.4$, i) and unpassivated ($x = 0$, j). The samples were illuminated and the PL acquired continuously with a 532-nm laser at an excitation intensity equivalent to ~1 sun (~60 mW.cm^{-2}) in ambient atmosphere. (k) Center of mass for the PL wavelength of the passivated perovskite films (*x* = 0.4).

Extended Data Figure 5. Time-resolved microwave conductivity measurements on passivated (Cs,FA,MA)Pb($I_{0.85}Br_{0.15}$)$_3$ films. (a-e) Time-resolved microwave conductivity measurements for (Cs,FA,MA)Pb($I_{0.85}Br_{0.15}$)$_3$ perovskite films with different fractions of K (*x* = 0 – 0.4) showing the change in photoconductance after pulsed excitation at 600 nm, with excitation densities (photons.cm^{-2}) as quoted on the panels. (f) Half lifetime extracted from the decays, with the excitation density quoted after accounting for the absorbed fraction and film thickness of each sample.

Extended Data Figure 6. STEM-EDX chemical maps of the passivated and unpassivated (Cs,FA,MA)Pb($I_{0.85}Br_{0.15}$)$_3$ samples. The HAADF image and corresponding STEM/EDX quantitative maps for iodine, lead, potassium and bromine in a (Cs,FA,MA)Pb($I_{0.85}Br_{0.15}$)$_3$ perovskite specimen with *x* = 0.20 fraction of potassium. (b) HAADF STEM cross sectional image of an unpassivated (Cs,FA,MA)Pb($I_{0.85}Br_{0.15}$)$_3$ perovskite thin film (*x* = 0). NMF decomposition results in (c) factor 1 associated to the perovskite layer and in (d) factor 2 indicating the presence of a Pb and Br rich phase. The profiles for (e) factor 1 and (f) factor 2.

Extended Data Figure 7. GIWAXS measurements of passivated (Cs,FA,MA)Pb($I_{0.85}Br_{0.15}$)$_3$ films. The diffraction patterns of thin (Cs,FA,MA)Pb($I_{0.85}Br_{0.15}$)$_3$ films collected at low angle using GIWAXS for (a) *x* = 0.00, (b) *x* = 0.05, (c) *x* = 0.10, (d) *x* = 0.20 and (e) *x* = 0.40. The high-resolution line profiles azimuthally integrated over the entire GIWAX profile for different fraction of potassium at (f) $0.5 \leq q \leq 0.8$ and (g) $0.8 \leq q \leq 1.1$.

Extended Data 8. HAXPES spectra for passivated (Cs,FA,MA)Pb($I_{0.85}Br_{0.15}$)$_3$ perovskite thin films. HAXPES spectra for (Cs,FA,MA)Pb($I_{0.85}Br_{0.15}$)$_3$ perovskite thin films ($0 \leq x \leq 20$) between 85-0 eV binding energy range recorded with a photon energy of (a) 758 eV, (b) 2200 eV and (c) 6600 eV. (d) Intensity ratio between core levels ([Cs]/[Pb] and [K]/[Pb]) calculated from the experimental results as a function of photon energy (measurements at 758, 2200 and 6600 eV). Intensity ratios between different core levels calculated from experimental results: (e) I/Pb and (f) Br/I of the perovskite thin films with different fraction of potassium ($0.0 \leq x \leq 0.20$). It is notable that we used Pb 5d, K 2p, Cs 4d, I 4d and Br 3d core levels for all different energies with the exception of K 1s, which is used for 6600 eV.

Extended Data Figure 9. Excitation-dependent PL quantum efficiency and time-resolved PL measurements of (Cs,FA,MA)Pb($I_{0.85}Br_{0.15}$)$_3$ device stacks. PLQE of reference (x=0) and passivated (x=0.1) (Cs,FA,MA)Pb($I_{0.85}Br_{0.15}$)$_3$ perovskite thin films with (a) n-type contact, (b) p-type contract and (c) both contacts, each measured under illumination with a 532-nm laser at different excitation intensity. Time-resolved PL decays of encapsulated (Cs,FA,MA)Pb($I_{0.85}Br_{0.15}$)$_3$ films ($x = 0$ and $x = 0.1$) with excitation at 407 nm and pulse fluence of 0.17 μJ.cm^{-2} (5×10^{15} cm^{-3}, equivalent to ~15 sun) when the perovskite is interfaced with (d) an n-type electron-collecting electrode (compact-TiO_2/thin-mesoporous TiO_2), (e) a p-type hole-collecting electrode (Spiro-OMeTAD), and (f) both electrodes in a full device stack.

Extended Data Figure 10. Current-voltage curves of passivated (Cs,FA,MA)Pb($I_{0.85}Br_{0.15}$)$_3$ devices and tabulated results for the (Cs,FA,MA)Pb($I_{0.85}Br_{0.15}$)$_3$ and (Cs,FA,MA)Pb($I_{0.4}Br_{0.6}$)$_3$ champion devices. Forward (open symbols) and reverse (closed symbols) J-V curves of champion solar cells with

$(Cs,FA,MA)Pb(I_{0.85}Br_{0.15})_3$ absorbers with (a) $x = 0.00$, (b) $x = 0.05$, (c) $x = 0.10$ and (d) $x = 0.20$ measured under full simulated solar illumination conditions (AM1.5, 100 $mW.cm^{-2}$) with a scan rate of 15 mVs^{-1}. The corresponding dark J-V curves are also shown. Preliminary stability tests of $(Cs,FA,MA)Pb(I_{0.85}Br_{0.15})_3$ perovskite devices: (e) Shelf-life of devices for $x = 0.00$ and $x = 0.10$ stored in a nitrogen glovebox over a month and tested regularly under full AM1.5 simulated sunlight. (f) Stability of a device with $x = 0.10$ aged at 0.8 V under continuous UV-filtered simulated sunlight in nitrogen atmosphere >350 hours. (g) Device parameters for the passivated $(Cs,FA,MA)Pb(I_{0.85}Br_{0.15})_3$ (upper) and $(Cs,FA,MA)Pb(I_{0.4}Br_{0.6})_3$ (lower) perovskite solar cells measured under full simulated solar illumination conditions (AM1.5, 100 $mW.cm^{-2}$).

Extended Data Figure 11. Device statistics. Box and whisker plots to summarise the statistics of photovoltaic parameters of (a-d) 10 devices with passivated $(Cs,FA,MA)Pb(I_{0.85}Br_{0.15})_3$ solar cells and (e-h) 8 devices of passivated $(Cs,FA,MA)Pb(I_{0.4}Br_{0.6})_3$ solar cells, each measured under full simulated solar illumination conditions (AM1.5, 100 $mW.cm^{-2}$) and scanned at a rate of 15 mV/s. The boxes represent the interquartile range, with the median represented by the line dividing the boxes, and the whiskers are determined by the 5th and 95th percentiles. The mean is given by the open square symbols, and the starred symbols represent the maximum and minimum values.