

ADVANCED ENERGY MATERIALS

Supporting Information

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Trap States, Electric Fields, and Phase Segregation
in Mixed-Halide Perovskite Photovoltaic Devices

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Johnston, and Laura M. Herz**

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1 Sample Fabrication

Substrate cleaning:

Fluorine-doped tin oxide (FTO) glass substrates (Tec 15, Pilkington) were washed using Hellamanex, acetone, isopropanol and ethanol. Thereafter, the FTO substrates were placed in the oxygen plasma asher for 10 minutes.

SnO₂ layer:

SnO₂ was prepared as reported previously.^{S1} In brief, SnCl₄·5H₂O in IPA (0.05 M) was spincoated on to clean FTO substrates at 3000 rpm and then annealed at 180 °C for 1 hour. The substrates were then placed in a chemical bath consisting of SnCl₂·2H₂O (108 mg), 3-Mercaptopropionic acid (10 µl), deionised water (40 ml), Urea (500 mg) and 37% HCl (500 µl). The chemical bath containing the substrates were placed in an oven for 3 hours at 70 °C. Afterwards, the films were washed with deionised water and annealed for 1 hour at 180 °C.

Perovskite thin-films:

CH₃NH₃Pb(Br_{0.5}I_{0.5})₃ thin films were prepared using the acetonitrile route as reported previously.^{S2} In brief, CH₃NH₃I, CH₃NH₃Br, PbI₂ and PbBr₂ were weighed out and dissolved in acetonitrile to give a 0.5 M solution as described by Noel *et al.*^{S2} The solution was then spincoated onto the substrate in a nitrogen filled glovebox at 2000 rpm. The films were then annealed for 1 hour at 100 °C.

CH₃NH₃PbI₃ thin films were prepared similarly to the CH₃NH₃Pb(Br_{0.5}I_{0.5})₃ thin films, except that a 1 M solution of CH₃NH₃I and PbI₂ in acetonitrile was made to ensure that the films were of the same thickness as the CH₃NH₃Pb(Br_{0.5}I_{0.5})₃ films.

Spiro-OMeTAD layer:

73 mg of 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD) was dissolved in 1 ml of chlorobenzene. Thereafter 38 µl of lithium bis(trifluoromethanesulfonyl)imide solution (170 mg ml⁻¹ in 1-butanol) and 21 µl of 4-tert-butylpyridine was added to the 1 ml solution of spiro-OMeTAD. The final solution was then spincoated in a nitrogen filled glovebox at 2000 rpm for 45 s. The resulting films were left to

oxidise in a desiccator for 24 hours.

Gold electrode:

Gold electrodes were deposited at 1×10^{-6} mbar in a thermal evaporator. The thickness of the electrodes was ~ 100 nm.

PMMA layer for thin-film samples:

PMMA (Sigma Aldrich, average M_W 97,000) was dissolved in chlorobenzene with a concentration of 150 mg mL^{-1} . The solution was spin coated at 2000 rpm for 45 seconds on top of the perovskite films.

2 Sample Characterization

2.1 Absorbance

Figure S1 shows an absorbance spectrum obtained from a $\text{MAPb}(\text{Br}_{0.5}\text{I}_{0.5})_3$ film spin-coated onto a quartz substrate and coated with a layer of poly(methyl methacrylate) (PMMA). The thin-film sample was created from the same batch of $\text{MAPb}(\text{Br}_{0.5}\text{I}_{0.5})_3$ solution that was used to create the mixed-halide perovskite devices used throughout the experiments described in the main text and this SI (other than those experiments that were explicitly done on MAPbI_3 devices). The measurements were conducted with a Bruker Vertex 80v Fourier-transform infrared spectrometer fitted with the reflection/transmission accessory, a tungsten halogen lamp source, a CaF beamsplitter, and a silicon diode detector. The reflectance reference spectrum was performed on a silver mirror, and the transmission reference spectrum was performed on a clean quartz substrate.

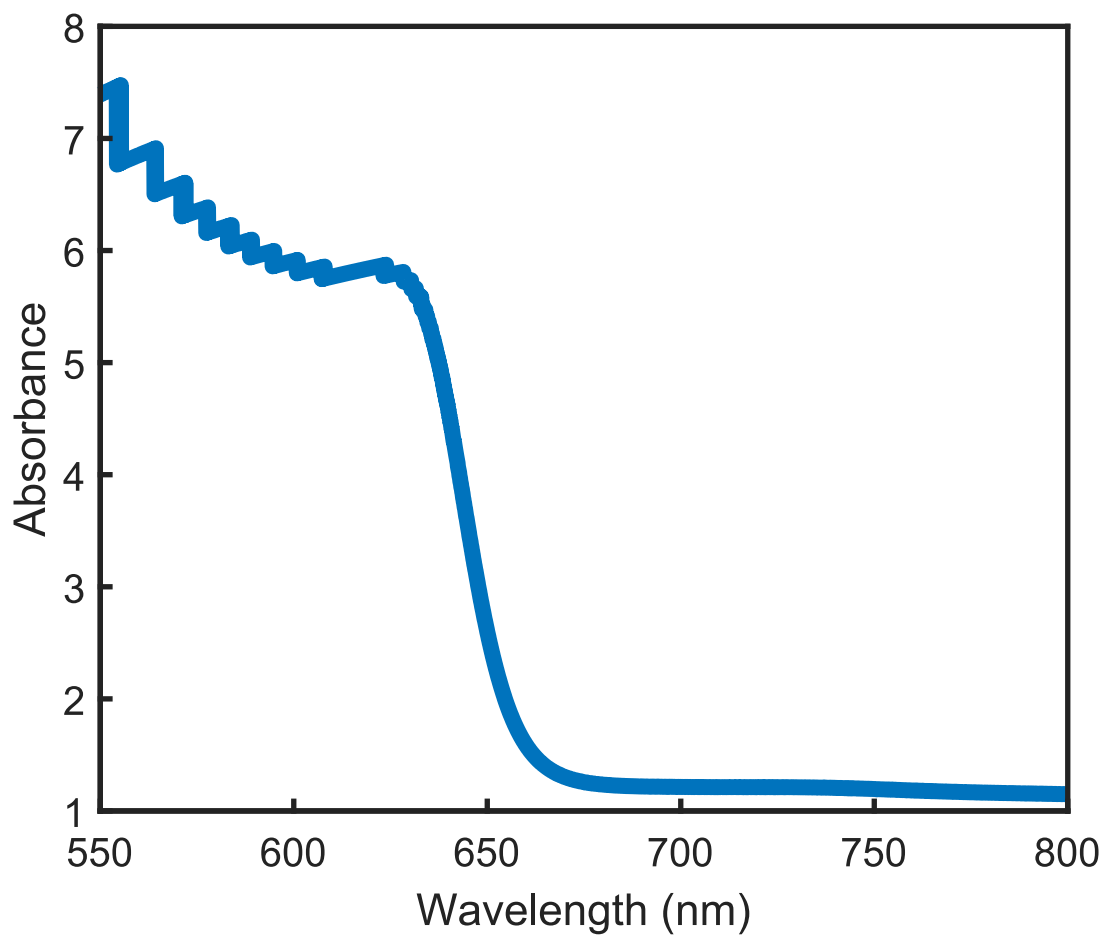


Figure S1: Absorbance spectrum of a MAPb(Br_{0.5}I_{0.5})₃ film on quartz coated with a layer of poly(methyl methacrylate) (PMMA). Steps in the spectrum below 630 nm are a quantization artefact associated with the transmitted/reflected signal dropping to the digitisation limit of the Fourier-transform infrared spectrometer's analogue to digital converter.

2.2 X-ray Diffraction

Figure S2 shows an X-ray diffraction (XRD) pattern obtained from a $\text{MAPb}(\text{Br}_{0.5}\text{I}_{0.5})_3$ film spin-coated onto a quartz substrate and coated with a layer of poly(methyl methacrylate) (PMMA). The thin-film sample was created from the same batch of $\text{MAPb}(\text{Br}_{0.5}\text{I}_{0.5})_3$ solution that was used to create the mixed-halide perovskite devices used throughout the experiments described in the main text and this SI (other than those experiments that were explicitly done on MAPbI_3 devices). The XRD pattern was taken from diffraction angle $2\theta = 5^\circ$ to 50° at a scan speed of $0.01^\circ \text{ s}^{-1}$ and obtained with a PANalytical X'Pert Powder X-Ray Diffractometer. The Cu-K_α line was used as incident radiation. In order to correct against sample tilt, the z-cut quartz peak in the data was used as a reference and fixed to $2\theta = 16.43^\circ$.

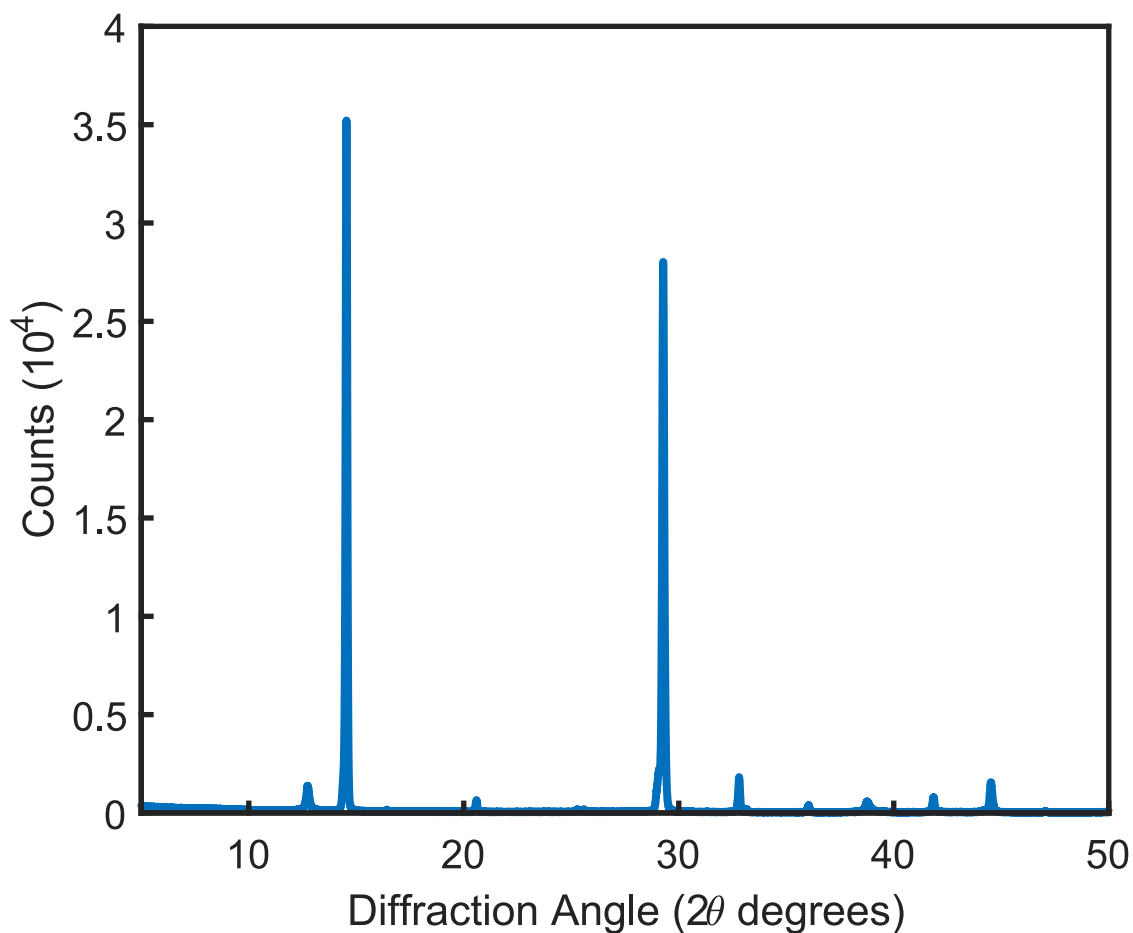


Figure S2: X-ray diffraction (XRD) pattern taken from a $\text{MAPb}(\text{Br}_{0.5}\text{I}_{0.5})_3$ film on quartz coated with a layer of poly(methyl methacrylate) (PMMA). The $\text{Cu-K}\alpha$ line was used as incident radiation. The peak at $\sim 12.7^\circ$ two theta is likely due to residual amounts of PbI_2 and PbBr_2 in the perovskite film.

2.3 Scanning Electron Microscopy

Scanning electron microscope (SEM) images were taken using a Hitachi S4300 microscope with a 3 kV accelerating voltage and an 11 μ A emission current. The images were acquired by detecting secondary electrons.

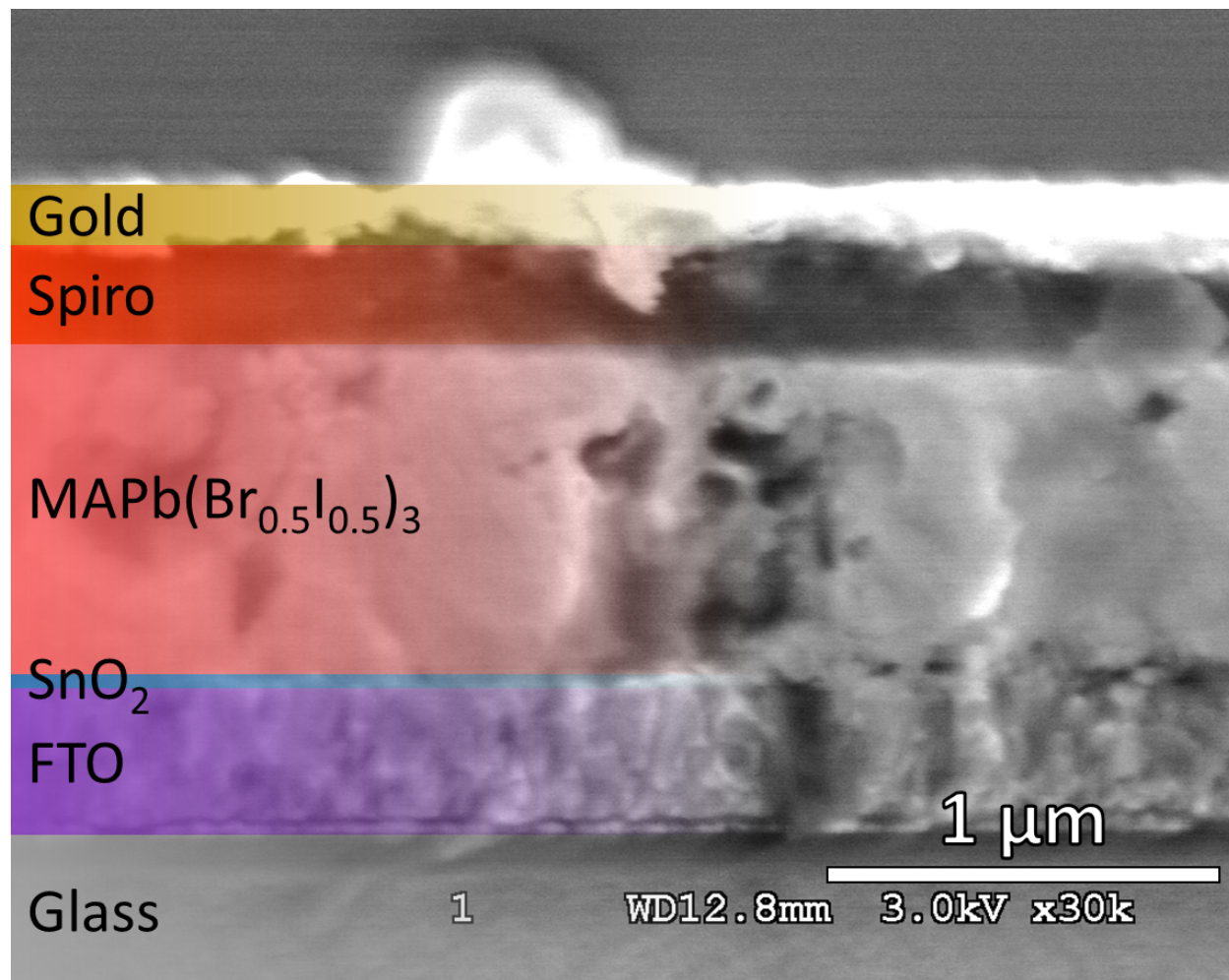


Figure S3: Cross-sectional scanning electron microscopy (SEM) images taken of a MAPb(Br_{0.5}I_{0.5})₃ perovskite solar cell. Highlighted in the image are the perovskite layer, the electron and hole transport layers (SnO₂ and spiro, respectively), the electrical contact layers (FTO and gold), and the glass substrate.

2.4 Device Statistics

The MAPb(Br_{0.5}I_{0.5})₃ perovskite solar cells were measured under simulated AM1.5, 100 mW cm⁻² sunlight (1 sun), using an ABET Technologies Sun 2000 and a Keithley 2400 Sourcemeeter in ambient conditions. The active area of each device was defined by a mask which exposed a 0.0919 cm² active area for testing of both the current voltage characteristics and stabilized power output. The devices were prebiased at 1.4 V for 5 s before initiating the reverse and forward scans. Device statistics are shown in Table S1, where the champion pixel is the one recorded to have the highest stabilised power output (SPO).

Figure S4 shows the forward and reverse J-V scans from the champion pixel, with the inset showing the SPO from this pixel.

Table S1: MAPb(Br_{0.5}I_{0.5})₃ device statistics for the champion pixel (the one with the highest standardised power output) and the average performance of all 36 pixels made.

	PCE (%)	J _{SC} (mA cm ⁻²)	V _{OC} (V)	Fill Factor	SPO (%)
Champion Pixel	5.79	11.90	0.98	0.49	5.32
Average of 36 Pixels	5.64	11.56	1.01	0.48	2.94

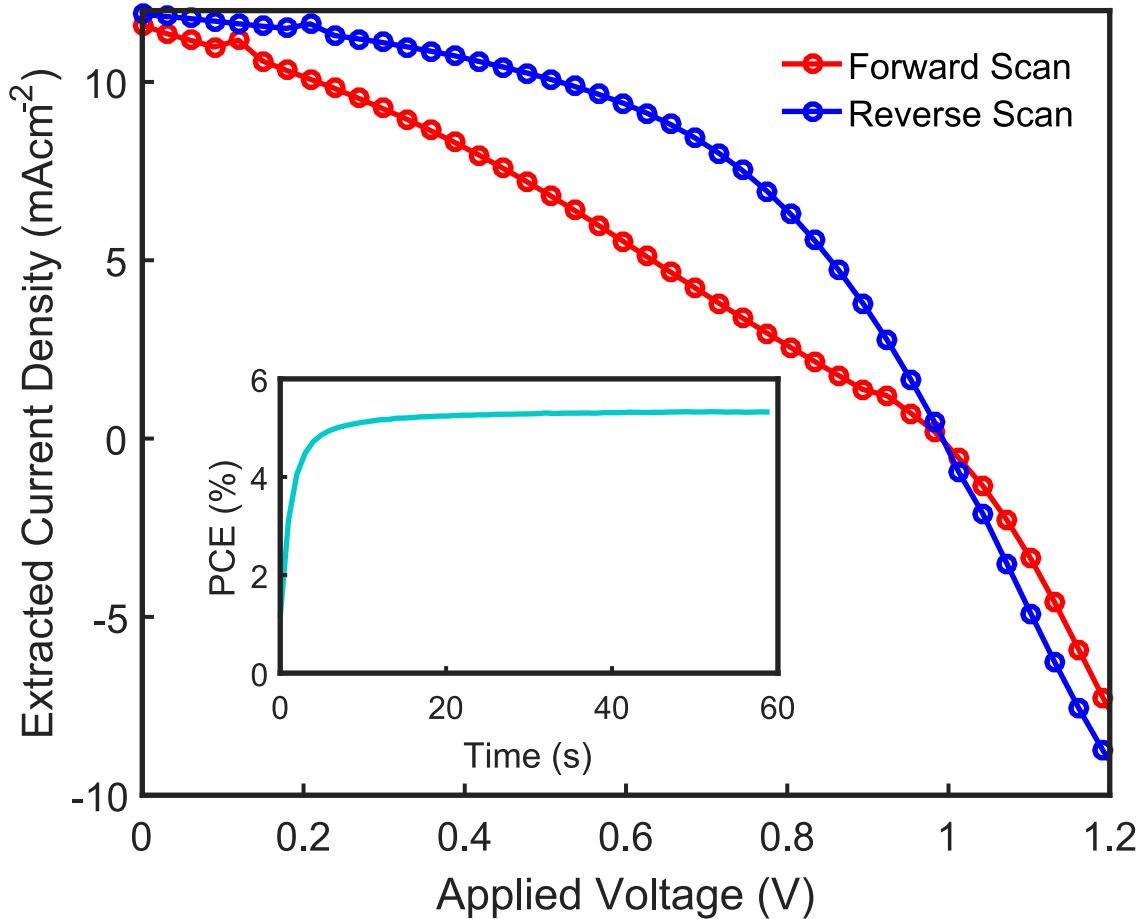


Figure S4: The forward and reverse current-voltage scans from the solution processed MAPb(Br_{0.5}I_{0.5})₃ device pixel with the highest measured stabilised power output. The stabilised power output for the same device pixel is plotted in the inset.

3 Photoluminescence under Applied Voltage

3.1 MAPb(Br_{0.5}I_{0.5})₃ Device Held at 0 and 0.85 Applied Volts

Figure 1b of the main text presents the photoluminescence (PL) from a MAPb(Br_{0.5}I_{0.5})₃ perovskite device under illumination as 0 and 0.85 V were alternatively applied across the device. The voltage held across the device was initially 0 V for 10 minutes, followed by 5 further periods of 10 minutes alternating between 0.85 and 0 V, resulting in 6 total periods in the hour-long experiment. The applied voltage was supplied by a Keithley 2450 Sourcemeter, and the same Keithley 2450 Sourcemeter also measured the extracted current from the device during the experiment (the extracted current is shown in Figure S5 below). The illumination source used was a continuous wave, 400 nm wavelength diode laser (PicoHarp, LDH-D-C-405M), and the illumination intensity used was 110 mW cm⁻², close to 1 sun intensity (100 mW cm⁻²). The PL from the device was collected and coupled into a grating spectrometer (Princeton Instruments, SP-2558), where the light was dispersed by its wavelength and detected by an iCCD camera (PI-MAX4, Princeton Instruments). The PL measurements were taken at 3 s intervals.

Figure S5 shows the current extracted from the device and the voltage applied across the device during the experiment described above. At 0 applied volts (short circuit) the extracted current is high, whereas at 0.85 applied volts (near to the open circuit voltage) little total current flows through the device.

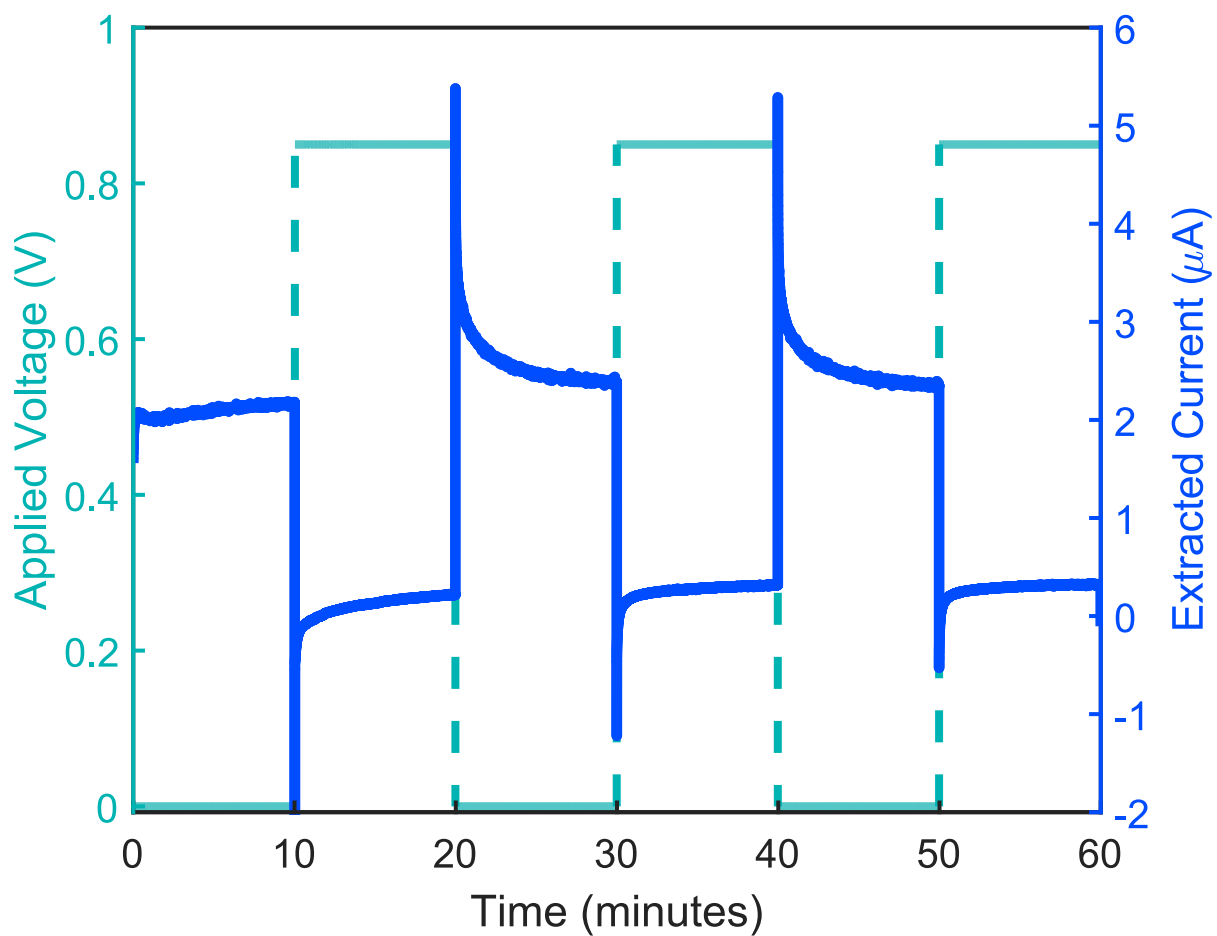


Figure S5: The current extracted from a $\text{MAPb}(\text{Br}_{0.5}\text{I}_{0.5})_3$ perovskite device (plotted in deep blue) as the applied voltage across the device was changed between 0 and 0.85 V every 10 minutes (plotted in turquoise).

3.2 MAPbI₃ Device Held at Various Applied Voltages

Figure S6 shows the PL recorded from a solution processed MAPbI₃ device under applied voltages ranging from 0 to 1 V. At the start of the experiment the voltage held across the device was 0 V, and the applied voltage was raised in 0.1 V steps up to 1 V over the course of 33 minutes. Each of the 11 voltages was held across the device for approximately 3 minutes to allow the device to reach equilibrium before the PL spectra were recorded. The applied voltage was supplied by a Keithley 2450 Sourcemeter. The illumination source used was a continuous wave, 400 nm wavelength diode laser (Picoharp, LDH-D-C-405M), and the illumination intensity used was 110 mW cm⁻², close to 1 sun intensity (100 mW cm⁻²). The PL from the device was collected and coupled into a grating spectrometer (Princeton Instruments, SP-2558), where the light was dispersed by its wavelength and detected by an iCCD camera (PI-MAX4, Princeton Instruments).

Figure S6 shows that as the applied voltage across the MAPbI₃ device increased, the emitted PL signal intensity from the perovskite increased. The increase in the applied voltage caused a decrease in the extracted current from the device, increasing the steady-state population of charge-carriers in the perovskite which caused a higher rate of radiative recombination. The PL behaviour of the MAPbI₃ device in Figure S6 contrasts against that of the MAPb(Br_{0.5}I_{0.5})₃ device presented in Figure 1b of the main text, where a higher applied voltage resulted in less emitted PL. In the main text we present evidence that mobile trap states have a greater influence on the PL emission from the MAPb(Br_{0.5}I_{0.5})₃ device than the level of current extraction.

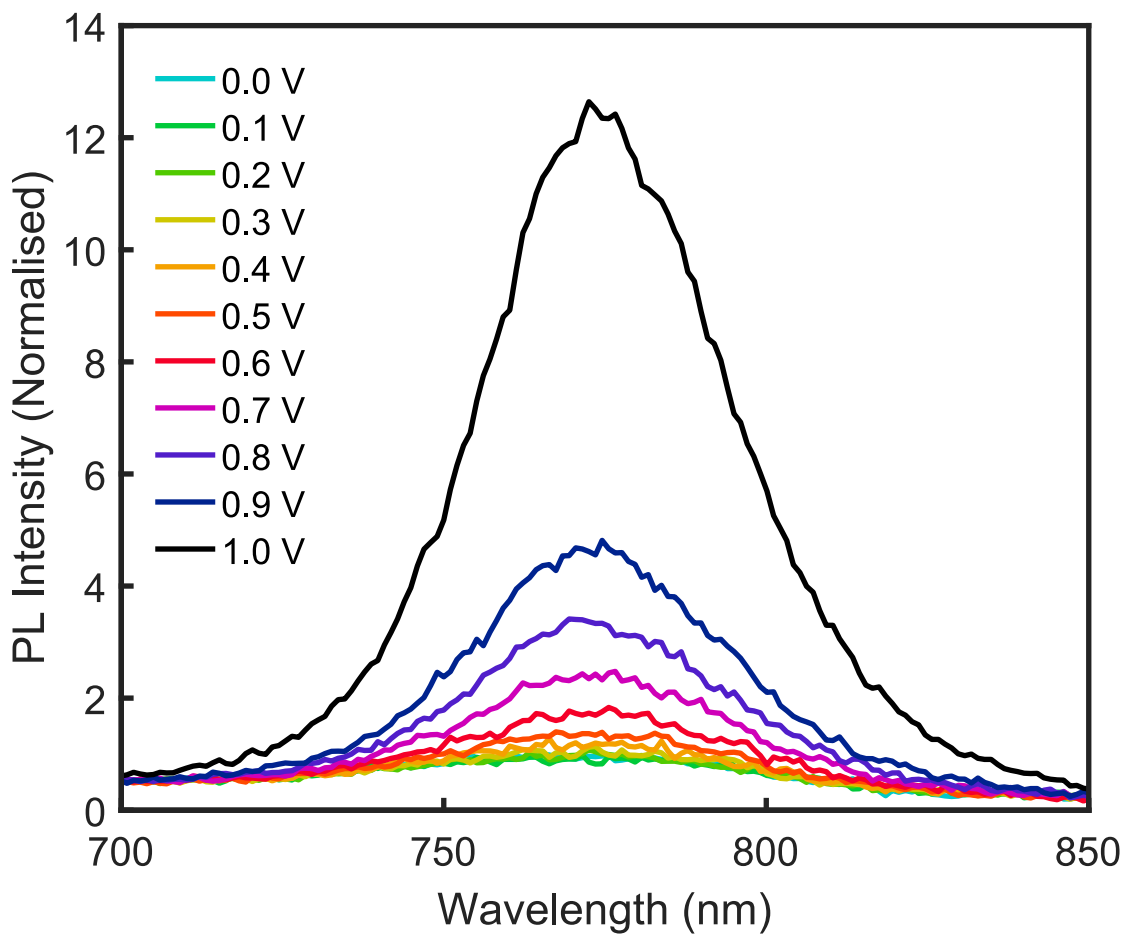


Figure S6: Normalised PL spectra from a MAPbI₃ device under various applied voltages between 0 and 1 V. The spectra have all been globally normalised so that the maximum intensity of the spectrum taken at 0 applied volts is 1.

4 Time Correlated Single Photon Counting under Applied Voltages

4.1 MAPb(Br_{0.5}I_{0.5})₃ Device

Figure 1c of the main text presents time correlated single photon counting (TCSPC) measurements from a MAPb(Br_{0.5}I_{0.5})₃ perovskite device under illumination and under various applied voltages. Initially a 1 V bias was held across the device for 1.5 hours before the first TCSPC measurement. Subsequently, 1 hour periods of held voltage were applied to the device before each TCSPC measurement, with the applied voltage dropping by 0.2 V after every TCSPC measurement. The experiment ended after 0 V had been applied across the device for 1 hour and the final TCSPC measurement had been made. The applied voltage was supplied by a Keithley 2450 Sourcemeter. The device was constantly held under pulsed illumination throughout the experiment, ensuring that the perovskite layer was fully segregated and at equilibrium during the TCSPC measurements. The pulsed illumination was provided by a 400 nm wavelength diode laser (PicoHarp, LDH-D-C-405M) at 5 MHz repetition rate and at 1400 mW cm⁻² average intensity. The PL wavelength measured was 750 nm, at the emission peak of the iodide-rich perovskite phase formed during the halide segregation process. The PL from the device was collected and coupled into a grating spectrometer (Princeton Instruments, SP-2558) fitted with a photon-counting detector (PDM series from MPD) with the timing controlled by a PicoHarp 300 TCSPC Event Timer. Each TCSPC measurement was taken over 120 s of accumulation time.

In the acquisition of the experimental data presented in Figure 1c of the main text, the voltages were applied in descending order. Figure S7 presents similar TCSPC measurements as shown in Figure 1c of the main text, except that during the experiment the voltages were applied in *ascending* order, with 0 V applied first. Initially a 0 V bias was held across the device for 1 hour before the first TCSPC measurement, and subsequent 1 hour periods of held voltage were applied to the device before each TCSPC measurement, with the applied

voltage increasing by 0.2 V after every TCSPC measurement. The experiment ended after 1 V had been applied across the device for 1 hour and the final TCSPC measurement had been made. The device was constantly held under pulsed illumination throughout the experiment, ensuring that the perovskite layer was fully segregated and at equilibrium during the TCSPC measurements. The pulsed illumination was provided by a 400 nm wavelength diode laser (PicoHarp, LDH-D-C-405M) at 5 MHz repetition rate and at 1400 mW cm^{-2} average intensity. The PL wavelength measured was 750 nm, at the emission peak of the iodide-rich perovskite phase formed during the halide segregation process. The PL from the device was collected and coupled into a grating spectrometer (Princeton Instruments, SP-2558) fitted with a photon-counting detector (PDM series from MPD) with the timing controlled by a PicoHarp 300 TCSPC Event Timer. Each TCSPC measurement was taken over 120 s of accumulation time.

4.2 MAPbI₃ Device

Figure S8 presents TCSPC measurements from a solution processed MAPbI₃ perovskite device under illumination and under various applied voltages. The voltage held across the device was initially 0 V for a 3.5 minute period, before the applied voltage was increased by 0.1 V approximately every 3.5 minutes, with the experiment ending after 1.0 V had been applied across the device for 3.5 minutes. The applied voltage was supplied by a Keithley 2450 Sourcemeter. The TCSPC measurements were made at the end of each 3.5 minute long constant-voltage period, and the device was constantly held under pulsed illumination throughout the experiment. The pulsed illumination was provided by a 400 nm wavelength diode laser (PicoHarp, LDH-D-C-405M) at 1 MHz repetition rate and at 320 mW cm^{-2} average intensity. The PL wavelength measured was 785 nm. The PL from the device was collected and coupled into a grating spectrometer (Princeton Instruments, SP-2558) fitted with a photon-counting detector (PDM series from MPD) with the timing controlled by a PicoHarp 300 TCSPC Event Timer. Each TCSPC measurement was taken over 30 s of

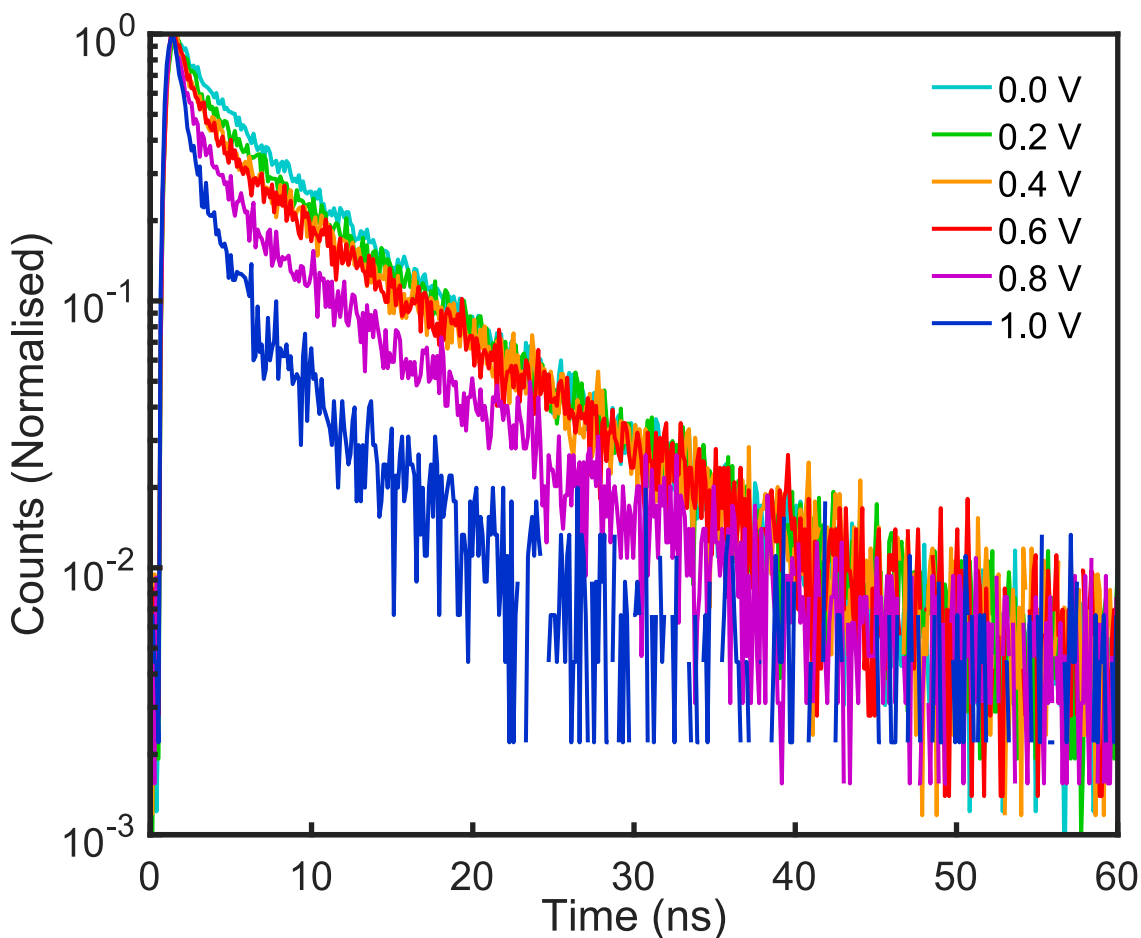


Figure S7: TCSPC decay traces measured at the low-energy PL peak (750 nm) of a mixed-halide perovskite device under various applied voltages and under 400 nm, 1400 mW cm^{-2} , 5 MHz pulsed laser illumination. The device was held at each target voltage for 1 hour before each 120 s TCSPC measurement was taken, and the applied voltages were applied in ascending order.

accumulation time.

Figure S8 shows that as the applied voltage across the MAPbI_3 device increased, the lifetimes of the photoexcited charge-carriers increased. The increase in applied voltage resulted in a decrease in the extracted current, lowering the loss rate of photoexcited charge-carriers from the perovskite layer and hence leading to flatter TCSPC traces. The behaviour of the charge-carrier lifetimes in the MAPbI_3 device in Figure S8 contrasts against that of the $\text{MAPb}(\text{Br}_{0.5}\text{I}_{0.5})_3$ device presented in Figure 1c of the main text, where a higher applied volt-

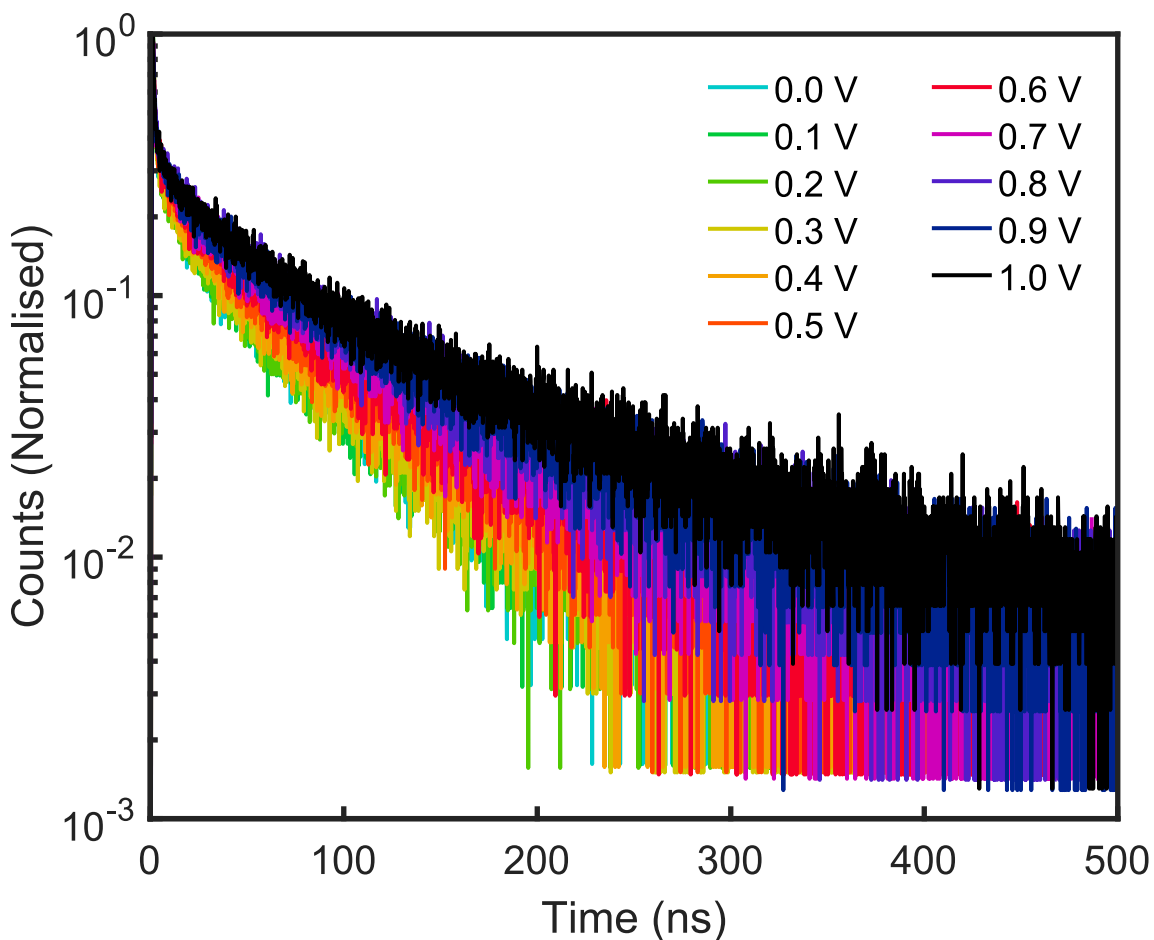


Figure S8: TCSPC measurements of a MAPbI₃ device under various applied voltages between 0 and 1 V. The TCSPC traces have been individually normalised such that the maximum number of counts from each trace is 1.

age resulted in a slight shortening of the charge-carrier lifetimes. In the main text we present evidence that mobile trap states have a greater influence on the charge-carrier dynamics in the MAPb(Br_{0.5}I_{0.5})₃ device than the level of current extraction.

5 Repeated Segregation Under Various Voltages

5.1 Experimental Overview

Figure 2 in the main text presents the PL (middle, bottom panels of Figure 2a) and extracted current (Figure 2c and also Figure S9 below) from a $\text{MAPb}(\text{Br}_{0.5}\text{I}_{0.5})_3$ device subjected to alternating periods of illumination and darkness. When under illumination, a variable applied bias was held across the perovskite device, and under darkness the device was held at short circuit (0 applied volts). The periods of illumination lasted 1 minute, and the periods of darkness lasted 30 minutes in order to allow any halide ions that segregated during the previous illumination period to remix. The illumination source used was a continuous wave, 400 nm wavelength diode laser (PicoHarp, LDH-D-C-405M), and the illumination intensity used was 110 mW cm^{-2} , close to 1 sun intensity (100 mW cm^{-2}). The PL from the device was collected and coupled into a grating spectrometer (Princeton Instruments, SP-2558), where the light was dispersed by its wavelength and detected by an iCCD camera (PI-MAX4, Princeton Instruments). The PL measurements were made at roughly 3 s intervals, and the spectra were integrated over the wavelength ranges 720 nm to 770 nm and 640 nm to 690 nm to create the iodide-rich phase PL and mixed phase PL signals in the middle and bottom panels, respectively, of Figure 2a in the main text. The applied voltage (plotted in Figure S9a) was supplied by a Keithley 2450 Sourceme-ter, and the same Keithley 2450 Sourceme-ter also measured the extracted current from the device during the experiment (plotted in Figure S9b). During the first illumination period, the applied voltage across the device was set to 0 V, and the applied voltage was then raised in 0.1 V steps per illumination period until 1 V was held across the device for an illumination period. After an additional illumination period at 1 applied volt, the applied voltage was decreased by 0.1 V per illumination period (in a symmetrical manner to the voltage up-ramp) until 0 V was held across the device for an illumination period. The completed up-down voltage ramp took place over 22 illumination periods, and was repeated 4 times for a total number of 88 illumination periods

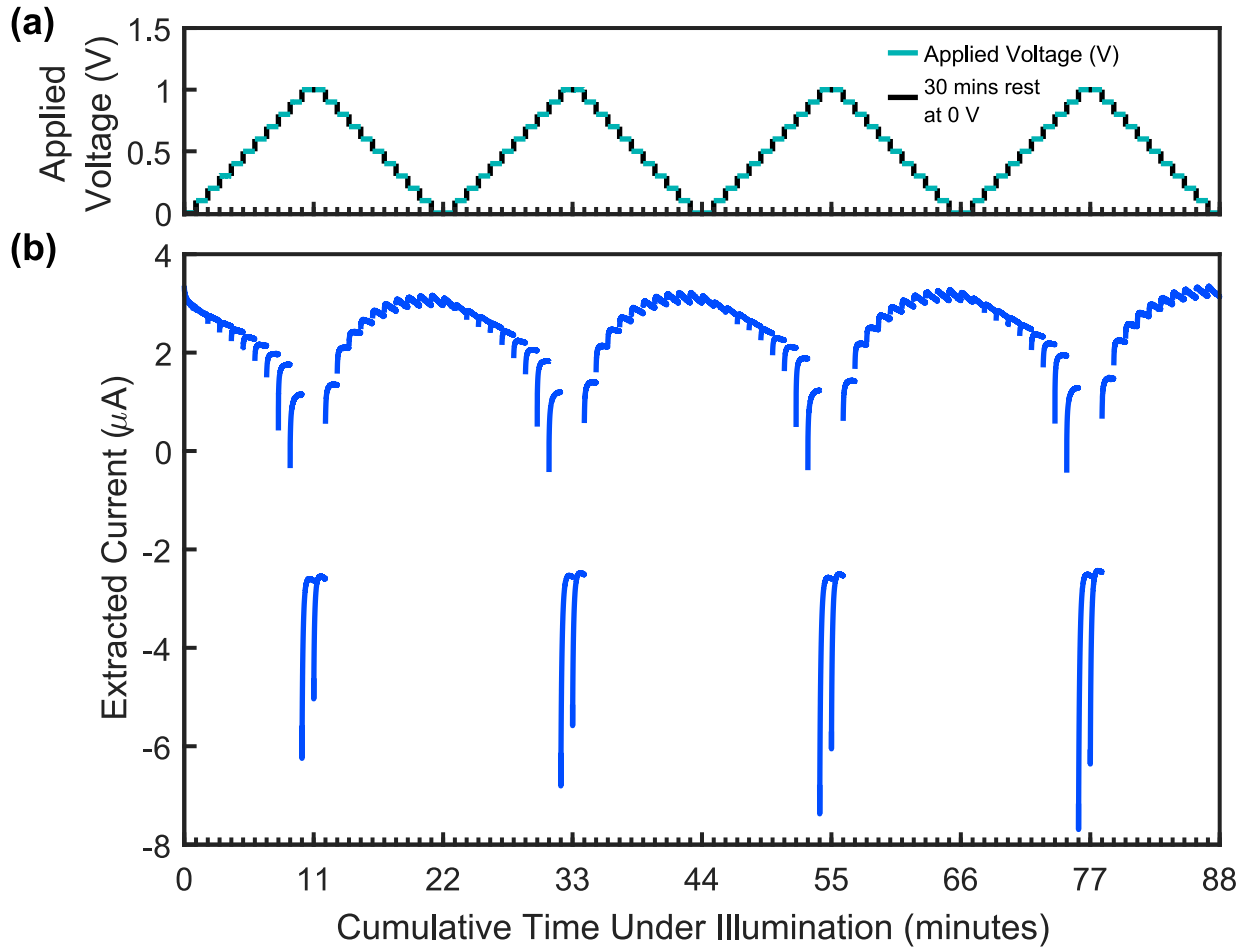


Figure S9: (a) Voltages applied across a $\text{MAPb}(\text{Br}_{0.5}\text{I}_{0.5})_3$ device during 1 minute illumination periods (blue) and indications of the 30 minute rest periods under darkness between the illumination periods (black). During the periods of darkness 0 applied volts were held across the device (b) Extracted current from the $\text{MAPb}(\text{Br}_{0.5}\text{I}_{0.5})_3$ device under illumination with the discrete voltage ramp shown in (a) applied. The current data shown in (b) corresponds to the experiment shown and discussed in Figure 2 of the main text, and the blue plots in Figure 2c of the main text are averages based on the data shown in (b).

over the course of the experiment. Figure S9a plots the applied voltages used during all 88 illumination periods.

5.2 Extracted Current

The extracted current from the device during the illumination periods of the experiment discussed above is shown in Figure S9b. The behaviour of the extracted current is a complex

result of the applied bias, changes in the material properties due to halide segregation, and ionic screening in the perovskite. The blue plots in Figure 2c in the main text were created by averaging the extracted current in Figure S9b over equivalent points in the last 3 voltage up-down ramps (the voltage ramps are plotted in turquoise in Figure S9a). ‘Equivalent points’ are measurements made at the same applied voltage, on the same part of the applied voltage up-down ramp, and at the same time after the start of an illumination period. The first applied up-down voltage ramp was discarded from the averaging process as the initial state of the device slightly influenced the measurements made during the first few illumination periods, and hence these measurements are not representative of the periodic behaviour of the device.

5.3 Example Spectra from Experiment

Figure S10 and Figure S11 present certain normalised PL spectra taken during the experiment discussed above and which were integrated over to form data points in the middle and bottom panels of Figure 2a in the main text. Figure S10 shows the first and last PL spectra taken during the illumination period at 0.7 applied volts on the 2nd voltage up-ramp (the 30th illumination period), both normalised to the maximum intensity of the first PL spectra of the illumination period. Figure S10 shows a clear rise of a low-energy PL peak over the course of the illumination period, attributed to the forming regions of iodide-rich perovskite. Figure S10 represents an illumination period over which a maximal amount of halide segregation was observed. Figure S11 shows the first and last PL spectra taken during the illumination period at 0.3 applied volts on the 2nd voltage down-ramp (the 41st illumination period), normalised to the maximum intensity of the first PL spectra of the illumination period. Figure S11 represents the minimal amount of halide segregation observed over one illumination period. While both Figures S10 and S11 show the growth of a low-energy PL peak attributed to halide segregation,^{S3} the peak growth is clearly more prominent in Figure S10, indicating that more halide segregation occurred over this illumination period. Figure

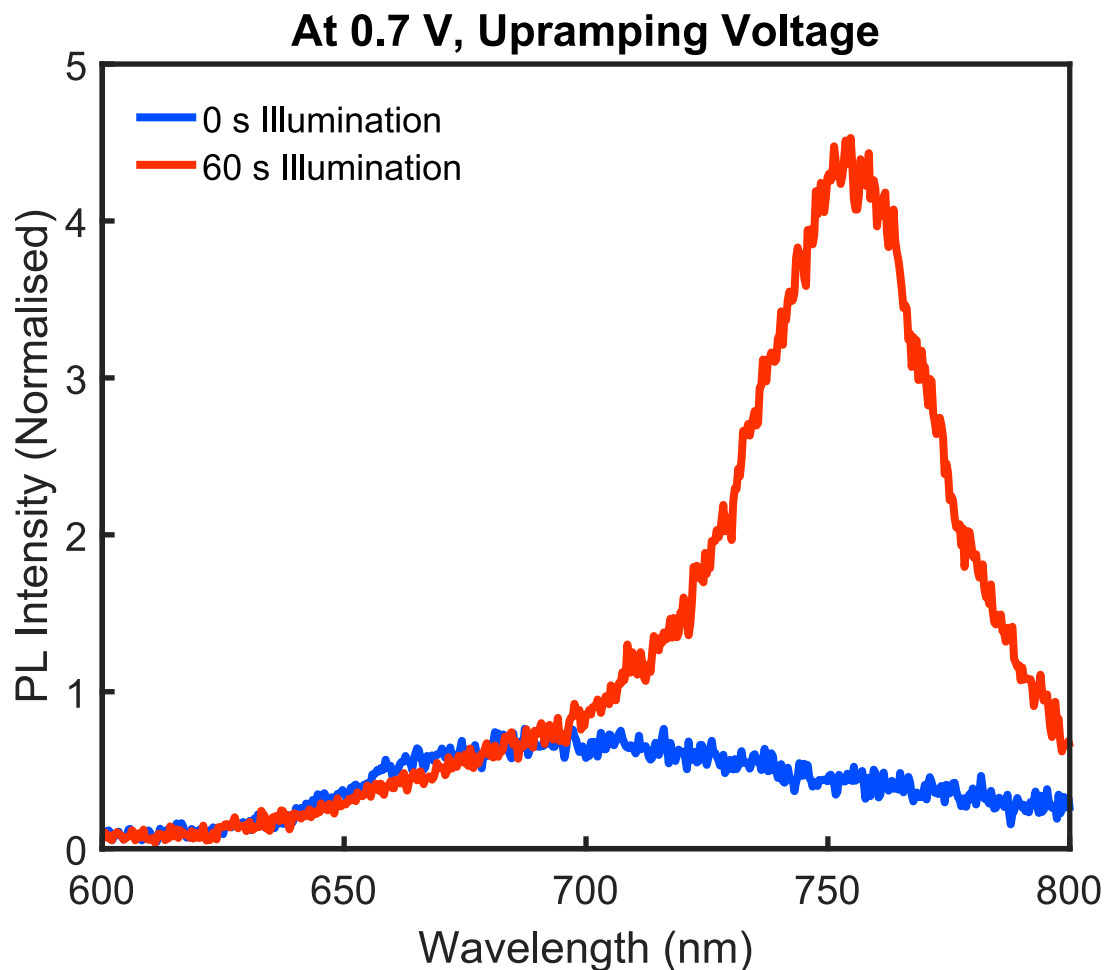


Figure S10: Normalised PL spectra from a $\text{MAPb}(\text{Br}_{0.5}\text{I}_{0.5})_3$ device taken at the start and at the end of a 60 s illumination period while 0.7 V was applied across the device. The spectra are both globally normalised such that the maximum signal of the initial spectrum is set to 1. The PL spectra were taken on the 2nd voltage up-ramp of the experiment presented in Figure 2 of the main text, and so the illumination period was the 30th out of 88 in the experiment. The spectra are plotted here as an example of the maximum amount of halide segregation that was observed over the course of one illumination period in the experiment shown in Figure 2 in the main text.

2b in the main text presents the ratio of PL signals from the iodide-rich and mixed regions of perovskite (averaged over equivalent points in the last 3 voltage up-down ramps), which is a quantified measure of how much halide segregation occurred over each illumination period.

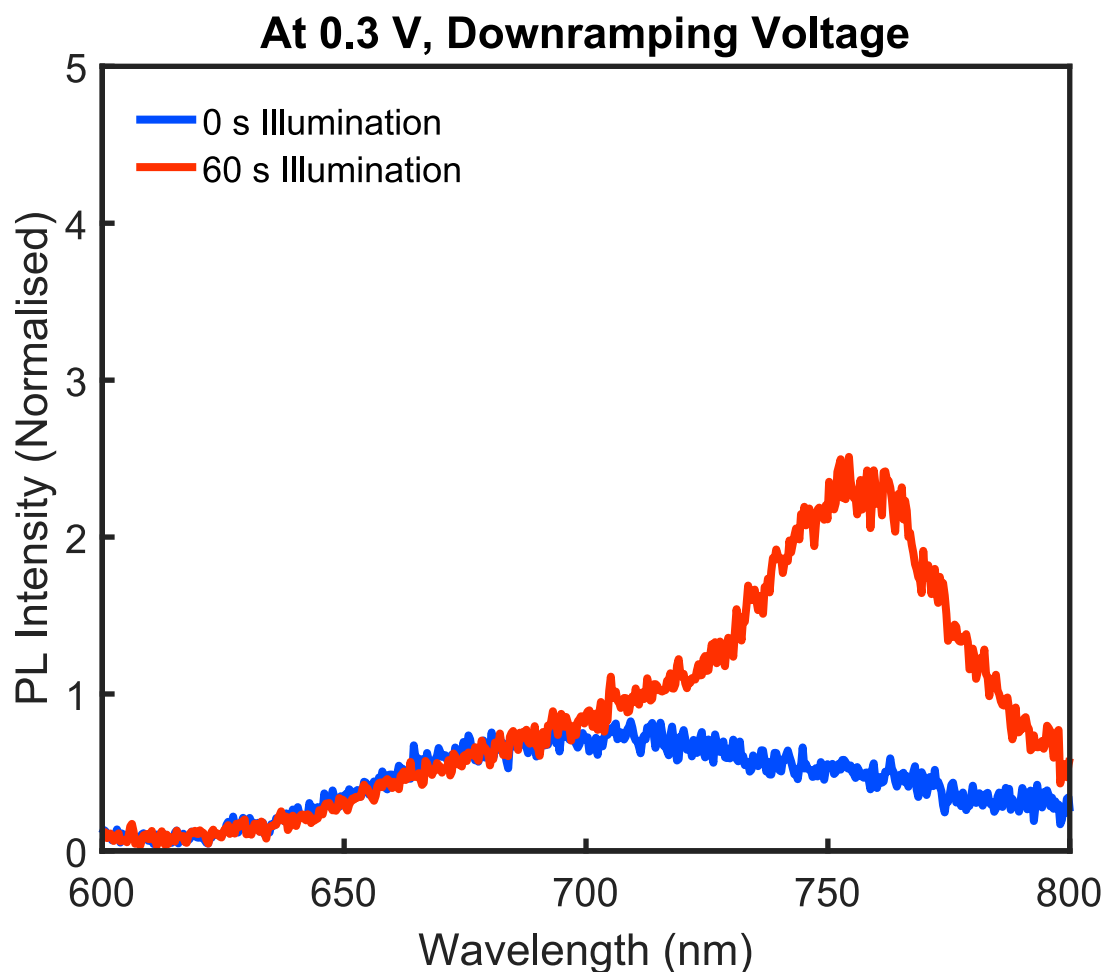


Figure S11: Normalised PL spectra from a $\text{MAPb}(\text{Br}_{0.5}\text{I}_{0.5})_3$ device taken at the start and at the end of a 60 s illumination period while 0.3 V was applied across the device. The spectra are both globally normalised such that the maximum signal of the initial spectrum is set to 1. The PL spectra were taken on the 2nd voltage down-ramp of the experiment presented in Figure 2 of the main text, and so the illumination period was the 41st out of 88 in the experiment. The spectra are plotted here as an example of the minimum amount of halide segregation that was observed over the course of one illumination period in the experiment shown in Figure 2 in the main text.

6 Repeated Segregation Under Various Voltages with Pre-Biasing Period

6.1 Experimental Overview

Figure S12 presents the PL and extracted current from a $\text{MAPb}(\text{Br}_{0.5}\text{I}_{0.5})_3$ device subjected to repeated periods of illumination and darkness, with a 5 minute period of pre-biasing applied during the periods of darkness. When under illumination, a variable applied bias was held across the perovskite device (plotted in blue in Figure S12a), and under darkness the device was held at short circuit (0 applied volts) when a pre-bias was not applied. The periods of illumination lasted 1 minute, and the periods of darkness consisted of an initial 25 minute period at 0 applied volts before a further 5 minute period over which the device was held at the voltage of the next illumination period. The illumination source used was a continuous wave, 400 nm wavelength diode laser (Picoharp, LDH-D-C-405M), and the illumination intensity used was 110 mW cm^{-2} , close to 1 sun intensity (100 mW cm^{-2}). The PL from the device was collected and coupled into a grating spectrometer (Princeton Instruments, SP-2558), where the light was dispersed by its wavelength and detected by an iCCD camera (PI-MAX4, Princeton Instruments). The PL measurements were made at roughly 3 s intervals, and the spectra were integrated over the wavelength intervals 720 nm to 770 nm and 640 nm to 690 nm to create the iodide-rich phase PL and mixed phase PL signals in Figure S12b and Figure S12c, respectively. The applied voltage (plotted in blue in Figure S12a) was supplied by a Keithley 2450 Sourcemeter, and the same Keithley 2450 Sourcemeter also measured the extracted current from the device during the experiment, which is presented in Figure S12d (current measured during the illumination periods) and Figure S13b and S14b (current measured during the 5 minute pre-biasing periods under darkness). During the first illumination period, the applied voltage across the device was set to 0 V, and the applied voltage was then raised in 0.1 V steps per illumination period until 1 V was held across the device for an illumination period. After an additional illumination

period at 1 applied volts, the applied voltage was decreased by 0.1 V per illumination period (in a symmetrical manner to the voltage up-ramp) until 0 V was held across the device for an illumination period. The completed up-down voltage ramp took place over 22 illumination periods, and was repeated 4 times for a total number of 88 illumination periods over the course of the experiment. Figure S12a presents the applied voltages used throughout the 88 illumination periods.

The behaviour of the PL shown in Figure S12 is broadly very similar to that shown in Figure 2 of the main text. During each individual illumination period the PL signal attributed to the iodide-rich regions of perovskite increased as halide segregation took place, and the PL signal attributed to the mixed perovskite phase decreased as photoexcited charge-carriers funnelled from the mixed perovskite phase into the iodide-rich regions. At the start of each illumination period – when negligible halide segregation had occurred – the first measurement of the mixed phase PL signal modulated up and down over the course of the experiment, a phenomenon we attribute in the main text to the slow movement of charged trap states according to the applied voltage across the device. The bottom panel of Figure 2a in the main text displays hysteresis in the initial mixed phase PL signal across the voltage up-down ramp, meaning that the PL measurements made at a given voltage were not all similar across the experiment. This hysteresis in the PL measurements suggests that the mobile trap states were not returning to equilibrium in the 30 minutes of darkness, highlighting that the trap states are essentially stationary unless under illumination. Similar hysteresis to that in the mixed phase perovskite PL measurements in Figure 2a of the main text is shown in Figure S12c, despite the 5 minutes of pre-bias under darkness, which further highlights that the mobile trap states are only mobile under illumination.

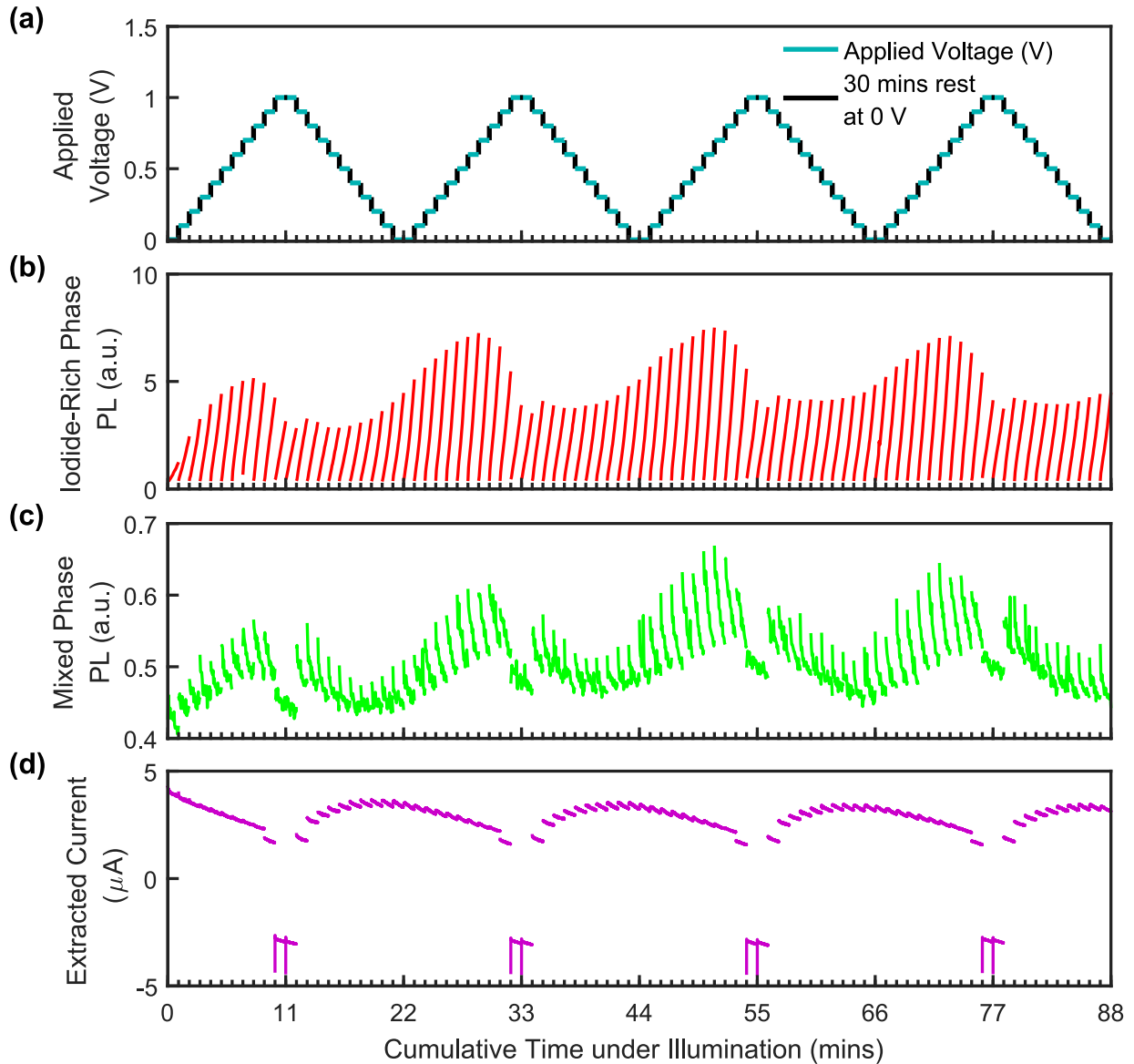


Figure S12: (a) Voltages applied across a $\text{MAPb}(\text{Br}_{0.5}\text{I}_{0.5})_3$ device when under illumination (blue) and indications of the 30 minute rest periods under darkness (including 5 minutes of pre-bias) that were applied to the device between 1 minute illumination periods (black). (b) The integrated low energy PL (720 nm to 770 nm) from the device under 400 nm, 110 mW cm^{-2} , continuous wave illumination. (c) The integrated higher energy PL (640 nm to 690 nm) from the device under illumination. (d) Extracted current from the $\text{MAPb}(\text{Br}_{0.5}\text{I}_{0.5})_3$ device under illumination with the discrete, voltage ramp shown in (a) applied. The purple plots in Figure 2c of the main text are averages based on the data shown in (d).

6.2 Current Comparison Between Pre-Biased and Not Pre-Biased Experiments

Figure 2 in the main text and Figure S12 present the results from similar experiments where a $\text{MAPb}(\text{Br}_{0.5}\text{I}_{0.5})_3$ device was repeatedly subjected to alternating periods of illumination and darkness. During both experiments, a variable voltage was applied across the device during the 1 minute periods of illumination (the applied voltage is plotted in the top panel of Figure 2a in the main text and in Figure S12a). For one experiment (results plotted in Figure 2 of the main text) the device was held at short circuit (0 applied volts) during the 30 minute periods of darkness between illumination periods. In the other experiment (results presented in Figure S12), between illumination periods the device was held under darkness at short circuit (0 applied volts) for 25 minutes, before a 5 minute pre-biasing period under darkness was applied. The voltage held across the device during the 5 minute pre-biasing periods was equal to the voltage held across the device during the illumination period that immediately followed. The PL recorded from these two experiments (presented in the middle and bottom panels of Figure 2a in the main text and Figure S12b and Figure S12c for the not pre-biased and pre-biased experiments, respectively) were similar, however the extracted current from the devices during the periods of illumination (Figure S9b and Figure S12d, respectively) were not. Without a pre-bias period (Figure S9b), the extracted current increased rapidly at the start of each illumination period. In the main text we attribute this rapid increase in current to the change in the ionic screening within the perovskite material upon the change in applied voltage that occurs at the start of each illumination period (short circuit to various applied voltages). With a pre-biasing period applied before each illumination period, there was no such rapid increase in extracted current observed (Figure S12d). A similar rapid increase in extracted current is instead seen at the start of the pre-biasing periods under darkness, as highlighted by Figure S13b and Figure S14b. The increase in current observed in Figure S14b at the start of the pre-biasing periods is attributed to the same change in the ionic screening within the perovskite that caused the similar increases in current at the start

of the illumination periods of the experiment with no pre-biasing period (results plotted in Figure S9b and Figure 2 of the main text). The increases in current observed in Figure S14b also explains why no increase in current was observed during the following illumination periods, as seen in Figure S12d.

6.3 Measurements made at 1 Applied Volt

It can be seen from Figure S12c that, during the illumination periods when 1 V was held across the device, the mixed perovskite phase PL (and to a lesser extent the iodide-rich phase PL in Figure S12b) measured was considerably dimmer than the PL measured at the corresponding points in other illumination periods. This dimness of PL at 1 applied volt was not observed in Figure 2a in the main text, suggesting that the period of pre-biasing unique to the experiment reported in Figure S12 was responsible for lowering the PL signal. Birkhold *et al.* reported that the presence of charge-carriers and electric fields in MAPbI₃ perovskites caused the formation of defects and trap states in the perovskite crystal, which were observed to quench the PL signal from the perovskite.^{S4} These trap states were observed to slowly heal when the charge-carrier injection and electric field generation were stopped. Figure S13b shows that during the experiment reported in Figure S12, a significant number of charge-carriers were injected into the perovskite device during the pre-biasing periods at 1 applied volt. Figure S13b also shows that, other than the pre-biasing periods under darkness at 1 applied volt, the current injected during all other pre-biasing periods was much less significant. We therefore suggest that the combination of 5 minutes under the total net electric field generated by the built-in and applied electric fields and a significant degree of current injection under darkness was enough to (reversibly) create trap states in the perovskite, as observed by Birkhold *et al.*^{S4} The generation of these trap states during the pre-bias period caused a dimness of PL during the following illumination period at 1 applied volt, as shown in Figure S12c. The PL measurements made during the later illumination periods following the ones at 1 applied volt showed a relative increase in the PL signal

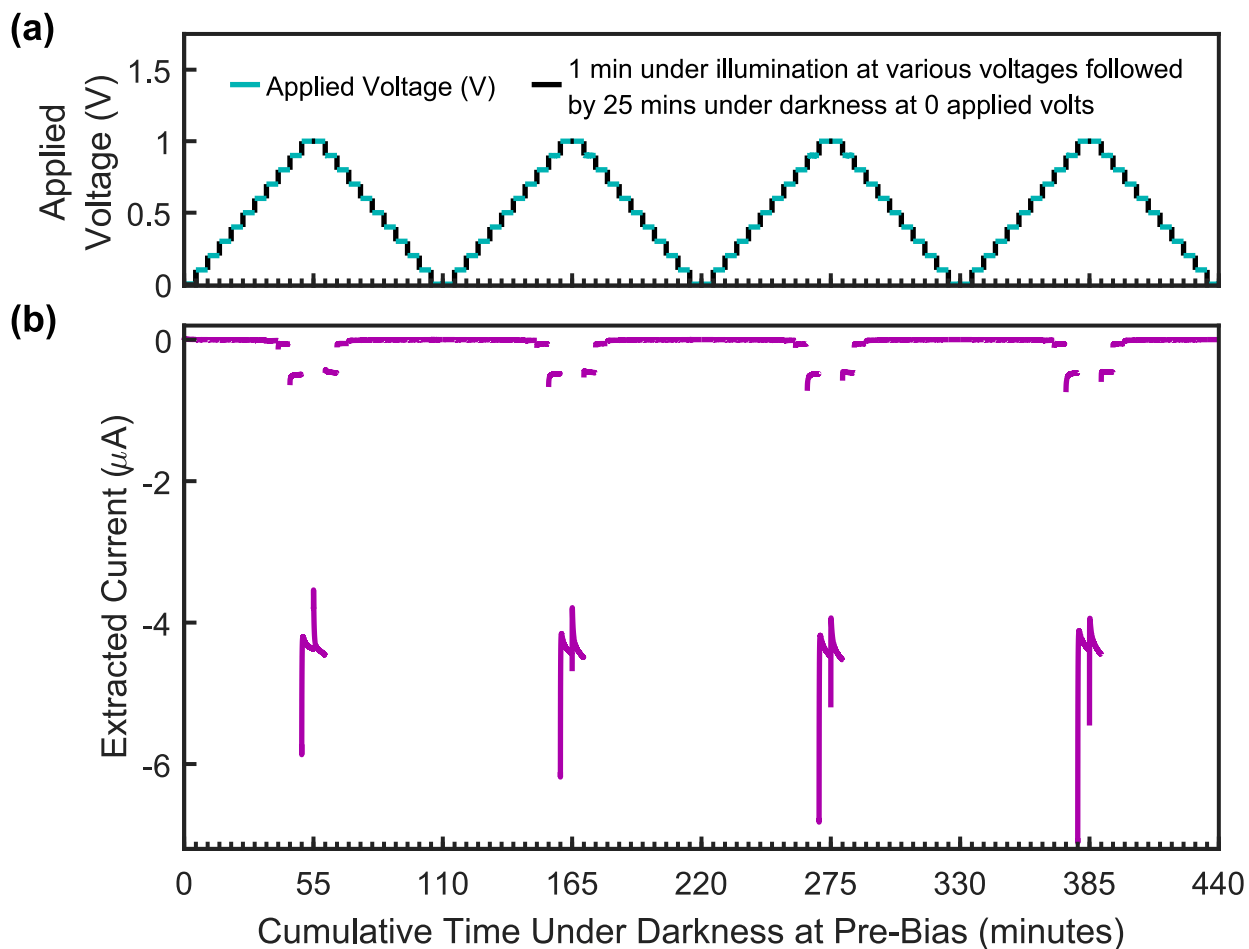


Figure S13: (a) Voltages applied across a $\text{MAPb}(\text{Br}_{0.5}\text{I}_{0.5})_3$ device during 5 minute pre-biasing periods under darkness (blue) and indications of the 1 minute of illumination at various applied voltages followed by the 25 minutes of darkness at 0 applied volts that were applied to the device between the 5 minute pre-biasing periods (black). (b) Extracted current from the $\text{MAPb}(\text{Br}_{0.5}\text{I}_{0.5})_3$ device under darkness with the discrete, voltage ramp shown in (a) applied.

brightness, verifying that the formed defect states were healed when the perovskite was allowed to relax without the injection of charge-carriers.

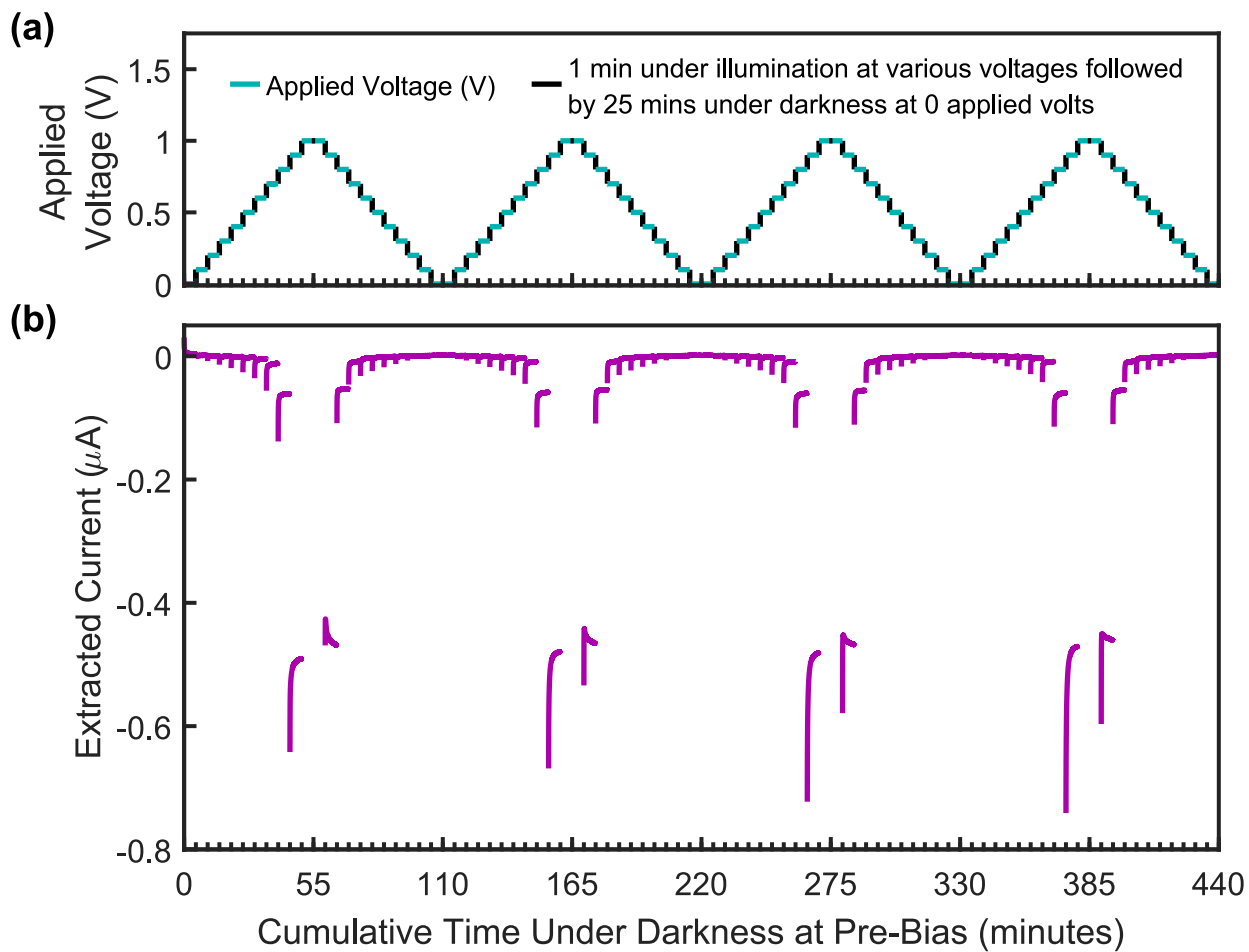


Figure S14: (a) Voltages applied across a $\text{MAPb}(\text{Br}_{0.5}\text{I}_{0.5})_3$ device during 5 minute pre-biasing periods under darkness (blue) and indications of the 1 minute of illumination at various applied voltages followed by the 25 minutes of darkness at 0 applied volts that were applied to the device between the 5 minute pre-biasing periods (black). (b) Zoomed region of Figure S13b.

7 External Quantum Efficiency Measurements

External quantum efficiency (EQE) was measured via a custom built Fourier transform photocurrent spectrometer based on a Bruker Vertex 80v Fourier Transform Interferometer. Devices were illuminated with simulated sunlight with a class AAA Oriel solar simulator. Devices were calibrated to a Newport-calibrated reference silicon solar cell with a known external quantum efficiency. The solar cells were masked with a metal aperture with a defined active area of 0.0625 cm^2 . The spikes observed between 450 and 500 nm in the EQE spectra presented in Figure 3a of the main text are artefacts resulting from slight fluctuations in the intensity of the solar simulator.

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