Nanoscale chemical heterogeneity dominates the optoelectronic response of alloyed perovskite solar cells

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Halide perovskites perform remarkably in optoelectronic devices. However, this exceptional performance is striking given that perovskites exhibit deep charge-carrier traps and spatial compositional and structural heterogeneity, all of which should be detrimental to performance. Here, we resolve this long-standing paradox by providing a global visualization of the nanoscale chemical, structural and optoelectronic landscape in halide perovskite devices, made possible through the development of a new suite of complementary, multimodal microscopy measurements combining quantitative optical spectroscopic techniques and synchrotron nanoprobe measurements. We show that compositional disorder dominates the optoelectronic response over a weaker influence of nanoscale strain variations even of large magnitude. Nanoscale compositional gradients drive carrier funnelling onto local regions associated with low electronic disorder, drawing carrier recombination away from trap clusters associated with electronic disorder and leading to high local photoluminescence quantum efficiency. These measurements reveal a global picture of the competitive nanoscale landscape, which endows enhanced defect tolerance in devices through spatial chemical disorder that outcompetes both electronic and structural disorder.

Halide perovskites have shown tremendous success in solar cell and other optoelectronic applications. The highest performing and most reproducible perovskites are alloyed compositions, such as FA0.79MA0.16Cs0.05Pb(I0.83Br0.17)3 (where FA is formamidinium and MA is methylammonium), found through empirical device optimization. Yet the unprecedented performance of halide perovskite devices comes in spite of the fact that these materials are optoelectronically, chemically and structurally heterogeneous across multiple length scales. It has been shown that the bulk stoichiometry of halide perovskites governs their optoelectronic performance and stability at the macroscale. Recent microscopy studies have shown that nanoscale trap clusters caused by structural disorder, as well as chemical heterogeneity, are both linked to reduced device performance in line with classical understanding of semiconductor behaviour. However, high photo-voltages can be achieved in perovskite solar cells despite chemical segregation, which in turn promotes radiative recombination through photodoping. A global understanding of the influence of the nanoscale landscape on device performance, and how the apparently detrimental and beneficial disorder can be reconciled, will be crucial for progressing the field.

Quantitative optical microscopy of halide perovskite devices. We solution-processed mixed-cation, mixed-halide FA0.79MA0.16Cs0.05Pb(I0.83Br0.17)3 perovskite films on glass, as well as solar cells in which the perovskite is sandwiched between contacts composed of poly(bis(4-phenyl)(2,4,6-trimethylphenyl)amine) (PTAA) and poly(9,9-bis(3’-N,N-dimethyl)-N-ethylammonium-propyl-2,7-fluorene-alt-2,7-(9,9-dioctylfluorene)) dibromide (PFN-Br) on the top side, with the complete stack as glass/indium tin oxide (ITO)/PTAA:PFN-Br/perovskite/PCBM/bathocuproine (BCP)/Ag (Supplementary Fig. 1). We developed a technique based on a wide-field, hyperspectral microscope to assess important optoelectronic properties of the samples, namely absorption and luminescence, in a quantitative manner at the nanoscale. The setup is calibrated to measure the spectrally resolved, absolute number of photons leaving the sample locally at each point of the region of interest (Fig. 1a and Methods). We assess local non-radiative recombination processes of bare perovskite films (see Supplementary Fig. 1 for equivalent measurements of a full device stack), which negatively affect the performance of solar cell devices, through extraction of absolute photoluminescence (PL) maps as a function of emission wavelength (Fig. 1b). The 405-nm continuous wave laser excitation intensity is set to roughly 90 mW cm−2, equivalent to illumination with roughly 1.4 suns for this bandgap (Methods), which emulates the conditions of a functioning solar cell device; we do not see considerable transient light soaking effects under these conditions and so we assert the variations we observe here are not due to light-induced phase segregation (Supplementary Fig. 2)39,40. The samples show PL spectra centred at approximately 1.62 eV (765 nm), with local variations in intensity, peak position and shape on the hundreds of nanometres scale (see example spectra in Fig. 1b, taken from map in Fig. 1d). By fitting the absolute PL spectra using the generalized Planck law, we extract the quasi-Fermi level.

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splitting (QFLS) from each point and plot this in Fig. 1f (Methods and Supplementary Fig. 3), which provides information about the excited state carrier distributions and gives an upper bound for the open-circuit voltage of a solar cell for the device under analysis. In films, we find variations above 20 meV in the local QFLS values, including local performance hot spots with values above 1.24 eV, corresponding to roughly 93% of the radiative limit of roughly 1.32 eV for this bandgap (1.62 eV). This spatial heterogeneity is particularly evident in the full device stack (Supplementary Fig. 1) where QFLS values range from below 1.07 eV to above 1.11 eV, with the increased spread probably due to additional spatially varying carrier quenching from the contacts. The spatially averaged QFLS in the bare film corresponds to an optically implied open-circuit voltage of roughly 1.23 V, with the full device exhibiting a value of 1.08 V, consistent with non-radiative losses associated with the contacts1,3,4 and comparable to the electrically measured value of 1.11 V.

Additionally, we used calibrated white light sources to extract local reflectance and transmittance spectra, and hence compute absorbance at each point, from the same area of thin films. To probe electronic disorder, we extract the local PLQE of 2.2% is in good agreement with standard macroscale methodologies (3.2%)5 (Methods), validating our approach. We note that both values are from external measurements, dictated by specific film outcoupling properties5,6, and there is small systematic underestimation of the PLQE from the local measurements due to light waveguided in the film or substrate or light emitted in the backwards hemisphere that is not collected. The PLQE (η) is logarithmically related to the QFLS (Δμ) of a material through the Ross relation7:

\[Δμ = Δμ_{rad} + k_b T \ln(η)\]

where Δμ_{rad} is the radiative limit QFLS for a given bandgap, \(k_b\) is the Boltzmann constant and \(T\) is temperature. We compare the local QFLS and PLQE extracted from each point as shown in Fig. 1g and find that their relationship matches well with the Ross relation. Therefore, our quantitative optical microscopy represents a self-consistent picture of local optoelectronic properties that links directly to device performance metrics.

We now seek to understand how the heterogeneous sample properties affect other local optoelectronic parameters. Figure 2a,b shows PLQE and Urbach energy (E_U) maps, respectively, extracted from the same area of a thin film. To probe electronic disorder, we extract the local E_U from the red tail of the PL spectrum at each pixel18 (Methods and Supplementary Fig. 5); a low E_U is associated with clean semiconducting behaviour19–21. As shown in the two-dimensional (2D) kernel density estimation plot in Fig. 2c, there is a clear spatial anticorrelation between the PLQE and the E_U (Spearman’s \(r = -0.44, \ P < 0.0001\)), highlighting the regions that are the most emissive also show the cleanest subbandgap tail, consistent with what we would expect for a semiconductor. Figure 2d shows the spatially averaged PL spectrum from the highest PLQE (>80th percentile) and lowest PLQE (<20th percentile) regions. These spectra show that the highest PLQE regions exhibit a distinctly red-shifted (low-energy) shoulder in the emission, which is absent in the low PLQE regions. By contrast, there is negligible difference in spectra between low and high PLQE regions in analogous

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**Fig. 1 | Hyperspectral microscopy of perovskite solar cell device stacks.** a. Schematic of the hyperspectral microscopy setup used to characterize the FA_{0.79}MA_{0.16}Cs_{0.05}Pb(I_{0.83}Br_{0.17})_3 perovskite films and devices. b. PL spectra from the black and red highlighted regions in d, e and f. c. Reflectance (R), transmittance (T) and absorbance (A) spectra from the region highlighted in black in those panels. d-f. Absolute PLQE (d), broadband reflectance (e) and QFLS maps (f) of a FA_{0.79}MA_{0.16}Cs_{0.05}Pb(I_{0.83}Br_{0.17})_3 perovskite device stack (without the back metal contact). Reflectance is normalized (norm.) to the mean value of the map. g. Scatter plot of QFLS versus PLQE extracted from the maps in d and f (blue) and of a full device stack (orange, Supplementary Fig. 1) compared to the Ross relation. All scale bars, 2 μm.
single-halide $\text{FA}_{0.79}\text{MA}_{0.16}\text{Cs}_{0.05}\text{PbI}_3$ thin film controls, and luminescence yields are an order of magnitude lower than the mixed-halide counterparts (Supplementary Fig. 6). These quantitative hyperspectral microscopy results thus suggest that the mixed-halide composition and its effects on the local energetic landscape and structure play a key role in the observed optoelectronic quality of the perovskite films.

**Nanoscale chemical and strain mapping of halide perovskites.** To unveil the nature of the nanoscale landscape and how it influences the optoelectronic performance, we probe the chemical and structural properties locally on the same scan area as the luminescence measurements by performing simultaneous synchrotron-based nano-X-ray fluorescence (nXRF) and nano-X-ray diffraction (nXRD) measurements, respectively, with a spatial resolution of roughly 50 nm (Methods, including discussion of beam sensitivity). The spatial variation in chemistry is extracted by tracking the characteristic Pb L$\alpha$, I L$\alpha$ and Br K$\alpha$ lines in nXRF (see spectrum in Supplementary Fig. 7), and we use ratios of the halide and lead XRF signal intensities to assess compositional variations independent of the map is net tensile strained, which has been previously shown to be caused by a mismatch in the thermal expansion coefficient (CTE) between the perovskite and the substrate during heating and cooling steps in the processing$^{12}$; calculations of the expected magnitude of strain from such a CTE mismatch yield strains of roughly 0.35–1% (Methods), consistent with the values that we experimentally observe, although we note that there may be multiple contributions to the observed strain. We spatially correlate these strain variations with the $E_U$ and find that there is a very weak but statistically signifi-

![Image](https://example.com/image.png)
Spatial relationships between halide composition, structural and optoelectronic variations in FA0.79MA0.16Cs0.05Pb(I0.83Br0.17)3 perovskite films. a, Normalized Br:Pb ratio map of a thin film. b, Strain map of the (210) family of planes extracted from nXRF and nXRD of the same area as in a. c, Histograms of the lattice constants extracted from nXRF (A\text{\tiny nXRF}) and from nXRD (A\text{\tiny nXRD}) from the (100), (200) and (210) peaks. d, 2D kernel density estimation plot of Urbach energy versus (210) strain showing a weak positive correlation between the two properties (Spearman’s \( r = 0.07, P = 4 \times 10^{-3} \)). e, f. Urbach energy maps overlaid with the regions of highest Br (e) (>80th percentile, light blue) and lowest Br (<20th percentile, light grey) content, respectively. g, h. Histograms of the Urbach energies (g) and PLQEs (h) in the highest Br (>80th percentile, blue) and lowest Br content regions (<20th percentile, light grey). The populations are statistically different in both cases as determined by two-sample Kolmogorov–Smirnov testing (\( P \ll 0.0001 \)). i, Schematic highlighting emission behaviour in high and low Br regions. All scale bars, 2 \( \mu \)m a.u., arbitrary units.
correlation between clusters with high subgap trap density, ascertained through local photo-emission microscopy (PEEM), and lower Br:Pb content, through nXRF measurements, confirms this proposition (Supplementary Fig. 15). Therefore, these multimodal measurements reveal the important features of nanoscale heterogeneity. Specifically, there are two primary, distinct types of site that influence local performance: sites with high Br content with low electronic disorder but an intriguing low-energy emission shoulder corresponding to hot spots of high performance, and sites with low Br content containing deep trap states associated with non-radiative recombination and electronic disorder (Fig. 3).

Optical tracking of carriers in alloyed halide perovskites. To understand the nanoscale charge-carrier recombination competition between these sites and the nature of the low bandgap recombination in a nominally Br-rich region, we perform transient absorption microscopy (TAM) measurements spatially correlated with nXRF measurements (Supplementary Fig. 16). The wide-field TAM methodology allows us to simultaneously monitor the temporally and spectrally resolved differential transmittance signal ($\Delta T/T$) for each spatial point (Methods). Here, we focus on characterizing the ground state bleaching (GSB) band of the transient absorption spectra, which are positive changes in $\Delta T/T$ stemming from a bleaching of the transitions between the valence and conduction bands$^{46}$. Monitoring the GSB signal allows us to track the extent of the excited carrier population as a function of energy, therefore enabling us to infer the size of the bandgap that carriers experience as a function of space and time. In Fig. 4a, we show the Br:Pb ratio of an nXRF line scan correlated with the PL profile reconfirming the earlier trend of increased steady-state PL intensity in regions of higher Br:Pb ratio on the region of interest for TAM. We then plot the centre-of-mass energy of GSB band as a function of time in Fig. 4b. We further highlight areas rich in Br (blue dashed line) and areas deficient in Br (grey dashed line) and compare the local energetic evolutions of those two distinct regions (Supplementary Fig. 17). In the Br-rich region, photoexcited carriers initially occupy higher energy states (roughly 1.66 eV) relative to the Br-poor region (roughly 1.64 eV). The GSB band in the Br-rich region then rapidly red-shifts towards 1.63 eV on the timescale of hundreds of picoseconds, which is evident in the local transient absorption spectra snapshots shown in Fig. 4c. In contrast, the Br-poor region behaves in a very different manner (Fig. 4d, grey dashed line) with the GSB centre-of-mass energy remaining constant at roughly 1.64 eV throughout the 500-ps window, consistent with carrier trapping. The GSB centre-of-mass, energy shift profile in Fig. 4c highlights this considerable disparity between the two regions. The continuous red shift of the peak in the Br-rich region indicates that charge carriers are funnelled to slightly lower-energy (roughly 20 meV) domains, consistent with the lower-energy emission behaviour observed in the steady-state hyperspectral PL measurements (Fig. 2d). Moreover, larger local energy shifts are linked to sample areas with higher PL intensity (Supplementary Fig. 18). The local transient absorption signal from the Br-poor region shows a higher energy peak at roughly 1.65 eV that drops in intensity and a low-energy shoulder at roughly 1.56 eV that remains constant with time (Fig. 4d). This suggests that in the Br-rich regions there are local inclusions of lower bandgap material onto which the carriers transfer, whereas this energetic transfer is not observed in the I-rich regions.

Nanoscale energetic landscape of alloyed halide perovskites. Taking all of the microscopic observations together, we explain a global picture of the nanoscale landscape and how it endows enhanced defect tolerance on the seemingly highly disordered perovskite material. Mixed-composition perovskites exhibit a spatially heterogeneous landscape of chemical composition, structural variation in the form of strain and trap state density imprinted onto the sample on film formation (Fig. 4f) that dictates where charges accumulate and recombine. Large, micrometre-size bulk regions slightly rich in bromide also contain low bandgap inclinations (below detection limits for the compositional maps) that are of very high optoelectronic quality. Photons absorbed in these areas excite charge carriers in the Br-rich bulk that readily funnel down a shallow energy gradient to these lower-energy, more ordered inclinations. This provides a complete nanoscale visualization and hence a mechanistic understanding of the macroscopic observations of photodoping$^{27}$ in which holes locally accumulate at lower bandgap regions. Such hole accumulation leads to high carrier densities and extremely efficient radiative recombination (Fig. 1f). These regions are composed of multiple morphological grains and are up to the order of micrometres (Figs. 3 and 4a) in size, leading to an effective, large capture cross-section for harvesting charges in the funnel. By contrast, the deep trap clusters with low electronic quality that trap holes are tens to hundreds of nanometres in size and uniquely associated with Br-poor regions (Supplementary Fig. 15). Therefore, the larger capture radius of the shallow energy funnel setup by the compositional disorder effectively outcompetes the smaller capture cross-section of carrier traps associated with electronic disorder, leading to high luminescence yields and device performance (Fig. 4f). By contrast, single-halide, iodide-only analogues exhibit a more homogeneous halide distribution while maintaining a similar strain distribution (Supplementary Fig. 19) and have an order of magnitude lower luminescence yield as they do not exhibit such carrier funnelling (Supplementary Fig. 6). This strengthens our arguments that the high Br areas and the resulting nanoscale chemical variations are the cause of high performance.

Conclusions
Our study has notable implications for the fundamental understanding of defect tolerance in these materials and the design of halide perovskite solar cells. Using a suite of multimodal microscopy techniques, we unveil the complex energetic landscape that charge carriers must navigate in halide perovskites. We provide a nanoscale picture of how this energetic landscape influences photodoping, carrier recombination and trapping. We find that the pursuit of homogeneous chemical compositions is not necessarily the best way to maximize the performance of this family of semiconductors, at least while the material still possesses deep trap clusters that lower device performance from the radiative limits. The existence of mixed Br and I samples induces the formation of beneficial local heterostructures that confer enhanced defect tolerance to these materials. In these regions, charge-carrier photogeneration and radiative recombination occurs through a rapid wide-to-narrow bandgap funnelling process, more efficient than in the chemically homogeneous counterparts. The chemical disorder in these regions allows the effective capture of diffusing carriers over micrometre-length scales to lead to radiative recombination, outcompeting the capture of carriers in more electronically disordered and trap-rich regions, thus resulting in strong luminescence and performance. Furthermore, nanoscale strain variations even of order 0.5% do not strongly affect initial performance, providing further confirmation of the purported defect tolerance and the dominance of the chemical properties. The beneficial chemical disorder in these perovskite compositions is key to their impressive device performance, where the small penalty to pay in QFLS (voltagel) of roughly 10–20 meV due to accumulation of carriers in slightly lower bandgap performance hot spots (with low energetic disorder) outweighs the potentially larger loss if carriers find regions of high energetic disorder such as deep trap clusters. This process is in part analogous to energy funnelling in mixed thickness, quasi-2D perovskites used for high efficiency LEDs$^{45,56}$. We note that there are also spatially heterogeneous distributions of the A site cations...
in these materials\cite{1,2,3}, but given the strong spatial correlations we show between high Br:Pb regions and optoelectronic behaviour, we expect the effects of cation disorder on the funnelling of carriers to be comparatively minor. Nevertheless, such heterogeneity may eventually become detrimental in solar cells as we approach the radiative limit in which deep trap states are at negligible levels where defect tolerance is no longer necessary. Furthermore, although we expect the effects of cation disorder on the funnelling of carriers to be needed to maintain such favourable energetic landscapes. This multimodal methodology represents a large step forwards in the understanding of the fundamental processes and nanoscale landscape governing these intriguing defect-tolerant materials and is widely applicable to the study of other emerging semiconductors at the nanoscale.

**Online content**

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41565-021-01019-7.

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**Fig. 4 | TAM of FA$_{0.79}$MA$_{0.16}$Cs$_{0.05}$Pb(I$_{0.83}$Br$_{0.17}$)$_3$ perovskite films correlated with local chemical mapping.**

- **a.** Line scan of the Br:Pb nXRF intensity ratio (black dots) and normalized PL intensity (red squares) of the region used for correlation. The Br-rich and Br-poor regions are denoted with blue and grey rectangles, respectively. **b.** TAM line scan showing the centre-of-mass value of the GSB as a function of time after excitation. The Br-rich and Br-poor regions are denoted with blue and grey rectangles, respectively. **c,d.** The GSB transient absorption spectra of the Br-rich (c) and Br-poor regions (d) at different delay times. **e.** The relative GSB energy centre-of-mass shift profile of the absorption spectra of the Br-rich (c) and Br-poor regions are denoted with blue and grey rectangles, respectively. **f.** Schematic of the model proposed in this work showing carriers funnelling to highly emissive low bandgap regions in Br-rich regions, outcompeting carrier trapping in Br-poor regions.

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Methods

Film and device fabrication. ITO substrates (12 x 12 mm², Kintec) and glass cover slips were cleaned with the following steps: deionized water with 1.5% v/v solution of Decon 90 detergent, deionized water, acetone and finally isopropanol for 15 seconds per step in an ultrasonic bath. ITO and glass substrates were further treated by ultraviolet (UV) ozone for 15 min and transferred to the glovebox immediately. SiN X-ray transparent grids (Noraca, product number NX7100C) were treated in an oxygen plasma cleaner for 5 min before immediately transferring to the glovebox. PTAA (2 mg ml⁻¹, Sigma) in anhydrous chlorobenzene (Sigma) was prepared and dropped on the middle of the substrate and then spin coated at 5,100 rpm (1,000 s⁻¹ ramp) for 30 s. PTAA films were annealed at 100°C for 10 min. To improve the surface wetting and passivate the PTAA layer, a PFN-Br layer (0.3 mg ml⁻¹, dissolved in anhydrous methanol) was spun on the top of the PTAA at 5,100 rpm (2,500 s⁻¹ ramp) for 30 s and annealed at 100°C for 10 min. For perovskite solution preparation, a composition of (Cs⁰.⁰⁵FA⁰.⁷⁹MA⁰.¹⁶)₂PbI₄, (FA)₂PbBr₄ and a delay time of 100 ms. The active area of solar cell was 4.5 mm², defined by the overlapping area between Ag and ITO. All the devices were measured in air without encapsulation.

Solar cell device characterization. Current–voltage (I–V) curve measurements were performed using a xenon lamp (Abet Sun 2000 Solar Simulators, AAB class) at 1 sun intensity illumination (100 mW cm⁻², AM 1.5G), calibrated with a reference silicon diode (no window filter). The spectrum mismatch factor was calculated and applied onto the solar simulator power. We recorded the device performance with a Keithley 2636A, source meter, controlled by a home-built LabVIEW program. We started the I–V measurements from 1.2 to 0.1 V (forward scan) with a step size of 20 mV and a delay time of 100 ms. The active area of solar cell was 4.5 mm², defined by the overlapping area between Ag and ITO. The Ag metal layer was thermally evaporated on the samples to achieve the desired thickness. At each step, the SiN substrates were transferred onto the hotplate on a glass slide to avoid thermal shock of the thin window.

Hyperspectral microscope characterization. Wide-field, hyperspectral microscopy measurements were carried out using a Photon etc. IMA system. For all measurements, ×100 air and oil, chromatic aberration corrected objective lenses from Olympus (MPLFN and MPLAPON) were used. All samples were stored in a nitrogen filled glovebox until immediately before measurement to mitigate oxygen and humidity related transient behaviour. A 405-nm continuous wave laser was used as excitation for luminescence excitation. Then 50-W halogen lamps were used for transmission and reflection measurements. The excitation laser was filtered by a dichroic mirror. The lamp light used for reflection measurements travels through the objective to the sample. The lamp used for transmission measurements was focused on the sample by a condenser lens from below the sample and is collected by the objective lens. The emitted/transmitted/reflected light from the sample was incident on the volume Bragg grating, which splits the light spectrally onto a CCD camera. The detector was a 1.040 x 1.392 resolution silicon CCD camera kept at 0°C with a thermoelectric cooler and has an operational wavelength range of 400–1,000 nm. By scanning the angle of the grating relative to the incident light, the spectrum of light coming from each point on the sample could be obtained. For excitation of the system to extract the absolute number of photons per point at each point, a two-step process was used for each objective lens used. First, a calibrated white light lamp from Ocean Optics was coupled into an integrating sphere. The objective lens was also coupled into the integrating sphere. Comparing the measured spectrum of the lamp at each point to the calibrated spectrum gives the relative sensitivity of the system both spectrally and spatially. Second, a 657-nm laser was coupled directly to the microscope by an optical fibre. The power of the laser was measured precisely at the output of the fibre using a power meter before coupling to the objective lens. Measuring the laser on the system allows direct conversion between number of counts and photons at this wavelength. Combining this absolute calibration with the relative calibration from the calibrated white light lamp and integrating sphere allows absolute calibration across the spectrum at each point of the sample.

To determine local absolute reflectance, the macroscopic reflectance spectrum of a calibration mirror was measured. Before each hyperspectral measurement of a given perovskite sample, a hyperspectral measurement of the calibration mirror was also measured. A spatial median filter was applied to these data to reduce influence from local imperfections in the mirror. The reflected spectrum from the mirror at each point was divided by the macroscopic reflectance spectrum to obtain the calculated incident lamp spectrum. Once a sample had been measured in reflection, data were divided by this lamp spectrum obtain the absolute reflectance of the sample. An equivalent process was also performed for transmittance using a reference glass cover slip. This is summarized in the following equation, where R(E,x,y) is the reflectance from the sample at position (x,y) and energy E, \( I_{\text{sample}}(E,x,y) \) is the intensity of light reflected from the surface of the sample at point (x,y) and \( I_{\text{mirror}}(E) \) is the same for the reference mirror and \( \rho_{\text{sample}}(E) \) is the measured reflectance of the mirror at an energy E:

\[
R(E,x,y) = \frac{I_{\text{sample}}(E,x,y)}{\rho_{\text{mirror}}(E)} \times \frac{I_{\text{mirror}}(E)}{I_{\text{sample}}(E,x,y)}
\]

Suns intensity calculation. To calculate the equivalent number of suns for a given monochromatic excitation of a given power, we used an interpolated AM 1.5G spectrum and converted from units of spectral irradiance (W m⁻²×nm⁻¹) to photons m⁻²×nm⁻¹×s⁻¹ by dividing the photon energy at each point of the spectrum. Then the spectrum was integrated over wavelength from 300 nm to the bandgap energy of the material (in this case roughly 765 nm) to obtain the total flux of above bandgap photons, photons m⁻²×s⁻¹. This flux was compared to the photon flux incident on the sample from the monochromatic excitation to obtain the equivalent number of suns.

QFELS extraction. QFELS can be extracted from absolute PL intensity on the basis of the generalized Planck law. The intensity of PL, Iₚₑₐₑ, can be thought of as the product of the photon density of states (\( g(E) \)), the Bose–Einstein occupation function (\( f_{\text{BE}}(E) \)) and the absorbance spectrum of the material (\( a(E) \))

\[
I_{\text{PL}}(E) = \rho(E) \times f_{\text{BE}}(E) \times \alpha(E)
\]

where \( E \) is energy, \( \beta \) is Planck's constant, \( c \) is the speed of light, \( k_b \) is Boltzmann's constant and \( \Delta \rho \) is the QFELS. The most common approach for QFELS extraction in the literature is first to approximate the Bose–Einstein occupation function as a Boltzmann distribution, one then takes the logarithm of both sides, and assuming the absorbance spectrum is approximately constant at the high energy side of the PL spectrum, the QFELS spectrum can be extracted with a linear fit.\(^{13,28}\)

\[
\ln(\frac{I_{\text{PL}}(E)}{E^2}) = \ln(\frac{2\pi e^2}{\hbar^2 c^2}) - \frac{E}{k_b T} \times \frac{\Delta \epsilon}{\epsilon}
\]

\( I_{\text{PL}}(E) \) is the measured PL spectrum of the sample, \( E \) is the photon energy, \( \Delta \epsilon \) is the bandgap (eV), \( T \) is the temperature, \( a \) is the absorbance, \( k_b \) is Boltzmann's constant and \( \epsilon \) is the refractive index.

An alternative approach where a model for the absorbance is also included and the entire PL peak can be fit was described by Katahara and Hillhouse.\(^{13,28}\) The model for the absorbance coefficient is a convolution of the above bandgap density of states, which varies with energy for a conventional three-dimensional semiconductor as:

\[
a(E) = a_0 \sqrt{E - E_g}
\]

where \( a_0 \) is a parameter that depends on the oscillator strength of the material and \( E_g \) is the bandgap, and a below bandgap density of states:

\[
a \propto \exp \left( \frac{E - E_g}{\gamma} \right)
\]

where \( \gamma \) is the characteristic energy broadening of the low-energy tail and \( \theta \) determines the form of the exponential tail. When \( \theta = 1 \), \( \gamma \) is the Urbach energy. For values of \( \theta \) greater than 1, this can be intepreted as longer-range disorder in the material.\(^{56}\) The combination of the two can be approximated as:

\[
a = a_0 \sqrt{\theta G \left( \frac{E - E_g}{\gamma}, \theta \right)}
\]

where \( G(\mathbf{x}, \theta) \) is a function where the convolution integral has been explicitly evaluated and lookup tables provided by Braly et al.\(^{55}\). Assuming that the absorption coefficient is occupation independent at low excitation densities, one can then write the overall intensity of PL as:

\[
I_{\text{PL}}(E) = \rho(E) \times f_{\text{BE}}(E) \times a(E)
\]
\[ I_{\text{PL}} (E) = \frac{2\hbar^2 E^2}{h^2} \times \left( 1 - \exp \left( -\alpha_k \frac{\pi}{\hbar} G \left( \frac{E - E_g}{T} \right) \right) \right) \times \exp \left( -\frac{E - \Delta \mu}{k_b T} \right) \]

d where \( d \) is the thickness of the film. The model has been successfully used on perovskites amongst other systems\(^1\). The \( \alpha \) product was set to be ten as is common for perovskite materials and has little impact on the fitted values of other parameters\(^2\). The temperature was set to the temperature of the room, generally 300 K. The remaining parameters to be fit are \( E_g \), \( \theta \), and \( \Delta \mu \). The data were fitted using the Levenberg–Marquardt, non-linear least squares fitting algorithm implemented in Python (Supplementary Fig. 1). To set initial guess parameters, the average PL spectra of the region of interest was fit and the output manually inspected before automatic fitting of the individual pixels was performed.

**Urbach energy extraction.** The Urbach energy was extracted from the red, low-energy portion of the PL spectrum. To be directly comparable to other works, the standard Urbach energy was reported rather than the more complicated coupled energy broadening and exponential powers mentioned above. The generalized Planck law was rearranged for absorptance:

\[ a (E) = I_{\text{PL}} (E) \times \frac{\hbar^2 \omega^2}{2 \pi^2} \times \exp \left( -\frac{E - \Delta \mu}{k_b T} \right) \]

The absorptance is related to the absorption coefficient as mentioned previously as:

\[ a (E) = 1 - \exp (-\alpha d) \]

For small values of \( \alpha d \) below the bandgap, one can perform a Maclaurin expansion of the exponential, which is to first order:

\[ a (E) \approx 1 - (1 - \alpha d) \]

The absorptance therefore follows the same functional form as the absorption coefficient for small arguments. We write the absorption coefficient in the Urbach tail as:

\[ a = a_0 \exp \left( \frac{E_g - E}{E_0} \right) \]

Therefore, if we take the log of both sides:

\[ \ln (a) = \ln \left( I_{\text{PL}} (E) \times \frac{\hbar^2 \omega^2}{2 \pi^2} \times \exp \left( -\frac{E - \Delta \mu}{k_b T} \right) \right) \]

Finding the inverse slope of this function using a Huber loss function, linear regression to eliminate effects of noisy outliers of data when mass fitting entire maps at the red edge of the PL gives the Urbach energy as shown in Supplementary Fig. 2.

**Local PLQF extraction.** To extract the local PLQF, the first flux of absorbed photons from the excitation laser must be determined. First, the power of the 405-nm laser at the objective of the microscope was measured using a power meter. The spot size of the laser was then measured to determine incident laser power. The 405-nm laser at the objective lens of the microscope was measured using a power meter. The spot size of the laser was then measured to determine incident laser power.

**Bulk XRD measurements.** Bulk XRD measurements were performed with a Bruker D8 ADVANCE system with a Copper focus X-ray tube (\( K_\alpha \): 1.54 Å, 40 kV). The scan range of 2θ was from 3° to 40° with a step size of 0.01° and a delay time of 0.15 s, corresponding to a \( q \) range of roughly 0.2–2.8 Å\(^{-1}\). The sample was measured in air.

**Synchrontron nXRD and nXRF.** Measurements were performed on the i4 Hard X-ray Nanoprobe beamline at Diamond Light Source Ltd, Didcot, UK. Samples were stored in nitrogen before measurements. The full experimental setup has been described elsewhere\(^3\). Briefly, X-rays from an undulator source are monochromatized to produce a 19 keV, monochromatic X-ray beam. The beam travels along a 186-m long channel, along the path, the X-rays are focused with Kirkpatrick Baez mirrors to produce a beam with full-width at half-maximum of roughly 50 nm at the focus. A sample is placed on a scanning stage and is raster scanned across this focal point. The energy resolved nXRF signal is collected with a four-element silicon drift detector in a back-scattering geometry. The diffracted X-rays are collected in transmission with an Encalibur 3 M detector consisting of three Medipix 2,048 × 512 pixel arrays\(^4\) at a sample–detector distance of 20.2 cm. For measurements involving nXRD/nXRF correlations, samples were deposited on X-Ray transparent, SiN windows from Norcarada (product number NTX7106C). The step size for the measurements was 50 nm and the dwell time was 0.75 s per point. All samples were stored in a nitrogen filled glovebox before measurement, and held under a nitrogen flow during measurements. Multidimensional nXRD and nXRF datasets were handled and analysed using the open-source Python package Hyperspy\(^5\). We note that we cannot rule out some damage to the perovskite following measurements owing to the highly focused X-ray nanoprobe. However, given that the acquired nXRD patterns (acquired simultaneously to the nXRF) index to the expected cubic FAPbI\(_3\) model (without any impurity phases) and previous work has shown that the nXRF signal is more beam stable than the nXRD\(^6\), we assert that our measured maps and conclusions are not influenced by beam damage. Furthermore, the strong agreement between our diffraction/chemical-based conclusions from scanning probe measurements with metrics obtained from optical measurements further support our conclusions.

**Chemistry normalized strain extraction.** The simultaneous measurement of nXRD and nXRF on the same sample allows us to remove the contribution of local chemistry and just focus on variations in the lattice parameter due to strain. We assume a Vegard’s law holds for the FA\(_x\)MA\(_{1-x}\)Cs\(_y\)PbI\(_{1−2y}\)Br\(_y\) family over the range we look at in these samples. The lattice parameter of the pure iodide FA\(_x\)MA\(_{1−x}\)Cs\(_y\)PbI\(_{1−2y}\)Br\(_y\) is roughly 6.36 Å and the nominal composition of the sample here, FA\(_x\)MA\(_{1−x}\)Cs\(_y\)PbI\(_{1−2y}\)Br\(_y\), has a lattice parameter of 6.30 Å. We look at the Br:Pb ratio, and to explore the variations we assume the same that the composition in our solution is the same as that in the film and thus set the mean value of the Br:Pb ratio to correspond to this 17% Br composition. We note that although the stoichiometry of the film may differ from that of the solution\(^7\), the deviation in these films appears to be small (Supplementary Fig. 10) and any error in the assumed stoichiometry and thus this mean point will only change the position of the otherwise arbitrary 0% strain point, but will not affect the distribution of strain in the sample, which is the key parameter under analysis here. Variations about this mean value are converted to lattice parameters (\( A_{\text{XRD}} \)) by inserting the extracted composition into Vegard’s law as mentioned above. Simultaneously, the assumed cubic lattice parameter is extracted at each point from the various nXRD peaks using:

\[ \frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{A_{\text{XRD}}^2} \]

where \( d \) is the plane spacing extracting from the \( q \) value of the peak; \( h \), \( k \), and \( l \) are the Miller indices of the plane and \( A_{\text{XRF}} \) is the cubic lattice parameter extracted from XRD. Percentage strain is then calculated as:

\[ \text{Strain (\%)} = \left( \frac{A_{\text{XRD}}}{A_{\text{XRF}}} - 1 \right) \times 100 \]

Strain due to CTE mismatch between the substrate and the perovskite thin film after annealing can be calculated using the equation:

\[ \epsilon_{\text{CTE}} = \frac{1}{1 - v_p} (\alpha_{\text{sub}} - \alpha_{\text{film}}) \Delta T \]

where \( \epsilon_{\text{CTE}} \) is the strain on cooling, \( v_p \) is the Poisson ratio, assumed to roughly 0.3 for most materials and \( \alpha_{\text{sub}} \) and \( \alpha_{\text{film}} \) are the CTEs of the substrate and film, respectively. SiN\(_x\) has a CTE of roughly \( 3.3 \times 10^{-5} \cdot \text{K}^{-1} \), whereas formamidinium and methylammonium containing either I or Br have CTEs in the range of \( 30 \times 10^{-5} \cdot \text{K}^{-1} \). In this work, we anneal the perovskite at 100 °C for 1 hour before exposing to room temperature of 20–25 °C, in the calculation we assume a \( T \) of 80 °K. Thus we calculate that the expected strain at the interface between SiN\(_x\) and the perovskite is tensile in nature and in the range of 0.35–1%, similar to the maximum values we extract however, there may be multiple contributions to the observed strain beyond CTE mismatch.

Small variations in the mean value of strain extracted for different families of planes could be caused by small variations in the CTE between different crystallographic directions. Additionally, given the nature of the nXRD experiment only showing in general only one diffraction spot per pixel, the peak maps are spatially orthogonal and do not overlap. Given there is nanoscale compositional and structural heterogeneity, minor variations in the mean strain are to be expected.

**Image registration for correlations.** A suspension of pseudo-planar Au nanoparticles with distinctive shapes (hexagons and triangles) were used as fiducial markers as per our previous works\(^8\). The gold nanoparticles were dispersed in
chlorobenzene (Sigma) and spun onto the perovskite film. For image alignment, optical and nXRF images of the same region were overlaid in the open-source image editing software GIMP. The optical images were transformed using the unified transform tool in GIMP, which includes all of the operations associated with an affine transformation (translation, scaling, shearing and rotation) along with a perspective transform to account for distortions in the detectors as well as any relative sample tilt between the measurements. The transform was applied until the Au fiducial markers were overlaid and simultaneously features from the Pb nXRF signal matched those from the reflectance images.

**Statistical analysis.** Differences in the populations of lower and higher Br/Pb regions were calculated using a two-sample Kolmogorov–Smirnov test implemented in the Scipy Python library<sup>54</sup> using the ks_2amp functionality. Output P values < 0.0001 were interpreted as the null hypothesis of the two samples being part of the same population being rejected and a statistically significant difference between them.

Correlations between data were tested using the Spearman’s ρ value, which tests whether the relationship between two datasets can be described with a monotonic function. This was also implemented in the Scipy Python library using the spearmanr function. P < 0.0001 were interpreted as a statistically significant relationship between the two variables.

**TAM.** A Yb:KGW laser system (Pharo, Light Conversion) provided the fundamental output beam of 200 fs, 30-p pulses at 1.030 nm with a 200-kHz repetition rate. The output beam was divided into two broadband white light continuum (WLC) stages. The WLC for the probe beam was generated in a 3-mm yttrium aluminium garnet crystal, covering the wavelength range from 650 to 950 nm selected using a 10-piece silica prism-based spectral filter. In contrast, the WLC for pump beam was generated in a 3-mm sapphire crystal to extend the WLC to 500 nm, and short-pass filtered at 650 nm (FESH650, Thorlabs). A set of chirped mirrors (pump, 109911, Layertec; probe, DCM9, Ventcon) and a pair of fused-silica wedges (Layertec) were used to compress the pulses to 9.2 fs (pump) and 8.6 fs (probe). The time resolution was then verified by second-harmonic generation frequency-resolved optical gating. A closed-loop piezo translation stage (M-ILS100HA, Newport) was used to delay the probe with respect to the pump. Both pump and probe beams were loosely focused onto the sample with a focal spot size of 30 μm by a dispersion-free concave mirror. This allowed even illumination over the region of interest. The transmitted probe pulse was then collected by an oil immersion objective (×100, an effective numerical aperture, NA, of 1.1) and sent to an electron-multiplying CCD camera (Roper Thunder, QImaging). The total magnification of the imaging system was ×288. The scattered pump light was rejected by a 650-nm long-pass filter (FE650L, Thorlabs) inserted in front of the camera. Differential imaging was achieved by modulating the pump beam at 30 Hz by a mechanical chopper. In the current experimental scheme, we adopted a slit–prism combination and used the configuration to achieve simultaneous spatial, temporal and spectral imaging. First, the dimension of the collimated probe beam was reduced by inserting a slit in an image plane. The transmitted one-dimensional probe beam is then dispersed by a prism, enabling us to simultaneously obtain 2D spatial and spectral map as a function of time<sup>56</sup>.

**PEEM.** The fundamental output of a 4-MHz, 650-nm Ti:sapphire oscillator (FemtoLasers XL650), delivering 45 fs pulses at 800 nm, was used to generate UV pulses for PEEM measurements. The 4.65-eV UV pulses are generated as the third harmonic of the 1.55-eV (800 nm) radiation by sum frequency generation of the fundamental and the 3.10-eV (400 nm) second harmonic. The UV beam is focused into the ultra-high-vacuum chamber of the PEEM instrument (SPELEEM, Elmitec GmbH), where it is incident on the sample at a grazing angle of approximately 17°. The probe spot size was approximately 250 μm full-width at half-maximum. The UV pulses were set to p polarization. Typical UV pulse fluences used were approximately <100 nJ cm<sup>−2</sup>.

**Data availability.** The data and code that support the findings of this study are available in the University of Cambridge Apollo repository at https://doi.org/10.17863/CAM.76854.

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**Author contributions.** K.F. and M.A. conceived the project. K.F. and M.A. developed the quantitative optical microscopy and performed the measurements, which were analysed by K.F. K.F., M.A., S.M., T.A.S.D., K.W.P.O., J.P. and P.D.O. performed the synchrotron nXRF and nXRD experiments that were analysed by K.F. and T.A.S.D. S.M. and J.S. performed the TAM measurements and analysed the data supervised by A.R. K.F., M.A. and S.M. performed the correlational analysis of the multimodal data. Y.-H.C. fabricated the thin film and device perovskite samples and performed bulk XRD experiments. A.J.W. performed the PEEM measurements supervised by K.M.D. S.D.S. supervised and funded the work. K.F. and M.A. wrote the draft of the manuscript with the input of S.D.S. All authors contributed to the revision of the final paper.

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**Additional information.**

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