Large guanidinium cation mixed with methylammonium in lead iodide perovskites for 19% efficient solar cells

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Organic–inorganic lead halide perovskites have shown photovoltaic performances above 20% in a range of solar cell architectures while offering simple and low-cost processability. Despite the multiple ionic compositions that have been reported so far, the presence of organic constituents is an essential element in all of the high-efficiency formulations, with the methylammonium and formamidinium cations being the sole efficient options available to date. In this study, we demonstrate improved material stability after the incorporation of a large organic cation, guanidinium, into the MAPbI3 crystal structure, which delivers average power conversion efficiencies over 19%, and stabilized performance for 1,000 h under continuous light illumination, a fundamental step within the perovskite field.

Hybrid perovskites have recently emerged as outstanding materials for efficient and low-cost solar technology. Unique properties, including high absorption coefficient1, large charge-carrier diffusion length2, small exciton binding energy3 and high photovoltaic performance. With this approach, solar cells display an average photoconversion efficiency (PCE) of 19.2 ± 0.4% at enhanced stability.

Here we introduce a perovskite based on the organic cation guanidinium (CH3N3+, Gua) as a more stable and efficient alternative to the state-of-the-art MAPbI3. Gua features an ionic radius of ~278 pm (ref. 17), slightly above the upper limit of the tolerance factor (t ~1.03), forming low-dimensional perovskites (LDPs) when mixed with PbI2 (refs 19,20). In this work, we demonstrate that when combined with methylammonium in a mixed MA1−xGuaPbx composition (0 < x < 0.25) the Gua cation inserts in the crystal unit, forming a 3D perovskite with enhanced thermal and environmental stability. Our results widen the exploration of cations with a radius beyond the tolerance limit, while preserving a 3D structure and high photovoltaic performance. With this approach, solar cells display an average photoconversion efficiency (PCE) of 19.2 ± 0.4% at enhanced stability.

Structural characterization of MA1−xGuaPbx perovskites
To gain insight into the arrangement of the Gua cations in the MA1−xGuaPbx crystal structure, X-ray diffraction (XRD) measurements of the thin films were performed (see Methods for details). Figure 1a shows the diffraction patterns of the perovskite films containing MA/Gua mixtures, where 0 < x < 0.25 (x represents the Gua molar ratio), compared with MAPbI3. The incorporation of Gua cations yields a gradual decrease of the reflection peak intensity, but retaining the MAPbI3 tetragonal phase even for xGua = 0.25. Larger Gua percentages significantly decrease the diffraction signal, while the appearance of new diffraction peaks at 8.54° and 11.31° indicates the formation of a 1D GuaPbI3 phase, as previously reported11. Interestingly, a closer inspection of the reflection peaks reveals a notable shift to lower angles, as shown in the zoom of Fig. 1b.

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It is worth noting that these results are in contradiction to those of previous reports, where Gua has been proposed as a passivating agent that does not incorporate into the perovskite structure due to its larger size\(^{11}\). Nevertheless, significant variations in the preparation method could account for the different crystallization dynamics. Here, we incorporate Gua within the precursor solution, ensuring the desired stoichiometry during crystallization.

The relative composition and chemical environment of the constituents in the perovskite materials have been analysed by X-ray photoelectron spectroscopy (XPS). Measurements performed for the pure MA and Gua phases and four representative mixtures \(x = 0, 12.5, 25, 30, 50, 100\) (for clarity, traces are shifted vertically). The relative composition and chemical environment of the constituents in the perovskite materials have been analysed by X-ray photoelectron spectroscopy (XPS). Measurements performed for the pure MA and Gua phases and four representative mixtures \(x = 0, 12.5, 25, 30, 50, 100\) (for clarity, traces are shifted vertically). The results demonstrate an increased number of micro-strains and distortions of the MAPbI\(_3\) lattice at larger percentages of Gua, supporting its inclusion in the crystal. However, further increments do not incorporate into the crystalline network and lead to a phase-separated 1D GuaPbI\(_3\), as suggested by the XRD. It is worth noting that these results are in contradiction to those of previous reports, where Gua has been proposed as a passivating agent that does not incorporate into the perovskite structure due to its larger size\(^{11}\). Nevertheless, significant variations in the preparation method could account for the different crystallization dynamics. Here, we incorporate Gua within the precursor solution, ensuring the desired stoichiometry during crystallization.

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![Fig. 1](image-url) | XRD and XPS characterization of Gua-based perovskites. a. Normalized XRD data for the mixed MA/Gua perovskite films containing different percentages of Gua. b. Magnification of the XRD peaks at (220) (left) and (440) (right) on variation of the Gua content (indicated in per cent). c. Lattice parameter variation (\(a\) and \(c\)) of the MA\(_{x}\)-Gua\(_{1-x}\)PbI\(_3\) unit cell obtained from the crystallographic analysis of the experimental XRD patterns. d. XPS spectra of N 1s for thin films of typical MA\(_{x}\)-Gua\(_{1-x}\)PbI\(_3\) perovskite mixtures \((x = 0, 12.5, 25, 30, 50, 100)\) (for clarity, traces are shifted vertically). e. Quantification of the percentage of Gua obtained from the XPS analysis (Gua\(_R\) corresponds to the measured values; Gua\(_T\) corresponds to theoretical values, initially incorporated into the precursor solution). f. Optimized simulated structure of the unit cell of MA\(_{0.75}\)Gua\(_{0.25}\)PbI\(_3\) including the six H-bond distances with respect to I atoms.
correlation functional were conducted. An estimation of the formation enthalpies at zero temperature, \( \Delta H_p \), for the pure MA and Gua phases, as well as for that containing \( x_{\text{Gua}} = 0.25 \) was performed (Supplementary Note 1). A remarkable difference for the three perovskite structures was found, with a clear tendency when increasing the Gua content: \( \Delta H_{\text{MA, pure}} = -0.149 \text{eV} > \Delta H_{\text{MAPbI}_3} > \Delta H_{\text{MA0.75Gua0.25PbI}_3} = -1.484 \text{eV} \). Compared with the pure MAPbI\(_3\) phase, which exhibits a value close to zero, consistent with previous reports, the 1D GuaPbI\(_3\) points to enhanced stability, as expected for LDP\(^{27}\). However, a striking result appears for the mixed MA\(_{0.75}\)Gua\(_{0.25}\)PbI\(_3\) perovskite, which also exhibits a highly negative formation enthalpy: \( \Delta H_{\text{MA0.75Gua0.25PbI}_3} \approx -2.045 \text{eV} \). This can be related to the different organic–inorganic interactions mediated by the larger cation could be compensated at the expense of the neighbouring cavities where the small MA cation localizes, preserving its 3D structure.

**Optical and electronic properties**

The effect of the lattice expansion on the optoelectronic properties was also analysed by DFT–GGA calculations. The electronic band structures and density of states for MAPbI\(_3\) and two representative mixtures (12.5% and 25% of Gua content) show no appreciable difference, with I 5p states mainly contributing to the top valence band and Pb 6p states dominating the lowest conduction band (Supplementary Fig. 3). Nevertheless, there is a small but gradual increase in the bandgap energy with the insertion of Gua, showing values equal to 1.77 eV, 1.79 eV and 1.82 eV for MAPbI\(_3\), 12.5% and 25% of Gua, respectively. The direct character of the MAPbI\(_3\) bandgap is also conserved in the two mixtures, with the minimum bandgap occurring at the \( \Gamma \) symmetry point. Moreover, the three samples display a similar dispersion of the valence and conduction bands, which ensures low carrier effective masses.

Consequently, the incorporation of Gua preserves the optical properties of the material. Figure 2a shows the normalized absorption spectra for four typical MA\(_{1-x}\)Gua\(_x\)PbI\(_3\) thin films with \( x_{\text{Gua}} \leq 0.5 \). In agreement with the theoretical calculations, no significant changes in the shape of the spectrum are observed for mixtures containing \( x_{\text{Gua}} < 0.5 \). However, an appreciable lowering of the absorption capacity along with a blueshift of the band edge (~0.02 eV), indicative of a widening of the bandgap. This can be related to the different organic–inorganic interactions mediated by the new hydrogen bonds, which lead to

![Graph](image-url)
local distortions at the Gua neighbouring positions, and expand the crystal unit. Results for higher Gua percentages are also reported in Supplementary Fig. 4a. A sharp band edge at ~500 nm, with a remarkable excitonic peak at 390 nm appears for pure 1D GuaPbI3 (ref. 7). This is also detected for $x_{\text{Gua}} > 0.5$, which, together with the absorption band edge of $\text{MA}_{1-x} \text{Gua}_x \text{PbI}_3$ at ~775 nm, confirms the preservation of both individual phases. Accordingly, the photoluminescence (PL) spectra shown in Fig. 2b (Supplementary Fig. 4b–d) manifest a gradual shift towards higher energy for samples with $x_{\text{Gua}} < 0.2$ (see inset to Fig. 2b), which becomes more apparent for $x_{\text{Gua}} = 0.25$, and is preserved for larger Gua amounts, consistent with the results observed in Fig. 2a. These findings provide compelling evidence that the substitution of Gua for MA efficiently stabilizes a 3D perovskite phase while retaining extended and efficient absorption similar to MAPbI3.

In addition, the electronic structure was also investigated by ultraviolet photoelectron spectroscopy (UPS). The results reveal a slight gradual shift of the valence band onset (by 0.04–0.09 eV) towards the Fermi level from MAPbI3 to $\text{MA}_{1-x} \text{Gua}_x \text{PbI}_3$, samples containing up to 25% Gua, while retaining the main valence band features of MAPbI3, as depicted in Fig. 2c. Concomitantly, the ionization energy becomes slightly reduced (by up to 0.14 eV). However, larger amounts of Gua (> 25%) result in a shift of the valence band onset away from the Fermi level. A solid change in the valence band features, increasingly resembling those corresponding to pure GuaPbI3 (binding energy region between 5.5 eV and 8.7 eV), suggests the coexistence of GuaPbI3 at the surface above 25% Gua content, which is corroborated also by scanning electron microscopy (SEM; as discussed below). As GuaPbI3 contains an increased number of Pb 0-related surface states, which tend to pin the Fermi level close to the conduction band minimum29 (Supplementary Fig. 2a), the wider gap of GuaPbI3, as compared with MAPbI3, results in the shift of the valence band onset towards higher binding energy for $x_{\text{Gua}} > 0.3$.

Photovoltaic performance

To demonstrate the applicability of Gua-containing perovskites, we embodied the $\text{MA}_{1-x} \text{Gua}_x \text{PbI}_3$ (0 < $x$ < 0.25) into solar cells sandwiched in between the mesoporous (mp)-TiO2, used as the electron-transporting material, and 2,2′,7,7′-tetakis(N,N′-di-p-methoxyphenylamine)-9,9′-spirobifluorene (spiro-OMeTAD), as the hole-transporting material (Fig. 3a and Supplementary Fig. 5). The average photovoltaic parameters obtained from the cells are shown in Fig. 3b and listed in Table 1, which also includes the champion cells obtained for each condition (see also Supplementary Table 1). The short-circuit current density ($J_S$) hardly changes for Gua fractions up to 20%, but gradually lowers for increased Gua contents, with 14% of Gua outstanding among the others. This behaviour can be related to the decreased absorption detected for $x_{\text{Gua}} > 0.2$, as supported by the external quantum efficiency (EQE) spectra shown in Fig. 3c (photographs of the as-prepared $\text{MA}_{1-x} \text{Gua}_x \text{PbI}_3$ solar cells are provided in Supplementary Fig. 6). In addition, the average open-circuit voltage ($V_{oc}$) increases progressively with the Gua incorporation, from 1.04 ± 0.02 V for $x = 0$ to 1.085 ± 0.02 V for $x = 0.25$ (see Table 1), as expected from the optical bandgap observations. Notably, the fill factor (FF) remains almost unaltered, with high average values over 0.75 (and maxima close to 0.80). As a result, the PCE of the prepared cells increases from 17 ± 1% for MAPbI3, to 19.2 ± 0.4% for the Gua/MA mixed system containing 14% Gua, with a champion cell efficiency of 20.15%. Moreover, even for perovskites containing 25% Gua, the photovoltaic performance remains similar to that of the MAPbI3, with an average PCE of 17.1 ± 0.8% and a record efficiency of 18.30% (Supplementary Fig. 7). The current density versus voltage ($J$–$V$) curve and EQE obtained for the champion device are presented in Fig. 4a,b, respectively. The EQE demonstrates high photon-to-current conversion over 80% throughout the entire ultraviolet–visible spectrum, leading to an integrated current density of 22.09 mA cm$^{-2}$. $J$–$V$ hysteresis measurements are reported in Supplementary Fig. 8. We also analysed the charge dynamics by electro-chemical impedance spectroscopy (Supplementary Figs. 9 and 10), which suggest an increased recombination resistance and longer electron lifetime with Gua incorporation, possibly related to a more efficient charge extraction and better crystal formation.

Device stability and phase segregation analysis

The device stability has been tested under AM1.5 G Sun illumination at maximum power point (MPP) tracking, for more than 1,000 hours, at 60 °C and under an Ar atmosphere. The results (Fig. 4d) reveal an enhanced stability for higher Gua contents, providing evidence of the beneficial effect on the material stability, as predicted by the simulations. Despite the initial decrease, recently
associated with the inter-penetration of spiro-OMeTAD and gold electrode\textsuperscript{22}, a gradual stabilization and recuperation of the performance is observed, which is reproducible (Supplementary Fig. 11a) and clearly correlated with the Gua content. Alternatively, we have performed an initial light stress test at 85 °C using triarylamine polymer, a more stable hole-transporting material, under 300 h of illumination, which further confirms the enhanced stability compared with MAPbI\textsubscript{3}, for the mixed MA/Gua perovskite systems measured under AM1.5G Sun illumination. In brackets are indicated the averaged values for each condition (scan rate: 0.01 V s\textsuperscript{-1}; stabilization time: 5 s).

### Table 1 | Photovoltaic performance

| Gua (%) | J\textsubscript{SC} (mA cm\textsuperscript{-2}) | V\textsubscript{OC} (V) | FF | PCE (%) |
|---------|------------------|----------------|-----|--------|
| 0       | 22.50 (22.0 ± 0.8) | 1.050 (1.04 ± 0.02) | 0.80 (0.74 ± 0.04) | 18.88 (17 ± 1) |
| 5.00    | 22.49 (22 ± 1) | 1.070 (1.05 ± 0.01) | 0.782 (0.76 ± 0.02) | 18.81 (17 ± 1) |
| 10.0    | 22.53 (23 ± 0.3) | 1.090 (1.07 ± 0.02) | 0.777 (0.75 ± 0.03) | 19.09 (17 ± 0.9) |
| 14.0    | 23.19 (22.8 ± 0.3) | 1.082 (1.07 ± 0.01) | 0.803 (0.79 ± 0.01) | 20.15 (19.2 ± 0.4) |
| 17.0    | 22.54 (21.7 ± 0.5) | 1.091 (1.08 ± 0.02) | 0.785 (0.78 ± 0.02) | 19.29 (18.1 ± 0.7) |
| 20.0    | 21.31 (21.2 ± 0.5) | 1.095 (1.08 ± 0.01) | 0.790 (0.77 ± 0.03) | 18.43 (17.7 ± 0.8) |
| 25.0    | 20.85 (20.6 ± 0.7) | 1.107 (1.09 ± 0.02) | 0.790 (0.77 ± 0.02) | 18.30 (17.1 ± 0.8) |

Photovoltaic parameters obtained for the best performing cells containing MA/Gua perovskite with Gua contents up to 25%.

These results are confirmed by the micro-Raman and micro-PL analysis (Fig. 5e,f). Averaged over a diffraction-limited spot size of 300 nm, this technique can provide further information about local heterogeneities within the film\textsuperscript{24}. The emission of four different samples was investigated, with a particular focus on the distribution of the PL peak position. The latter is intimately linked to the material bandgap, which changes with composition\textsuperscript{1,25} and/or local disorder\textsuperscript{26} over microscopic areas of the samples. Fig. 5e shows the map of the PL peak position over 6 x 6 μm\textsuperscript{2} regions. In the wavelength emission range between 710 nm and 780 nm, no appreciable change in the PL peak is observed for x\textsubscript{Gua}  < 0.25, remaining around 770 nm, as for the pure MAPbI\textsubscript{3} (Supplementary Fig. 14). On the contrary, the addition of 75% Gua leads to the appearance of a contrasted PL map with regions extending up to a few micrometres, with a remarkable PL shift down to 710 nm. This behaviour indicates a phase segregation in the material, resulting in a distribution of different bandgaps across the film. On the same areas, micro-Raman spectra were recorded (Fig. 5f). For Gua contents up to 25%, the Raman spectra closely resemble that of the pure MAPbI\textsubscript{3}. Characteristic broad peaks in the region below 200 cm\textsuperscript{-1} are observed related to the Pb–I stretching and bending modes\textsuperscript{31,32}, along with a broad feature around 250 cm\textsuperscript{-1} related to the vibrations of the organic cation. Remarkably, as recently observed with FA incorporation to the MAPbI\textsubscript{3}, a gradual shift of the peak to lower wavenumber appears.
suggesting a shrinking of the mode due to the incorporation of the distinct Gua cation in the unit cell. For Gua content above 25%, we could identify a position-dependent signal that changes in line with the PL variation. Some regions show a similar spectrum as for the lower Gua content, while on the regions presenting the ‘rod-like’ morphology, a redistribution of the relative peak intensity happens with a dominant peak at 120 cm$^{-1}$ and an additional peak at 135 cm$^{-1}$, both with a reduced broadening of the signal. This peak shift is usually attributed to isolated Pb–I planes, similarly to the case of PbI$_2$ intercalated with large organic molecules$^{33}$, which suggest the formation of a LDP as for the pure GuaPbI$_3$ arranging into the 1D phase. As corroborated in the figure, GuaPbI$_3$ shows apparent peaks at 120 cm$^{-1}$ and 135 cm$^{-1}$ as previously asserted for the 75% sample. These results further confirm the phase homogeneity of the mixed MA$_{1-x}$Gua$_x$PbI$_3$ for Gua < 25%, which, on the contrary, reveals a severe phase segregation into a 3D/1D mixture for larger Gua amounts, while retaining the individual features of the single constituents. No visible degradation signs are observed during the PL measurements, as shown in Supplementary Fig. 14b.

Conclusions
We present a perovskite composition based on a combination of Gua/MA cations that exhibits superior photovoltaic performance and material stability compared with MAPbI$_3$. We demonstrate that the incorporation of large Gua cations unexpectedly forms a highly stable 3D crystalline structure, plausibly mediated by the increased number of H bonds within the inorganic framework. The prepared MA$_{1-x}$Gua$_x$PbI$_3$ perovskites preserved the good optoelectronic properties associated with the organic lead halide materials, leading to a high PCE surpassing 20% for a Gua content of 14%. Our results emphasize the versatility of organic–inorganic lead halide perovskites, and invite further exploration of organic cations including those that are beyond the limit of the tolerance factor.

Methods
Solar cell fabrication. Perovskite solar cells were fabricated on F-doped SnO$_2$ (NSG10) substrates previously cleaned by a sequential sonication treatment in a 2% Hellmanex solution, acetone and isopropanol, followed by ultraviolet–ozone treatment for 15 min. A compact blocking layer of TiO$_2$ (bil-TiO$_2$, 30 nm in thickness) was then deposited onto the fluorine-doped tin oxide (FTO) glass substrate by spray pyrolysis, using a titanium disopropoxide bis(acetylacetonate) solution in ethanol (60% v/v), and then sintered at 450 °C for 30 min. A 200-nm-thick layer of mesoporous TiO$_2$ (mp-TiO$_2$, 30 NR-D titania paste from Dyesol) was prepared by spin-coating a diluted TiO$_2$ dispersion in ethanol, ratio 1:8 by weight, at 2,000 r.p.m. for 15 s followed by a sintering step at 500 °C for 30 min. Afterwards, the substrates were lithium-treated by spin-coating 40 µl of tris (bis(trifluoromethyl)sulfonyl)imide) (Li-TFSI) (14.67 mg ml$^{-1}$ in acetonitrile) onto the mesoporous layer, followed by a sintering step at 500 °C for 30 min. Stoichiometric precursor solutions were prepared by mixing MAI, GuaI (Dyesol) and PbI$_2$ (TCI) in N,N′-dimethylsulfoxide (DMSO) with MAI/GuaI gradually changing from 1:0 to 1:0.1, while keeping the PbI$_2$ molarity equal to 1.25. The perovskite layers were then fabricated by using a two-step spin-coating process reported previously$^{34}$ (first step 1,000 r.p.m. for 10 s, second step 4,000 r.p.m. for 30 s) and 15 s before the end of the programme. 100 µl of chlorobenzene was poured onto the films, and then the substrates were annealed at 100 °C for 45 min. After this time, spiro-OMeTAD was spin-coated at 4,000 r.p.m., for 30 s from a chlorobenzene solution (28.9 mg in 400 µl, 60 mmol) containing Li-TFSI (7.0 µl from a 520 mg ml$^{-1}$ stock solution in chlorobenzene). After drying under N$_2$, the active layer was completed by coating a 500-nm thick layer of Ag, followed by sintering at 90 °C for 30 min. The photovoltaic characteristics were measured under 1 sun illumination (AM 1.5G, 100 mW cm$^{-2}$) using a Keithley 2400 source meter. All processed substrates were stored in a desiccator prior to the measurement.

Fig. 5 | Morphology and phase segregation analysis. a-d, Top-surface SEM images of four representative samples, including pure MAPbI$_3$ (a), mixed MA$_{1-x}$Gua$_x$PbI$_3$ with $x = 0.14$ (b), with $x = 0.30$ (c), and pure GuaPbI$_3$ (d). Scale bars, 1 µm. e,f, Micro-PL wavelength peak shift map (e) and micro-Raman spectra (f) of the perovskite surface obtained for Gua contents equal to 0, 15, 25 and 75%. The traces are shifted vertically for clarity.
acetonitrile), TBP (11.5 µl) and Co(II)TSI (10 mmol%, 8.8 µl from a 40 mmol¹⁻¹ stock solution) as dopants. Finally, a 70 nm gold electrode was evaporated.

**Thin-film characterization.** The XRD patterns of the prepared films were measured using a D8 Advance diffractometer from Bruker (Bragg–Brentano geometry, with an X-ray tube Cu Kα, λ = 1,5406 Å). The absorption spectra were registered with an ultraviolet–visible–infrared spectrophotometer (PerkinElmer Instrument). Photoluminescence (PL) steady-state measurements were recorded with a spectrophotometer (Gilden Photonics). The micro-PL and micro-Raman measurements were performed on a Renishaw InVia Raman microscope with a 1,100x objective (spot size of about 300 nm). The PL map was recorded using 0.0005% laser intensity (corresponding to 100 µW/cm²), using a 532 nm green laser diode. The spectra were registered in the 710–820 nm region. Raman spectra were obtained using the same excitation monitoring the 50–250 cm⁻¹ range, particularly sensitive to the Pb–I modes. The final data were averaged over 50 accumulations to maximize the signal-to-noise ratio. To prevent sample degradation or thermal effects, the laser power intensity was kept below (excitation density of around 3 mW cm⁻² (0.0005%) and the light exposure time per measurement was 0.1 s. Photoelectron spectroscopy measurements were performed in an ultrahigh-vacuum system (base pressure of 2x10⁻¹⁰ mbar) using a He-discharge ultraviolet source (Omicron) with an excitation energy of 21.2 eV for UPS and an Al Kα X-ray source (excitation energy: 1486.6 eV) for XPS. The photoelectron spectra were recorded using a Phoibos 100 (Specs) hemispherical energy analyser at a pass energy of 5 eV for the valence band and a pass energy of 20 eV for the core levels. For the peak position determination, the secondary electron cut-off was applied by applying a −10 V sample bias to clear the analyser workfunction. The reported valence band spectra were background subtracted. The binding energies for all of the photoemission spectra are referenced to the Fermi level. For a comparison of the XPS core-level spectra, the binding energy values were all adjusted to the binding energy of 284.6 eV for C 1s. The Gaussian–Lorentzian peak shape and a Shirley-type background were employed for fitting the spectra.

**Device characterization.** The photovoltaic device performance was analysed using a VersaSol LED solar simulator (Newport) producing 1 Sun AM 1.5 (1,000 W m⁻²) sunlight. Current–voltage curves were measured in air with a potentiostat (Keithley 2604). The light intensity was calibrated with a NREL-certified KG5-filtered Si reference diode. The solar cells were masked with a metal aperture of 0.16 cm² to define the active area. The cells were measured in air, at room temperature and without encapsulation, at a constant rate 10 mV s⁻¹ for both forward and reverse bias. No special pre-conditioning protocol was used apart from 5 s of stabilization time before the measurement. No anti-reflective coating was used during the measurement. The stability test was performed in a sealed cell holder flushed with nitrogen for 2 h. EQE was measured with the IQE200B (Oriel) without bias light. Device characterization. This is indirectly confirmed by the usually good agreement between the reported and theoretical band gaps of the perovskite layers.

**Data availability.** The data that support the plots within this paper and other finding of this study are available from the corresponding author upon reasonable request.

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Author contributions

A.D.J. planned the experiments and prepared and characterized the cells; M.S. performed the impedance measurements and analysis; S.A. supervised M.S.; G.M. performed the XPS, XRD and absorption analysis; G.G. carried out the Raman and PL characterization; C.R.-C. designed the experiments, carried out the SEM analysis and wrote the manuscript; L.C. performed the theoretical simulations; M.R. and N.K. performed UPS and XPS analysis; C.R.-C., G.M., L.C. and M.K.N. conceived the idea, and supervised the research project.

Competing interests

The authors declare no competing financial interests.

Additional information

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