# **Supporting information**

Balanced change in crystal unit cell volume and strain leads to stable halide perovskite with high guanidinium content

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# **Experimental section**

## Materials

Materials: All materials were reagent grade and were used as received. Lead iodide (PbI<sub>2</sub>, > 98%, from TCI), methylammonium iodide (MAI, 98%, from Greatcellsolar), Guanidinium iodide (GuI, > 99%, from Greatcellsolar), 2-propanol (99.7% from Carlo Erba), ethanol (96%) and acetone (99.25%) from PanReac, hydrochloric acid (HCl 37%), dimethyl sulfoxide (DMSO anhydrous 99.9%), clorobenzene (CB anhydrous 99.8%), acetonitrile (MeCN anhydrous 99.8%), ethylacetate (EA anhydrous 99.8%), 4tert-butylpiridine (TBP 96%). (99.995%) lithium zinc powder and bis(trifluoromethylsulfonyl)imide (Li-TFSI 99.95%) from Sigma aldrich, while 2,20,7,70-tetrakis [N,N-di(4-methoxyphenyl)amino]-9,90-spirobifluorene (spiro-OMeTAD 99% from Feiming chemical limited), and SnO<sub>2</sub> colloid precursor from Alfa Aesar (15% in H<sub>2</sub>O colloidal dispersion). Indium tin oxide (ITO) coated glass substrates (Pilkington TEC15, ~ 15  $\Omega$  sq<sup>-1</sup>).

#### **Device fabrication**

Substrates (indium tin oxide, ITO) were etched by using zinc powder and pour over it drops of HCl 2 M. Then glass was cleaned with deionized water, acetone and ethanol in an ultrasonic cleaner for 15 min for each solvent. After being dried by air flow, the substrates were put in an ultraviolet-ozone for 15 min to remove organic residues. Once cleaned, the electron transport layer ETL (SnO<sub>2</sub>) was deposited from dissolution of SnO<sub>2</sub> 3% from colloid precursor. Then, it is spin-coated onto the ITO substrates with an acceleration of 3,000 rpm for 30 s, and heated at 150 °C for 30 min. Once the ETL is prepared, substrates are submitted to 20 min of UV-Ozone before perovskite deposition. A quantity of 50  $\mu$ l of perovskite is deposited over SnO<sub>2</sub> ETL by one-step spin coating at 4,000 rpm for 20 s. Perovskite solutions were prepared by weighting the MAI precursors and PbI<sub>2</sub> at 1.4 M concentration and mix them to obtain MAPbI<sub>3</sub> 1.4 M concentration in 4:1 DMF:DMSO (v:v).The same procedure was followed for GuPbI3 by weighting GuI 1.4 M and PbI2 1.4 M. Once both solutions were prepared they were mixed in different proportions. According to this, the perovskite mixtures MAPbI<sub>3</sub>:GUPbI<sub>3</sub> where mixed in the following volume ratio: 1:0, 0.98:0.02, 0.95:0.05, 0.93:0.07, 0.90:0.10 and 0.85:0.15.Then, the sample was moved to a hotplate and annealed for 10 min at a temperature of 130 °C. After perovskite deposition, 50 µl of hole transporting layer made with spiro-OMeTAD in chlorobenzene (85.5 mg/mL), doped with 28.8 µL of TBP and 17.8 µL of a stock solution of 520 mg mL<sup>-1</sup> of Li-TFSI in acetonitrile, is spin-coated at 4,000 rpm for 20 s onto the top annealed perovskite layers as hole transport material (HTM). Finally, Au electrode with a thickness of 80 nm is deposited by thermal evaporation.

### **Film characterization**

*Optical Characterization*: UV-VIS absorption of the thin films are measured using a UV-VIS-absorption spectrophotometer (Varian, Cary 300) in the wavelength range of 400-850 nm.

Steady state photoluminescence emission (PL): PL of the films were carried out by using the 514 nm excitation wavelength coupled with a CCD detector (InGaAsAndoriDUS DU490A- 2.2) with an adaptive focus imaging spectrograph (Kymera KY-193i-B2). A commercial continuous laser (532 nm, GL532RM-150) was used as an excitation source.

*Scanning electron microscopy (SEM):SEM* is performed by the equipment JEOL 3100 F equipped with an electron gun employing 5 kV which allow us to magnifications from 5000X up to 50000X to analyze surface. By using INCA 350 (Oxford) and INCA Wave 200 (Oxford) it was employed microanalysis by X-ray energy dispersion (EDX) or by wavelength dispersion (WDX) respectively.

*X-Ray Diffraction (XRD)*: The*x-ray diffraction (XRD)* profiles were registered by a diffractometer (Bruker AXS, D8 Advance) equipped with a primary monochromator of Ge. Measurements were taken using Cu Karadiation (wavelength of I= 1.5406 A) over a 20 range between 5° and 70° with a step size of 0.02°.

#### **Device characterization**

*Current-voltage (J-V) measurement* :n-i-p devices parameters are obtained using Abet sun 2000 solar simulator which gives an AM 1.5G (100 mW/cm<sup>2</sup>) light illumination conditions coupled with a Keithley 2612 sourcemeter to measure current-voltage. Each measured was taken with Tracer software and done at ambient conditions (T=25°C, RH~40-60%) using a scan rate of 10 mV/s and a shadow mask of 0.121 cm<sup>2</sup>.

*Incident photon to current efficiency (IPCE):* IPCE measurements are performed using a Xenon lamp with a monochromator Oriel Cornestone 130 which was used to measure along the wavelength of the spectrum. Before measurement, calibration is done using a reference photodiode of silicon and each measurement is obtained using TRACQ BASIC software. Finally, IPCE scans were taken from 300 nm to 810 nm in steps of 10 nm.

*Chronoamperometry*: data is obtained by a Potentiostat Autolab PGSTAT30 employing 1 sun illumination over devices at ambient conditions of 40 % R.H measuring at mpp for 1 Hour.

Impedance spectroscopy (IS): The(IS) is measured by using a Potentiostat Autolab PGSTAT30 employing different filters to change light intensity up to 1 sun. For each voltage point ( $V_{OC}$ ) IS was measured with an AC 10mVvoltage perturbation from 1 MHz to 100 mHz. Nova software was used to generate data and Z-View software for modelling the equivalent circuit model used to fit the spectra, respectively.

### **Volume calculation**

On the basis of the tetragonal phase of MAPbI<sub>3</sub>the characteristic peak at approximately  $14^{\circ}$  was considered to correspond to the plane (110) and the peak at 20° to the plane (112). These peaks can be observed for the references and MA<sub>1-x</sub>Gu<sub>x</sub>PbI<sub>3</sub> samples with Gu content of up to 20% preserving the same crystalline structure and increasing its volume. In consequence, the tetragonal phase will consist of a square base of side "a" and height "c" that will result in a volume of "a<sup>2</sup>c". However for higher values than 20% peaks at ~8.5° and ~11°, which are related to 2D structures appear, and the volume cannot be calculated as a tetragonal structure.

#### PbS QDs synthesis and ligand exchange procedure

PbS QDs were synthesized and added according to previous reports. In a three-necked round-bottom0.9 g (4 mmol) of PbO, 2.0 g(7 mmol) of Oleic acid and 36 ml of 1-octadecene (ODE)were mixed and heated at 150 °C under N<sub>2</sub> while stirring. After 1 h, 3 ml (6.7 mmol)of trioctylphosphine (90%) were injected. Then, 0.42 ml (2 mmol) of hexamethyldisilathiane(HMDS) and 4 ml ODE were introduced once flask decreases its temperature to  $110^{\circ}$ C. Finally, solution was left to decrease its temperature to room temperature. QDs were obtained after performed three time washes with ethanol/acetone (1:1, v/v), centrifuged (3000 rpm for 10 minutes) and dispersed in toluene (100 mg/ml).

To perform the ligand exchange PbS in octane is mixed with 0.25 M of perovskite in 1:3 volume ratio. The latter leaves one phase of PbS in octane separated from another phase of perovskite in its solvents. Then, after stirring by 30 min the ligand exchange is produced leading to one phase of PbS/perovskite in the bottom and octane in the upper part. To recover the QDs with perovskite capping ligand it is perform three washing and finally the QDs are precipitated with toluene. Then, the remainder is dried by vacuum pump for 2 hours. Finally, perovskite solution is added in proper way to have PbS/perovskite embedded in perovskite solution. To have mixed cationperovskite capping ligand the same procedure was followed.

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Figure S1. A) Absorbance spectra of perovskite with different amount of Gu; Tauc plots and second derivative to determine their bandgap. B) SEM measurements of fresh samples with different quantities of Gu.

**Table S1.** Photoluminescence Full Width Half Maximum (PL FWHM) of perovskitepeaks with different Gu %.

Gu%	FWHM		
0	44.65 ± 0.36		
2	47.18 ± 0.53		
5	45.74 ± 1.23		
7	44.34 ± 0.26		
10	48.94 ± 0.09		
15	49.11 ± 0.03		



Figure S2. Grain size of different mixtures of perovskite observed at surface measured by SEM images.



**Figure S3.** XRD patterns for studies cases: **A)** XRD with < 20% of Gu (sample over FTO); **B)** XRD with > 20% of Gu: peaks corresponding to 2D phase are indicated with \* (~8.4° and ~11.2°).

**Table S2.** Photovoltaic parameter of samples measured under 1 sun illumination for different quantities of Gu in the perovskite at day 0.

Gu %	Jsc (mA/cm2)	Voc (V)	FF (%)	PCE (%)
0	20.3 ± 0.9	1.05 ±0.02	72.9 ± 1.8	15.6 ± 0.3
2	20.7 ± 0.7	1.06 ±0.01	74.6 ± 1.8	16.3 ± 0.6
5	20.9 ± 0.9	1.04 ±0.02	76.0 ± 3.0	16.6 ± 0.7
7	21.5 ± 0.6	1.06 ±0.01	76.2 ± 2.1	17.4 ± 0.5
10	19.8 ± 1.0	1.05 ±0.03	74.2 ± 2.3	15.4 ± 0.7
15	20.3 ± 0.7	1.06 ±0.02	71.0 ± 4.0	15.2 ± 0.7



**Figure S4. A)** J/V curve of highest efficiency devices for different quantities of Gu**B**) showing the highest performance among all the mixed devices and **C**) the respective IPCE to assert the Jsc obtained.



**Figure S5**. Photovoltaic parameters for 15 devices of each Gu percentage for the mixed cation perovskite measured at different days while they remain at 30-40% RH in dark conditions and 22 °C.



**Figure S6**.Normalized photovoltaic parameters for 15 devices of each Gu percentage for the mixed cation perovskite measured at different days while they remain at 30-40% RH in dark conditions and 22 °C.



Figure S7. A) PL intensity measured at 532 nm for Gu samples without and with QDs and B) their respective wavelength of maximum PL.



**Figure S8.A)**. Absorbance spectra, Tauc plot and 2<sup>nd</sup> derivative for perovskite with PbS QDs.

**Table S3.** Photoluminescence Full Width Half Maximum (PL FWHM) of perovskitepeaks with different Gu % with QDs.

Gu %	FWHM				
0	50.50 ± 0.40				
2	48.51 ± 0.06				
5	49.90 ± 0.30				
7	48.99 ± 0.02				
10	50.06 ± 0.15				
15	50.83 ± 0.08				



Figure S9. A) XRD patterns of films with QDs using different Gu quantities and B) SEM top view images of the corresponding films.



**Figure S10. A)** Grain size of different perovskite MAGuPbI<sub>3</sub> mixtures with QDs. **B)** Crystal size determination.

Table S4.	Photovoltaic	parameter	of sa	mples	measured	under	1	sun	illumination	for
different qu	uantities of G	u in perovsl	cite w	ith en	nbedded Pb	S QDs	at	day	0.	

Gu %	Jsc (mA/cm2)	Voc (V)	FF (%)	PCE (%)
0	$20.2 \pm 0.4$	0.99 ±0.01	67.7 ± 1.0	14.3 ± 0.2
2	19.9 ± 0.6	1.01 ±0.02	70.1 ± 1.9	14.1 ± 0.5
5	20.7 ± 0.6	1.00 ±0.02	73.1 ± 1.8	15.1 ± 0.4
7	20.5 ± 0.6	1.03 ±0.02	72.0 ± 3.0	15.2 ± 0.5
10	19.3 ± 1.0	1.04 ±0.03	72.4 ± 2.5	14.6 ± 0.6
15	18.7 ± 0.5	1.05 ±0.02	74.1 ± 2.3	14.6 ± 0.5



**Figure S11** .Photovoltaic parameters for 15 devices of each Gu percentage for the mixed cation perovskite with PbS QDs measured at different days while they remain at 30-40% R.H. in dark conditions and 22 °C.

![](_page_16_Figure_0.jpeg)

**Figure S12**. Normalized photovoltaic parameters for 15 devices of each Gu percentage for the mixed cation perovskite with PbS QDs measured at different days while they remain in dark conditions at 30-40 % RH and 22 °C.

![](_page_17_Figure_0.jpeg)

**Figure S13.** Williamson-Hall linear fitting for each Gu amount without and with QDs which determines the strain coefficient corresponding to the slope.

![](_page_17_Figure_2.jpeg)

Figure S14. A) Microstrain of QD/ (W/O QDs) and  $J_{sc}$  of QD/  $J_{sc}$  W/O QDs for each Gu percentage at 0 day B) and 300 day.

 $MAPbI_3 = MA_{0.98}Gu_{0.02}PbI_3 = MA_{0.95}Gu_{0.05}PbI_3 = MA_{0.93}Gu_{0.07}PbI_3 = MA_{0.90}Gu_{0.10}PbI_3 = MA_{0.85}Gu_{0.15}PbI_3 = MA_{0.95}Gu_{0.15}PbI_3 = MA_{0.95}Gu_{0.17}PbI_3 = MA_{0.85}Gu_{0.15}PbI_3 = MA_{0.85}PbI_3 = MA$ 

![](_page_18_Figure_0.jpeg)

Figure S15. A) Photovoltaic parameters of 15 devices W/O QDs and W QDs measure at 1 sun in reverse mode after 300 days. B) Chronoamperometry of devices measured at  $V_{mpp}$  for 1 hour at 40 % R.H..

![](_page_18_Figure_2.jpeg)

**Figure S16.A)** Equivalent circu.it used for IS analysis <sup>1</sup>B) Recombination resistance ( $R_{rec}$ ) at 1 sun illumination ranging voltage from 0 to 1.1 V for devices W/O QDs and W QDs **C**).

![](_page_19_Figure_0.jpeg)

**Figure S17.(A)** XRD patterns of reference and  $GU_{7\%}$  after 20 days of humidity exposition at 45% R.H. and 22 °C W/O QDs and with QDs. **(B)** XRD patterns of each Gu percentage at 20 days W/O QDs and W QDs.

# References

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