# Supporting information

Efficient Large Guanidinium Mixed Perovskite Solar Cells with Enhanced Photovoltage and Low Energy Losses

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### **Experimental Section**

*Materials*: All the commercial materials were used as received, including N, Ndimethylformamide (99.99%, J&K), chlorobenzene (99.9%, J&K), dimethyl sulfoxide (99.50%, J&K), PbI<sub>2</sub> (99.999%, TCI), PbBr<sub>2</sub> (99.9%, TCI), spiro-OMeTAD (Lumtec), 4-tertbutylpyridine (99.90%, Sigma-Aldrich), lithium bis(trifluoromethylsulphonyl)imide (99.95%, Sigma-Aldrich), tris(2- (1H-pyrazol-1-yl)-4tert-butylpyridine)cobalt(iii)-tris(bis(trifluoromethylsulfonyl)imide) (99.95%, Sigma-Aldrich) (FK209) and ITO substrates. The HC(NH<sub>2</sub>)<sub>2</sub>I, CH<sub>3</sub>NH<sub>3</sub>Br, CsI, GuaI and MoO<sub>3</sub> were purchased from Xi'an Polymer Light Technology Corporation.

*Preparation of*  $SnO_2$  *nanoparticle film*:  $SnO_2$  colloid precursor was purchased from Alfa Aesar (Tin (IV) oxide, 15% in H<sub>2</sub>O colloidal dispersion). The precursor diluted by DI water to 2 % was spin coated onto glass/ITO substrates at 4000 rpm for 30 s, and then baked on a hot plate at 150 °C for 30 min in ambient.

Solution Preparation and Perovskite Film Deposition: ITO glass (15  $\Omega$  sq<sup>-1</sup>) was sequentially cleaned by sonication with detergent (Decon 90), deionized water, acetone, and isopropyl alcohol for 15 min, respectively. The cleaned ITO substrates were then treated by UV ozone for 25 min before use. Mixed cation perovskite precursor solution was prepared by previous reports <sup>1-2</sup>, which mixed FAI (1 M, 171.97 mg), PbI<sub>2</sub> (1.1 M, 507.1 mg), MABr (0.2 M, 22.4 mg), PbBr<sub>2</sub> (0.2 M, 73.4 mg) in anhydrous DMF: DMSO (4: 1, 800 ul DMF and 200 ul DMSO) followed by adding 89 ul of CsI stock solution (1.5 M in DMSO) to form (CsI)<sub>0.133</sub>(FAPbI<sub>3</sub>)<sub>0.85</sub>(PbI<sub>2</sub>)<sub>0.085</sub>(MAPbBr<sub>3</sub>)<sub>0.15</sub> (shorten as Cs<sub>0.12</sub>FA<sub>0.76</sub>MA<sub>0.16</sub>PbI<sub>2.79</sub>Br<sub>0.4</sub>). To be simple, we use CsFAMA to represent Cs<sub>0.12</sub>FA<sub>0.76</sub>MA<sub>0.16</sub>PbI<sub>2.79</sub>Br<sub>0.4</sub> in our paper. Gua incorporated perovskite solution was prepared by adding different molar ratio of GuaPbI<sub>3</sub> into CsFAMA precursor solution. The perovskite solutions with different composition were spin-coated on glass/ITO/SnO<sub>2</sub> at 1000 and 4000 rpm for 10 s and 30 s, respectively. 110 uL of chlorobenzene (CB) as an anti-solvent was quickly dropped on the center of film 5 s before the end of spin-coating and the perovskite was baked on hotplate at 100°C for 30 min. Then, 72.3 mg spiro-OMeTAD in 1 mL chlorobenzene with additives of 28.8 µL tert-butylpyridine, 17.5 µL Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI) stock solution (520 mg mL<sup>-1</sup> in acetonitrile) and 28.9 µL tris(2-(1H-pyrazol-1-yl)-4-tertcobalt(iii)-tris(bis(trifluoromethylsulfonyl)imide) butylpyridine) (FK209) stock solution (300 mg mL<sup>-1</sup> in acetonitrile), was spin coated at 4000 rpm for 30 s. Finally, 8 nm MoO<sub>3</sub> and 100 nm silver electrode was evaporated under high vacuum ( $<4 \times 10^{-6}$ Torr). The device area was defined and characterized as 0.16 cm<sup>2</sup> by metal shadow mask.

*Characterization*: *J*–*V* characteristics of photovoltaic devices were measured in glove box at room temperature by using a Keithley 2400 source meter under simulated sunlight from a solar simulator (Enlitech, SS-F5, Taiwan). A National Renewable Energy Laboratory calibrated silicon solar cell was used to obtain the AM 1.5G solar simulator's light intensity. X-ray diffraction (XRD) characterization was carried out on a D2 Phaser instrument with a Cu K $\alpha$  ( $\lambda$ =0.154 nm) radiation. The morphology of the samples was monitored by scanning electron microscopy (SEM, Philips XL30 FEG) PL and TRPL spectrum was recorded with a FLS980 spectrofluorometer (Edinburgh). UV-Vis absorption spectra were recorded on a UV-Vis spectrometer (PerkinElmer model Lambda 2S). Impedance of the samples was measured with a ZAHNER IM6 workstation with a frequency range from 0.5 to  $10^6$  Hz. EQEs were carried out by an EnLi Technology (Taiwan) EQE measurement system. All photoemission studies are carried out in a VG ESCALAB 220i-XL surface analysis system equipped with a He-discharge lamp (hv = 21.22 eV) and a monochromatic Al–K $\alpha$  X-ray gun (hv = 1486.6 eV) for UPS and XPS investigation, respectively.

### The fitting of PL decay times

The PL decay times were fitted by using bi-exponential function of time (t)

$$f(t) = A_1 \times e^{-\frac{t}{\tau_1}} + A_2 \times e^{-\frac{t}{\tau_2}}$$

where  $A_1$  and  $A_2$  are the relative amplitude fraction for each decay component, and  $\tau_1$ and  $\tau_2$  are defined as the time constant of the fast and long decay species, respectively.

### The calculation of $V_{\rm OC}$ loss from different items

According to the previous work from to Rau and Kirchartz,  $V_{OC}$  of solar cell can be deduced from the following equation:

$$V_{OC} = \frac{k_B T}{q} \ln \left( \frac{J_{SC}}{J_0} \right)$$
(S1)

where  $k_B$  is Boltzmann constant, T is temperature, q is element charge,  $J_{SC}$  is short-circuit current,  $J_0$  is dark saturation current. The expressions of  $J_{SC}$  and  $J_0$  are given by:

$$J_{SC} = q \int_{0}^{\infty} EQE_{PV}(E)\phi_{AM1.5}(E)dE$$
(S2)

$$J_0 = \frac{q}{EQE_{EL}} \int_0^\infty EQE_{PV}(E)\phi_{BB}(E)dE$$
(S3)

$$\phi_{BB}(E) = \frac{2\pi E^2}{h^3 c^2} \frac{1}{\exp\left(\frac{E}{k_B T}\right) - 1}$$
(S4)

where  $^{EQE_{PV}}$  is photovoltaic external quantum efficiency,  $^{EQE_{EL}}$  is electroluminescence external quantum efficiency,  $\phi_{AM1.5}$  is solar cell radiative spectrum,  $\phi_{BB}$  is black-body radiative spectrum,  $^{c}$  is light speed in vacuum. For Schokley-Queisser limit (S-Q limit): (1) The  $EQE_{PV}$  is described with Heaviside step

 $EQE_{PV}(E) = \begin{cases} 1, E \ge E_g \\ 0, E < E_g; (2) \text{ only the photos with energy larger than bandgap} \\ (^Eg) \text{ are absorbed; (3) all recombination is radiative } (^{EQE}_{EL} = 1). \text{ Therefore, } J_{SC} \text{ and } J_0 \text{ in } S-Q \text{ limit are written as:} \end{cases}$ 

$$J_{SC}^{SQ} = q \int_{E_g}^{\infty} \phi_{AM1.5}(E) dE$$

$$J_0^{SQ} = q \int_{E_g}^{\infty} \phi_{BB}(E) dE$$
(S5)
(S6)

Therefore,  $V_{OC}$  in S-Q limit is:

$$V_{OC}^{SQ} = \frac{k_B T}{q} \ln \left( \frac{f_{SC}^{SQ}}{f_0^{SQ}} \right)$$
(S7)

Considering the assumption of *S*-*Q* limit,  $V_{OC}^{SQ}$  can be described in several terms. The first  $V_{OC}$  loss component is due to the non-ideal  $EQE_{PV}$ , which is less than 100%. In this condition, short-circuit current is expressed as:

$$J_{SC} = q \int_{0}^{\infty} EQE_{PV}(E)\phi_{AM1.5}(E)dE$$
(S8)

and the  $V_{\rm OC}$  loss from  $\Delta V_{OC}^{sc}$  can be is calculated from:

$$\Delta V_{OC}^{sc} = V_{OC}^{SQ} - \frac{k_B T}{q} \ln \left( \frac{J_{SC}}{J_0^{SQ}} \right) = \frac{k_B T}{q} \ln \left( \frac{J_{SC}^{SQ}}{J_{SC}} \right)$$
(S9)

The second  $V_{OC}$  loss component comes from the energy loss associated with extra thermal radiation of solar cell in dark. In experiment, the  $EQE_{PV}$  extends into the sub-bandgap region, where the black-body radiation increases with the photo energy lowering. Thus, this sub-bandgap  $EQE_{PV}$  increased the dark saturation current. The short-circuit current,  $J_{SC}^{rad}$ , is equal to  $J_{SC}$ , and dark saturation current in this condition are written as:

$$J_{0}^{rad} = q \int_{0}^{\infty} E Q E_{PV}(E) \phi_{BB}(E) dE$$
(S10)

therefore, the radiative  $V_{\rm OC}$  loss,  $\Delta V_{OC}^{rad}$ , is:

$$\Delta V_{OC}^{rad} = \frac{k_B T}{q} \ln \left( \frac{J_{SC}}{J_0^{SQ}} \right) - \frac{k_B T}{q} \ln \left( \frac{J_{SC}}{J_0^{rad}} \right) = \frac{k_B T}{q} \ln \left( \frac{J_0^{rad}}{J_0^{SQ}} \right)$$
(S11)

The third  $V_{\text{OC}}$  loss component,  $\Delta V_{OC}^{nonrad}$ , is ascribed to the nonradiative recombination in device, which can be calculated as:

$$\Delta V_{OC}^{nonrad} = \frac{k_B T}{q} \ln \left( \frac{J_{SC}}{J_{0}^{rad}} \right) - V_{OC}$$
(S12)

#### The Calculation of trap density of states (tDOS)

To characterize both shallow and deep trap states ( $N_T$ ) and quantize the reduction of  $N_t$ in the films, admittance spectroscopy was applied accordingly. The energetic profile of tDOS can be deduced from the angular frequency ( $\omega$ ) dependent capacitance by using the following equation:

$$N_T(E_w) = -\frac{V_{bi} \, dC \, w}{qW dw k_B T} \tag{S13}$$

where  $V_{bi}$  is the built-in potential, q is the elementary charge, W is the depletion width, C is the capacitance,  $\omega$  is the angular frequency,  $k_B$  is Boltzmann constant, and T is the temperature.  $V_{bi}$  and W can be derived from  $C^{-2}$ -V plots.  $E_{\omega}(E_{\omega} = E_{T} - E_{V})$ , where  $E_{T}$  and  $E_{V}$  are the trap state energy and valence band edge) is defined as energetic demarcation,

$$E_w = k_B T ln(\frac{w_0}{w}) \tag{S14}$$

where  $\omega_0$  is the attempt-to-escape frequency.

# TOC



A large guanidinium cation (Gua<sup>+</sup>) is incorporated into perovskite lattice, leading to a significantly improved  $V_{OC}$  of 1.19 V with a high power conversion efficiency beyond 21%.



**Fig. S1** Comparison of the figure-of-merit (open-circuit voltage loss,  $V_{oc, loss}$ ) for PVSCs reported in literatures with the bandgap ( $E_g$ ) in the range of 1.48-1.82 eV.



Fig. S2 (a) Full XPS spectra, (b) N 1s and (c) C 1s high-resolution XPS spectra for

CsFAMA and CsGuaFAMA perovskite.



Fig. S3 Top-view SEM image of perovskite films with different molar ratio of Gua on

ITO substrate.



Fig. S4 AFM image of perovskite films with different molar ratio of Gua.



Fig. S5 Tauc plot of CsFAMA with 0 and 10% of Gua (calculated from UV-vis spectra).



Fig. S6 Normalized PL spectra of perovskite with 0, 5, 10, 20 and 40% of Gua.



**Fig. S7** Ultraviolet photoelectron spectroscopy (UPS) for thin films of CsFAMA and CsGuaFAMA perovskite.



**Fig. S8** J-V curves of the best performing devices for CsFAMA and CsGuaFAMA at forward scan and reverse scan.



Fig. S9 J-V curves of PVSCs with 5%, 20% and 40% of Gua.



**Fig. S10** External quantum efficiency (EQE) spectra of CsFAMA and CsGuaFAMA based devices.



**Fig. S11** Statistics of (a)  $J_{sc}$ , (b)  $V_{oc}$ , (c) *FF* and (d) PCE of PVSCs with different concentration of Gua<sup>+</sup> (fabricated from different batches).



Fig. S12 Nyquist plot of CsFAMA and CsGuaFAMA PVSCs measured at room temperature.



Fig. S13 Capacitance-frequency (C-*f*) curves for CsFAMA and CsGuaFAMA.

Samples	Lattice constant (Å)	Crystallite size (nm)	
0% Gua	6.264	63.37	
5% Gua	6.269	41.72	
10% Gua	6.276	62.63	
20% Gua	6.295	52.38	
40% Gua	6.287	48.02	

 Table S1. The Lattice parameters and crystallite size of perovskite with different ratio

between Gua and CsFAMA

Samples	$\tau_{ave} [ns]$	$\tau_1 [ns]$	% of $\tau_1$	$\tau_2 [ns]$	% of $\tau_2$
0% Gua	767.00	72.48	5.16	771.55	94.84
5% Gua	1216.25	90.92	4.27	1219.00	95.73
10% Gua	2659.88	100.00	1.05	2660.90	98.95
20% Gua	1839.21	150.00	4.27	1845.34	95.73
40% Gua	1303.27	273.68	17.19	1346.73	82.81

 Table S2. The parameters of carrier lifetime by fitting spectroscopy based on
 glass/perovskite structure.

Device	$J_{\rm sc}$ [mA cm <sup>-2</sup> ]	$V_{\rm OC}$ [V]	FF	PCE [%]
0% Gua	23.55	1.11	0.71	18.56
5% Gua	23.43	1.14	0.75	20.03
10% Gua	23.66	1.19	0.75	21.12
20% Gua	22.69	1.18	0.72	19.28
40% Gua	20.49	1.20	0.57	14.02

**Table S3**. Solar cell performance parameters, extracted from J-V curves.

**Table S4.** Parameters measured and calculated for quantifying the different  $V_{OC}$  loss terms.

Device	$V_{\rm oc}$	$V_{ m oc, SQ}$	$\Delta V_{ m oc, \ SC}$	$\Delta V_{ m oc, \ rad}$	$\Delta V_{ m oc, nonrad}$
CsFAMA	1.11 V	1.34 V	1.35 mV	29.78 mV	201.86 mV
CsGuaFAMA	1.19 V	1.33 V	1.54 mV	5.42 mV	137.03 mV

## Reference

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