## **Supplementary Information**

## Influence of A-Site Cation on the Open-Circuit Voltage of Efficient Perovskite Solar

Cells: A case of Rubidium and Guanidinium Additives

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**Fig. S1.** Statistics of photovoltaic parameters for the Cs,  $Rb_5Cs$ , and  $GA_5Cs$  PSCs, (a)  $V_{oc}$ , (b)  $J_{sc}$ , (c) FF, and (d) PCE.



Fig. S2. AFM images of (a) Cs, (b) Rb<sub>5</sub>Cs (c) and (d) GA<sub>5</sub>Cs perovskite films.



**Fig. S3**. Three-dimensional AFM images of (a) Cs, (b) Rb<sub>5</sub>Cs and (c) GA<sub>5</sub>Cs perovskites deposited on glass slide.



**Fig. S4**. UV-visible and PL spectra of Cs, Rb<sub>5</sub>Cs and GA<sub>5</sub>Cs perovskites deposited on glass slide.



**Fig. S5**. Time-resolved PL (TRPL) spectra of Cs, Rb<sub>5</sub>Cs and GA<sub>5</sub>Cs based perovskite films deposited on glass slides.



Fig. S6. XRD patterns of Cs, Rb<sub>5</sub>Cs and GA<sub>5</sub>Cs perovskite films, zoomed on (110) peak.

V<sub>oc</sub>(V) FF (%) PCE (%) Device J<sub>sc</sub> (mA/cm<sup>2</sup>) Cs 1.12 22.7 76 19.7 78 Rb<sub>5</sub>Cs 1.16 22.8 21 1.2 23.6 70 20.3 GA<sub>5</sub>Cs

**Table S1**. Photovoltaic parameters of the best performing Cs, Rb<sub>5</sub>Cs and GA<sub>5</sub>Cs PSCs

**Table S2**. Fitting parameters of the corresponding TRPL curves

Perovskite	А	τ (ns)
Cs	2.9	29.7
Rb <sub>5</sub> Cs	1.59	49.6
GA <sub>5</sub> Cs	1.6	56.5