Supporting Information

Solvation Effect in Precursor Solution Enables over 16% Efficiency in Thick 2D Perovskite Solar Cells

Xiaomei Lian,[a,b] Jiehuan Chen,[a,b] Yingzhu Zhang,[a,b] Minchao Qin,[c] Thomas Rieks Andersen,[a,b] Jun Ling,[a] Gang Wu,*[a,b] Xinhui Lu,[c] Deren Yang,[b] and Hongzheng Chen*[a,b]

[a]MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China. E-mails: samy@zju.edu.cn, hzchen@zju.edu.cn
[b]State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, P. R. China
[c]Department of Physics, The Chinese University of Hong Kong, New Territories 999077, Hong Kong, P. R. China

Keywords: Thick 2D perovskite film; Solvation effect; Guanidinium; Large grains; Orientation

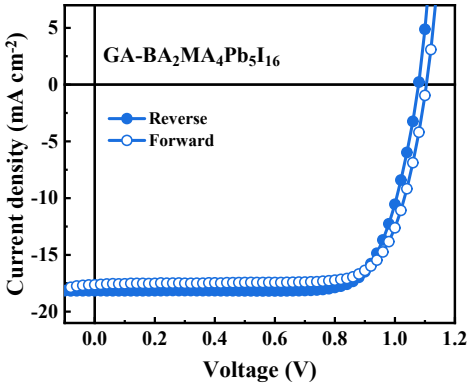

Figure S1. The forward-reverse *J-V* curves of the GA-$BA_2MA_4Pb_5I_{16}$ based PVSCs with precursor concentration of 0.6 M.

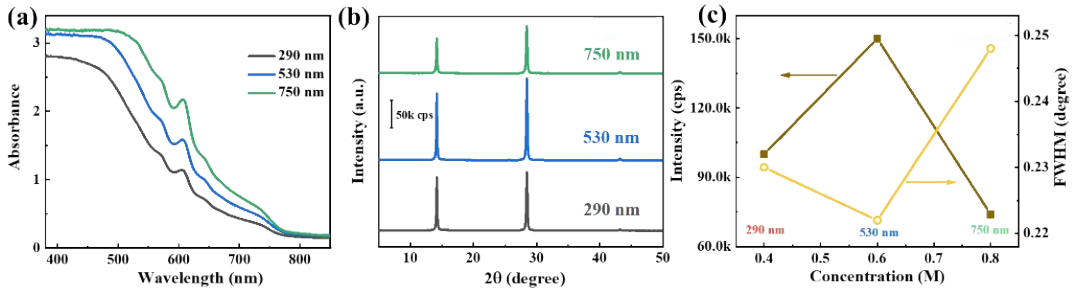

Figure S2. (a) Absorption spectra, (b) X-ray diffraction (XRD) patterns and (c) XRD peak intensity and FWHM of the (202) peak for the GA-$BA_2MA_4Pb_5I_{16}$ films with different thicknesses.

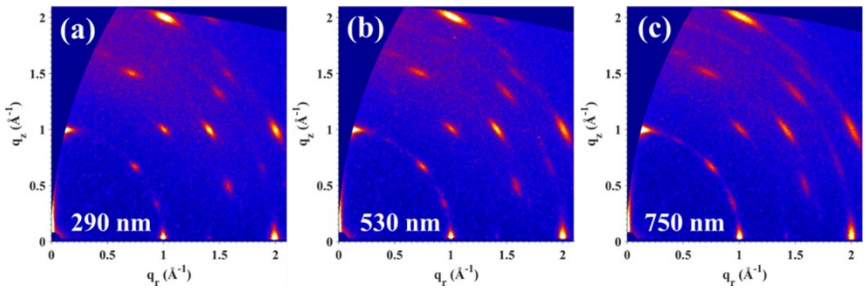

Figure S3. 2D GIWAXS patterns of the GA-$BA_2MA_4Pb_5I_{16}$ films with different thicknesses.

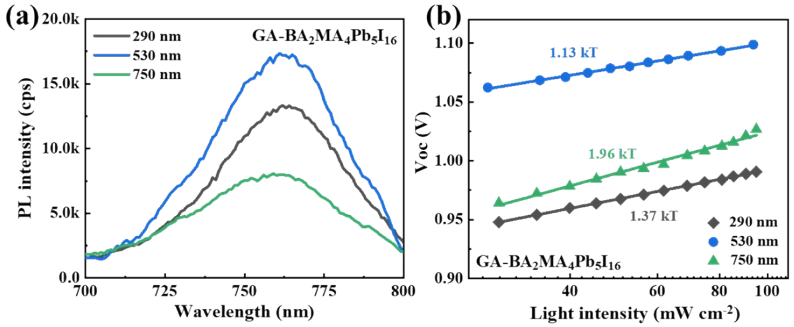

Figure S4. (a) Steady-state PL spectra, (b) Measured *Voc* of the PVSCs based on GA-$BA_2MA_4Pb_5I_{16}$ films with different thicknesses on quartz substrate.

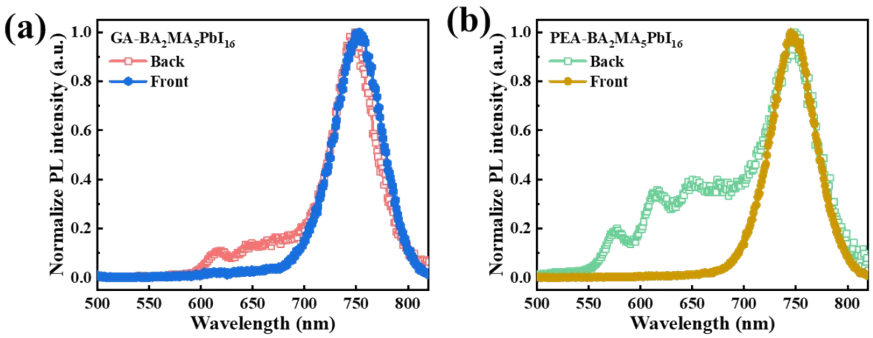

Figure S5. Normalized steady-state PL spectra of the perovskite films with (a) GA^+ and (b) PEA^+ addition excited from back (glass side) and front (perovskite side) sides.

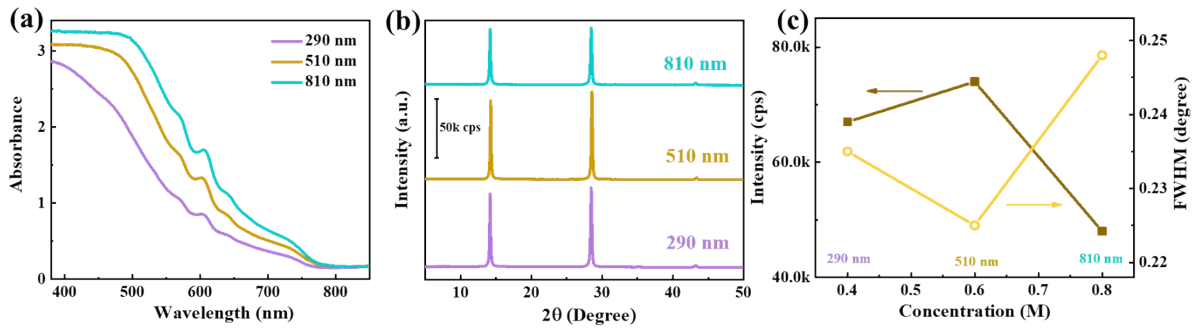

Figure S6. (a) Absorption spectra, (c) X-ray diffraction (XRD) patterns and (d) XRD peak intensity and FWHM of the (202) peak for the PEA-$BA_2MA_4Pb_5I_{16}$ films with different thicknesses.

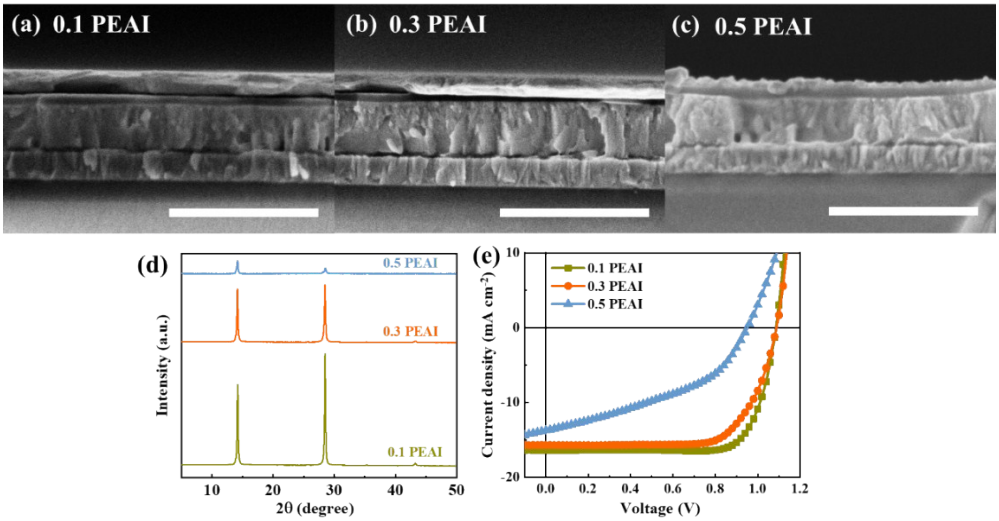

Figure S7. (a-c) Cross-sectional SEM images (the scale bar is 1 μm), (d) XRD patterns and (e) *J-V* curves of the PEA-$BA_2MA_4Pb_5I_{16}$ films or PVSCs deposited from precursor solutions with different ratio of PEAI addition at concentration of 0.4M.

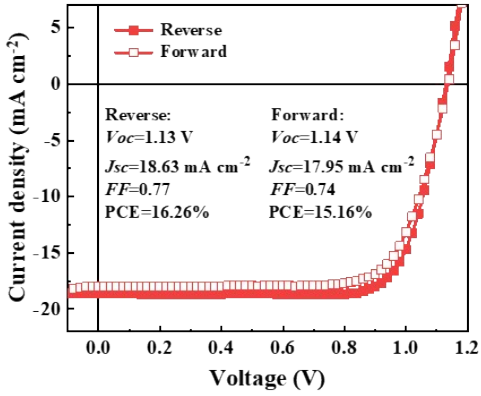

Figure S8. The forward-reverse *J-V* curves of the PVSCs based on GA-$BA_2MA_4Pb_5I_{16}$ film deposited from precursor solution (0.6 M) with MACl addition.

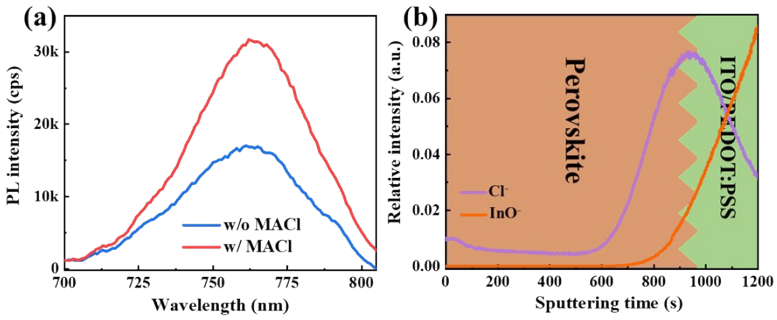

Figure S9. (a) Steady-state photoluminescence (PL) spectra of GA-$BA_2MA_4Pb_5I_{16}$ perovskite films (0.6M) with and without MACl on quartz substrates. (b) SIMS profiles showing Cl^-, InO^- elements from the top to the bottom of the optimized GA-$BA_2MA_4Pb_5I_{16}$ perovskite film (0.6M) with MACl on quartz substrate.

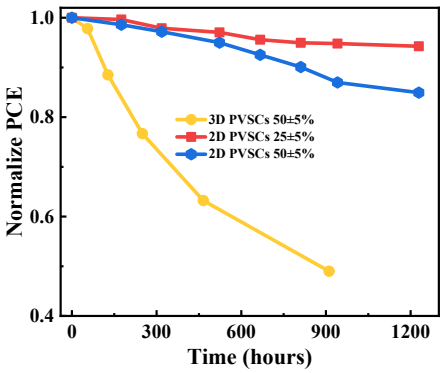

Figure S10. Storage stability of the unsealed devices based on GA-$BA_2MA_4Pb_5I_{16}$ (0.6 M, with MACl) and 3D $MAPbI_3$ films in air with different humidities.

Table S1. A summary of the film thickness for the reported high 2D PVSCs with inverted structure.

Perovskite	Thickness [nm]	*Voc* [V]	*Jsc* [mA cm^{-2}]	*FF*	PCE [%]	Reference
$(PEA)_2(MA)_4Pb_5I_{16}$	300	1.11	15.01	0.67	11.01	*Adv. Energy Mater*. 2018, 8, 1702498
$(PEA)_2(MA)_3Pb_4I_{13}$	310	1.16	14.7	0.71	12.1	*Adv. Energy Mater*. 2018, 1800185
$(PEA)_2(MA)_4Pb_5I_{16}$	300	1.19	15.8	0.75	14.1	*ACS Energy Lett*. 2018, 3, 2086
$(BA)_2(MA)_2Pb_3I_{10}$	300	1.23	13.61	0.72	12.07	*J. Mater. Chem. A*, 2018, 6, 18010
$(BA)_2(MA)_3Pb_4I_{13}$	235	1.01	16.76	0.74	12.51	*Nature* 2016, 536, 312
$(BA)_2(MA_{0.8}FA_{0.2})_3Pb_4I_{13}$	300	1.00	18.12	0.71	12.81	*J. Am. Chem. Soc*. 2018, 140, 459
$(PDA)_2(MA)_3Pb_4I_{13}$	315	0.97	18.0	0.74	13.0	*Adv. Mater.* 2018, 30, 1800710
$GAMA_4Pb_4I_{13}$	300	1.00	17.5	0.73	12.8	*J. Mater. Chem. A*, 2018, 6, 18871
$(ThMA)_2(MA)_2Pb_3I_{10}$	370	1.07	18.89	0.76	15.42	*J. Am. Chem. Soc*. 2018, 140, 11639

Table S2. The forward-reverse *J-V* photovoltaic parameters of the GA-$BA_2MA_4Pb_5I_{16}$ based PVSCs with precursor concentration of 0.6M.

	Voc [V]	*Jsc* [mA cm^{-2}]	*FF*	PCE [%]	HI [%]	*Jcal* [mA cm^{-2}]
Reverse	1.08	18.16	0.76	14.94	4.6	17.86
Forward	1.08	17.63	0.75	14.25		

Table S3. XRD pattern parameters of the GA-$BA_2MA_4Pb_5I_{16}$ films with different thicknesses.

Thickness	Plane	(111)	(202)
290 nm	FWHM [°]	0.178	0.230
	Intensity [cps]	9.5×10^4	1.0×10^5
530 nm	FWHM [°]	0.176	0.222
	Intensity [cps]	1.2×10^5	1.5×10^5
750 nm	FWHM [°]	0.203	0.248
	Intensity [cps]	6.2×10^4	7.4×10^4

Table S4. XRD pattern parameters of the PEA-$BA_2MA_4Pb_5I_{16}$ films with different thicknesses.

Thickness	Plane	(111)	(202)
290 nm	FWHM [°]	0.191	0.235
	Intensity [cps]	6.1×10^4	6.7×10^4
510 nm	FWHM [°]	0.183	0.225
	Intensity [cps]	6.7×10^4	7.4×10^4
810 nm	FWHM [°]	0.210	0.248
	Intensity [cps]	4.6×10^4	4.8×10^4

Table S5. The *J-V* photovoltaic parameters of the PVSCs based on PEA-$BA_2MA_4Pb_5I_{16}$ films fabricated with different ratios of PEAI addition at concentration of 0.4M.

PEAI ratio	*Voc* [V]	*Jsc* [mA cm^{-2}]	*FF*	$PCE_{max/avg}$ [%]
0.1 PEAI	1.09	16.39	0.78	13.83/13.30
0.3 PEAI	1.09	15.69	0.71	12.21/11.54
0.5 PEAI	0.95	13.73	0.42	5.43/4.65