

## **Guanidinium Doping Enabled Low-temperature Fabrication of High-efficiency All-inorganic CsPbI<sub>2</sub>Br Perovskite Solar Cells**

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**Author Contributions:** # J.M. and M.Q. contributed equally to this work.

## Experimental Section

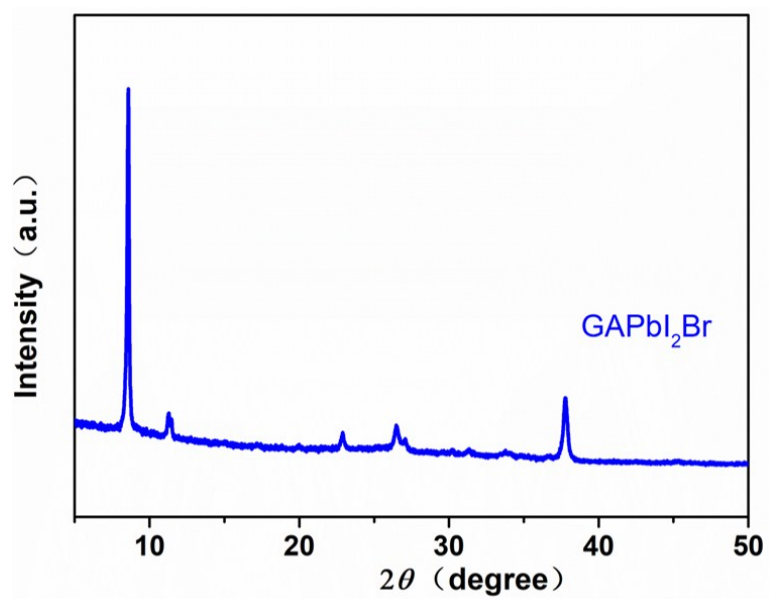
*Materials:* Zn (CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, 2-Methoxyethanol, Ethanolamine were purchased from J&K Scientific LTD. PbI<sub>2</sub>, PbBr<sub>2</sub>, GABr were purchased from TCI. CsI, anhydrous dimethylformamide (DMF), dimethylsulfoxide (DMSO), isopropanol (IPA), acetonitrile, 4-tert-butylpyridine (TBP), bis(trifluoromethane) sulfonimide lithium salt (Li-TFSI) and [tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) tris(bis(trifluoromethylsulfonyl)imide) (FK209) were obtained from Sigma-Aldrich. Spiro-OMeTAD was purchased from Ying Kou You Xuan; All the chemicals were used without further purification.

*Device Fabrication:* ITO-based glass substrate was sequentially rinsed by sonication in detergent, deionized water, acetone, and ethanol, and dried with an N<sub>2</sub> blow gun. ZnO electron transport layers were prepared according to previously published works. ZnO precursor (100mg Zn(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O and 28.29 μL E-thanolamine dissolved in 973 μL 2-Methoxyethanol) spin coated on the ITO substrates with a spin-rate of 4000rpm for 30s and then annealing for 30 min at 200°C. The neat CsPbI<sub>2</sub>Br precursor was prepared by dissolving CsI (1.05M), PbI<sub>2</sub> (0.525M) and PbBr<sub>2</sub> (0.525M) in mixed solvent DMSO and DMF(6:4, v/v). The GAPbI<sub>2</sub>Br solution was obtained by dissolving 0.1M GABr and PbI<sub>2</sub> in mixed solvent DMSO and DMF (6:4, v/v). CsPbI<sub>2</sub>Br precursor solution mixed with GAPbI<sub>2</sub>Br solution to achieve a doping concentration within 1%. The perovskite precursor solution was spin coated on substrate at 2500 rpm for 45 s. After the spin coating, the films were heated on a hotplate from 40 °C to 140 °C for 10 min. To realize the surface treatment, the GABr first dissolved into IPA solvent (3 mg/ml), and then spin coated onto the perovskite surface at the speed of 5000 rpm for 30s, followed by annealing at 140 °C for 3 min. A layer of the hole transporting material composed of 72.3 mg spiro-OMeTAD, 28.8 μL TBP, and 28.8μL FK209 (300mg in 1 mL acetonitrile and 17.5 μL Li-TFSI solution (520 mg in 1 mL acetonitrile) in 1 mL chlorobenzene was spin coated on perovskite film at 4000 rpm for 30 s. Finally, a 70 nm Au electrode contact layer was deposited by thermal evaporation.

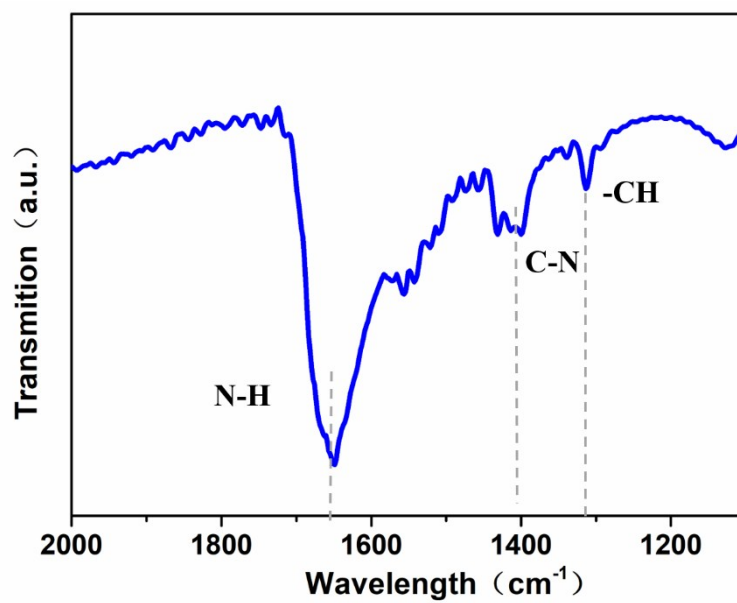
*In Situ GIWAXS Experiments:* In situ GIWAXS measurements were performed at 23A small and wide-angle X-ray scattering (SWAXS) beamline at the National Synchrotron

Radiation Research Center (NSRRC), Hsinchu, Taiwan. The wavelength of X-ray was 1.240 Å (10 keV). The scattering signals were collected by a C9728DK area detector. The lanthanum hexaboride (LaB6) sample was used to calibrate. The incident angle was kept at 2° to enhance the signal resolution with a frame exposure time of 3 s. The spin-coating process was conducted in an air-tight chamber under N<sub>2</sub> flow at a designated timing during the whole 300 s spinning process at 1500 rpm. GIWAXS measurement and sample spinning could be triggered simultaneously.

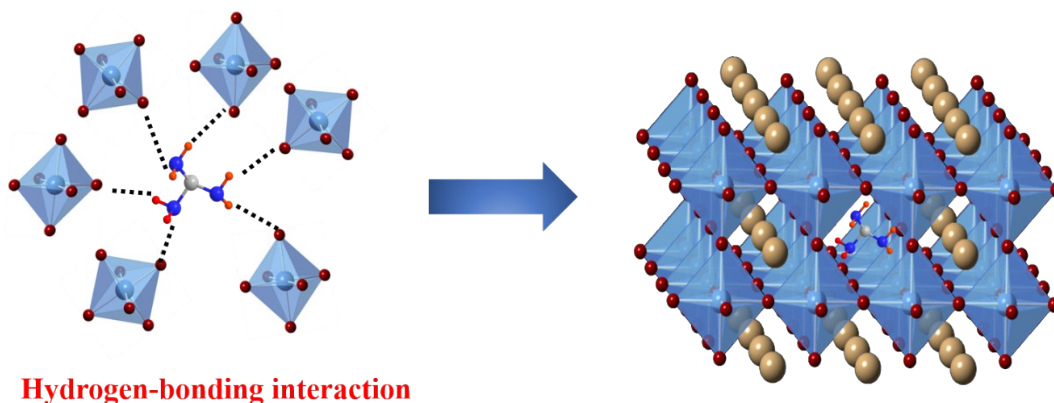
*Materials Characterizations:* UV–vis absorption spectra were taken on a Hitachi U-3501 UV/visible/NIR spectrophotometer. The current density–voltage (J–V) curves were measured by a Keithley 2400 source meter unit under an AM 1.5G solar simulator (100 mW cm<sup>-2</sup>). The devices were measured without pretest illumination and bias poling. The SEM images of the perovskite films were observed by high-resolution field emission scanning electron microscopy (HR-FESEM) (FEI, Quanta 400). The crystalline structures of the prepared perovskite films were measured by X-ray diffraction (Rigaku, Smart Lab). Steady-state PL spectra measurements were taken at room temperature using commercially available Raman/PL spectrometer (Horiba, Inc.). The functional groups of GA were measured by FTIR (Thermo Nicolet, Nexus). The ex-situ GIWAXS measurements were carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300K detector. The incidence angle is 0.3°. XPS characterization of the prepared perovskite films was measured at BL09A2 U5 beamline at the National Synchrotron Radiation Research Center (NSRRC), Taiwan, with an incident photon energy of 750 eV. Before testing the samples, we calibrate the standard deviation using an Au sample. The reference binding energies (eV) (Mg Kα) of Au (4f 7/2) is 84.00 eV.



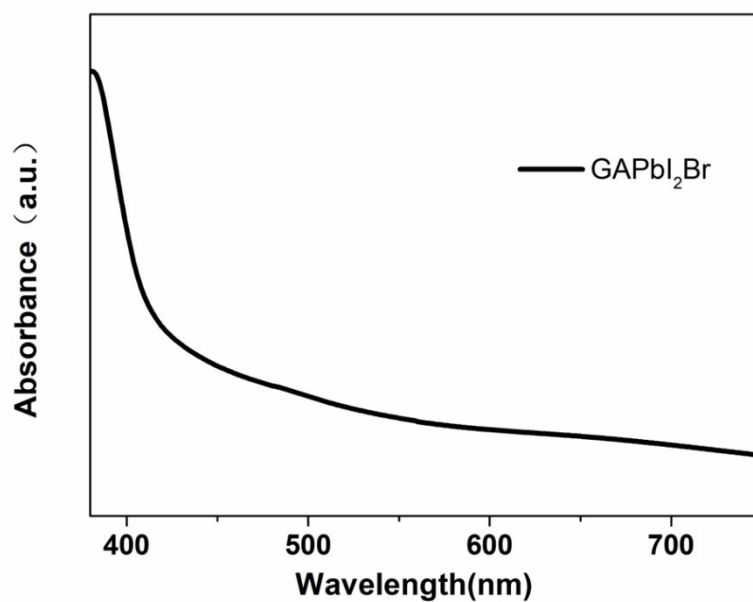
**Fig S1.** The XRD pattern of GAPbI<sub>2</sub>Br.



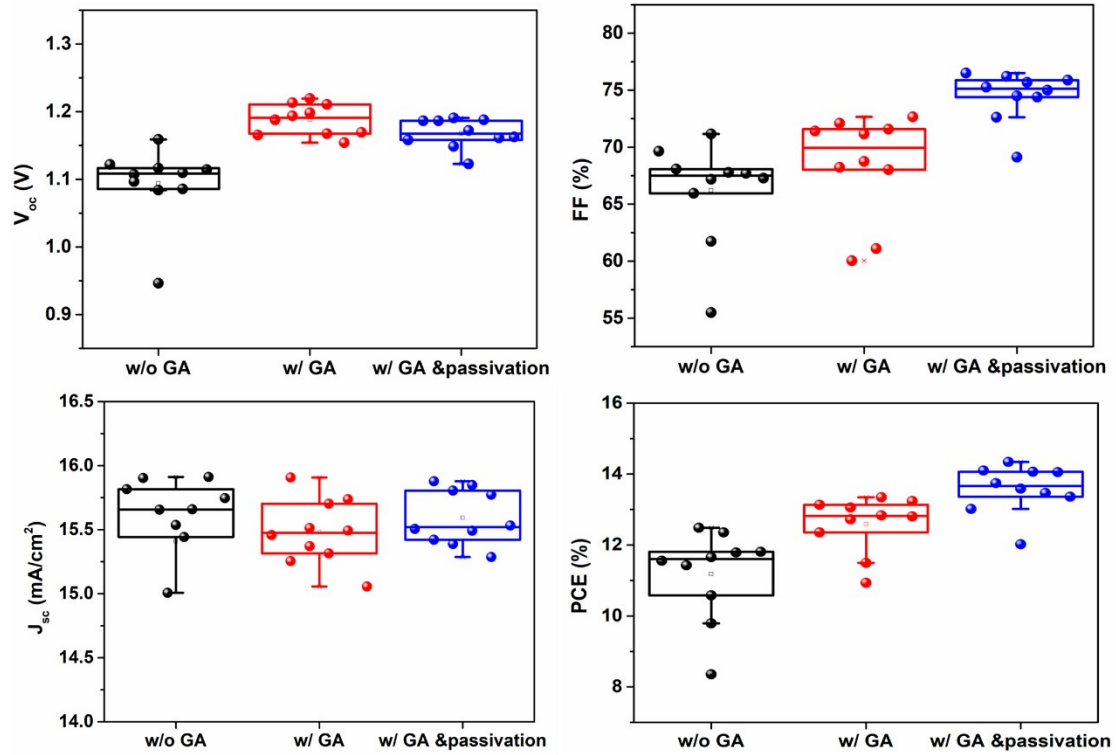
**Fig S2.** The FTIR spectrum of GAPbI<sub>2</sub>Br.



**Fig S3.** Schematic illustration of role of the GA in crystallization process and hydrogen-bonding interaction between GA and lead-halide framework



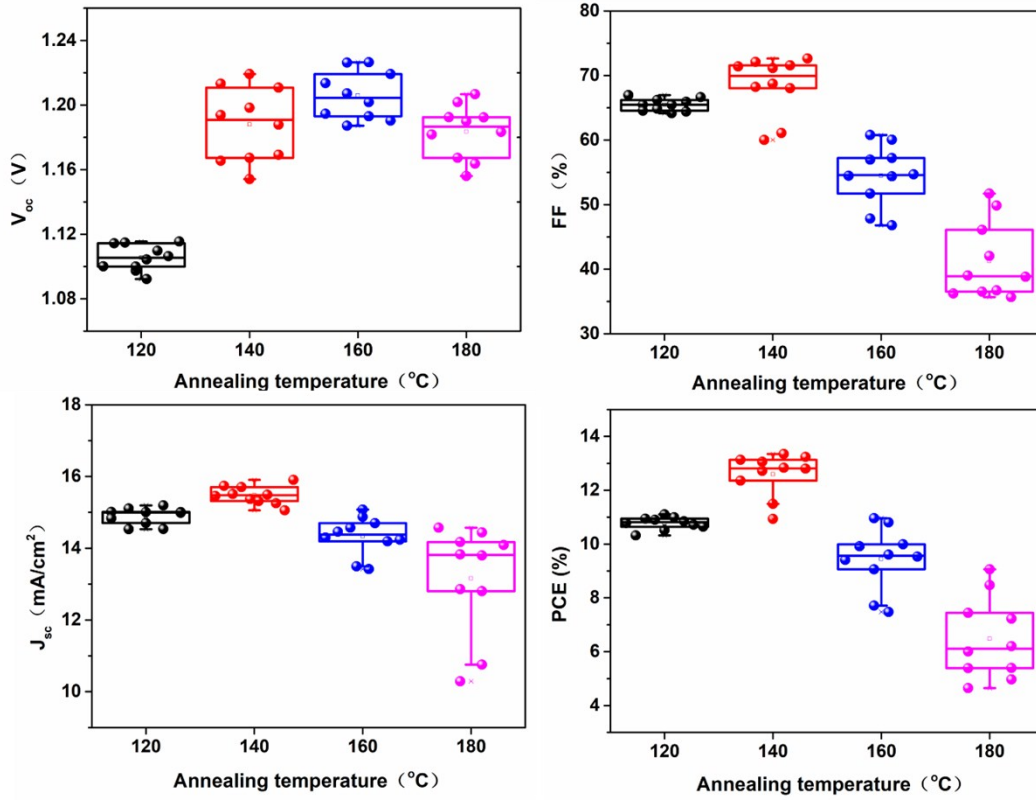
**Fig S4.** Ultraviolet-visible (UV-vis) spectra of GAPbI<sub>2</sub>Br films.



**Fig S5.** Box plots of the 10 devices performance parameters for the PSCs based on the perovskite film without GA, with GA, and with GA and passivation.

**Table S1.** The average photovoltaic parameters of the PSCs based on the perovskite film without GA, with GA, and with GA and passivation.

Devices	$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA cm}^{-2}$ )	FF	PCE (%)
w/o GA	$1.09 \pm 0.15$	$15.40 \pm 0.74$	$0.66 \pm 0.11$	$11.18 \pm 2.83$
w/ GA	$1.18 \pm 0.03$	$15.48 \pm 0.43$	$0.68 \pm 0.04$	$12.59 \pm 1.66$
w/GA& passivation	$1.17 \pm 0.05$	$15.59 \pm 0.31$	$0.74 \pm 0.05$	$13.57 \pm 0.77$



**Fig S6.** Box plots of the 10 devices performance parameters for the PSCs based on the GA doped perovskite film with different annealing temperature.

**Table S2.** The average photovoltaic parameters of the PSCs based on the on the GA doped perovskite film with different annealing temperature.

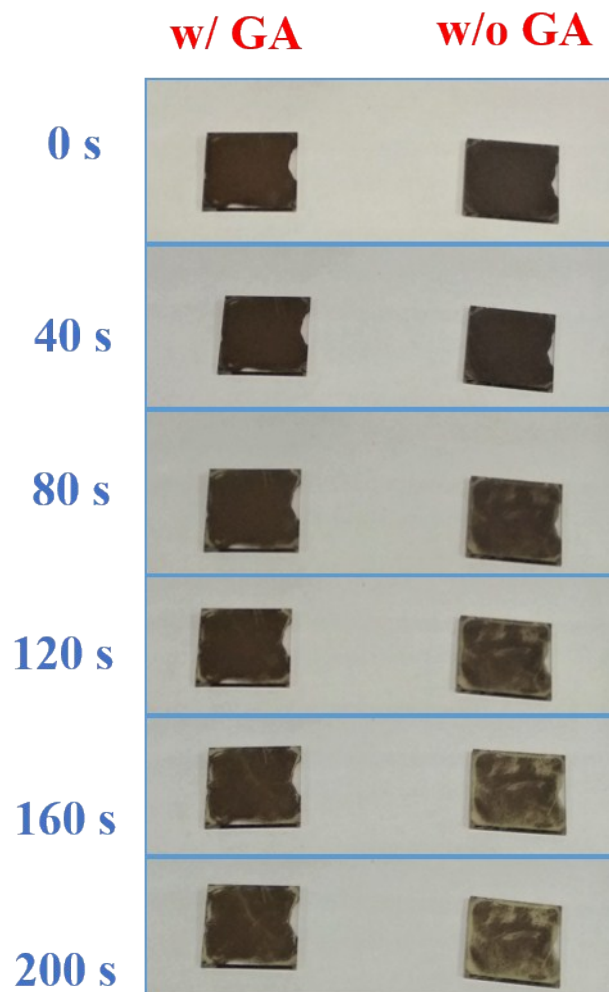
Temperature (°C)	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF	PCE (%)
120	1.10±0.02	14.89±0.30	0.65±0.13	10.77±0.33
140	1.18±0.03	15.48±0.43	0.68±0.04	12.59±1.66
160	1.20±0.02	14.33±0.74	0.54±0.09	9.44±0.51
180	1.18±0.03	13.16±1.41	0.41±0.15	6.48±1.84

**Table S3.** The summary of photovoltaic parameters of the All-reported CsPbI<sub>2</sub>Br PSCs prepared at a low fabrication temperature (<150 °C)

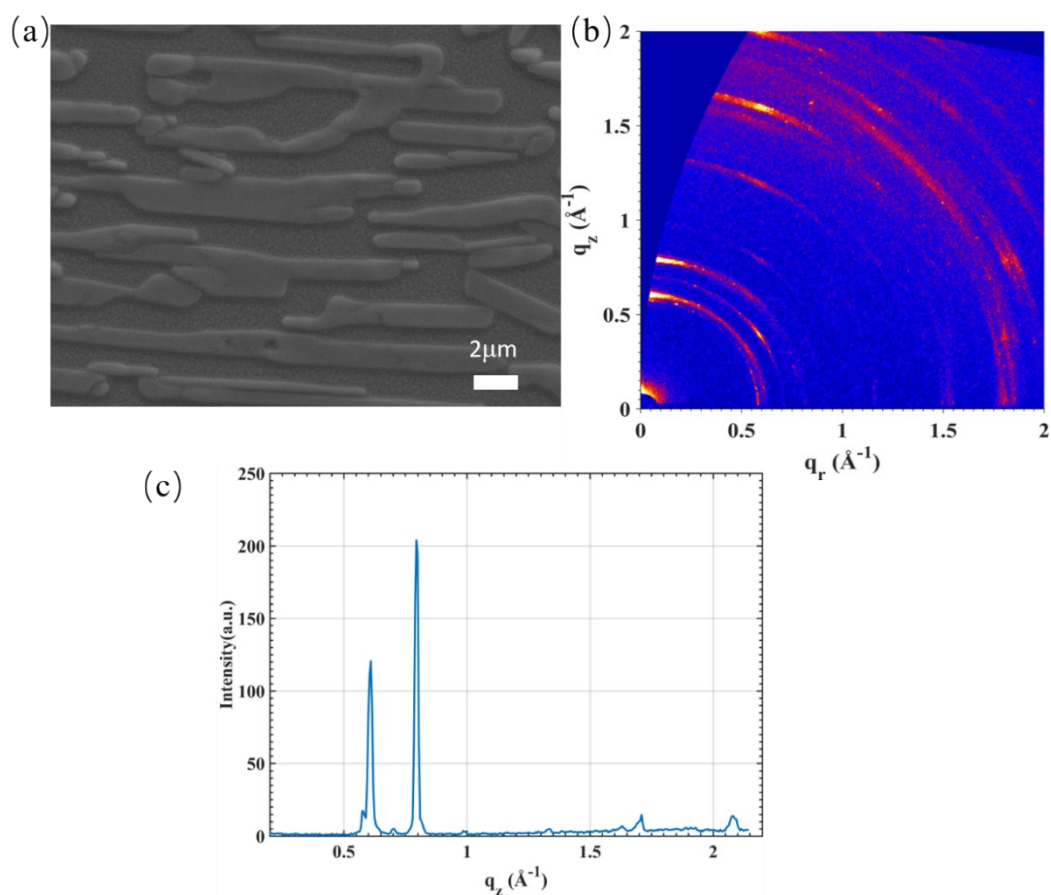
Device structure	Temperature (°C)	$V_{OC}$ (V)	$J_{SC}$ (mA cm <sup>-2</sup> )	$FF$	PCE (%)	Ref.
FTO/TiO <sub>2</sub> /CsPbI <sub>2</sub> Br/spiro-OMeTAD/Au	130	1.13	13.6	0.69	10.6	[1]
FTO/TiO <sub>2</sub> /CsPbI <sub>2</sub> Br/P3HT/Au	100	0.96	13.4	0.60	7.7	[2]
FTO/TiO <sub>2</sub> /CsPb <sub>0.95</sub> Sr <sub>0.05</sub> I <sub>2</sub> Br/P3HT/Au	100	1.06	14.9	0.71	11.3	[2]
ITO/NiO <sub>x</sub> /CsPbI <sub>2</sub> Br/C60/Bathocuproine (BCP)/Ag	120	1.05	12.6	0.79	10.4	[3]
PET/ITO/NiO <sub>x</sub> /CsPbI <sub>2</sub> Br/C60/BCP/Ag	120	0.97	11.5	0.65	7.3	[3]
FTO/TiO <sup>[1]</sup> /CsPbI <sub>2</sub> Br/spiro-OMeTAD/Au	120	1.18	14.9	0.77	13.5	[4]
PET/ITO/Nb <sub>5</sub> O <sub>2</sub> /CsPbI <sub>2</sub> Br/spiro-OMeTAD/Au	130	1.19	14.6	0.77	11.7	[4]
ITO/SnO <sub>2</sub> /CsPbI <sub>2</sub> Br/PTAA/Au	100	1.16	15.56	0.79	14.31	[5]



ITO/PEDOT:PSS / CsPbI <sub>2</sub> Br /PCBM/BCP/Al	135	1.06	10.9	0.58	6.8	[6]
ITO/SnO <sub>2</sub> / CsPbI <sub>2</sub> Br /Spiro- OMeTAD/Au	100	1.10	14.3	0.70	10.99	[7]
ITO/ZnO/CsPbI <sub>2</sub> Br/ spiro- OMeTAD/Au	140	1.19	15.8	0.76	14.34	This work



**Fig S7.** A series of photographs of the CsPbI<sub>2</sub>Br film with and without GA for different amount of time durations in ambient condition with around 50% relative humidity.



**Fig S8.** (a) SEM images of the GAPbI<sub>2</sub>Br film. (b) GIWAXS patterns of the of the GAPbI<sub>2</sub>Br film perovskite. (c) Diffraction intensity along  $q_z$  direction.

## References

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