## Amidinium additives for high-performance perovskite solar cells

Yue Ma<sup>1§</sup>, Na Liu<sup>1§</sup>, Huachao Zai<sup>2\*</sup>, Rundong Fan<sup>2</sup>, Jiaqian Kang<sup>3</sup>, Xiaoyan Yang<sup>1</sup>, Fengtao Pei<sup>2</sup>, Wentao Zhou<sup>2</sup>, Hao Wang<sup>1</sup>, Yihua Chen<sup>1</sup>, Lina Wang<sup>1</sup>, Jiawang Hong<sup>3</sup>, Yang Bai<sup>1</sup>, Huanping zhou<sup>2</sup> and Qi Chen<sup>1\*</sup>

<sup>1</sup>Beijing Key Laboratory of Construction Tailorable Advanced Functional Materials and Green Applications, Experimental Center of Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China.

<sup>2</sup>Beijing Key Laboratory for Theory and Technology of Advanced Battery Materials, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, BIC-ESAT, School of Materials Science and Engineering, Peking University, Beijing 100871, China.

<sup>3</sup>School of Aerospace Engineering, Beijing Institute of Technology, Beijing 100081, China

<sup>§</sup>These authors contributed equally to this work.

\*Correspondence: zaihuachao@pku.edu.cn; qic@bit.edu.cn



**Figure S1.** Atomic force microscopy (AFM) of perovskite films with and without BRCl additive.



**Figure S2.** Size distributions of PbI<sub>2</sub> complexes in complex-precursor system detected by dynamic light scattering (DLS).



**Figure S3.** Top-view scanning electron microscope (SEM) images and grain size distribution of perovskite films a) without, and b) with 1 mg/mL BRCl additive annealed at 150°C for different times.



**Figure S4.** (a) The perovskite grain size is summarized as a function of annealing time, (b) and corresponding derivative curve.



Figure S5. (a) Thermogravimetric analysis (TGA) results of BRCl powder, (b) and corresponding derivative curve.



**Figure S6.** Energy dispersive spectroscopy (EDS) results of perovskite films. (a) 0 mg/mL BRCl. (b) 0.5 mg/mL BRCl. The blue line represents the Pb signal, green line represents the Cl signal, red line represents the I signal. The accelerating voltage is 7 kV.



**Figure S7.** Energy dispersive spectroscopy (EDS) results of grain boundaries. (a) 0 mg/mL BRC1. (b) 0.5 mg/mL BRC1. The accelerating voltage is 7 kV. Energy dispersive spectroscopy (EDS) results of grain interior. (c) 0 mg/mL BRC1. (d) 0.5 mg/mL BRC1. The accelerating voltage is 15 kV.



Figure S8. Reciprocal of FWHM of perovskite film with different BRCl concentrations.



**Figure S9.** UV-visible absorption spectra and its Tauc plot of perovskite films with 0 and 0.05 mg/mL BRCl additive.



Figure S10. XPS spectra of the perovskite film with 0 and 0.05 mg/mL BRCl additive.



**Figure S11.** (a) Steady-state photoluminescence (PL) spectra of control perovskite films with and without surface passivation. (b) Top-view SEM images of control perovskite films with and without surface passivation. The scale bars are 1  $\mu$ m.

Sample	$A_1$	$ au_1$	A <sub>2</sub>	$ au_2$
Control	0.61	71.60	0.27	293.23
BRC1	0.12	85.48	0.58	434.04

Control BRCI 650 700 750 800 850 900 Wavelength (nm)

**Figure S12.** Steady-state photoluminescence (PL) spectra of perovskite films prepared on glass with 0 and 0.05 mg/mL BRCl additive.

Sample	Thickness-1	Thickness-2	Thickness-3	Average
Control	609 nm	624 nm	645 nm	626 nm
BRC1	629 nm	624 nm	625 nm	626 nm

Table S2. Thickness of perovskite layer measured by step profiler.

Table S1. Parameters of the TRPL spectra of perovskite films deposited on glass substrates.



**Figure S13.** Box-chart for PCE of PSCs fabricated using different concentrations of BRCl additive.



Figure S14. Incident photon-to-current conversion efficiency (IPCE) spectra and integrated short-circuit current density  $(J_{SC})$  of the control and BRCl-assisted PSCs.



**Figure S15.** Transient photovoltage (TPV) curves for the hybrid PSCs with 0 and 0.05 mg/mL BRCl additive.



**Figure S16.** Thermal stability of the devices is tested at 85 °C in an N<sub>2</sub> filled glovebox, the results were verified in 16 cells, 8 for each condition. The tested devices are fabricated with the following device configuration: ITO/SnO<sub>2</sub>/perovskite/PTAA/Au. The initial average PCE values for control and BRCl-assisted are 21% and 22%.