

Supplementary Information

Passivation Effect of Halogenated Benzylammonium as Second Spacer Cation for Improved Photovoltaic Performance of Quasi-2D Perovskite Solar Cells

Guozhen Liu,^{ab} Xiao-Xiao Xu,^{ab} Shendong Xu,^{ab} Liying Zhang,^{ab} Huifen Xu,^{ac} Liangzheng Zhu,^a Xianxi Zhang,^d Haiying Zheng^{*c} and Xu Pan^{*a}

^aKey Laboratory of Photovoltaic and Energy Conservation Materials, Institute of Applied Technology, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei 230031, China.

^bUniversity of Science and Technology of China, Hefei 230026, China.

^cInstitutes of Physical Science and Information Technology, Anhui University, Hefei 230601, China.

^dShandong Provincial Key Laboratory/Collaborative Innovation Center of Chemical Energy Storage & Novel Cell Technology, School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252000, China.

Corresponding Authors

*E-mail: hyzheng@ahu.edu.cn (H. Zheng), xpan@rntek.cas.cn (X. Pan)

Experimental section

Materials

Lead (II) iodide (PbI_2), lead(II) bromide (PbBr_2) and cesium iodide (CsI) were obtained from TCI. N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), isopropanol and chlorobenzene were purchased from Innochem. 4-tert-butylpyridine (tBP), lithium bis (trifluoromethylsulphonyl) imide (Li-TFSI), titanium isopropoxide and bis(acetylacetonate) were acquired from Aldrich. Spiro-MeOTAD was purchased from Xi'an Polymer Light Technology Corp. Formamidinium iodide (FAI) and formamidinium bromide (FABr) were prepared in our laboratory which are consistent with ESI of previous work [34]. Other reagents have been come from Alfa or Sinopharm and all purchased reagents are used directly without further treatment.

Perovskite Solar Cells Fabrication

The compact layer of TiO_2 was deposited on the FTO by spray pyrolysis at 460 °C. For the TiO_2 solution, 0.6 mL of titanium diisopropoxide bis(acetylacetonate) was added into 6 ml anhydrous isopropanol. The mesoporous layer of TiO_2 was prepared by spin-coating Dyesol paste (30 nm particle size) which was diluted by ethanol with a mass ratio of 5.5 times to deposit on the substrate at 4000 r.m.p. for 20 s. Then the substrate was annealing at 510 °C for 30 minutes. The perovskite precursor solutions (1.35 M Pb^{2+}) of corresponding amount of material powder were dissolved in mixed solvent of DMF and DMSO (DMF:DMSO=4:1) and stirred at 65 °C for 1h. In the glove box with flowing dry air (about 20% RH), the quasi-2D perovskite light absorption layer was fabricated by spin-coating perovskite precursor solutions in two steps: the first step was 11 s at 1100 r.p.m. and the second step was 33 s at 4600 r.p.m. At the last 15 s of the second process, 120 μL of chlorobenzene was added to the perovskite layer rapidly and evenly by burette. Then, the substrate was rapidly annealed at 100 °C for 50 min. After cooling to room temperature,

the hole transport layer was deposited at 3000 r.p.m. for 20 s. The hole transport layer solution was made up of 73 mg spiro-OMeTAD, 29 μL 4-tert-butylpyridine (tBP), 17 μL Li^+ salt and 8 μL cobalt (III) salt dissolving in 1 mL of chlorobenzene. Finally, 60 nm of Au electrode was evaporated by thermal vacuum on the HTL layer.

Characterizations

XRD patterns were obtained by the Smartlab 9 KW. UV-vis absorption spectra were obtained by the Hitachi U-3900H UV-vis spectrophotometer. SEM images were scanned by high resolution field emission scanning electron microscope (FE-SEM, sirion200, FEI Corp., Netherlands). Photoluminescence (PL) spectra were measured via exciting the perovskites at 500 nm. The data were recorded on a Spectro fluorometer (photon technology international) using the standard 450 W Xenon CW lamp and analyzed by fluorescence software. An LKS (Applied photophysics) with laser device energy of 150 $\mu\text{J cm}^{-2}$ and repetition rate of 5 Hz was used to record the transient absorption (TA) spectra with a probe light of 760 nm and a laser light of 500 nm. The EIS was tested in the dark using an Autolab analyzer (Metrohm, PGSTAT 302N, Switzerland) with frequencies ranging from 1 Hz to 1 MHz. *J-V* curves were gained by using the solar simulator (Newport, Oriel a, 91195A) and a source meter (Keithley 2420). The solar simulator with 100 mW cm^{-2} illumination AM 1.5G was calibrated by using NREL certified silicon reference cell. By shielding a black mask, the device maintained an active area of 0.09 cm^2 . Incident photon-to-electron conversion efficiency (IPCE) with wavelength of 350-850 nm were measured in DC mode without biased light and executed on dual Xenon/quartz halogen light source (PV Measurements, Inc.). The water contact angles were tested by OCA15EC contact angle measuring instrument (Dataphysics, Germany). The humidity aging measurements were performed in sealed containers with relative humidity of $45\pm 5\%$ RH. These containers maintained at room temperature. The

thermal aging measurement was in a sealed container at 85 °C with a relative humidity of about 10%.

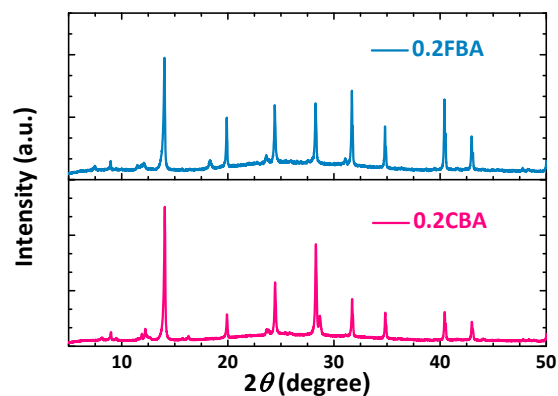


Figure S1. XRD patterns of 0.2FBA and 0.2CBA perovskite films.

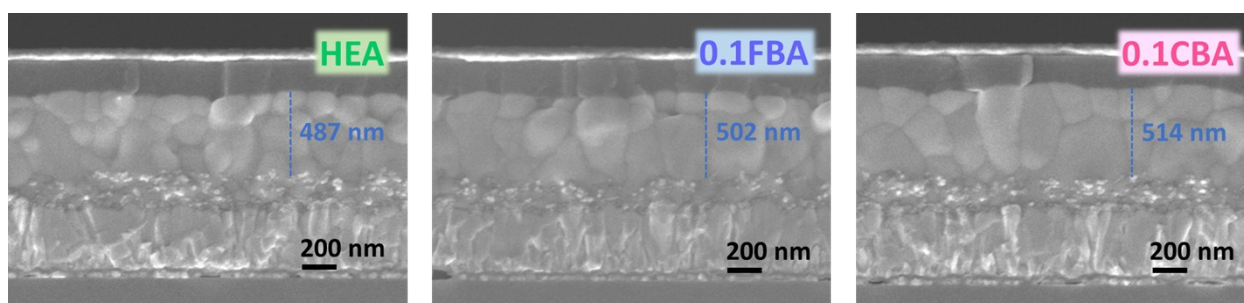


Figure S2. Cross-view SEM images of HEA, 0.1FBA and 0.1CBA perovskite devices.

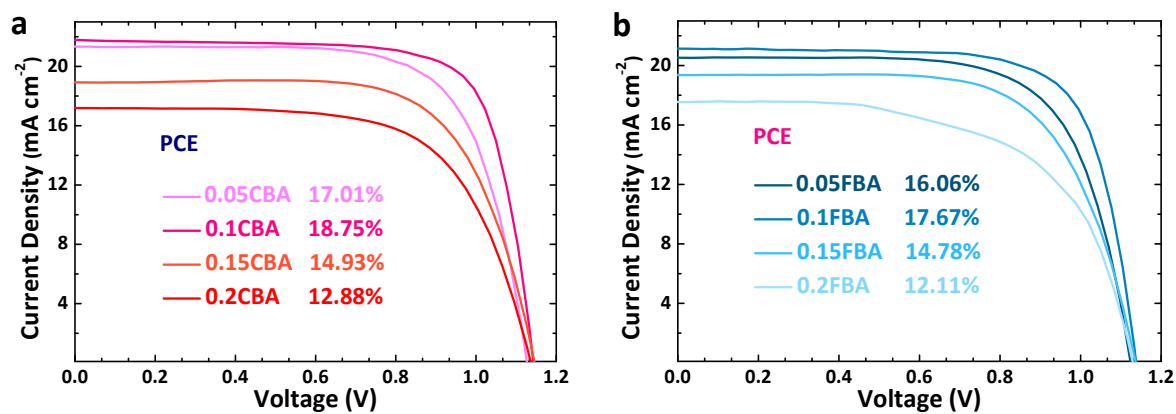


Figure S3. *J-V* curves of (a) xFBA and (b) xCBA ($x = 0.05, 0.1, 0.15$ and 0.2) perovskite devices.

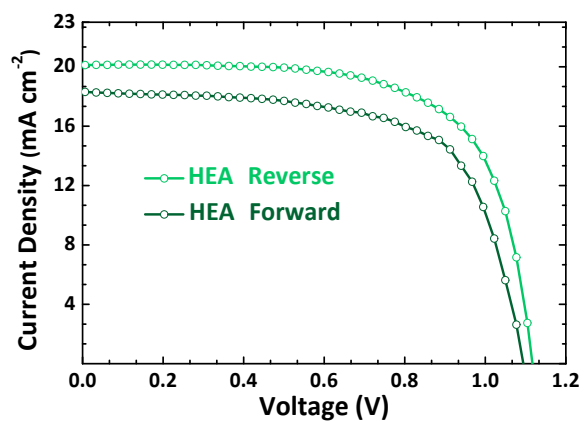


Figure S4. J - V curves of HEA perovskite devices under reverse and forward scan directions.

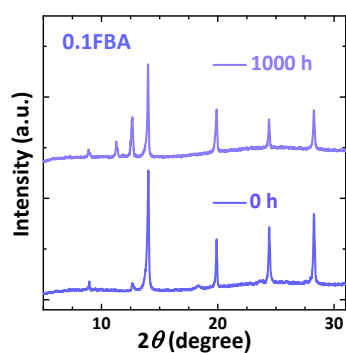


Figure S5. XRD patterns of 0.1FBA perovskite film before and after aging under 45±5% RH.

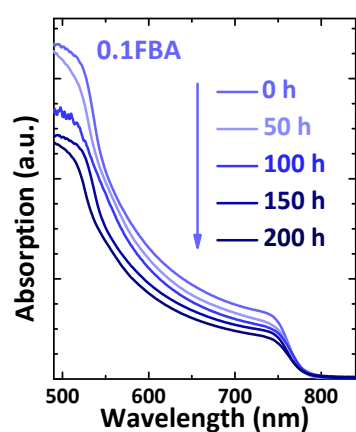


Figure S6. UV-vis absorption spectra of 0.1FBA perovskite film before and after aging at 85 °C.

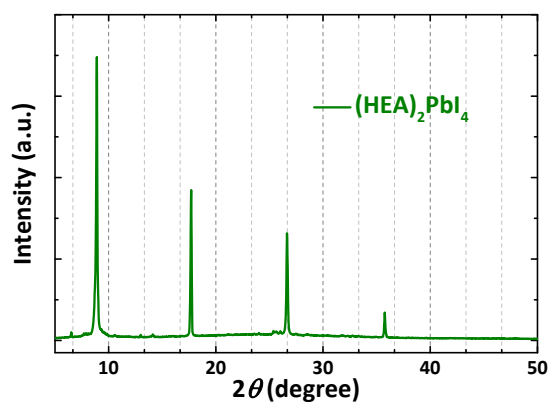


Figure S7. XRD pattern of 2D $(\text{HEA})_2\text{PbI}_4$ perovskite.

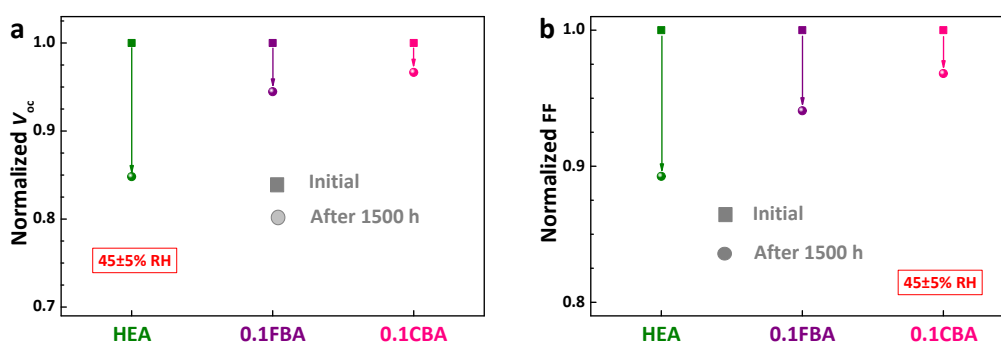


Figure S8. Normalized (a) V_{oc} and (b) FF variations of unsealed HEA, 0.1FBA and 0.1CBA perovskite devices aging at 45±5% RH for 1500 h.

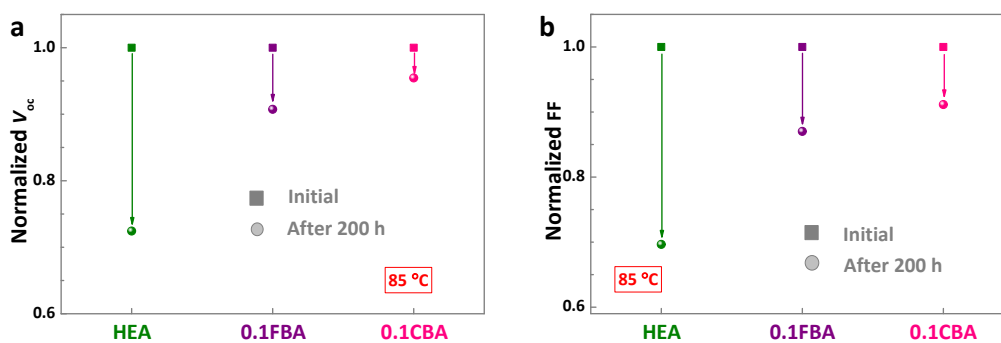


Figure S9. Normalized (a) V_{oc} and (b) FF variations of unsealed HEA, 0.1FBA and 0.1CBA perovskite devices aging at 85 °C for 200 h.

Table S1. Parameters of the EIS of HEA, 0.1FBA and 0.1CBA perovskite solar cells.

	R_s (Ω)	R_{rec} (Ω)	C (F)
HEA	26.05	4181	$5.22 \cdot 10^{-9}$
0.1FBA	21.57	7211	$1.08 \cdot 10^{-8}$
0.1CBA	18.77	8915	$2.09 \cdot 10^{-8}$

Table S2. Photovoltaic parameters of the HEA, 0.1FBA and 0.1CBA devices under reverse and forward scan directions.

Device		J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)
HEA	Reverse	20.12	1.117	67.56	15.19
	Forward	18.31	1.095	66.36	13.31
0.1FBA	Reverse	21.17	1.138	73.32	17.67
	Forward	20.56	1.136	70.95	16.54
0.1CBA	Reverse	21.75	1.143	75.39	18.75
	Forward	21.24	1.137	74.91	18.09

Table S3. Photovoltaic parameters of xFBA and xCBA (x= 0.05, 0.1, 0.15 and 0.2) PSCs.

Device	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)
0.05FBA	20.54	1.124	69.56	16.06
0.1FBA	21.17	1.138	73.32	17.67
0.15FBA	19.38	1.135	67.15	14.78
0.2FBA	17.55	1.130	61.08	12.11
0.05CBA	21.33	1.127	70.72	17.01

0.1CBA	21.75	1.143	75.39	18.75
0.15CBA	18.92	1.146	68.87	14.93
0.2CBA	17.19	1.137	65.87	12.88

Table S4. The measured electron trap-state density (N_t) of devices based on different perovskite films.

Device	HEA	0.1FBA	0.1CBA
L (nm)	487	502	517
V_{TFL} (V)	0.45	0.24	0.20
N_t (cm ⁻³)	7.35*10 ¹⁵	3.69*10 ¹⁵	3.01*10 ¹⁵

Table S5. The statistics photovoltaic parameters of HEA, 0.1FBA and 0.1CBA PSCs.

HEA	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
1	19.65	1.12	65.40	14.33
2	19.36	1.12	69.19	14.98
3	19.66	1.10	70.85	15.19
4	20.03	1.12	62.84	14.11
5	19.52	1.11	64.46	13.93
6	18.84	1.11	67.92	14.19
7	19.37	1.10	65.03	13.84
8	19.42	1.10	68.21	14.60
9	20.16	1.10	67.52	15.03
10	19.94	1.12	63.67	14.23
11	19.46	1.11	64.23	13.81
12	20.13	1.10	65.22	14.51
13	19.66	1.10	68.83	14.86
14	19.57	1.10	66.11	14.20

15	19.17	1.10	69.56	14.60
16	19.19	1.12	67.99	14.64
17	19.39	1.10	65.88	14.02
18	19.09	1.11	69.53	14.72
19	19.32	1.11	69.25	14.83
20	19.82	1.10	64.65	14.04
21	20.17	1.12	65.67	14.89
22	20.28	1.11	67.63	15.19
23	19.59	1.11	69.60	15.16
23	19.18	1.10	65.33	13.77
25	19.91	1.11	67.98	15.08
26	19.82	1.12	65.86	14.61
27	19.85	1.11	65.66	14.51
28	19.51	1.11	62.11	13.46
29	20.02	1.12	63.12	14.12
30	19.43	1.11	64.21	13.81
0.1CBA	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
1	20.21	1.12	75.12	16.97
2	21.12	1.13	74.83	17.84
3	22.16	1.13	71.23	17.75
4	21.70	1.12	72.90	17.67
5	21.78	1.14	69.88	17.29
6	21.09	1.13	73.51	17.55
7	21.93	1.12	74.33	18.30
8	21.18	1.14	75.06	18.16
9	21.93	1.13	74.41	18.39
10	20.51	1.14	75.04	17.59
11	21.32	1.15	76.02	18.57
12	21.09	1.14	72.55	17.37
13	20.91	1.14	75.92	18.12

14	21.13	1.12	73.92	17.56
15	21.08	1.13	75.74	17.96
16	21.37	1.11	77.29	18.40
17	21.95	1.12	74.48	18.38
18	21.35	1.13	76.66	18.53
19	20.38	1.13	74.86	17.29
20	21.78	1.13	71.29	17.51
21	20.73	1.13	77.28	18.15
22	21.94	1.13	75.85	18.75
23	21.25	1.14	69.62	16.82
23	21.59	1.14	73.95	18.13
25	22.07	1.13	71.04	17.64
26	21.37	1.13	74.13	17.97
27	21.41	1.13	73.93	17.87
28	21.26	1.13	75.91	18.22
29	21.57	1.14	75.40	18.48
30	20.99	1.13	72.72	17.17
0.1FBA	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
1	20.90	1.13	74.45	17.52
2	20.75	1.11	72.74	16.77
3	20.48	1.13	73.44	16.98
4	21.12	1.14	71.15	17.10
5	21.17	1.12	68.16	16.22
6	20.44	1.12	72.04	16.48
7	20.26	1.14	69.65	16.03
8	20.98	1.13	72.14	17.09
9	20.90	1.12	75.16	17.52
10	20.75	1.13	70.65	16.52
11	20.48	1.12	73.47	16.90
12	20.92	1.13	71.10	16.80

13	21.17	1.11	72.74	17.05
14	20.44	1.12	71.94	16.49
15	20.26	1.13	69.71	15.89
16	21.28	1.14	69.97	16.93
17	20.92	1.12	73.94	17.31
18	19.52	1.13	75.17	16.56
19	21.03	1.12	70.61	16.62
20	21.49	1.12	72.28	17.44
21	20.52	1.14	73.52	17.18
22	20.39	1.14	76.16	17.67
23	19.79	1.11	74.97	16.45
23	20.22	1.12	75.08	17.06
25	21.15	1.11	73.74	17.37
26	20.99	1.13	71.44	15.90
27	20.45	1.11	74.12	16.80
28	20.39	1.13	72.51	16.75
29	21.08	1.12	73.86	17.41
30	20.90	1.13	72.14	17.10