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# Alkali-Cation-Enhanced Benzylammonium Passivation for Efficient and Stable Perovskite Solar Cells Fabricated Through Sequential Deposition

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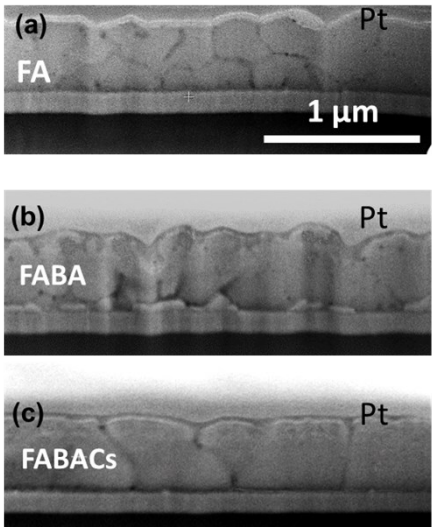


**Fig. S1** Cross-sectional SEM images of FA, FABA and FABACs films.

The measured thickness values of the FA, FABA and FABACs samples are 440 nm, 452 nm and 445 nm, respectively. There is a standard deviation of 6 nm in the thickness values. We believe this is a common variation seen in different fabrication batches. Note that we have also measured the thickness of our samples via other means (e.g., stylus profiler) and did not find the FABA samples are systematically thicker than the FA and FABACs samples. A few islanded small grains are observed at the bottom of the FABA perovskite, which might be induced by a special nucleation and crystallization process (Ref. [S1, S2]).

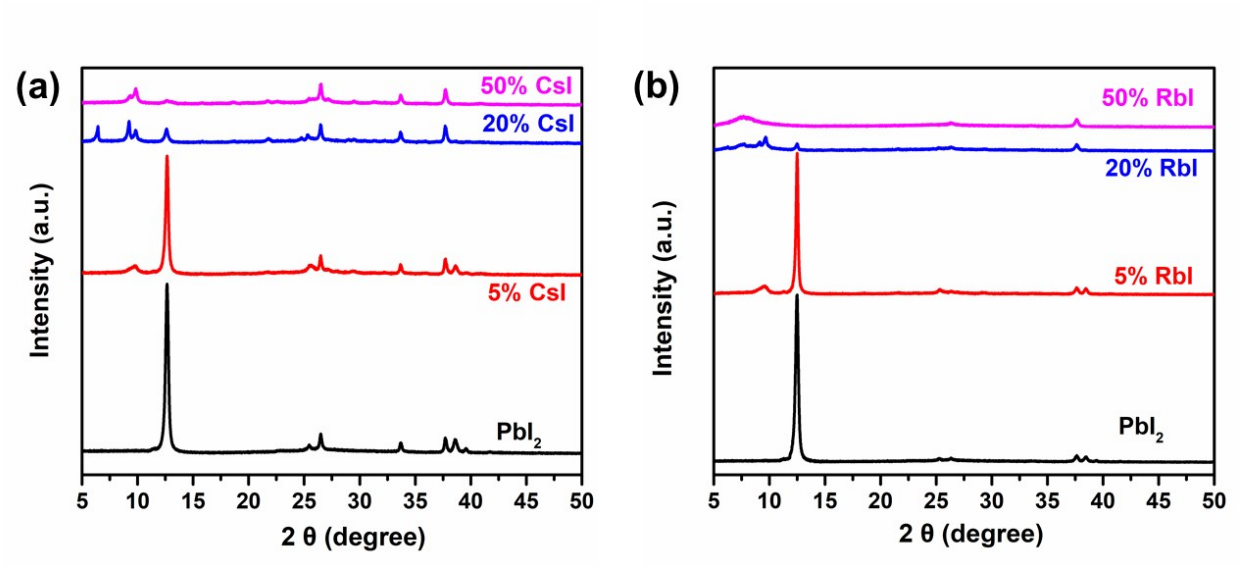


**Fig. S2** XRD patterns of the $PbI_2$ films with and without inclusion of (a) CsI or (b) RbI.

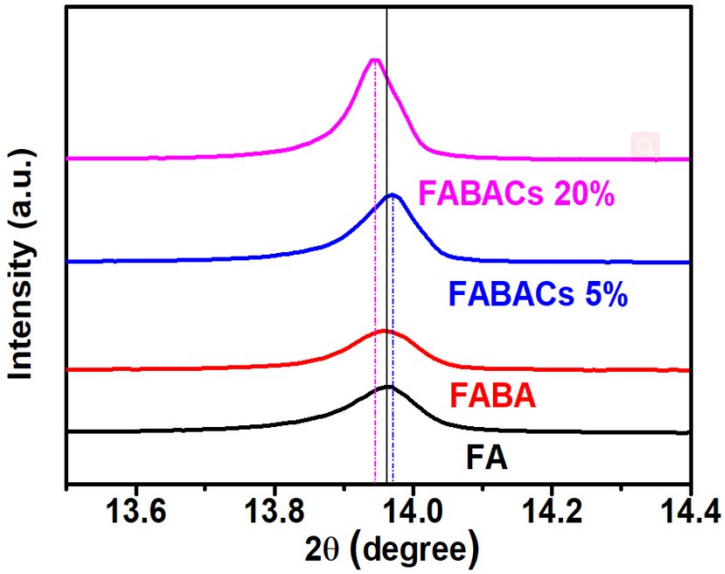


**Fig. S3** Perovskite diffraction peaks around 14° extracted from the XRD patterns of FA, FABA and FABACs films.

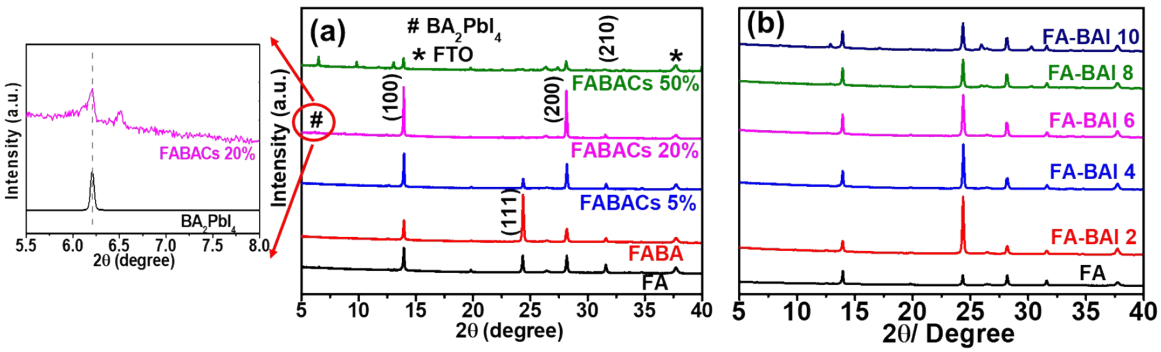


**Fig. S4** (a) XRD patterns of FA, FABA and FABACs incorporated with CsI of different molar ratios. (b) XRD patterns of FA and FABA incorporated with BAI of different weight concentration, the number stands for the weight concentration of BAI in the organic mixture solution, unit: mg/mL.

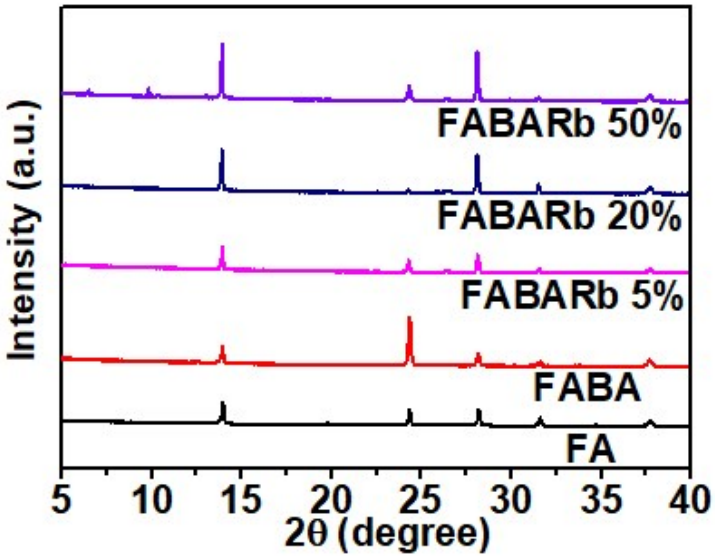


**Fig. S5** XRD patterns of FA, FABA and FABARb incorporated with RbI of different molar ratios.

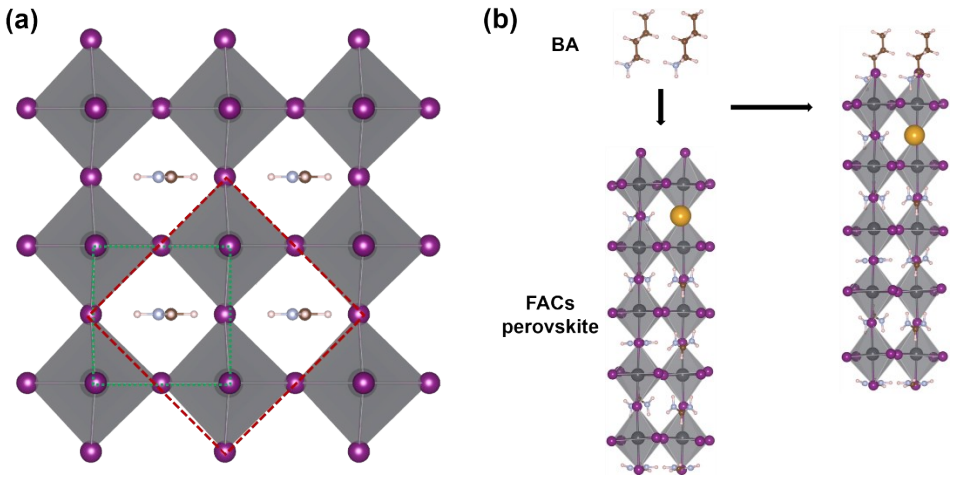


**Fig. S6** (a) Scheme of the construction of $\sqrt{2} \times \sqrt{2}$ supercell (top view). The green square indicates the unit cell of cubic $FAPbI_3$. The red square shows the $\sqrt{2} \times \sqrt{2}$ supercell of cubic $FAPbI_3$. The $BA^+$-passivated model is then constructed by replacing two $FA^+$ on the surface with two $BA^+$. (b) Schematic representation of the $BA^+$-passivated perovskite surfaces (side view).

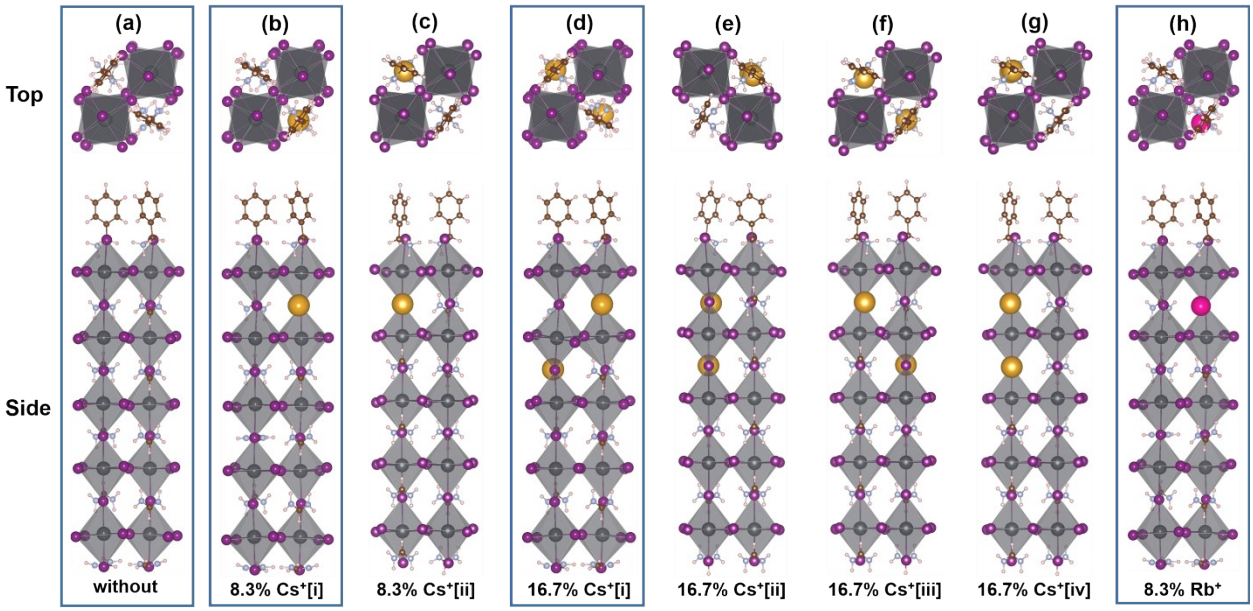


**Fig. S7** Top and side views of BA passivated perovskites with (a) 0%, (b) 8.3% $Cs^+$[i], (c) 8.3% $Cs^+$[ii], (d) 16.7% $Cs^+$[i], (e) 16.7% $Cs^+$[ii], (f) 16.7% $Cs^+$[iii], (g) 16.7% $Cs^+$[iv], and (h) 8.3% $Rb^+$ in the 3D $FAPbI_3$ perovskites. For 8.3% $Cs^+$, we consider two configurations, and for 16.7% $Cs^+$, we consider four configurations. The most stable configurations are highlighted by blue lines. The purple, light blue, brown, light pink, dark grey, dark yellow and rose-red spheres denote I, N, C, H, Pb, Cs and Rb atoms, respectively. The percentage of $Cs^+$ and $Rb^+$ are calculated as following: when one $Cs^+$ substituting for one $FA^+$, where twelve A-site cations (ten $FA^+$ and two $BA^+$) in total, the percentage of $Cs^+$ is 1/12 = 8.3%.

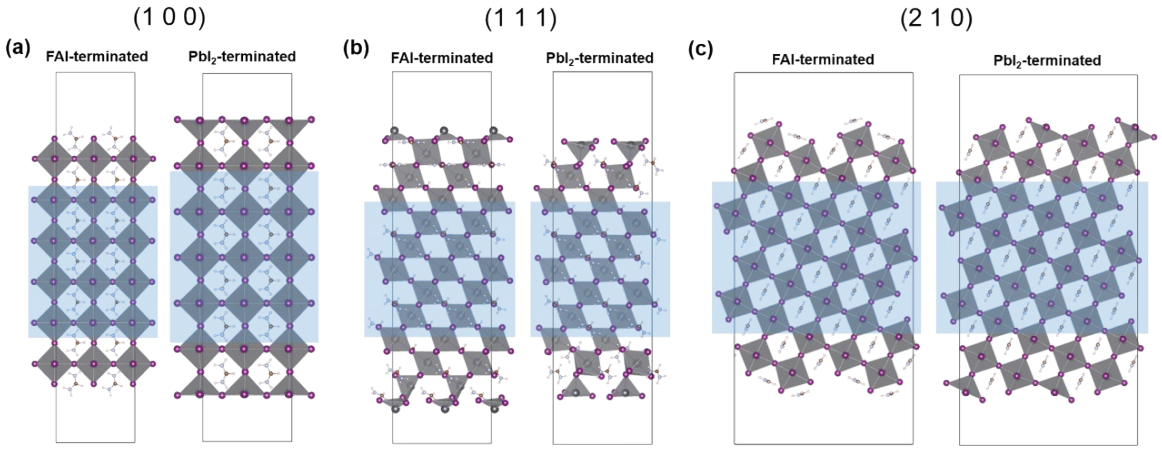


**Fig. S8** Structural models of $FAPbI_3$ surfaces: (1 0 0) (a), (1 1 1) (b) and (2 1 0) (c) with FAI- and $PbI_2$-terminations, respectively. The layers inside the blue rectangle regions were fixed while the top and bottom layers were relaxed.

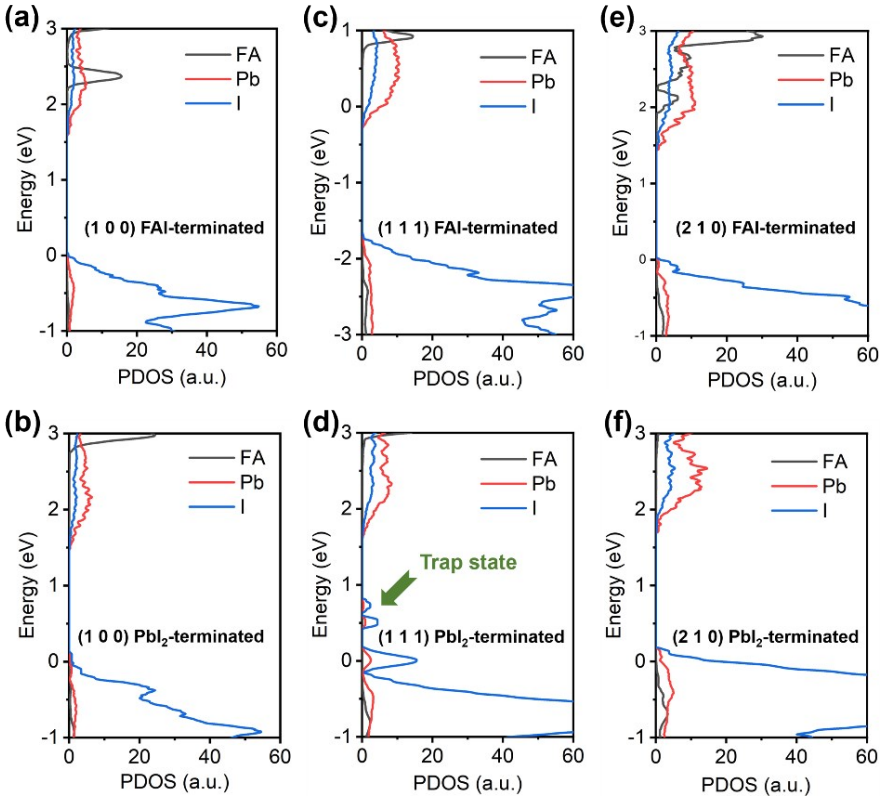


**Fig. S9** Projected density of states of FAI- and $PbI_2$-terminated $FAPbI_3$ surfaces of (1 0 0) (a, b), (1 1 1) (c, d) and (2 1 0) (e, f).

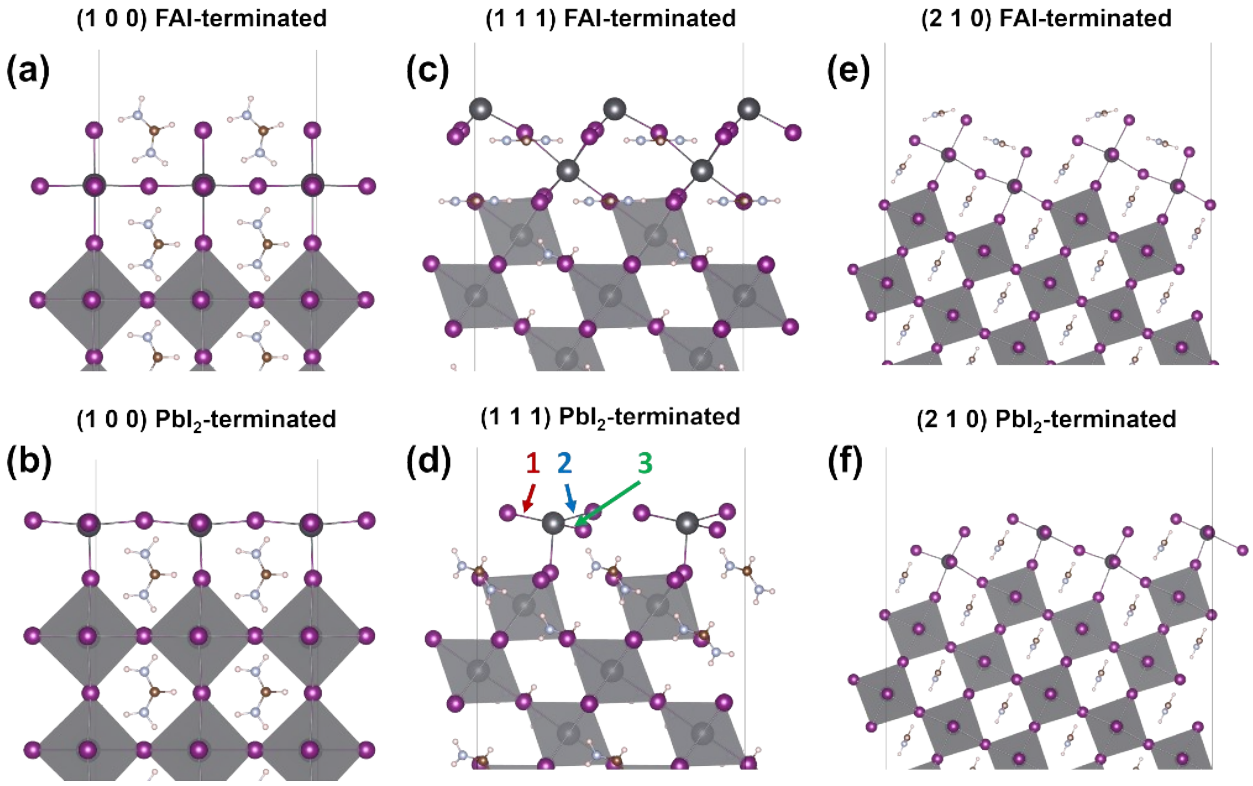


**Fig. S10** FAI- and $PbI_2$-terminated $FAPbI_3$ surfaces of (1 0 0) (a, b), (1 1 1) (c, d) and (2 1 0) (e, f). The three undercoordinated Pb-I bonds in a unit cell are indicated by red, blue, and green arrow, respectively. The two straight grey lines in the crystal structure indicate the 2×2 slab.

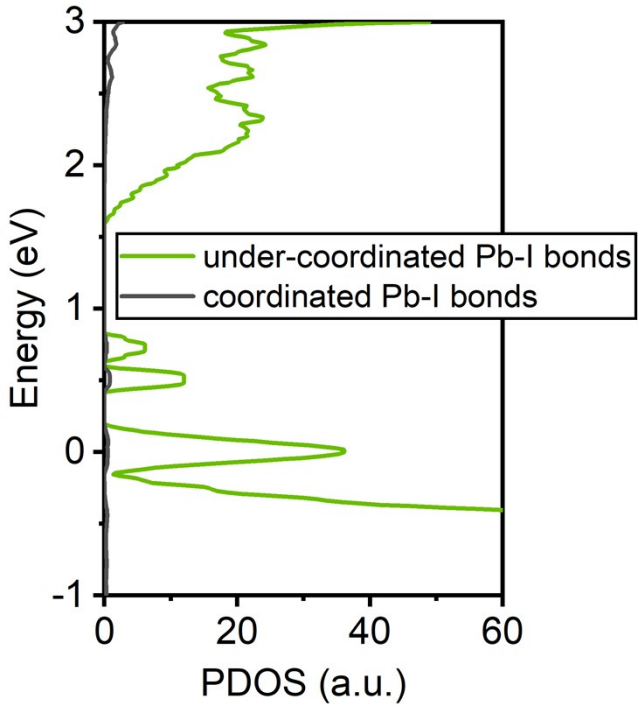


**Fig. S11** Projected density of states (PDOSs) of $PbI_2$-terminated $FAPbI_3$ (1 1 1). The green and black lines are the PDOS of atoms from undercoordinated Pb-I bonds on the surface and atoms from other regular Pb-I bonds, respectively.

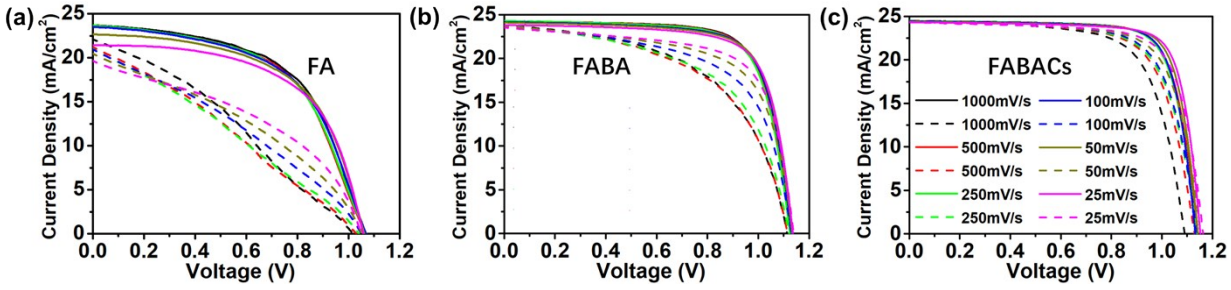


**Fig. S12** Reverse scanned (solid lines) and forward scanned (dash lines) J-V curves of (a) FA, (b) FABA and (c) FABACs devices with scan rate from 1000 mV/s to 25 mV/s.

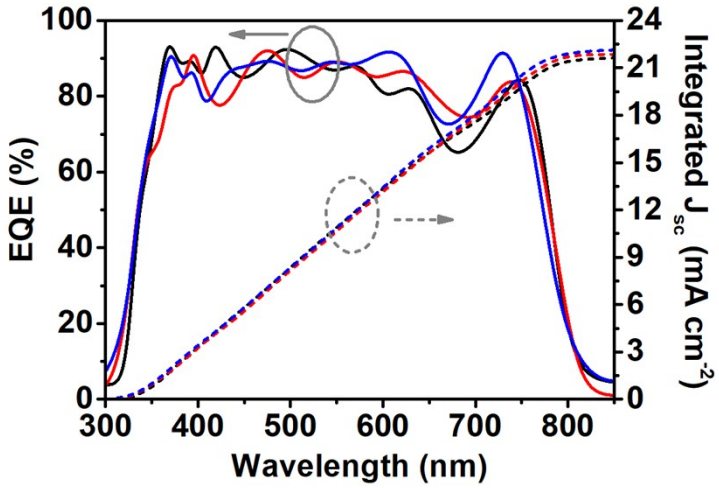


**Fig. S13** IPCE spectra (solid line) and integrated current density (dash line) of the corresponding PSCs.

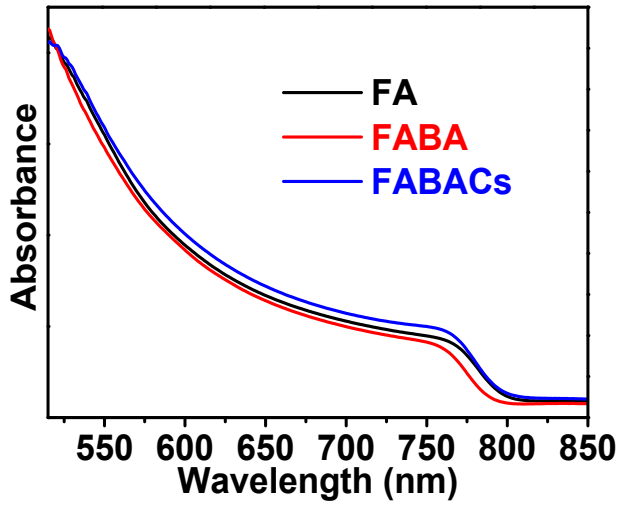


**Fig. S14** UV-vis absorption spectra of FA, FABA and FABACs perovskites.

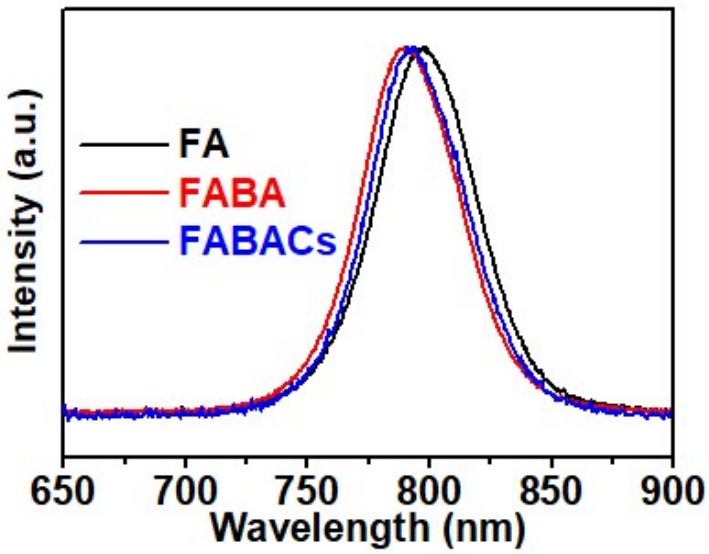


**Fig. S15** PL spectra of FA, FABA and FABACs perovskites.

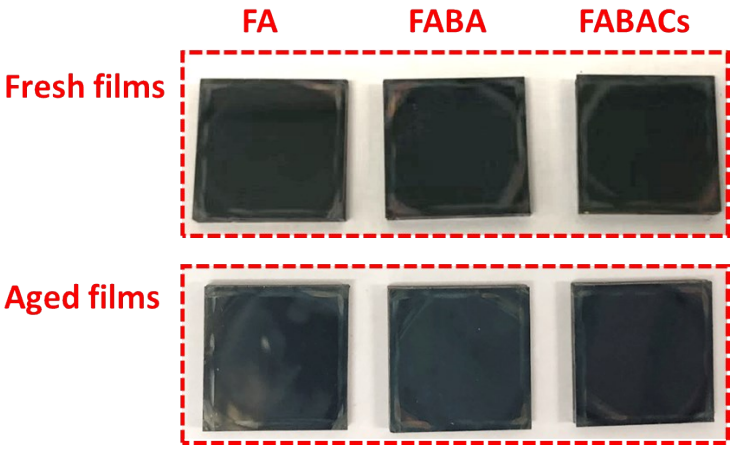


**Fig. S16** Photos of the FA, FABA, FABACs samples before (top row) and after (bottom row) aging at 100 ℃ under two-sun illumination for 8 h.

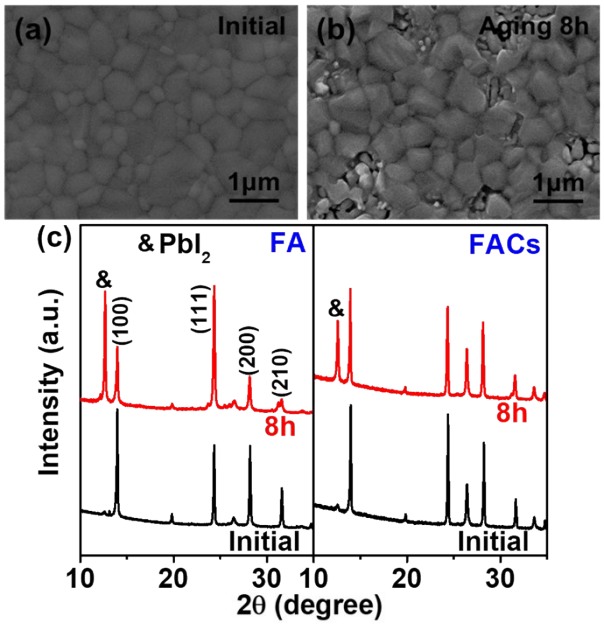


**Fig. S17** SEM images of the FACs perovskite: (a) initial film, (b) film after aging at 100 ℃ for 8 h under a white LED light source with an intensity of 2000 W/m$^2$; (c) XRD patterns of the FA and FACs perovskites after aging at 100 ℃ for 8 h under a white LED light source with an intensity of 2000 W/m$^2$.

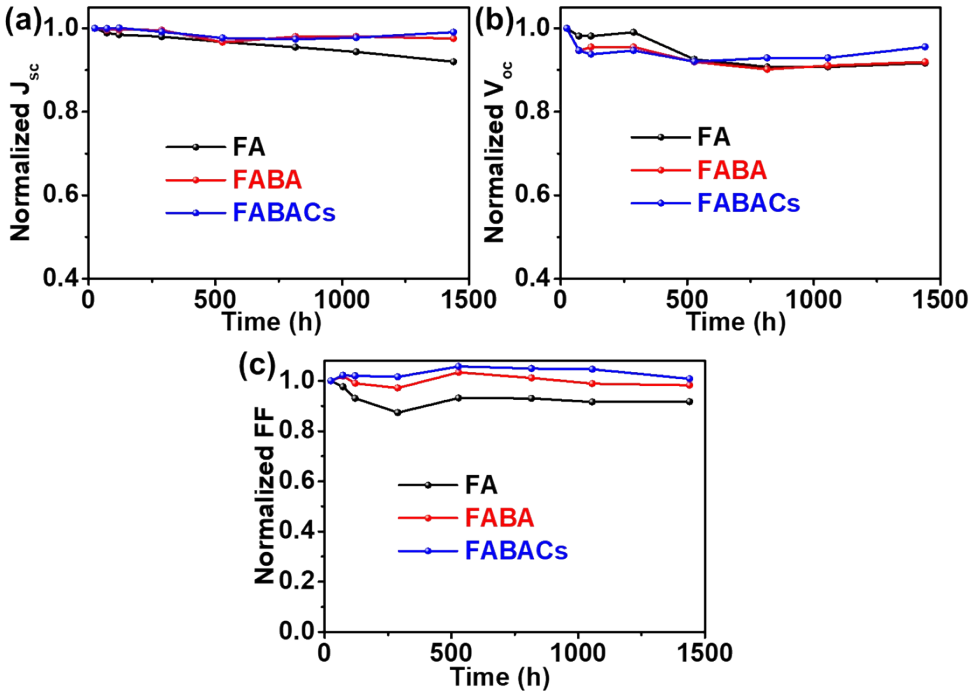


**Fig. S18** Variations of (a) $J_{sc}$, (b) $V_{oc}$ and (c) FF of PSCs based on FA, FABA and FABACs perovskites upon air exposure without encapsulation (humidity level: 60–65%).

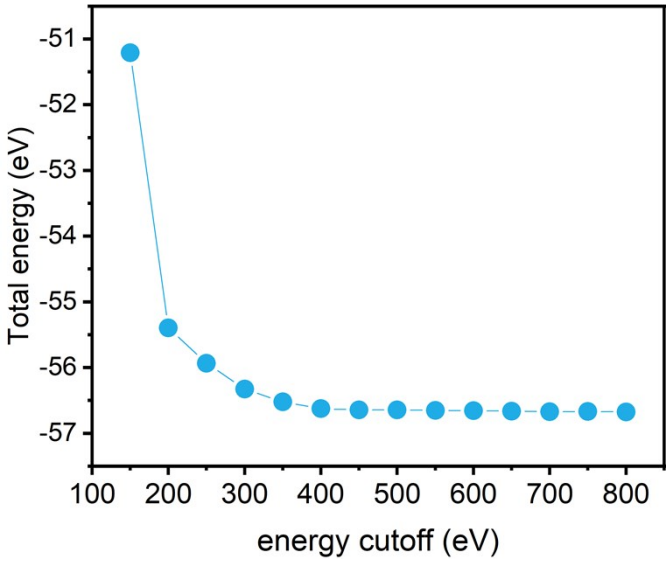


**Fig. S19** The total energy convergence with plane-wave energy cutoff for the unit cell of a bulk cubic $FAPbI_3$.

**Table S1**. Interface formation energies and structural details of the perovskites: lattice parameters, hydrogen bond lengths ($d_1$, $d_2$, $d_3$ and $d_4$), average bond length $d_{av}$, and lattice parameter.

| Type \ Composition | | without | 8.3% $Cs^+$ | 16.7% $Cs^+$ | 8.3% $Rb^+$ |
|---|---|---|---|---|---|
| **Interface formation energy (meV/Å²)** | | -317.95 | -321.78 | -322.35 | -323.73 |
| **Lattice parameter (Å)** | **a** | 9.12 | 9.08 | 9.04 | 9.08 |
| | **b** | 9.18 | 9.15 | 9.15 | 9.10 |
| **$d_1$ (Å)** | | 2.62 | 2.62 | 2.60 | 2.63 |
| **$d_2$ (Å)** | | 2.66 | 2.68 | 2.70 | 2.67 |
| **$d_3$ (Å)** | | 2.64 | 2.63 | 2.66 | 2.60 |
| **$d_4$ (Å)** | | 2.61 | 2.60 | 2.60 | 2.61 |
| **$d_{av}$ (Å)** | | 2.63 | 2.63 | 2.64 | 2.63 |

**Table S2.** Performance of the photovoltaic devices based on FA and FABA perovskites. The number behind FABA stands for the concentration (mg/mL) of the BAI in the organic mixture solution.

| | $V_{oc}$ (V) | $J_{sc}$ (mA·cm$^{-2}$) | *FF* (%) | *PCE* (%) |
|---|---|---|---|---|
| **FA** | 1.060±0.031 | 23.409±0.827 | 66.559±3.320 | 16.523±1.326 |
| **FABA 2** | 1.124±0.019 | 23.982±0.924 | 67.446±5.749 | 18.148±2.178 |
| **FABA 4** | 1.140±0.014 | 24.236±0.516 | 69.324±2.836 | 19.164±1.129 |
| **FABA 6** | 1.144±0.011 | 24.139±0.715 | 67.301±2.962 | 18.608±1.398 |
| **FABA 8** | 1.082±0.030 | 24.352±0.427 | 59.088±3.648 | 15.586±1.301 |
| **FABA 10** | 0.787±0.130 | 15.025±1.230 | 44.494±3.140 | 5.365±1.029 |

**Table S3.** Performance parameters (extracted from reverse scan and forward scan of the J-V curves) of the photovoltaic devices made of FA, FACs, FABA and FABACs perovskites.

| | | $V_{oc}$ (V) | $J_{sc}$ (mA·cm$^{-2}$) | *FF* (%) | *PCE* (%) |
|---|---|---|---|---|---|
| **FA** | Reverse | 1.060±0.031 | 23.409±0.827 | 66.559±3.320 | 16.523±1.326 |
| | Forward | 0.978±0.062 | 23.261±0.261 | 54.771±9.130 | 12.448±2.229 |
| **FACs** | Reverse | 1.089±0.017 | 24.237±0.376 | 73.925±2.653 | 19.517±0.870 |
| | Forward | 1.021±0.024 | 24.124±0.371 | 57.408±3.304 | 14.146±0.904 |
| **FABA** | Reverse | 1.140±0.014 | 24.236±0.516 | 69.324±2.836 | 19.164±1.129 |
| | Forward | 1.112±0.015 | 24.060±0.894 | 58.907±2.039 | 15.768±0.968 |
| **FABACs** | Reverse | 1.145±0.012 | 24.706±0.433 | 74.601±2.619 | 21.132±0.750 |
| | Forward | 1.113±0.008 | 24.451±0.460 | 68.749±2.444 | 18.705±0.731 |

**Table S4.** Conductivity of the fresh $SnO_2$ film and the ones coated with FACs and FABACs perovskites and subsequently washed with DMF.

| | $SnO_2$ | $SnO_2$-FACs | $SnO_2$-FABACs |
|---|---|---|---|
| Conductivity (S $cm^{-1}$) | $1.57\times10^{-4}$ | $1.57\times10^{-4}$ | $1.55\times10^{-4}$ |

## References


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2 C. Li, R. Ma, X. He, T. Yang, Z. Zhou, S. Yang, Y. Liang, X. W. Sun, J. Wang, Y. Yan and W. C. H. Choy, *Adv. Energy Mater.*, 2020, **10**, 1903013.