Electronic Supplementary Material (ESI) for RSC Advances.


# Supplementary information

## Additive effects of alkali metals on Cu-modified $CH_3NH_3PbI_{3-\delta}Cl_\delta$ photovoltaic devices

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**Table S1**. Preparation composition of the present perovskite crystals.

| Cells | $CH_3NH_3I$ | $PbICl_2$ | $PbI_2$ | $CuBr_2$ | NaI | KI | RbI | CsI |
|---|---|---|---|---|---|---|---|---|
| Standard | 2.4 M | 0.8 M | 0.08 M | | | | | |
| + $CuBr_2$ | 2.4 M | 0.792 M | 0.08 M | 0.008 M | | | | |
| + $CuBr_2$ + NaI | 2.376 M | 0.792 M | 0.08 M | 0.008 M | 0.008 M | | | |
| + $CuBr_2$ + KI | 2.376 M | 0.792 M | 0.08 M | 0.008 M | | 0.008 M | | |
| + $CuBr_2$ + RbI | 2.376 M | 0.792 M | 0.08 M | 0.008 M | | | 0.008 M | |
| + $CuBr_2$ + CsI | 2.376 M | 0.792 M | 0.08 M | 0.008 M | | | | 0.008 M |

**Table S2**. Energy levels of the HOMO and LUMO, and energy gap ($E_g$) of the perovskite structures without Cu, calculated by first-principles calculation.

| Perovskite | LUMO (eV) | HOMO (eV) | $E_g$ (eV) | $E_F$ (eV) |
|---|---|---|---|---|
| $MAPbI_3$ | -14.9 | -17.6 | 2.70 | -16.2 |
| $MA(Na)PbI_3$ | -14.9 | -17.6 | 2.71 | -16.2 |
| $MA(K)PbI_3$ | -14.9 | -17.6 | 2.71 | -16.2 |
| $MA(Rb)PbI_3$ | -14.9 | -17.6 | 2.71 | -16.2 |
| $MA(Cs)PbI_3$ | -14.9 | -17.6 | 2.71 | -16.2 |

**Table S3**. Calculated thermodynamic parameters of the perovskite structures without Cu. (*G*: Gibbs energy, *H*: enthalpy and *S*: entropy.)

| Perovskite | *G* (kJ $mol^{-1}$) | *H* (kJ $mol^{-1}$) | *S* (kJ $K^{-1}$ $mol^{-1}$) |
|---|---|---|---|
| $MAPbI_3$ | 946 | 2326 | 4.63 |
| $MA(Na)PbI_3$ | 728 | 2092 | 4.58 |
| $MA(K)PbI_3$ | 741 | 2090 | 4.53 |
| $MA(Rb)PbI_3$ | 721 | 2094 | 4.61 |
| $MA(Vs)PbI_3$ | 722 | 2097 | 4.61 |

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**Table S4.** Measured photovoltaic parameters of the present perovskite photovoltaic devices.

| | $J_{SC}$ (mA cm$^{-2}$) | $V_{OC}$ (V) | FF | $\eta$ (%) | $\eta_{ave}$ (%) | $R_S$ (Ω cm$^2$) | $R_{Sh}$ (Ω cm$^2$) |
|---|---|---|---|---|---|---|---|
| After 1 week | | | | | | | |
| Standard | 17.5 | 0.713 | 0.601 | 7.5 | 6.9 | 3.62 | 3788 |
| + $CuBr_2$ | 20.6 | 0.892 | 0.580 | 10.7 | 10.3 | 5.12 | 1344 |
| + $CuBr_2$ + NaI | 21.6 | 0.882 | 0.653 | 12.5 | 12.0 | 4.83 | 2440 |
| + $CuBr_2$ + KI | 21.6 | 0.878 | 0.676 | 12.8 | 12.1 | 4.88 | 2200 |
| + $CuBr_2$ + RbI | 22.1 | 0.900 | 0.625 | 12.5 | 12.0 | 5.10 | 1980 |
| + $CuBr_2$ + CsI | 21.4 | 0.863 | 0.701 | 13.0 | 12.6 | 4.44 | 2540 |
| After 2 weeks | | | | | | | |
| Standard | 18.8 | 0.734 | 0.562 | 7.8 | 6.8 | 4.49 | 674 |
| + $CuBr_2$ | 21.1 | 0.917 | 0.622 | 12.0 | 11.2 | 5.42 | 1926 |
| + $CuBr_2$ + NaI | 21.7 | 0.893 | 0.671 | 13.0 | 12.4 | 4.44 | 1810 |
| + $CuBr_2$ + KI | 20.6 | 0.891 | 0.681 | 12.5 | 12.1 | 4.97 | 1485 |
| + $CuBr_2$ + RbI | 22.3 | 0.925 | 0.637 | 13.1 | 12.3 | 5.23 | 7785 |
| + $CuBr_2$ + CsI | 21.0 | 0.883 | 0.695 | 12.9 | 12.6 | 4.81 | 1534 |
| After 3 weeks | | | | | | | |
| Standard | 17.5 | 0.787 | 0.622 | 8.6 | 8.1 | 3.89 | 20222 |
| + $CuBr_2$ | 20.6 | 0.928 | 0.652 | 12.5 | 11.5 | 4.65 | 4317 |
| + $CuBr_2$ + NaI | 21.5 | 0.887 | 0.681 | 13.0 | 12.4 | 4.34 | 1803 |
| + $CuBr_2$ + KI | 21.2 | 0.884 | 0.685 | 12.8 | 11.8 | 4.58 | 1230 |
| + $CuBr_2$ + RbI | 21.6 | 0.910 | 0.673 | 13.2 | 12.4 | 5.10 | 2224 |
| + $CuBr_2$ + CsI | 20.2 | 0.860 | 0.708 | 12.3 | 11.8 | 4.42 | 1067 |
| After 4 weeks | | | | | | | |
| Standard | 18.0 | 0.706 | 0.573 | 7.3 | 6.9 | 4.34 | 22089 |
| + $CuBr_2$ | 20.2 | 0.930 | 0.679 | 12.7 | 11.9 | 4.79 | 5675 |
| + $CuBr_2$ + NaI | 19.3 | 0.887 | 0.691 | 11.8 | 11.6 | 4.66 | 1361 |
| + $CuBr_2$ + KI | 20.8 | 0.890 | 0.691 | 12.8 | 11.6 | 4.55 | 654 |
| + $CuBr_2$ + RbI | 21.8 | 0.925 | 0.682 | 13.7 | 12.8 | 4.77 | 1814 |
| + $CuBr_2$ + CsI | 20.8 | 0.879 | 0.707 | 13.0 | 12.6 | 4.29 | 891 |
| After 5 weeks | | | | | | | |
| Standard | 17.0 | 0.722 | 0.578 | 7.1 | 6.8 | 4.48 | 18415 |
| + $CuBr_2$ | 20.7 | 0.940 | 0.679 | 13.2 | 11.5 | 4.71 | 18738 |
| + $CuBr_2$ + NaI | 21.8 | 0.894 | 0.684 | 13.3 | 12.8 | 4.54 | 1426 |
| + $CuBr_2$ + KI | 20.9 | 0.887 | 0.679 | 12.6 | 11.7 | 4.85 | 1325 |
| + $CuBr_2$ + RbI | 22.0 | 0.918 | 0.690 | 13.9 | 13.3 | 4.86 | 10343 |
| + $CuBr_2$ + CsI | 20.7 | 0.868 | 0.713 | 12.8 | 12.4 | 4.28 | 1017 |
| After 6 weeks | | | | | | | |
| Standard | 17.9 | 0.726 | 0.559 | 7.3 | 6.9 | 4.87 | 1733 |
| + $CuBr_2$ | 21.3 | 0.940 | 0.662 | 13.3 | 12.1 | 5.32 | 12829 |
| + $CuBr_2$ + NaI | 20.3 | 0.912 | 0.683 | 12.6 | 12.3 | 4.85 | 691 |
| + $CuBr_2$ + KI | 20.6 | 0.907 | 0.689 | 12.9 | 11.8 | 4.45 | 506 |
| + $CuBr_2$ + RbI | 21.0 | 0.921 | 0.690 | 13.3 | 13.3 | 5.07 | 1426 |
| + $CuBr_2$ + CsI | 21.0 | 0.892 | 0.712 | 13.3 | 12.8 | 4.05 | 723 |
| After 7 weeks | | | | | | | |
| Standard | 17.4 | 0.711 | 0.543 | 6.7 | 6.1 | 5.04 | 812 |
| + $CuBr_2$ | 20.2 | 0.946 | 0.682 | 13.0 | 12.1 | 4.90 | 5476 |
| + $CuBr_2$ + NaI | 21.2 | 0.918 | 0.678 | 13.2 | 12.1 | 4.71 | 972 |
| + $CuBr_2$ + KI | 20.3 | 0.909 | 0.688 | 12.7 | 11.4 | 4.85 | 894 |
| + $CuBr_2$ + RbI | 21.7 | 0.937 | 0.688 | 14.0 | 13.0 | 4.93 | 4077 |
| + $CuBr_2$ + CsI | 19.5 | 0.906 | 0.699 | 12.4 | 11.7 | 4.50 | 820 |

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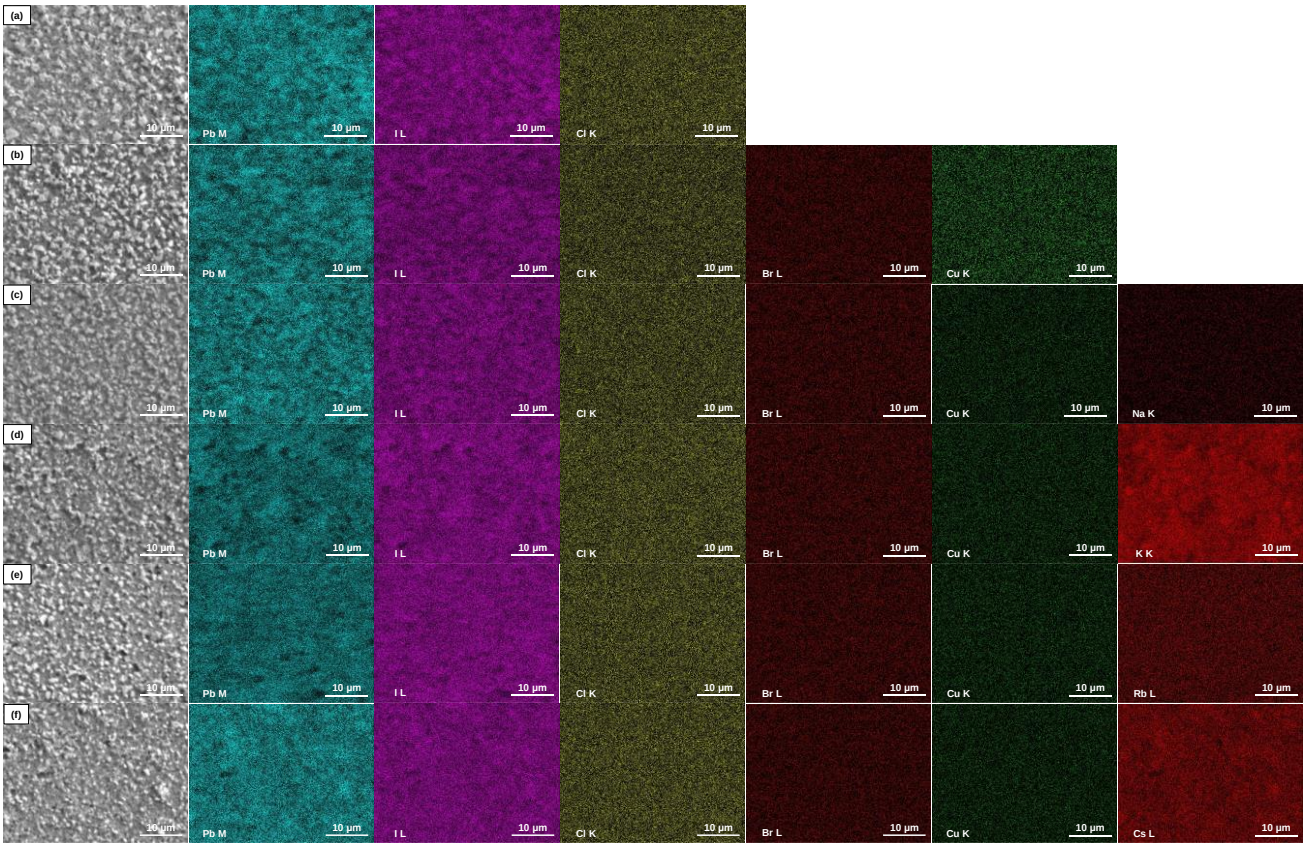


**Fig. S1**. SEM images and corresponding elemental mappings of the Pb M, I L, Cl K, Br L, Na K, K K, Rb L, and Cs L lines of (a) standard, (b) + $CuBr_2$, (c) + $CuBr_2$ + NaI, (d) + $CuBr_2$ + KI, (e) + $CuBr_2$ + RbI and (f) + $CuBr_2$ + CsI perovskite photovoltaic devices.

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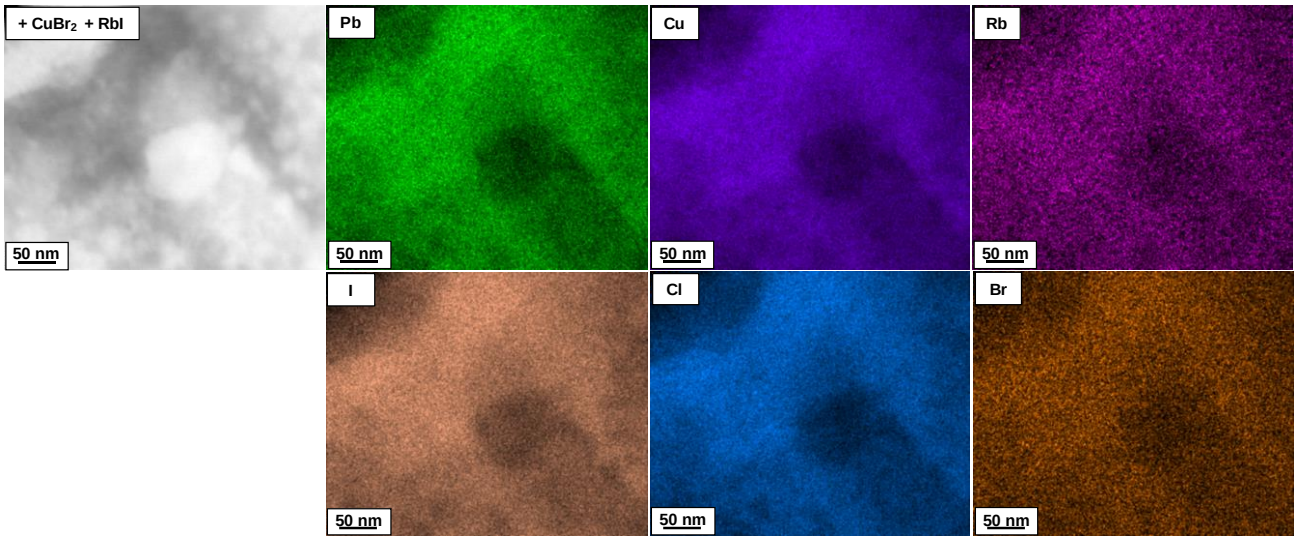


**Fig. S2**. High-angle annular dark-field scanning transmission electron microscopy image and corresponding elemental mappings of the Pb L, Cu K, Rb K, I K, Cl K, and Br K lines of + $CuBr_2$ + RbI perovskite photovoltaic device.

# Supplementary information

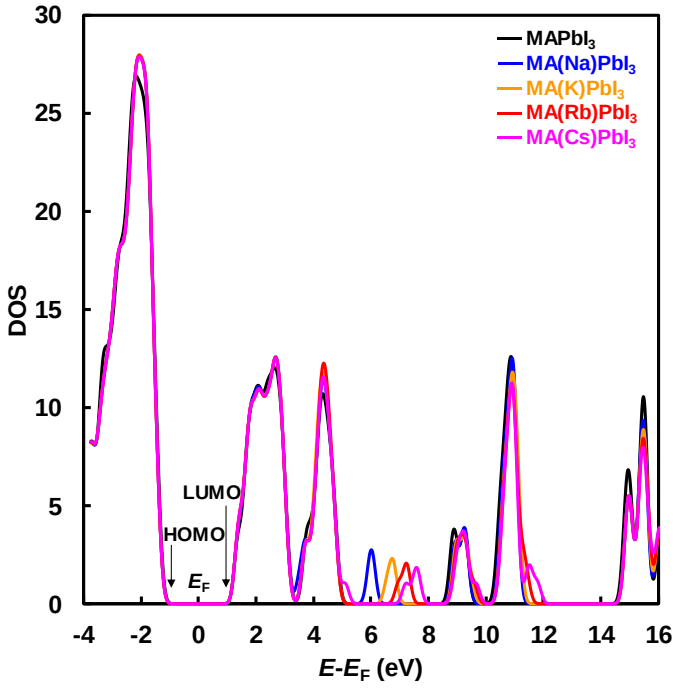


**Fig. S3**. Total density of states of the present perovskite structures without Cu.

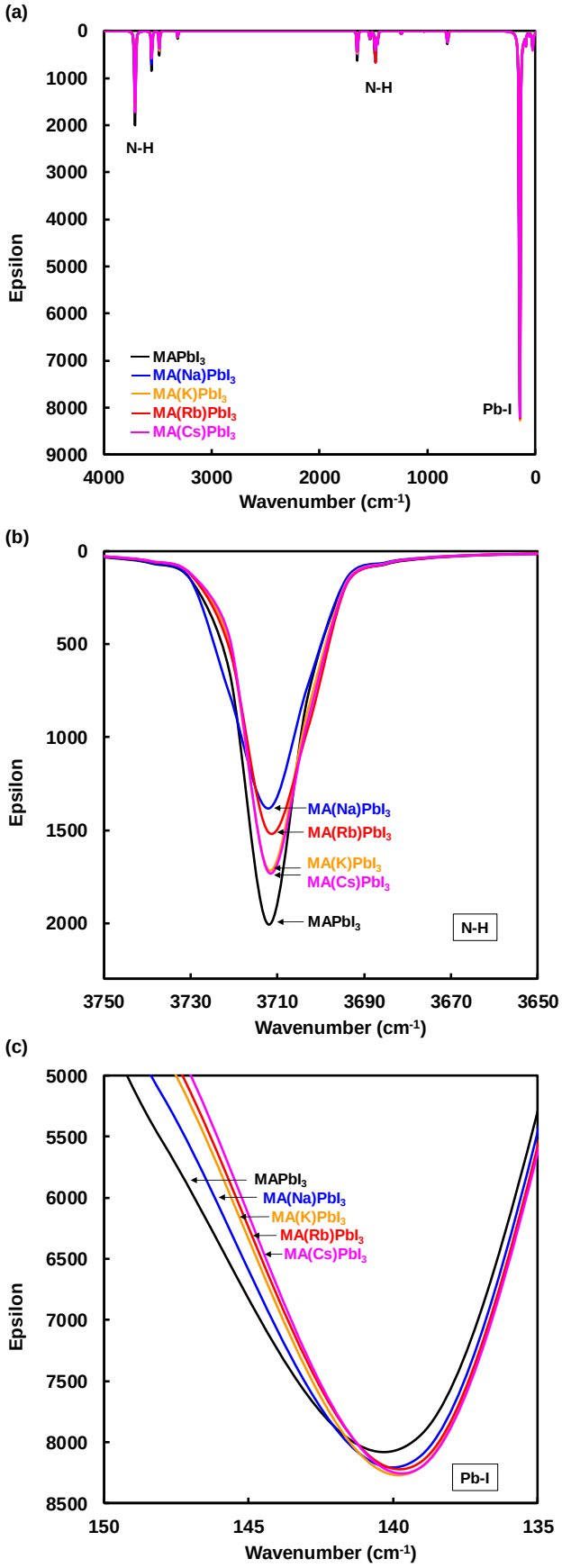


**Fig. S4**. IR spectra of (a) total view, (b) N-H, and (c) Pb-I stretching vibration of the perovskite structures without Cu.

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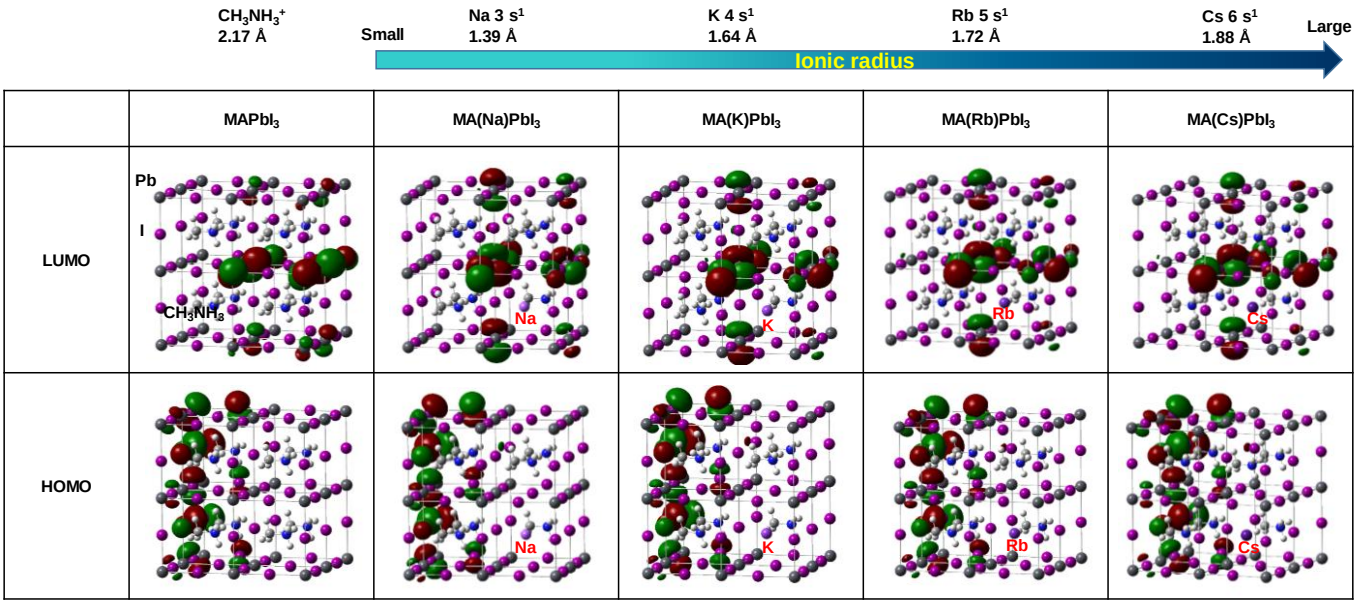


**Fig. S5**. Electronic structures at HOMO and LUMO of the present perovskite structures without Cu.