
Supporting Information

Orange to red, emission tunable Mn doped two-dimensional perovskites with high luminescence and stability

Chun Sun, Zhiyuan Gao, Yuchen Deng, Hanxin Liu, Le Wang, Sijing Su, Peng Li, Huanrong Li, Zihui Zhang, and Wengang Bi**

Dr. C. Sun, Z. Gao, H. Liu, L. Wang, S. Su, Prof. Z. Zhang, Prof. W. G. Bi.

State Key Laboratory of Reliability and Intelligence of Electrical Equipment,
Hebei University of Technology, 5340 Xiping Road, Tianjin, 300401, P. R.
China

Tianjin Key Laboratory of Electronic Materials and Devices, School of
Electronics and Information Engineering, Hebei University of Technology,
5340 Xiping Road, Tianjin, 300401, P. R. China

E-mail: cs@hebut.edu.cn and wbi@hebut.edu.cn

Dr. Y. Deng, Dr. P. Li, Prof. H. Li.

Hebei Provincial Key Lab of Green Chemical Technology and High Efficient
Energy Saving, School of Chemical Engineering and Technology, Hebei
University of Technology, Tianjin 300130, P. R. China

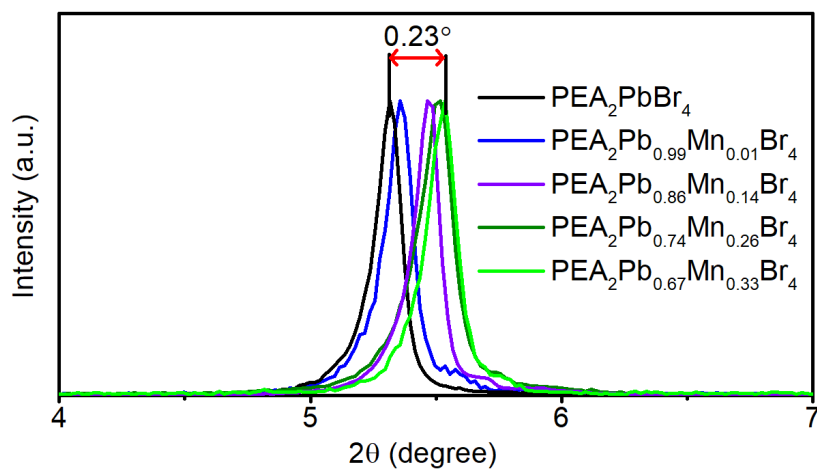


Figure S1. Small angle X-ray diffraction patterns of 2D $\text{PEA}_2\text{PbBr}_4$ and $\text{PEA}_2\text{Mn}_x\text{Pb}_{1-x}\text{Br}_4$.

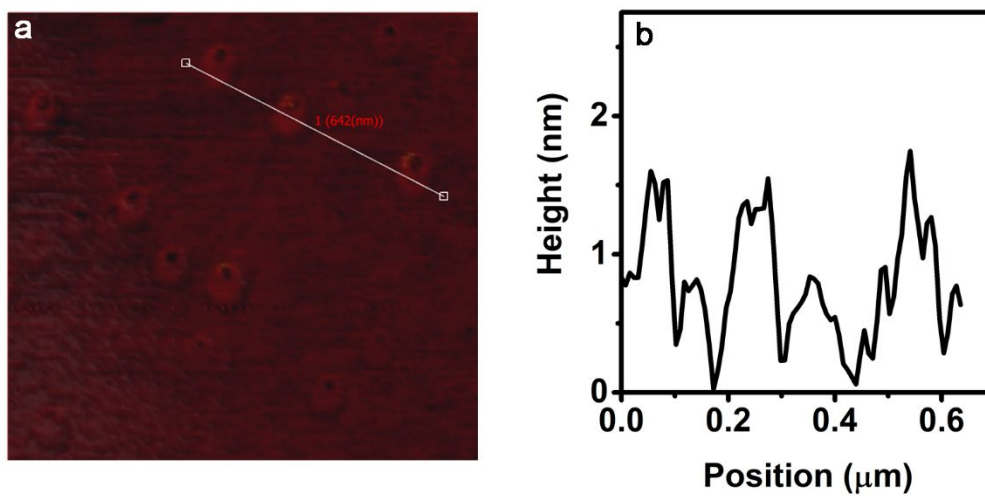


Figure S2. (a) AFM image of $\text{PEA}_2\text{PbBr}_4$ and (b) their height distribution.

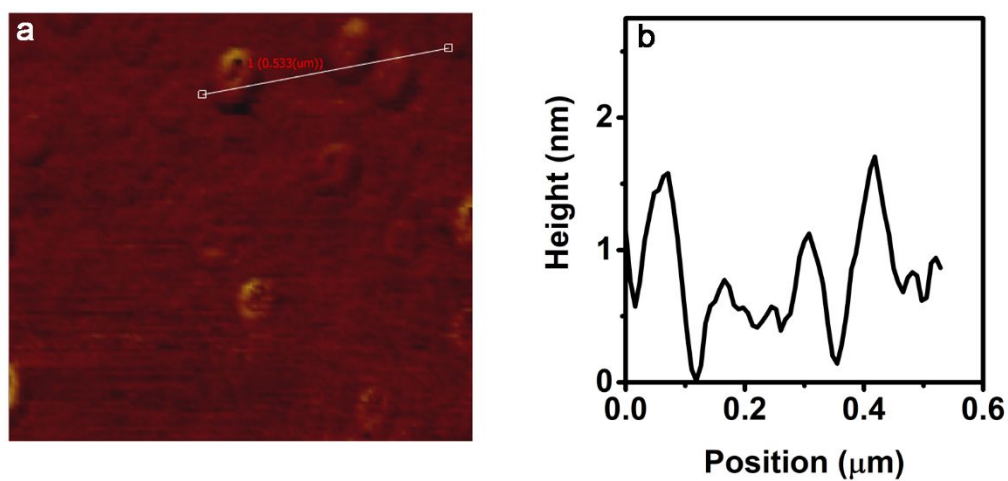


Figure S3. (a) AFM image of $\text{PEA}_2\text{Pb}_{0.74}\text{Mn}_{0.26}\text{Br}_4$ and (b) their height distribution.

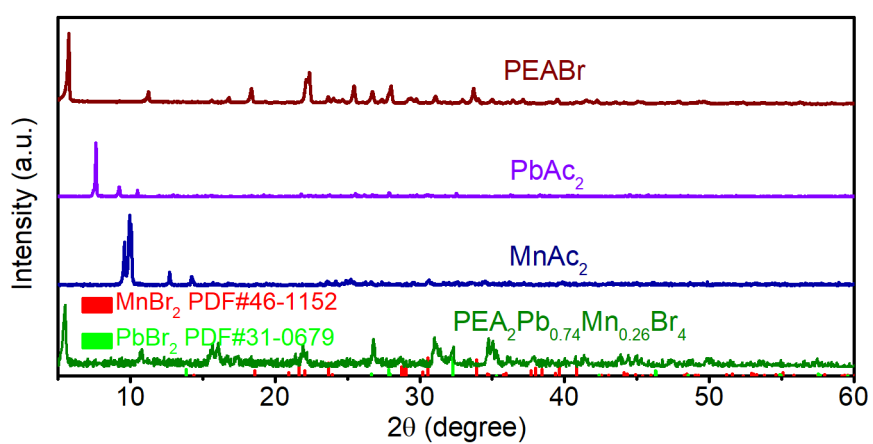


Figure S4. XRD patterns of PbAc_2 , MnAc_2 , PEABr , PbBr_2 , MnBr_2 and $\text{PEA}_2\text{Pb}_{0.74}\text{Mn}_{0.26}\text{Br}_4$.

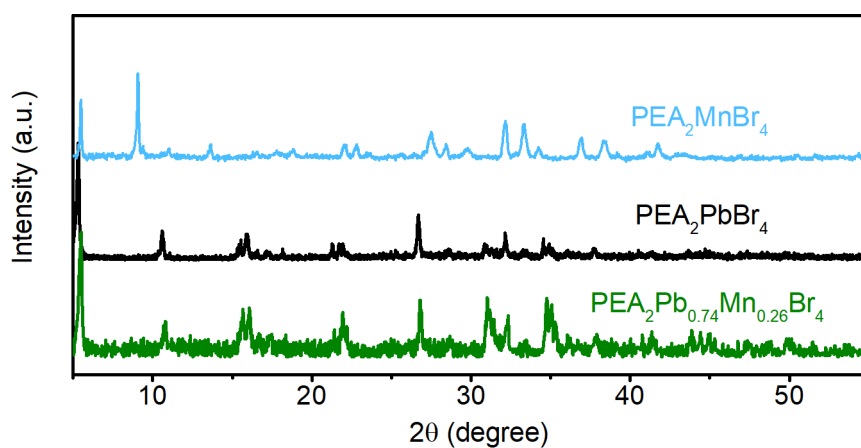


Figure S5. XRD patterns of $\text{PEA}_2\text{PbBr}_4$, $\text{PEA}_2\text{MnBr}_4$, and $\text{PEA}_2\text{Pb/MnBr}_4$.

Pure $\text{PEA}_2\text{MnBr}_4$ perovskite was synthesized using our above-described method without adding PbAc_2 .

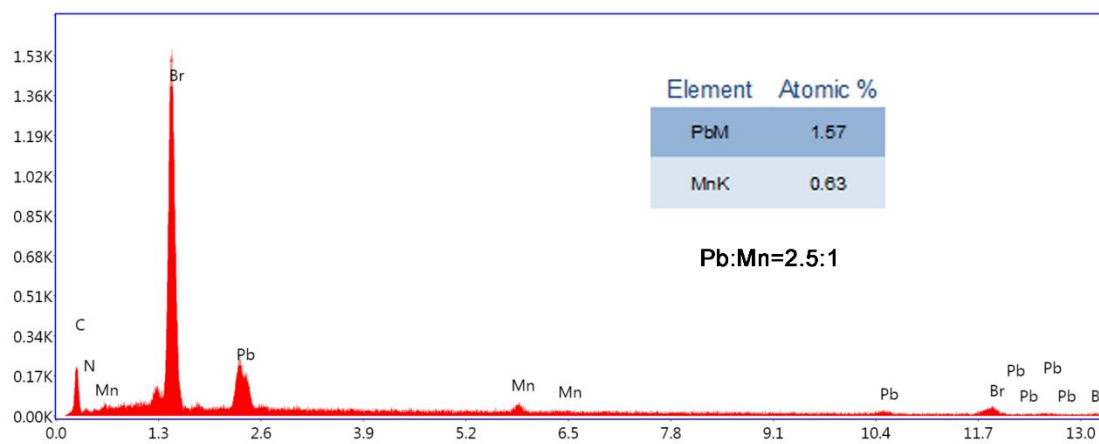


Figure S6. EDX image of $\text{PEA}_2\text{Pb}_{0.74}\text{Mn}_{0.26}\text{Br}_4$.

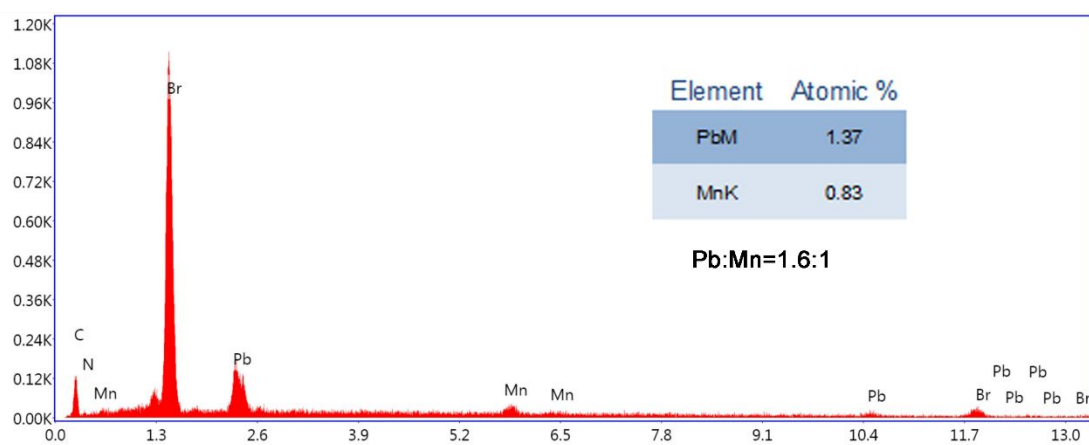


Figure S7. EDX image of $\text{PEA}_2\text{Pb}_{0.67}\text{Mn}_{0.33}\text{Br}_4$.

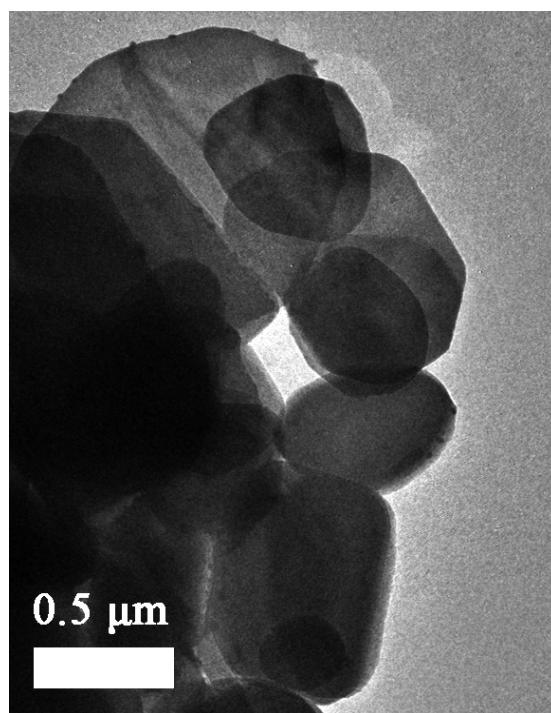


Figure S8. TEM image of $\text{PEA}_2\text{PbBr}_4$.

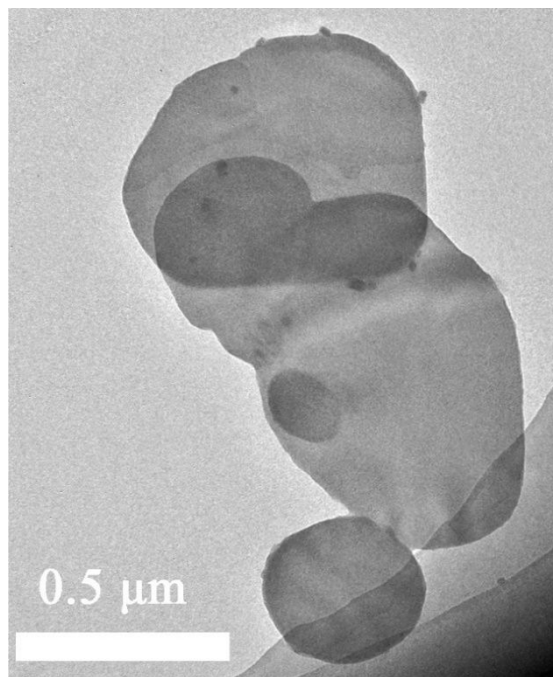


Figure S9. TEM image of $\text{PEA}_2\text{Pb}_{1-x}\text{Mn}_x\text{Br}_4$.

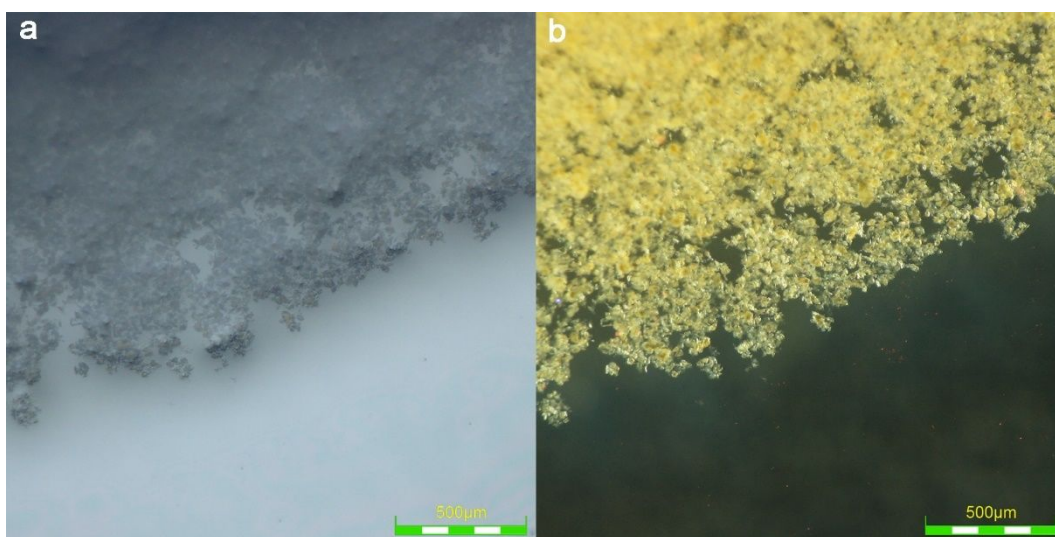


Figure S10. Optical microscopic image of $\text{PEA}_2\text{Pb}_{1-x}\text{Mn}_x\text{Br}_4$ under ambient light (a) and UV light (b).

No fluorescence was found in $\text{PEA}_2\text{MnBr}_4$, while $\text{PEA}_2\text{Pb}_{1-x}\text{Mn}_x\text{Br}_4$ exhibits strong orange fluorescence. In order to verify homogeneous phase, we have used optical microscope to observe the PL of the product. As can be seen from Figure S10, all these particles emitted strong orange fluorescence under UV light and no nonluminous particles were found in the optical microscopic image.

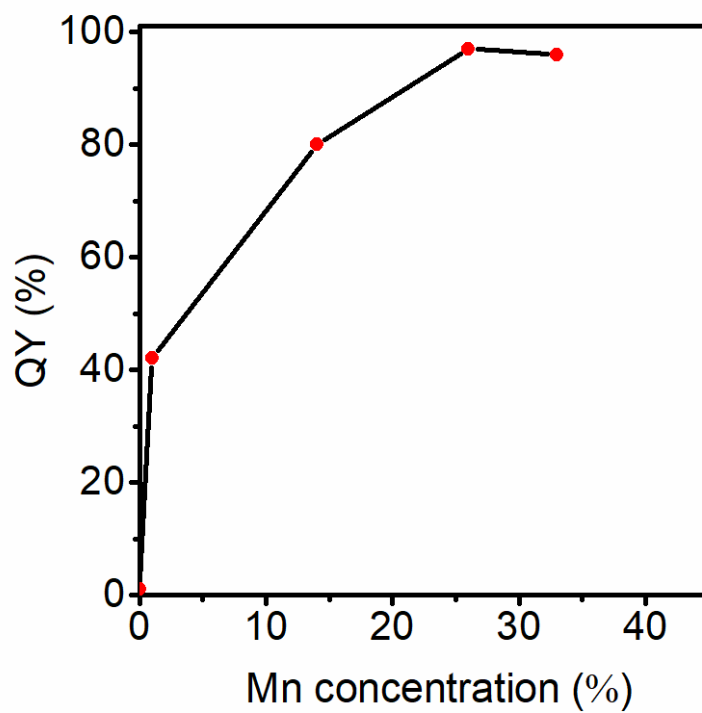


Figure S11. The QYs of $\text{PEA}_2\text{Pb}_{1-x}\text{Mn}_x\text{Br}_4$ with different Mn incorporated concentration.

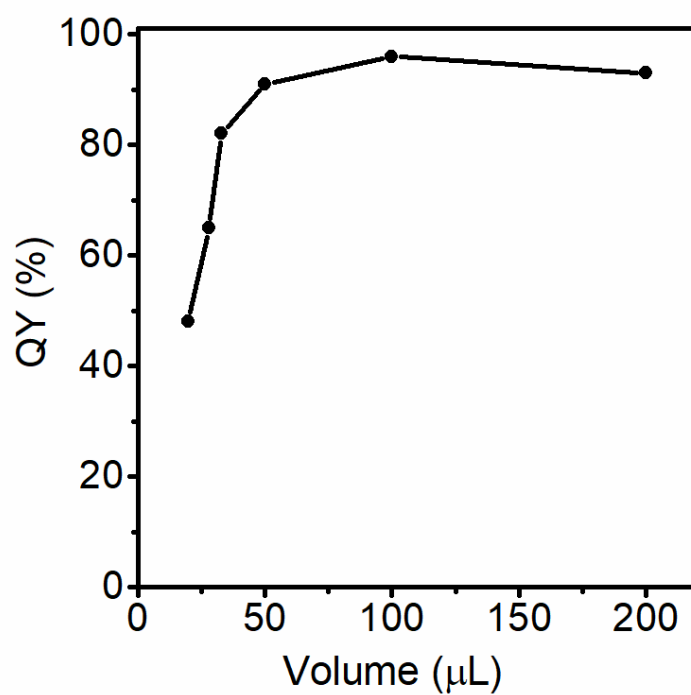


Figure S12. The QYs of $\text{PEA}_2\text{Pb}_{0.74}\text{Mn}_{0.26}\text{Br}_4$ with different PEA concentration.

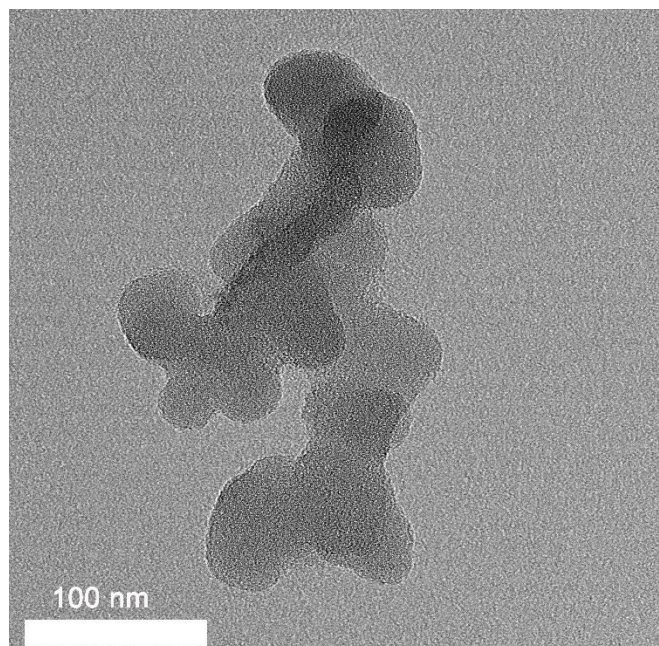


Figure S13. TEM image of P-33 after oxidation.

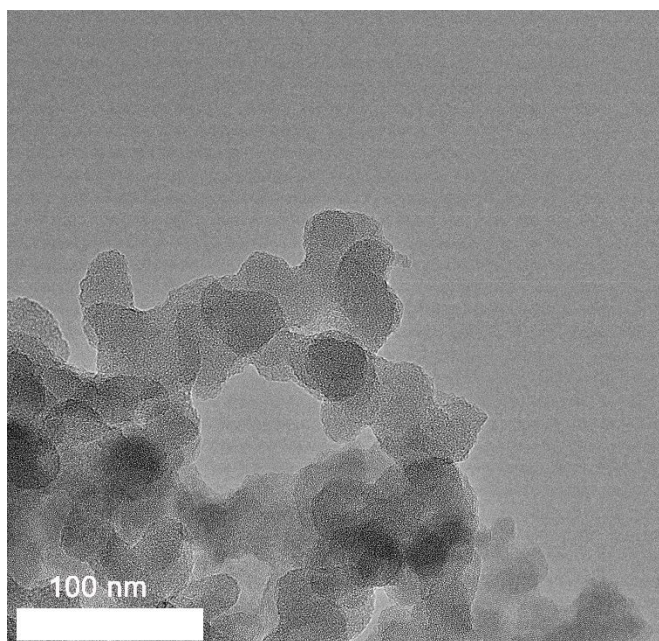


Figure S14. TEM image of P-20 after oxidation.

As can be seen, all these particles show irregular rectangular morphology. The sizes of perovskite with less PEA (33 μ L and 20 μ L) are about 100 nm, which are slightly smaller than that of P-100.

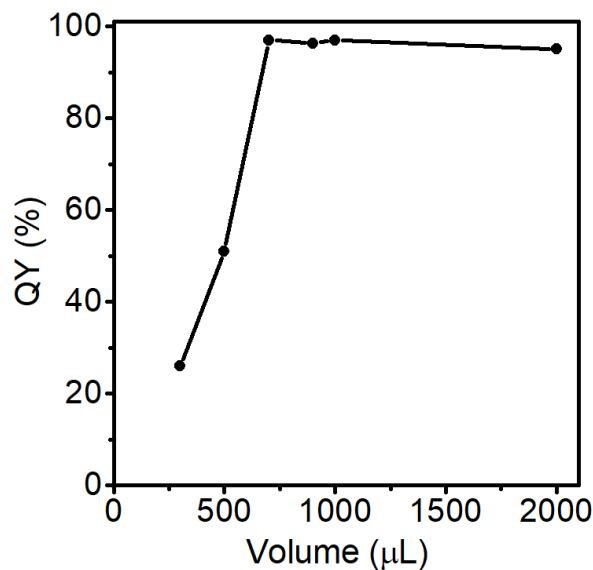


Figure S15. The QYs of $\text{PEA}_2\text{Pb}_{0.74}\text{Mn}_{0.26}\text{Br}_4$ with different OA addition.

In order to verify the effect of the oleic acid, a series of experiments were performed with different OA addition (0.3mL-2mL). As shown in Figure S15, at first, the QYs of Mn doped 2D perovskite increase with the addition of OA (0.3mL-0.7mL), and finally the QY reaches to the highest value. This indicates that OA can passivate the surface traps, leading to enhanced QY.

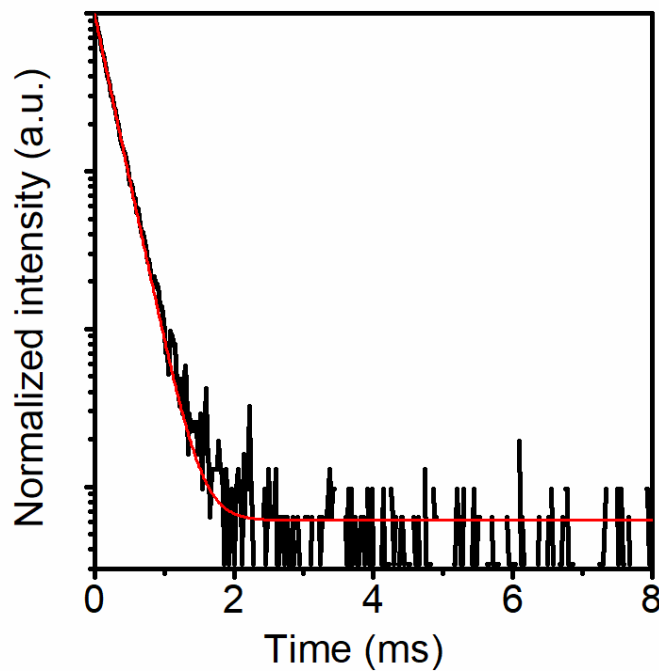


Figure S16. Time-resolved PL decay of P-33 perovskite.

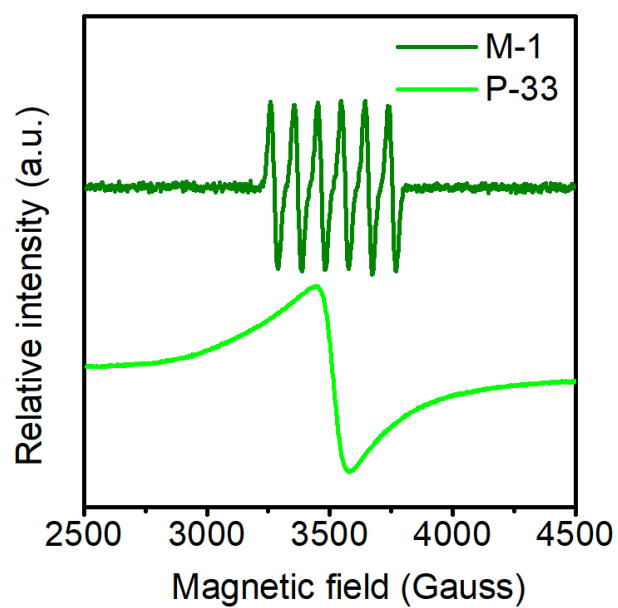


Figure S17. The EPR spectra of M-1 and P-33.

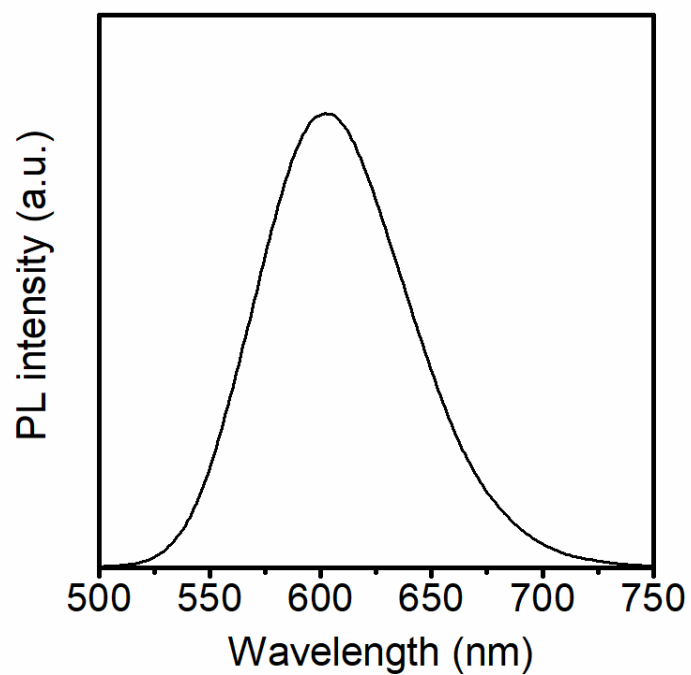


Figure S18. The PL spectrum of P-33 after oxidation.

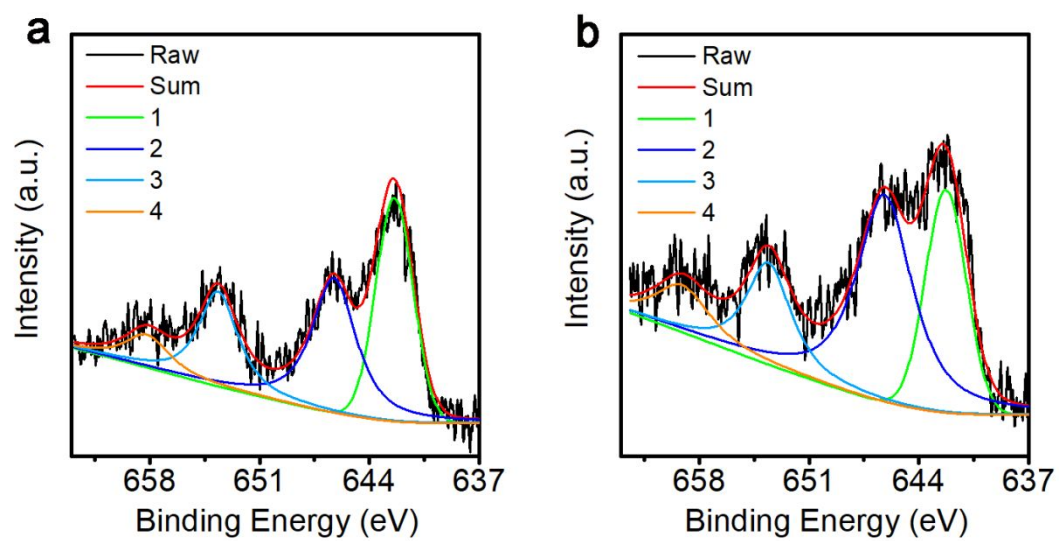
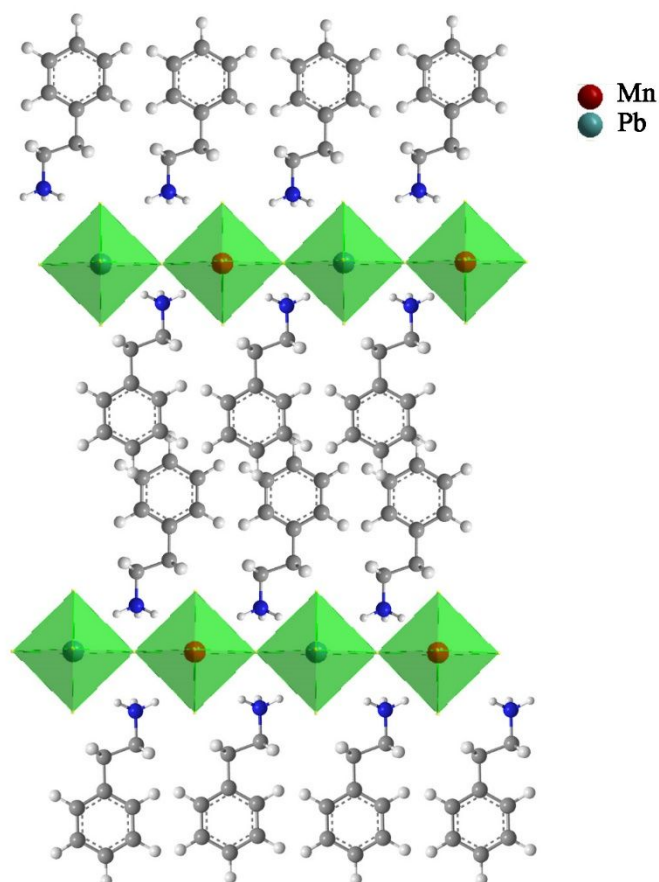
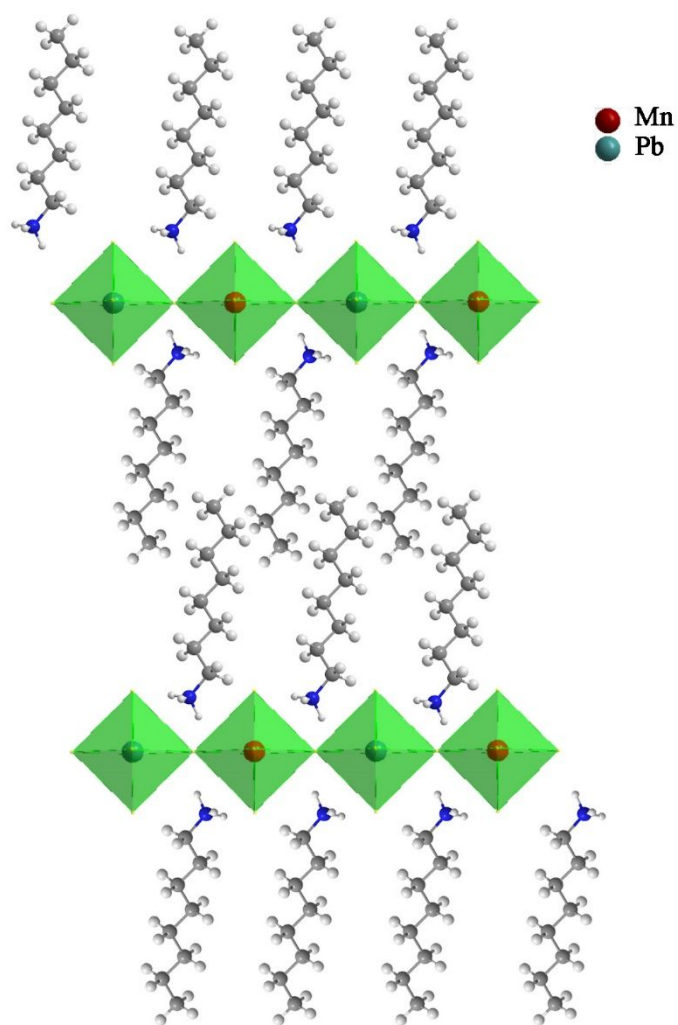


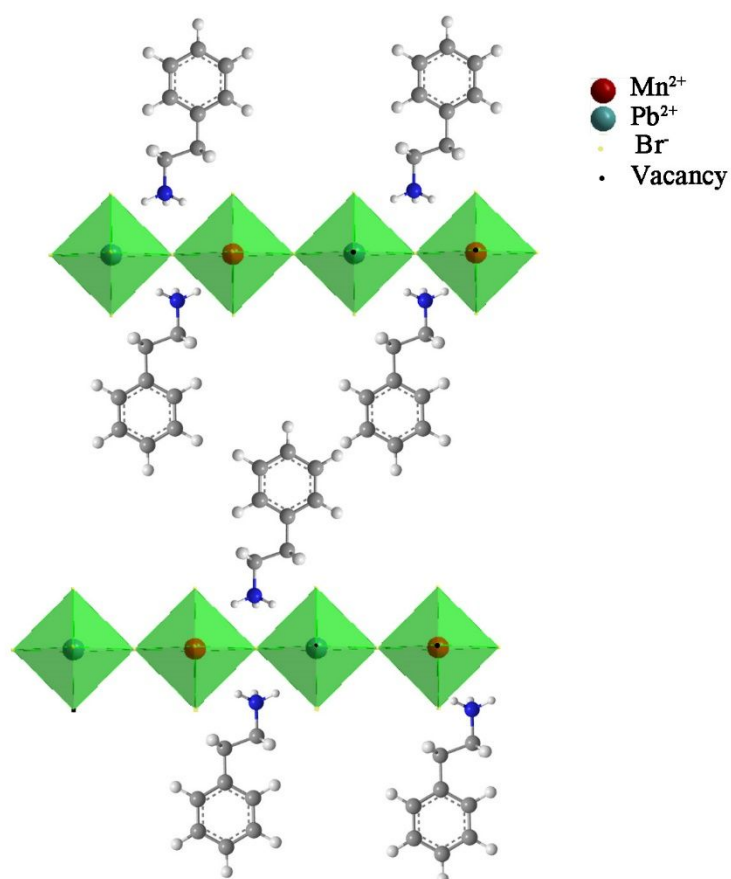
Figure S19. Mn 2p XPS spectra of P-100 (a) and P-33 after oxidation (b).



Scheme S1. Schematic representation of the $\text{PEA}_2\text{Pb}_{0.74}\text{Mn}_{0.26}\text{Br}_4$ 2D perovskite.

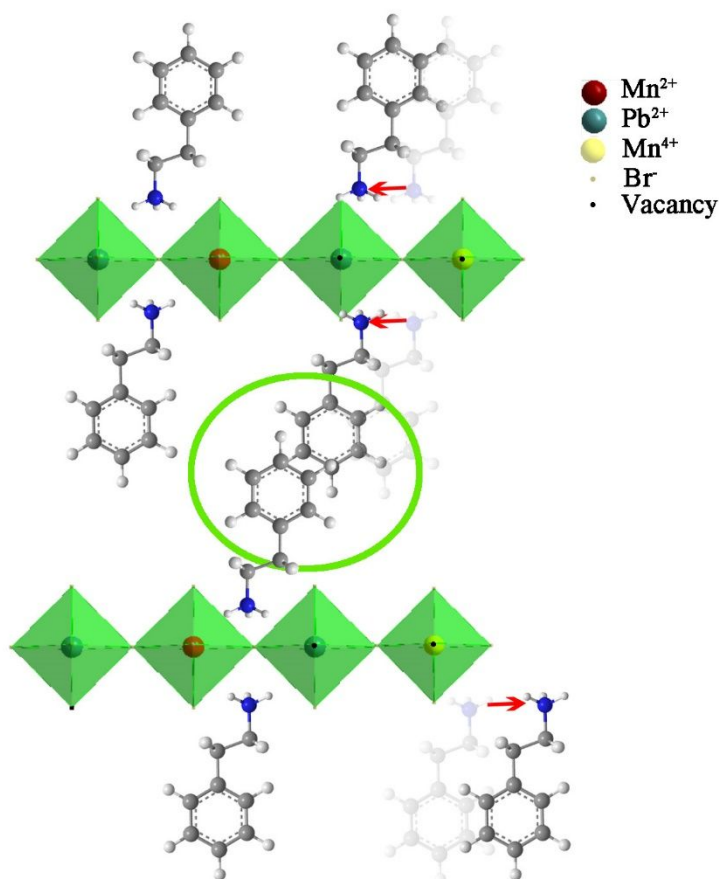


Scheme S2. Schematic representation of the $\text{OCA}_2\text{Pb}_{0.74}\text{Mn}_{0.26}\text{Br}_4$ 2D perovskite.



Scheme S3. Schematic representation of the P-33 2D perovskite.

As the amount of PEA ammonium cations decreases, the PEA ammonium cations will move away from each other due to the steric hindrance. In other words, the intervals between them become large and the local crystal-field symmetry increases.



Scheme S4. Schematic representation of the P-33 2D perovskite after oxidation.

After oxidation, Mn^{4+} ions exist in the inorganic lattice which have higher effective nuclear charge. Hence, the ability of the halides around Mn(IV) giving electrons will be impaired. One ammonium cation can be stabilized by hydrogen bonds with the halides of the nearby two octahedra.¹ After oxidation, the hydrogen bonds between the ammonium headgroup and the halides around Mn(IV) are impaired, resulting in that the ammonium cations are attracted by the nearby $[\text{PbX}_6]^{4-}$ or $[\text{MnX}_6]^{4-}$ octahedron. Large steric hindrance between ammonium cations around the Mn(II) appears again (the green circle in this figure), which makes the crystal-field symmetry around these unoxidized Mn^{2+} decreases again.

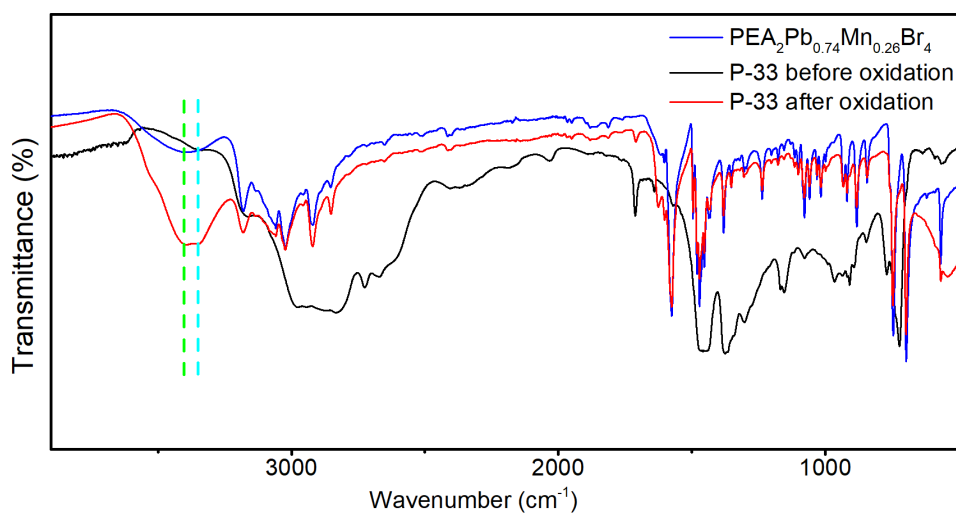


Figure S20. The FTIR spectra of $\text{PEA}_2\text{Pb}_{0.74}\text{Mn}_{0.26}\text{Br}_4$, P-33 before and after oxidation.

Hydrogen bond strength increases as the PEA reduces. After P-33 are oxidized, the hydrogen bond effect between the bromine ions and PEA molecules will decrease.

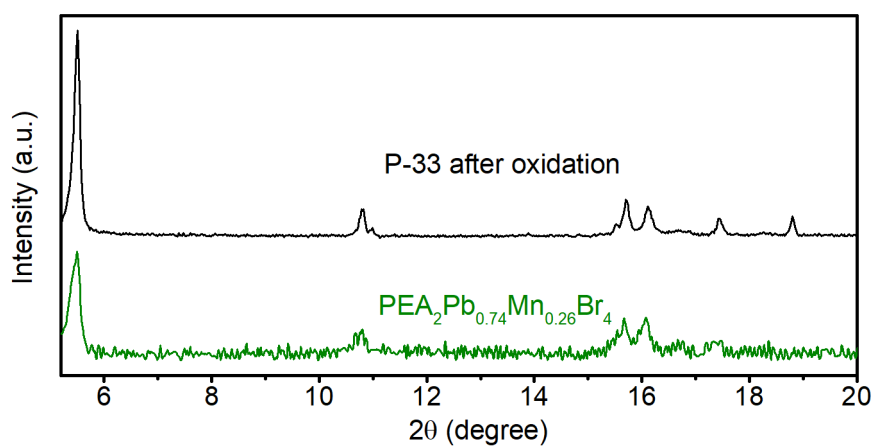


Figure S21. XRD patterns of $\text{PEA}_2\text{Pb}_{0.74}\text{Mn}_{0.26}\text{Br}_4$ and P-33 after oxidation.

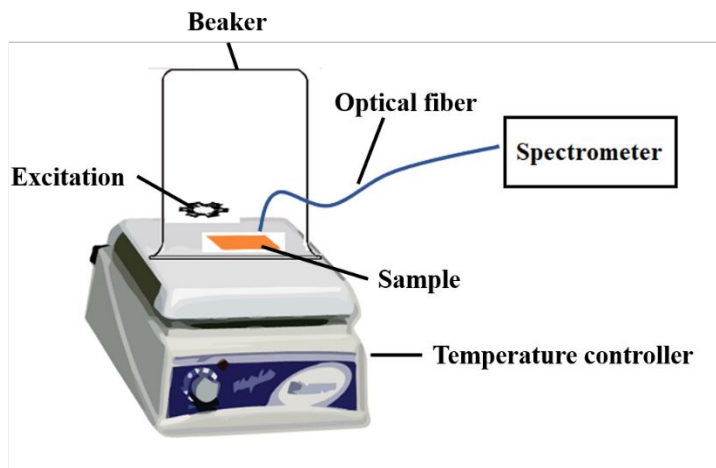


Figure S22. Schematic of the temperature and humidity controlling equipment.

The temperature of the whole room is controlled by air condition (20°). The temperature of the sample is precisely adjusted by temperature controller. In order to maintain the humidity condition, a large upside-down beaker is put on the sample. Besides, the gap is sealed by glue tape to form a closed system.

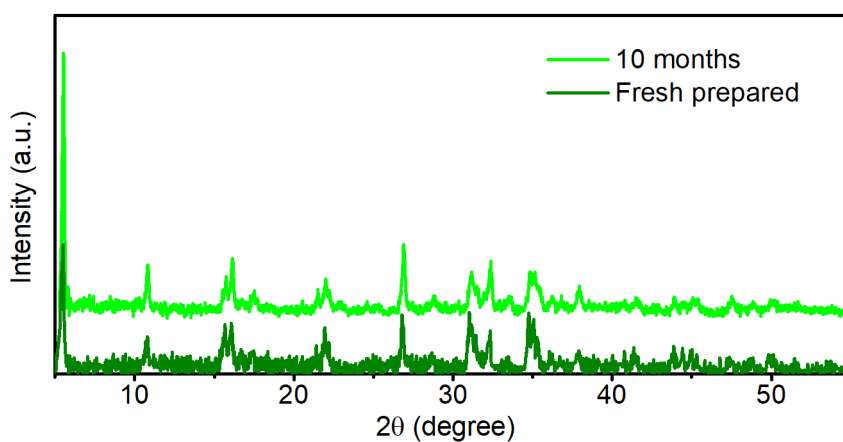


Figure S23. XRD pattern of $\text{PEA}_2\text{Pb}_{0.74}\text{Mn}_{0.26}\text{Br}_4$ after preserving in the ambient environment for 10 months.

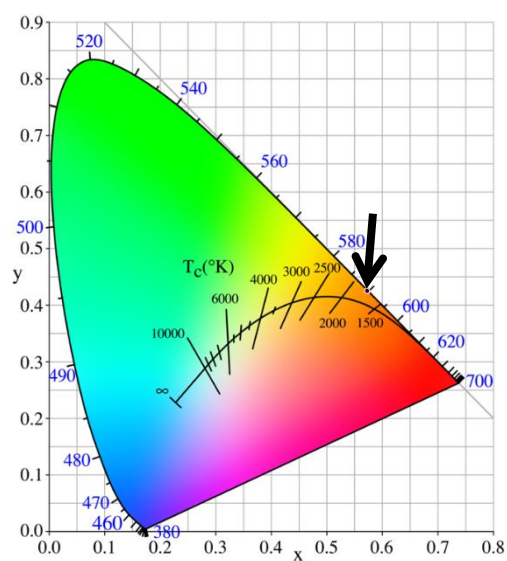


Figure S24. CIE chromaticity coordinate of the LED from P-100.

References

- (1) Ahmad, S.; Fu, P.; Yu, S.; Yang, Q.; Liu, X.; Wang, X.; Wang, X.; Guo, X.; Li, C. Dion-Jacobson Phase 2D Layered Perovskites for Solar Cells with Ultrahigh Stability. *Joule* **2019**, 3, 794-806.