Electronic Supplementary Information for:

Waterproof Perovskites: High Fluoresence Quantum Yield and Stability from a Methylammonium Lead Bromide / Formate Mixture in Water

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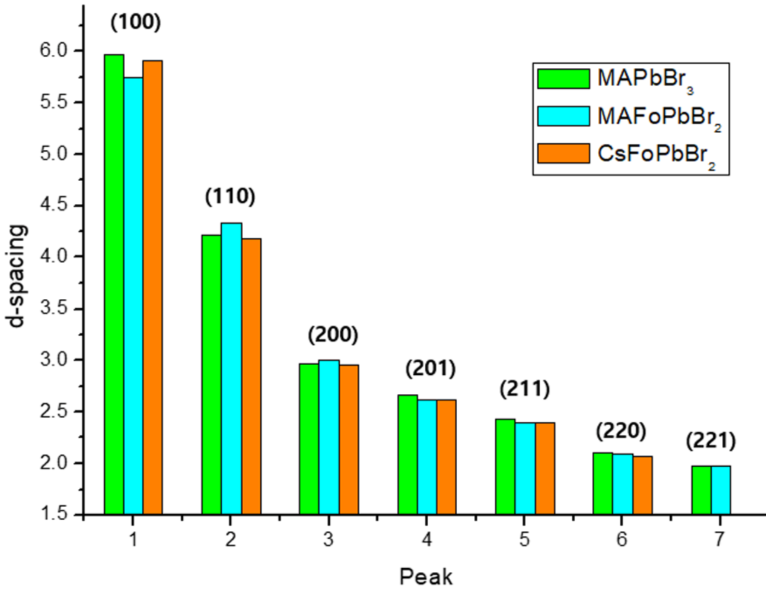


Figure S1. d-spacing comparison of $MAPbBr_3$, $MAFoPbBr_2$ and $CsFoPbBr_2$.

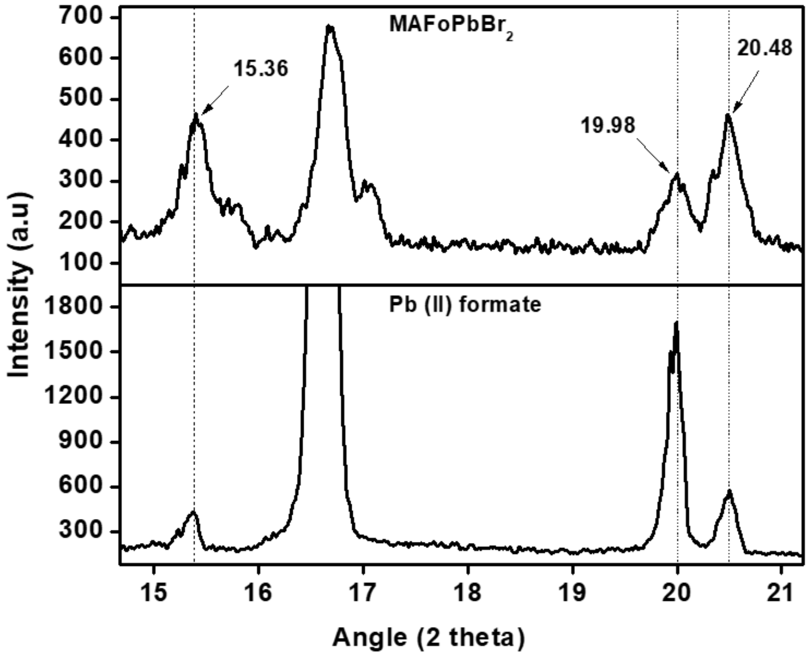


Figure S2. Comparative analysis of X-ray diffraction patterns of lead formate and 1:0.3 MAFo: $PbBr_2$.

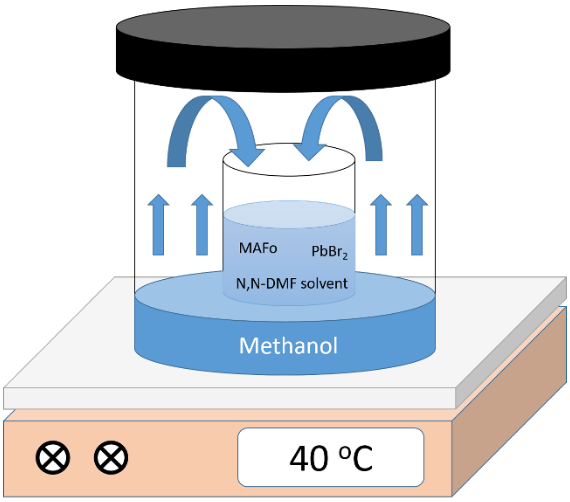
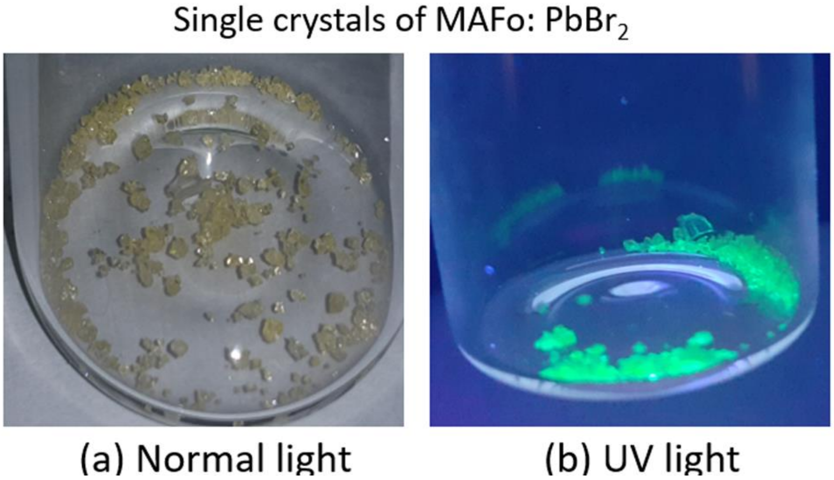
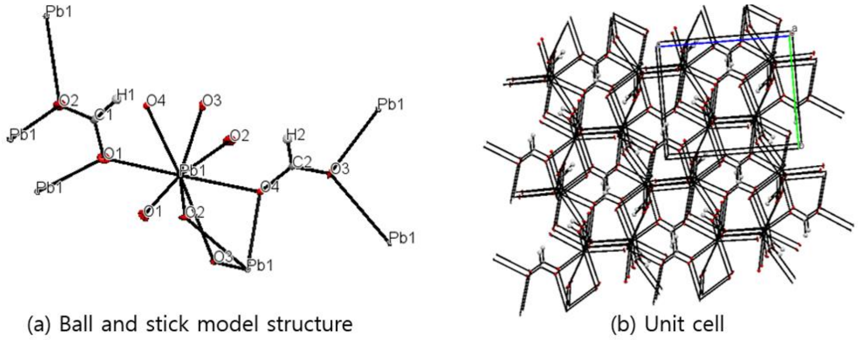


Figure S3. Vapor diffusion technique.



(a) Normal light (b) UV light

Figure S4. Photographs of single crystals prepared by vapor diffusion. (a) Crystals under normal light, (b) crystals under UV light.



(a) Ball and stick model structure (b) Unit cell

Figure S5. Single crystal analysis of MAFo: PbBr$_2$ crystals. (a) Ball and stick model and (b) unit cell.

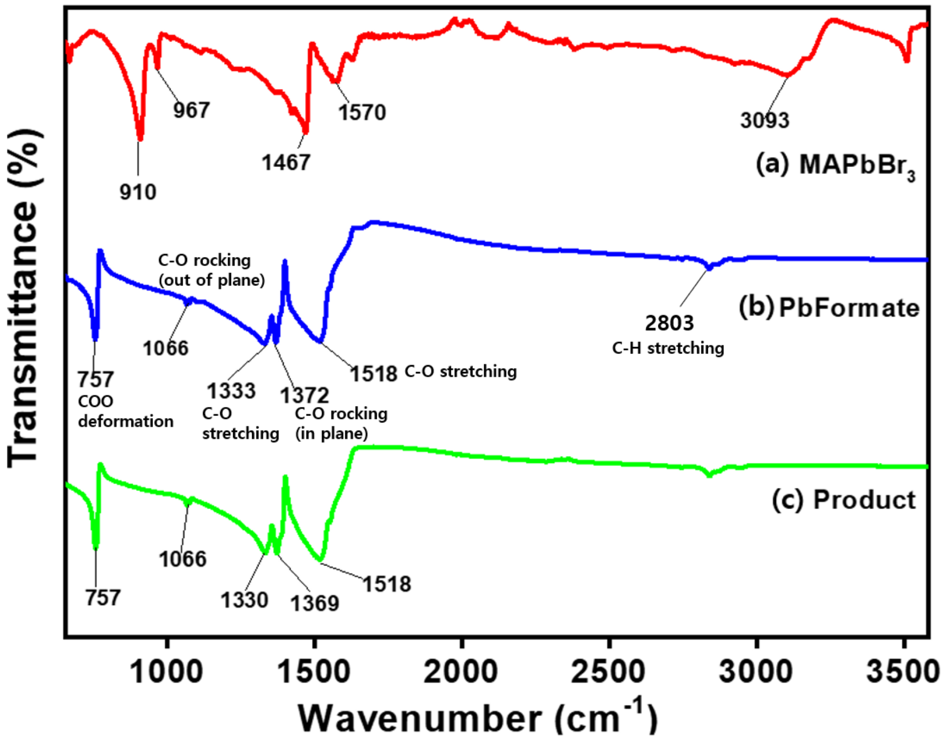


Figure S6. FT-IR comparison of (a) MAPbBr$_3$, (b) Lead formate and c) 1:0.3 MAFo: PbBr$_2$.

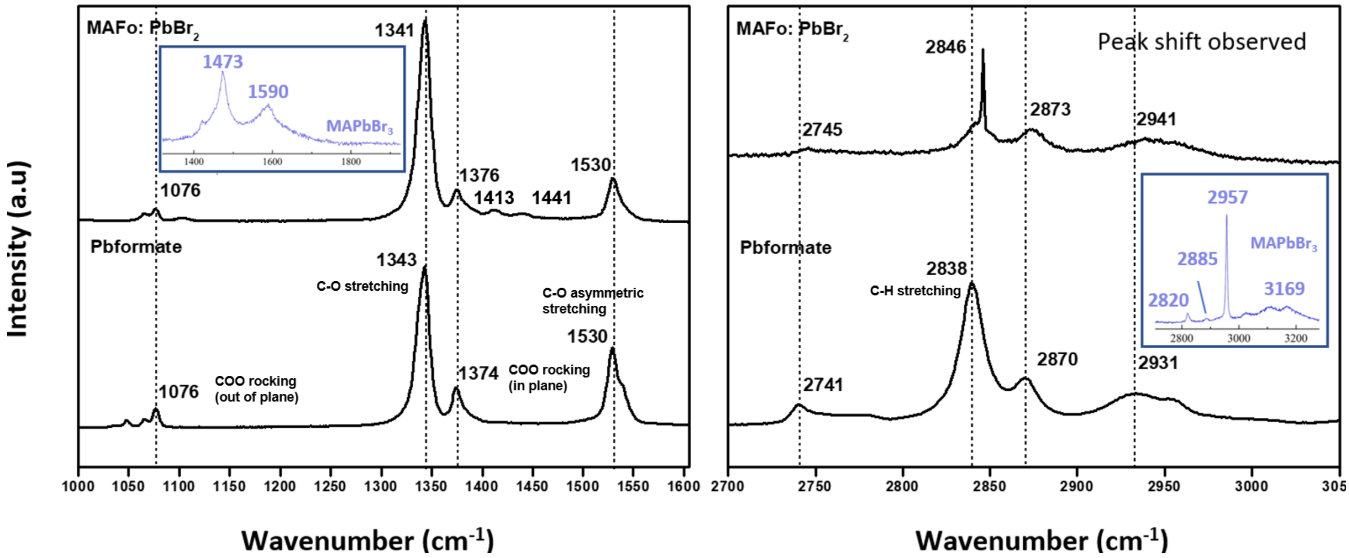
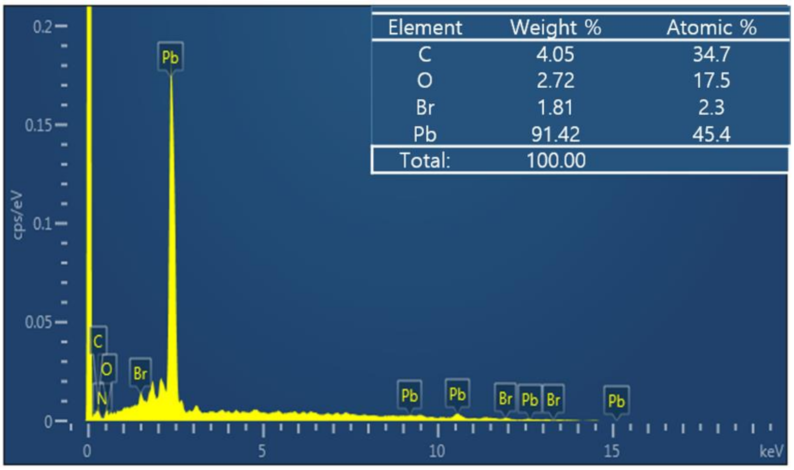


Figure S7. Raman spectra of MAFo:PbBr$_2$ fluorescent crystals and lead formate. MAPbBr$_3$ reference spectrum was reported by K. Wang et al[1]



Element	Weight %	Atomic %
C	4.05	34.7
O	2.72	17.5
Br	1.81	2.3
Pb	91.42	45.4
Total:	100.00	

Figure S8. EDX spectroscopy of 1:0.3 MAFo:PbBr$_2$ (1:0.3) crystals.

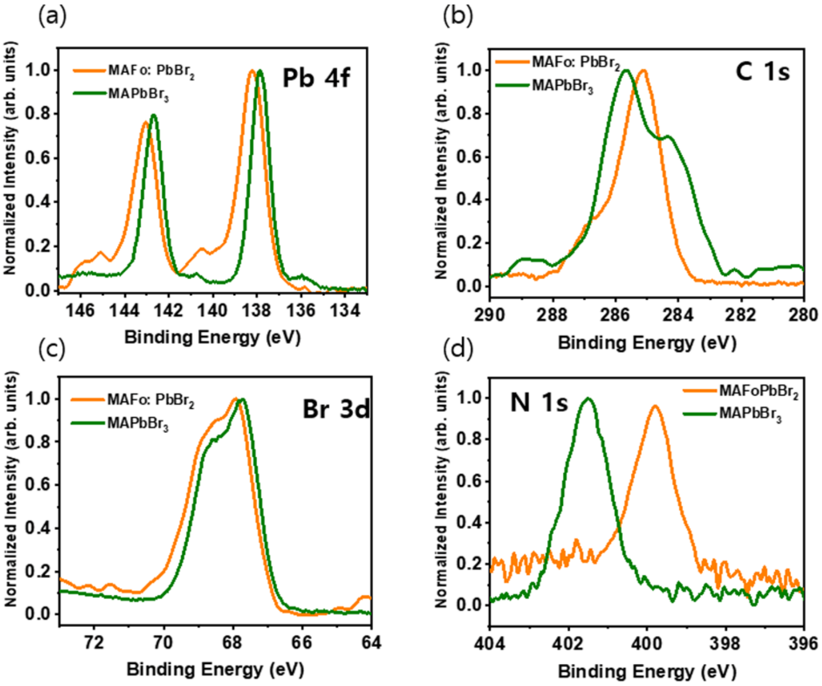
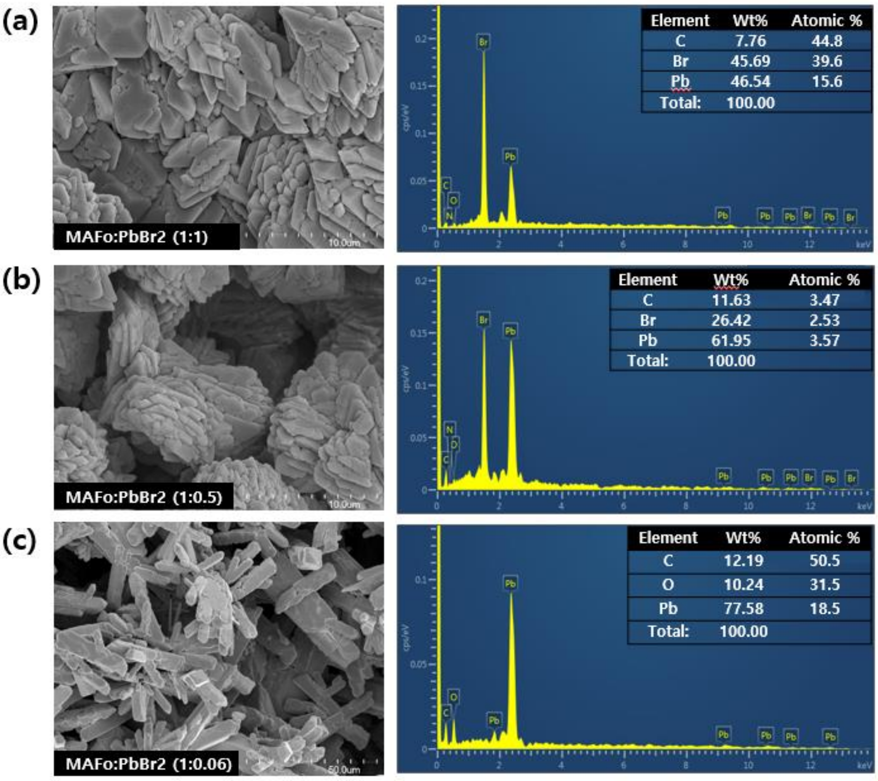


Figure S9. X-ray photoelectron spectroscopy (XPS) analysis. Core level binding energy comparison of MAFo: $PbBr_2$ and $MAPbBr_3$, (a)Pb 4f, (b) C 1s, (c) Br 3d and (d) N 1s.

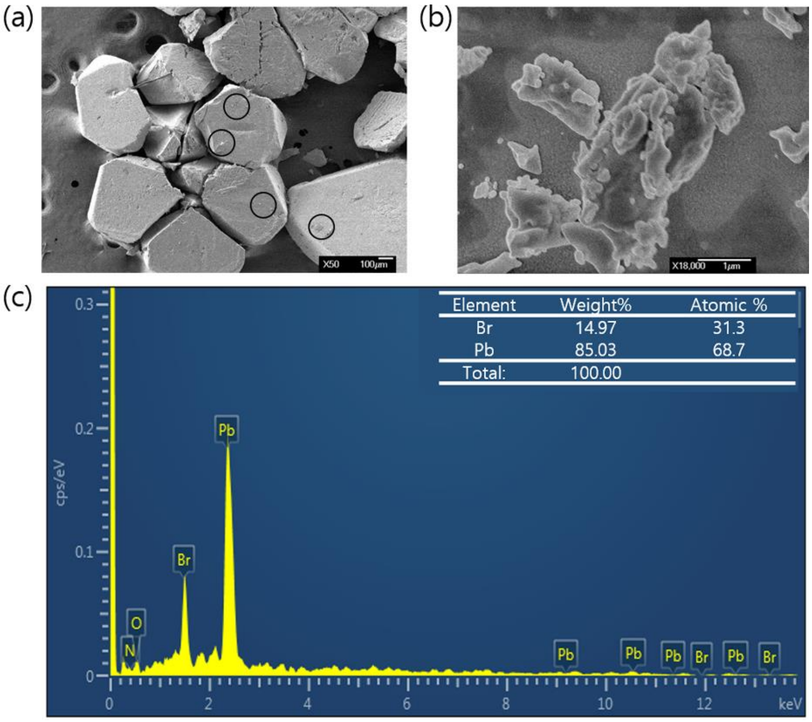


Element	Wt%	Atomic %
C	7.76	44.8
Br	45.69	39.6
Pb	46.54	15.6
Total:	100.00	

Element	Wt%	Atomic %
C	11.63	3.47
Br	26.42	2.53
Pb	61.95	3.57
Total:	100.00	

Element	Wt%	Atomic %
C	12.19	50.5
O	10.24	31.5
Pb	77.58	18.5
Total:	100.00	

Figure S10. SEM/EDX data of MAFo:$PbBr_2$ at ratios of (a) 1:1, (b) 1:0.5 and (c) 1:0.06.



Element	Weight%	Atomic %
Br	14.97	31.3
Pb	85.03	68.7
Total:	100.00	

Figure S11. FE-SEM images of (a) large sized crystal of MAFo:$PbBr_2$ (1:0.3); blisters are shown inside the circles, (b) blister shaped particles formed on the crystals. (e) EDX analysis of the blister shaped particles.

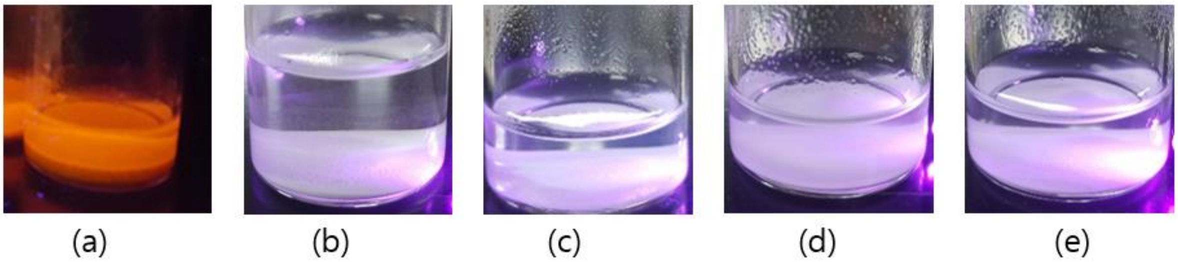


Figure S12. Photographs of material obtained upon replacement of MA with (a) cesium, (b) ethylammonium, (c) propylammonium, (d) iso-propylammonium and (e) tert-butylammonium ions illuminated under a UV lamp.

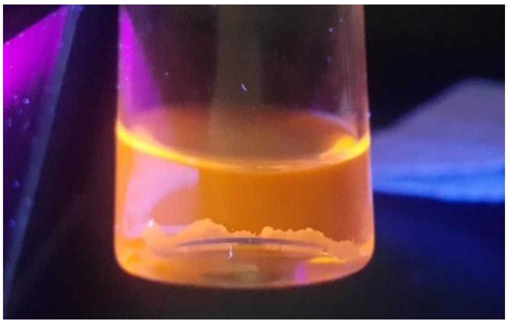


Figure S13. Image of lead bromide in DMF + methanol under UV lamp illumination.

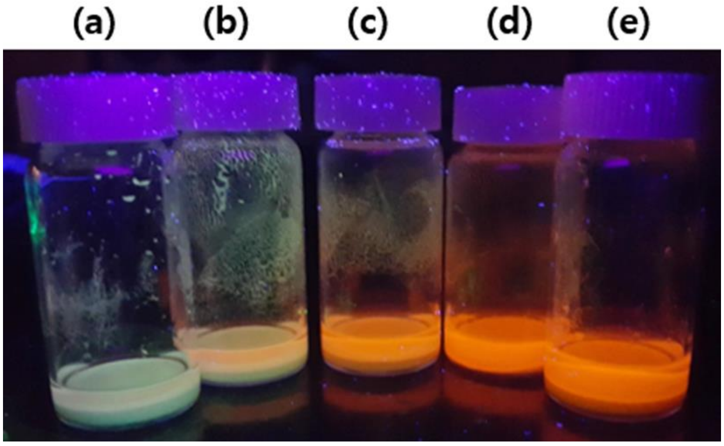


Figure S14. Increasing amount of PbBr2 in CsFo (a) 1:0.5, (b) 1:1, (c) 1:2, (d) 1:3, (e) 1:4

Orange fluorescence was observed when the amount of lead bromide was greater than cesium formate in mixed solution of DMF and MeOH. No fluorescence was observed when the reactant ratio was less than 1:0.5. In contrast, the MA cation in MAFo: $PbBr_2$ mixtures resulted in very high PLQY (70%) at ratios lower than 1:0.5. The intensity of fluorescence in case of cesium gradually increased when more lead bromide was introduced. However, the fluorescence was relatively dim compared to the green fluorescence of the 1:0.3 MAFo: $PbBr_2$ mixture.

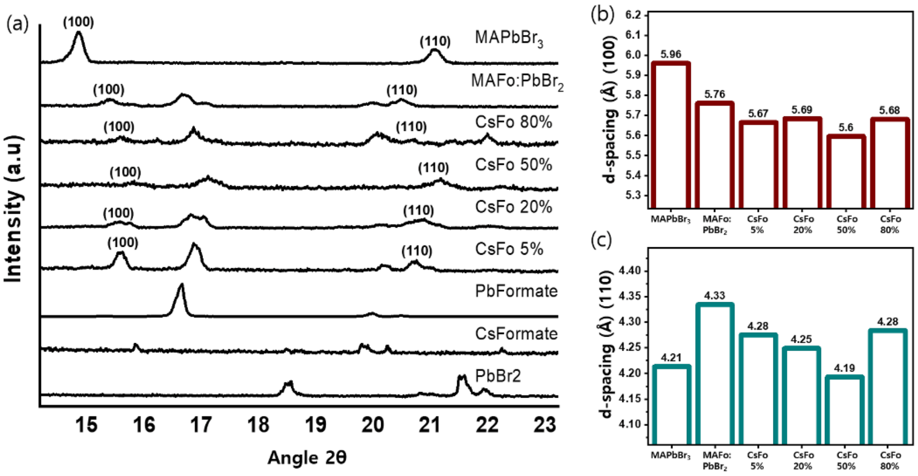


Figure S15. (a) XRD patterns, (b) d-spacing comparison of peak 100 and (c) peak 110 of MAFoPbBr$_2$ with the gradual addition of CsFo.

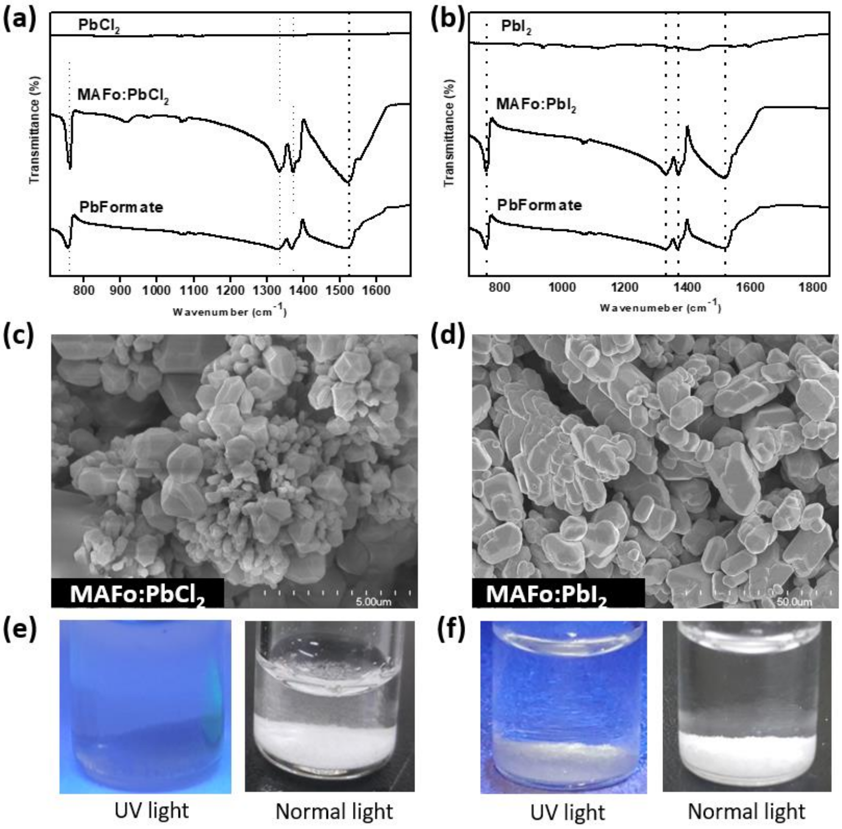


Figure S16. (a) FTIR data of MAFo: PbCl$_2$ (b) FTIR data of MAFo: PbI$_2$ (c) SEM image of MAFo:PbCl$_2$, (d) SEM image of MAFo:PbI$_2$. photographs of (e) MAFo:PbCl$_2$ under UV light and normal light and (f) MAFo:PbI$_2$ under UV light and normal light.

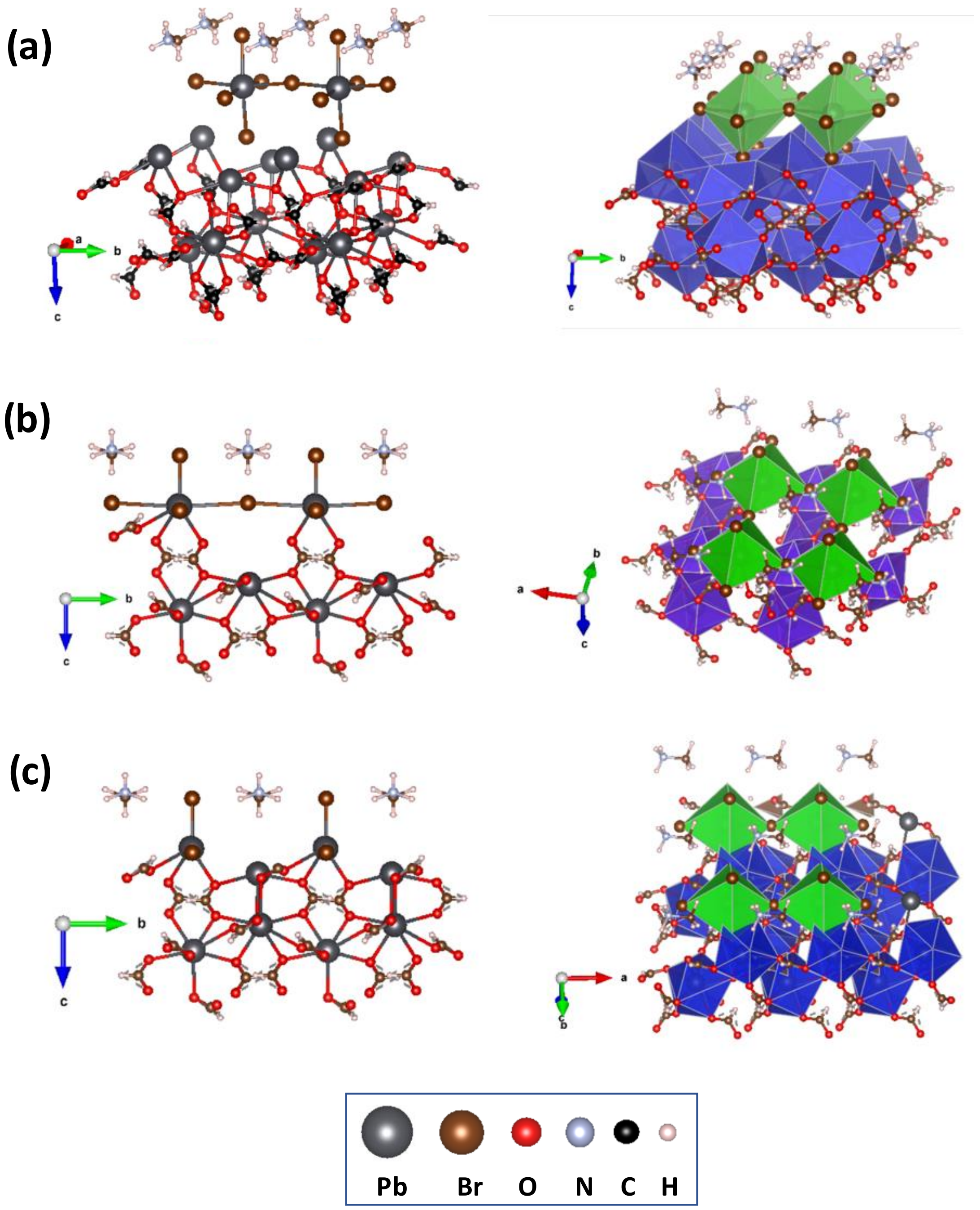


Figure S17. Proposed emissive surface structures of MAFo: $PbBr_2$. (a) Shows an $MAPbBr_3$ perovskite monolayer consisting of a sheet of $PbBr_6$ octahedra bound to the [001] surface of lead formate by electrostatic attraction between lead atoms on the surface of lead formate and bromine atoms in the perovskite layer. (b) Mixed coordination surface layer comprising square-pyramidal $PbBr_5$ units in which one Br site of the $PbBr_6$ octahedra is replaced by two formate ligands on the [001] surface of lead formate. (c) Mixed coordination surface layer comprising triangular $PbBr_3$ units in which three Br sites of the $PbBr_6$ octahedra are replaced by three formate ligands on the [001] surface of lead formate.

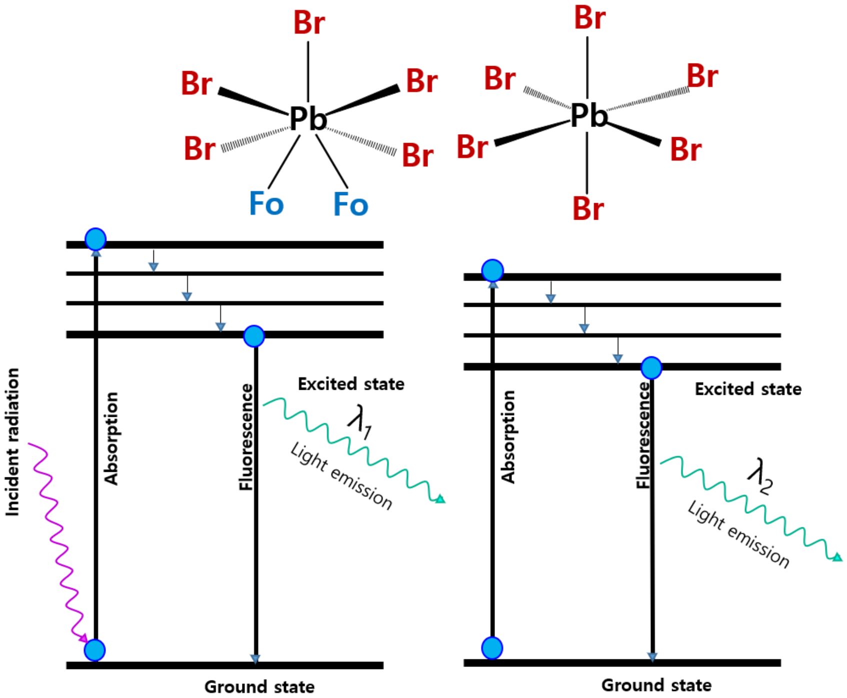


Figure S18. Jablonski diagram showing a possible mechanism for fluorescence with two bands. Since different emissive structures may have different energy gaps between their excited electronic states and ground states, light fluoresced from a mixture of the two structures may have different wavelengths or more than one local maximum.

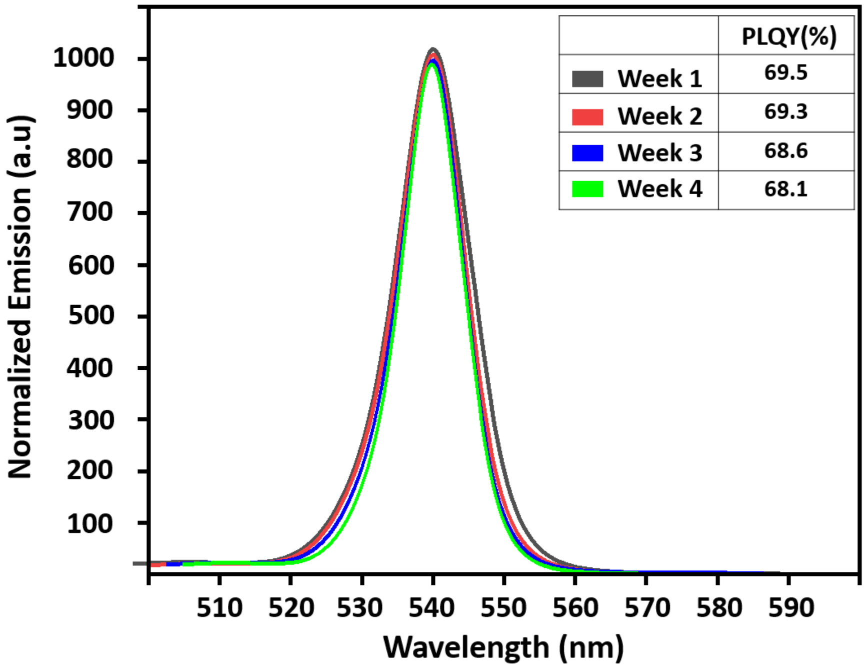


Figure S19. Stability of MAFo:PbBr$_2$ fluorescence spectrum upon immersion in water for a month.

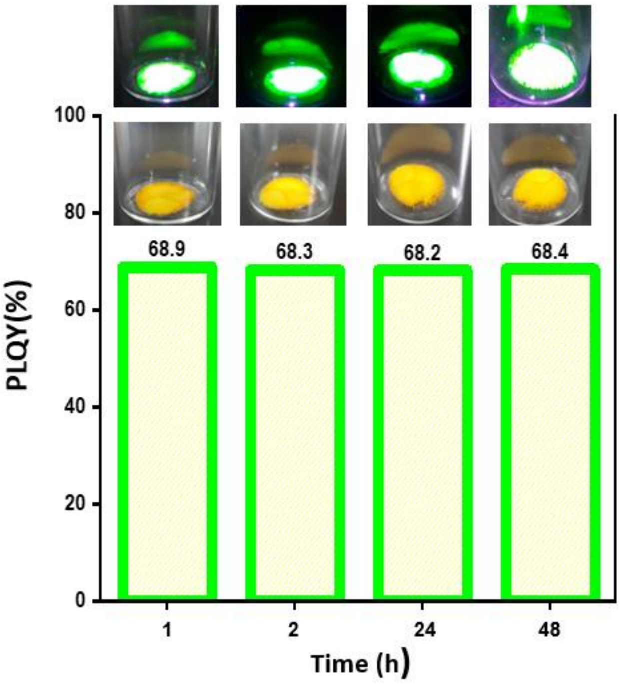


Figure S20. Stability of fluorescence quantum yield at 50 °C for 48 hours.

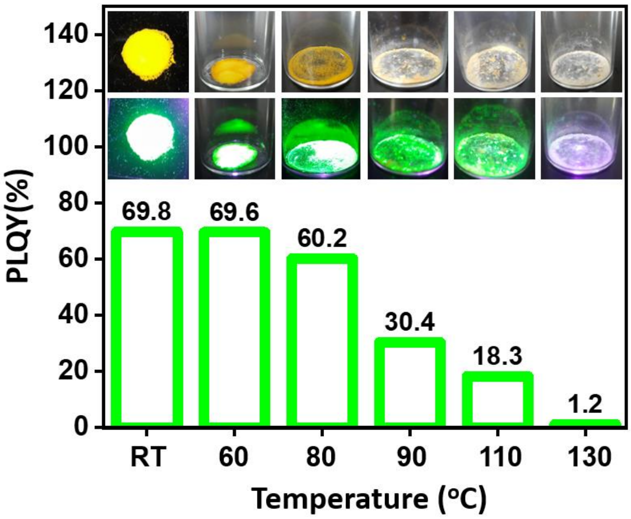


Figure S21. Stability of fluorescence at different temperatures.

Table S1 Single crystals analysis table.

	Obtained
Volume	423.92(8)
Space group	P 21 21 21
Hall group	P 2ac 2ab
Moiety formula	-
Sum formula	C2 H2 O4 Pb
Dx, gcm^{-3}	297.23
Z	4
Mu (mm^{-1})	39.405
F000	512.0
h,k,lmax	8,9,11
Nref	1021
Tmin, Tmax	0.013, 0.022

Table S2.Comparison of this work to other water stable perovskites

Title	Composition	PLQY	Stability	References
Waterproof Perovskites: High Fluoresence Quantum Yield and Stability from a Methylammonium Lead Bromide / Formate Mixture in Water **(This work)**	Composed of lead formate having a surface layer of emissive $MAPbBr_3$	70%	Air and water stable (**immersed**) for more than 6 months with no significant decrease in PLQY.	**This work**
Highly Luminescent and Water-Resistant $CsPbBr_3$–$CsPb_2Br_5$ Perovskite Nanocrystals Coordinated with Partially Hydrolyzed Poly(methyl methacrylate) and Polyethylenimine	Composed of $CsPbBr_3$-$CsPbBr_5$ perovskites stabilized by partially hydrolyzed PMMA and branched PEI	65% (solution) - 75% (film)	Water **(immersed)** heat and UV radiation stability. PLQY decreased to about 80% of its initial value after 40 days in water.	2
Water-Stable, Fluorescent Hybrid and Fully Inorganic Perovskites	Composed hybrid perovskites with a lead hydroxide protective layer for water resistance	70%	Water stable **(immersed)** for 6 months. PLQY of aged samples decreases from 53.9 % to 40.1%	3
Water resistant $CsPbX_3$ nanocrystals coated with polyhedral oligomeric silsesquioxane and their use as solid state luminophores in all-perovskite white light-emitting devices	Composed of CsPbX3 with surface protection provided by a polyhedral oligomeric silsesquioxane (POSS)	69% / 45% after silsequioxane treatment	Water **(dispersed)** resistance over 10 weeks; samples emitted strong green light after 10 weeks but PLQY of aged samples not reported	4

References:

1 K.-H. Wang, L.-C. Li, M. Shellaiah and K. Wen Sun, *Sci. Rep.*, 2017, **7**, 13643.

2 G. Jiang, C. Guhrenz, A. Kirch, L. Sonntag, C. Bauer, X. Fan, J. Wang, S. Reineke, N. Gaponik and A. Eychmüller, *ACS Nano*, 2019, **13**, 10386–10396.

3 A. Jana and K. S. Kim, *ACS Energy Lett.*, 2018, **3**, 2120–2126.

4 H. Huang, B. Chen, Z. Wang, T. F. Hung, A. S. Susha, H. Zhong and A. L. Rogach, *Chem. Sci.*, 2016, **7**, 5699–5703.