

Tunable optical and scintillation properties of two-dimensional tin-mixed halide perovskites

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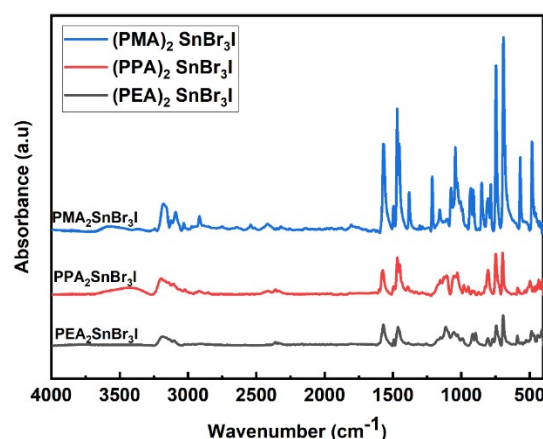


Fig. S1. FTIR spectra of mixed halide Sn based perovskite.

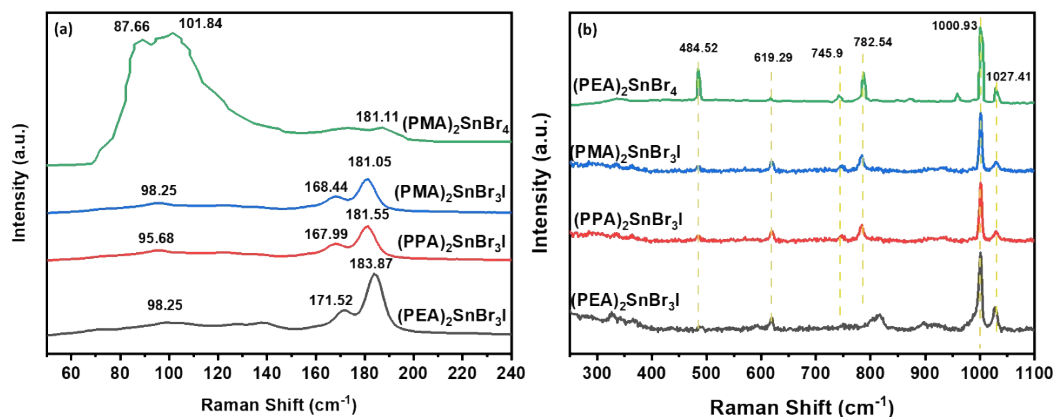


Fig. S2. Raman spectra of mixed halide Sn based perovskite (a) below 250 cm^{-1} and (b) 300-1100 cm^{-1} . Green vertical dashed lines are used for reference.

Fig. S2b represents the mid and high region Raman spectra of $(\text{PMA})_2\text{SnBr}_3\text{I}$, $(\text{PEA})_2\text{SnBr}_3\text{I}$ and $(\text{PPA})_2\text{SnBr}_3\text{I}$ exhibiting similar vibrational band with seven dominant Raman peaks at 619.29, 782.54, 1000.93, 1027.41 cm^{-1} . These indicates the prominent signal of electrostatic attractions and chemical interactions between organic cation and the inorganic SnBr_3I framework. Vibrational band at 783 cm^{-1} correspond to the CH_3NH_3^+ rocking. The observed stretching mode at 1001.54 cm^{-1} is from C-N stretching, which serves as an indication of strong interaction from the inorganic framework. The twisting mode NH_3^+ at 1600 in the $(\text{PMA})_2\text{SnBr}_3\text{I}$, $(\text{PEA})_2\text{SnBr}_3\text{I}$ and $(\text{PPA})_2\text{SnBr}_3\text{I}$ perovskites are too weak, this indicates that the vibrational of the PMA, PPA, and PEA cations are highly sensitive to the microenvironment. Meanwhile, peak 326.29 cm^{-1} only appear on $(\text{PEA})_2\text{SnBr}_3\text{I}$ that indicates in 2D-structured, the alkylammonium cations still interact with the SnBr_3I framework via the NH_3^+ .

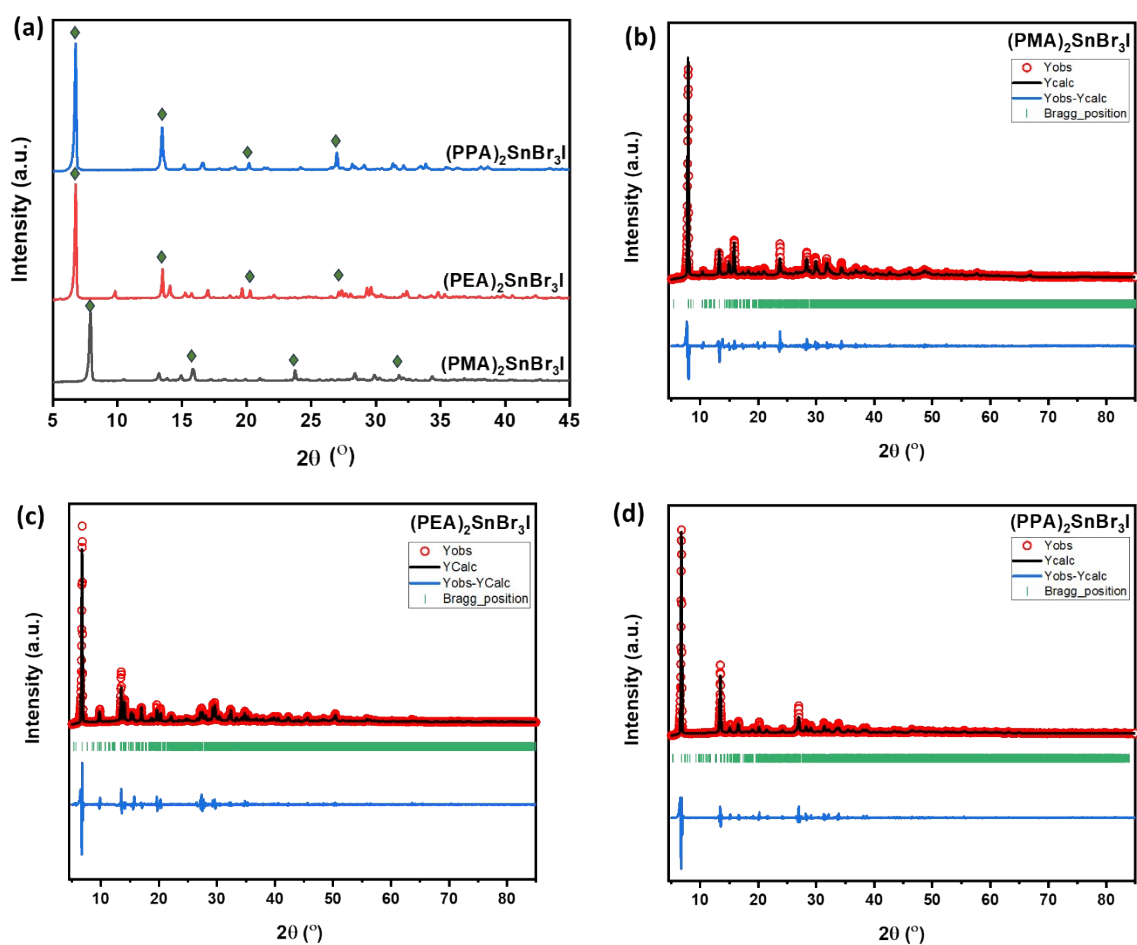


Fig. S3. (a) XRD pattern of tin-mixed halide perovskite and Rietveld refinement of (b) $(\text{PMA})_2\text{SnBr}_3\text{I}$, (c) $(\text{PEA})_2\text{SnBr}_3\text{I}$ and (d) $(\text{PPA})_2\text{SnBr}_3\text{I}$.

Supplementary Table 1. Summary of parameters obtained from Rietveld refinement of diffraction patterns.

Compound name	$(\text{PMA})_2\text{SnBr}_3\text{I}$	$(\text{PEA})_2\text{SnBr}_3\text{I}$	$(\text{PPA})_2\text{SnBr}_3\text{I}$
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P -1	P -1	P -1
χ^2	26.2	44	37.9
Bragg R-factor	2.19	2.66	1.08
R_f -factor	1.91	2.20	2.03
R_p	37.2	34.5	34.1
R_{wp}	37.5	38.4	34.0
R_e	7.33	5.75	5.52
$a/\text{\AA}$	11.4763	15.9449	13.2983
$b/\text{\AA}$	11.3655	11.8069	12.2002
$c/\text{\AA}$	17.0744	17.4328	17.2782
$\alpha/^\circ$	80.347	80.121	79.273
$\beta/^\circ$	75.146	75.080	80.771
$\gamma/^\circ$	90.613	90.038	90.771
$V/\text{\AA}^3$	2118.8101	3120.7913	2715.9031
2θ range	$5^\circ - 80^\circ$	$5^\circ - 80^\circ$	$5^\circ - 80^\circ$
GoF index	5.1	6.7	6.2
N sigma of GoF	1079.155	1868.296	1584.007

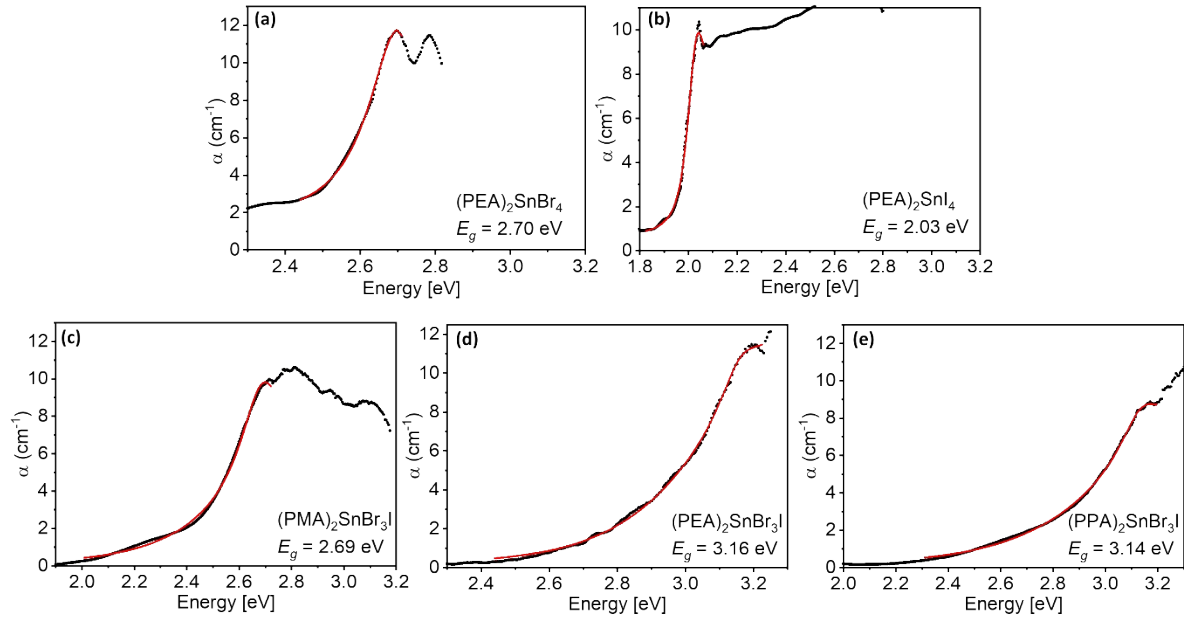


Fig. S4. Elliott fittings and the energy bandgaps of (a) $(\text{PEA})_2\text{SnBr}_4$, (b) $(\text{PEA})_2\text{SnI}_4$, (c) $(\text{PMA})_2\text{SnBr}_3\text{I}$, (d) $(\text{PEA})_2\text{SnBr}_3\text{I}$, and (e) $(\text{PPA})_2\text{SnBr}_3\text{I}$.

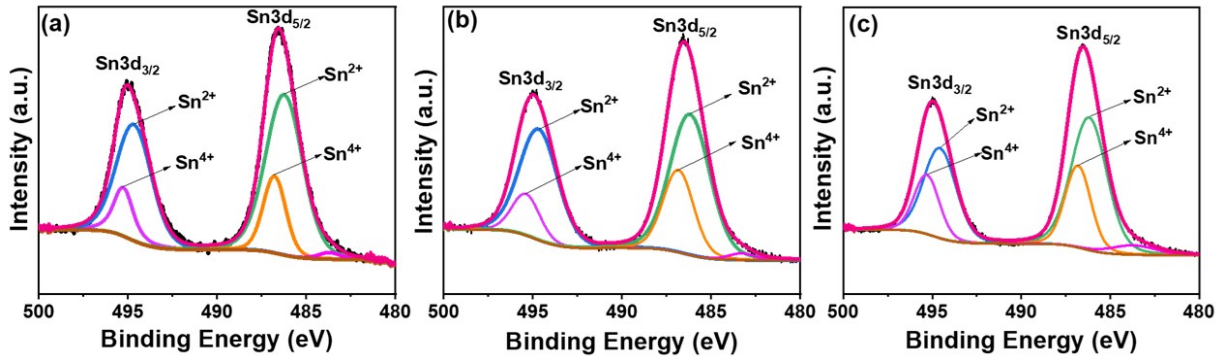


Fig. S5. XPS spectra Sn 3d of (a) $(\text{PMA})_2\text{SnBr}_3\text{I}$, (b) $(\text{PEA})_2\text{SnBr}_3\text{I}$, (c) $(\text{PPA})_2\text{SnBr}_3\text{I}$.

Supplementary Table 2. Summary of Sn peak position based on deconvoluted XPS spectra.

Sample	Sn 3d _{3/2}		Sn 3d _{5/2}		
	Peak Position				
	Sn ²⁺	Sn ⁴⁺	Sn ²⁺	Sn ⁴⁺	Sn ⁰
PMA ₂ SnBr _x I _y	494.66	495.26	486.24	486.78	483.7
PEA ₂ SnBr _x I _y	494.67	495.38	486.19	486.84	483.3
PPA ₂ SnBr _x I _y	494.57	495.31	486.19	486.81	483.73

Supplementary Table 3. Summary of Sn contents and Sn⁴⁺ ratio in Sn composition¹

Sample	% conc.						
	Sn 3d _{3/2}			Sn 3d _{5/2}			
	Sn ²⁺	Sn ⁴⁺	Sn ⁴⁺ ratio	Sn ²⁺	Sn ⁴⁺	Sn ⁰	Sn ⁴⁺ ratio
$\text{PMA}_2\text{SnBr}_x\text{I}_y$	31.45	8.77	0.218	45.36	13.29	1.13	0.222
$\text{PEA}_2\text{SnBr}_x\text{I}_y$	31.18	8.44	0.213	40.77	18.35	1.27	0.304
$\text{PPA}_2\text{SnBr}_x\text{I}_y$	25.15	12.83	0.338	40.22	18.17	3.62	0.293

Supplementary Table 4. Summary of FWHM of Sn peak based on deconvoluted XPS spectra

Sample	FWHM				
	Sn 3d _{3/2}		Sn 3d _{5/2}		
	Sn ²⁺	Sn ⁴⁺	Sn ²⁺	Sn ⁴⁺	Sn ⁰
PMA ₂ SnBr _x I _y	2.33	1.3	2.45	1.5	1.49
PEA ₂ SnBr _x I _y	2.53	1.83	2.63	2.03	1.75
PPA ₂ SnBr _x I _y	2.15	1.67	2.35	1.72	3

Supplementary Table 5. Extracted XPS parameter of Br 3d

Sample	Peak position		FWHM		Area	
	Br _{3/2}	Br _{5/2}	Br _{3/2}	Br _{5/2}	Br _{3/2}	Br _{5/2}
PMA ₂ SnBr _x I _y	69.3	68.24	1.63	2.1	2611.46	11459.54
PEA ₂ SnBr _x I _y	69.62	68.56	1.56	2.38	778.04	9862.23
PPA ₂ SnBr _x I _y	68.52	68.51	2.32	2.49	98.69	2636.24

Supplementary Table 6. Extracted XPS parameter of I 3d

Sample	Peak position		FWHM		Area	
	I _{3/2}	I _{5/2}	I _{3/2}	I _{5/2}	I _{3/2}	I _{5/2}
PMA ₂ SnBr _x I _y	629.62	618.11	2.81	2.58	1175.03	1677.31
PEA ₂ SnBr _x I _y	630.37	618.86	2.86	2.59	2219.17	2818.75
PPA ₂ SnBr _x I _y	630.04	618.34	1.25	3.39	383.84	1270.81

Supplementary Table 7. Summary of integrated area of Sn, Br and I peak extracted from the deconvoluted XPS spectra

Sample	Area					Br	I	Sn/Br,I ratio
	Sn 3d _{3/2}		Sn 3d _{5/2}					
	Sn ²⁺	Sn ⁴⁺	Sn ²⁺	Sn ⁴⁺	Sn ⁰			
PMA ₂ SnBr _x I _y	12963.06	3615.04	18815.28	5511.56	471.28	14071	2852.34	2.45
PEA ₂ SnBr _x I _y	12362.94	3344.32	16267.75	7320.43	506.73	10722.3	5037.92	2.53
PPA ₂ SnBr _x I _y	10068.72	5134.76	16200.81	7315.26	1462.13	2733	1654.65	9.153

Supplementary Table 8. Summary of parameters based on crystal lattice system

Samples	Layer Spacing (Å)	Chain Spacing (Å)	Organic Chain penetrations (Å)	Organic Chain distances (Å)
(PMA) ₂ SnBr ₃ I	9.88	0.70	1.27	5.67
(PEA) ₂ SnBr ₃ I	10.29	0.91	1.37	5.75
(PPA) ₂ SnBr ₃ I	10.06	0.75	1.41	6.42

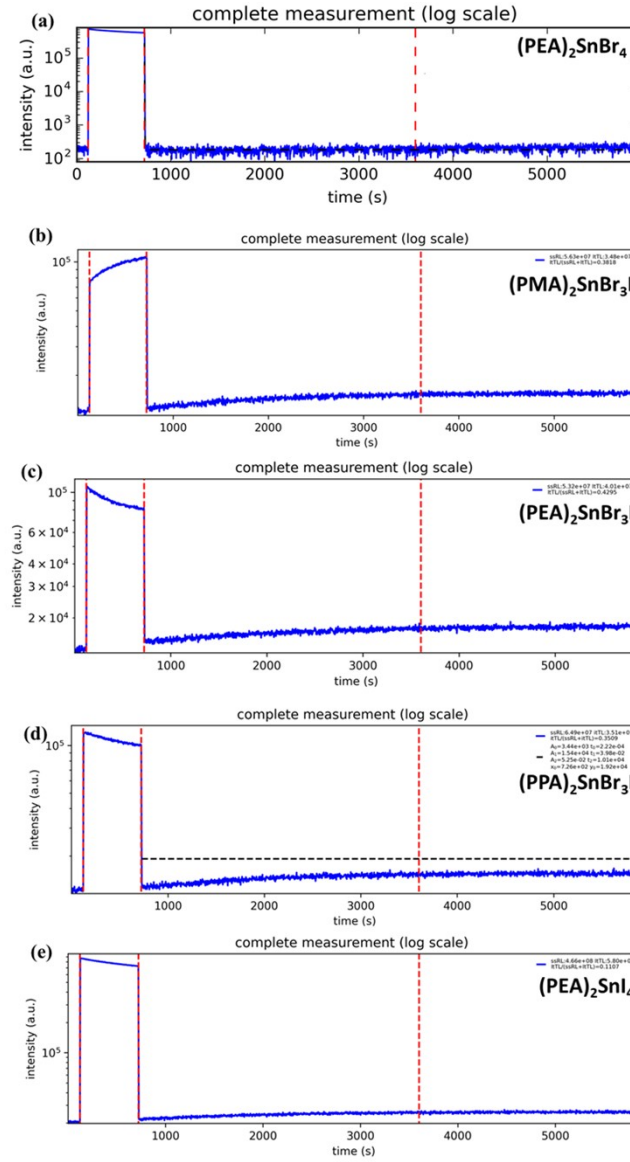


Fig. S6. Thermoluminescence of (a) $(\text{PEA})_2\text{SnBr}_4$, (b) $(\text{PMA})_2\text{SnBr}_3\text{I}$, (c) $(\text{PEA})_2\text{SnBr}_3\text{I}$, (d) $(\text{PPA})_2\text{SnBr}_3\text{I}$, (e) $(\text{PEA})_2\text{SnI}_4$. $(\text{PEA})_2\text{SnBr}_4$ and $(\text{PEA})_2\text{SnI}_4$ were used as the comparison for this study.

Negative Thermal Quenching Fitting

$$I(T) = A_0 \frac{1}{1 + C_1 \exp\left(\frac{-E_{d1}}{k_B T}\right)}$$

where A_0 is NTQ coefficient that related to the contribution from thermally excited electrons, C_1 are the thermal quenching coefficients related to non-radiative electrons excitation leading to thermal quenching, E_{d1} corresponds to the activation recombination energy of nonradiative processes, k_B is Boltzmann constant. All of energies have meV in Units.

Supplementary Table 9. Negative thermal quenching coefficients and the activation energy

Samples	I_0	C_1	E (meV)
$\text{PEA}_2\text{SnBr}_4$	1	2.77	6
PEA_2SnI_4	0.84	2.28	53
$\text{PMA}_2\text{SnBr}_3\text{I}$	0.96	4.85	13
$\text{PEA}_2\text{SnBr}_3\text{I}$	0.92	28.93	75
$\text{PPA}_2\text{SnBr}_3\text{I}$	0.91	14.02	43

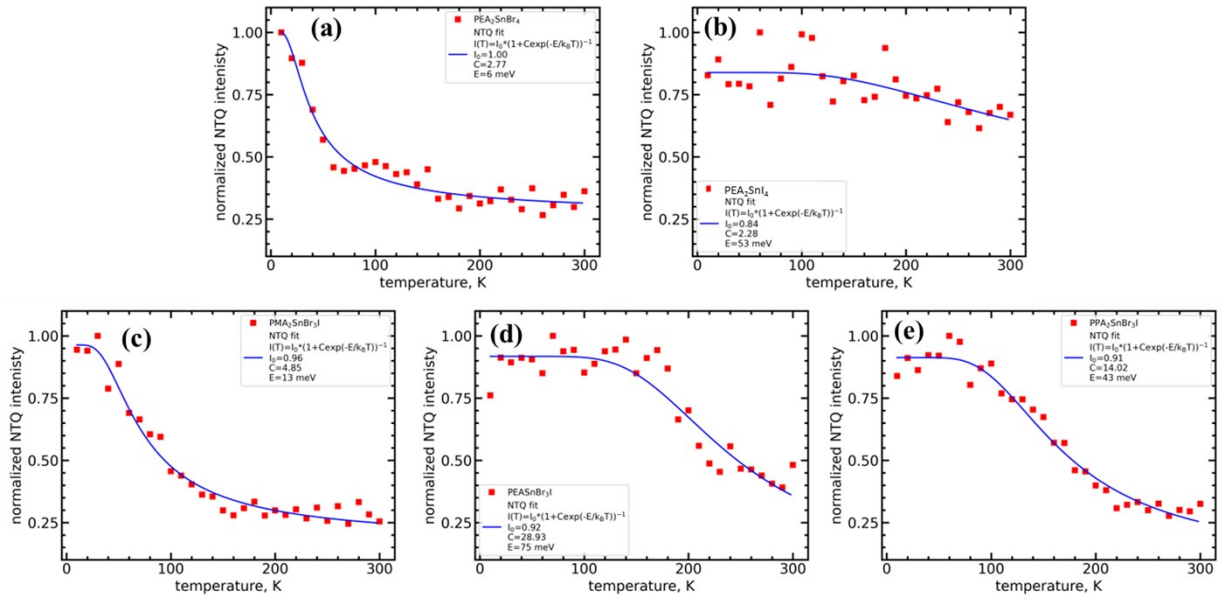


Fig. S7. Fitting of thermal quenching behavior of TMHPs.

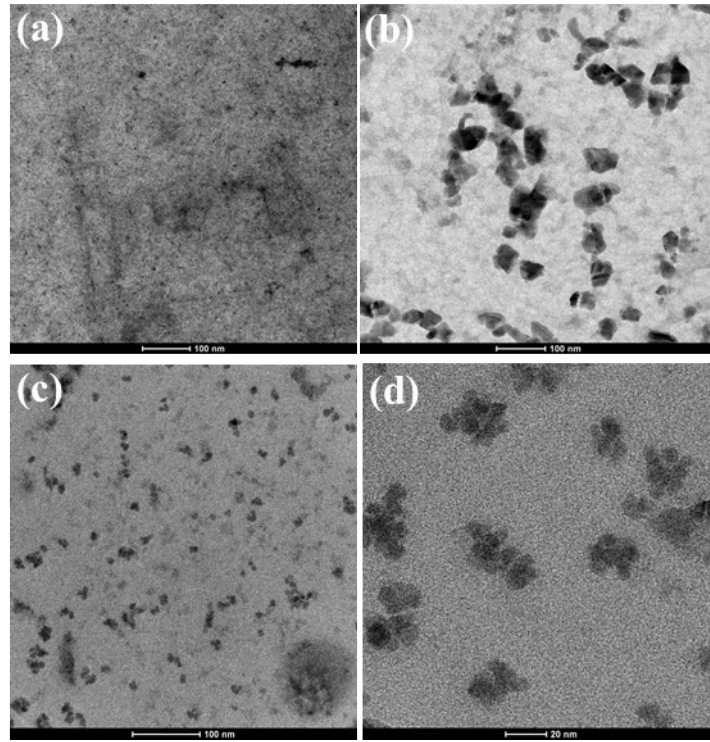


Fig. S8. TEM image of (a) $\text{PEA}_2\text{SnBr}_4$, (b) PEA_2SnI_4 , and (c) $\text{PEA}_2\text{SnBr}_3\text{I}$. (d) higher magnification TEM image of $\text{PEA}_2\text{SnBr}_3\text{I}$

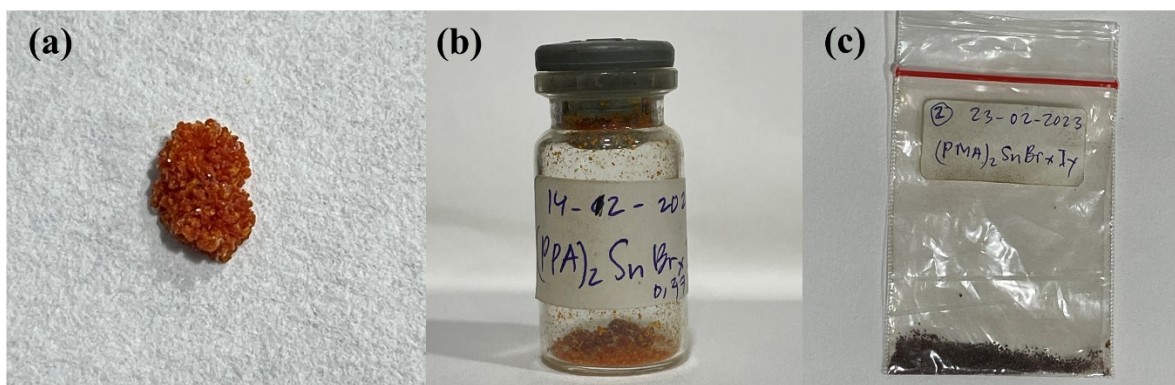


Fig. S9. Photograph sample of (a) $\text{PPA}_2\text{SnBr}_3\text{I}$, (b) saving up to 6 months in vial and (c) $\text{PMA}_2\text{SnBr}_3\text{I}$ saving up to 6 months in zip plastic.