Supporting information

Zero-Dimensional Hybrid Tin Halides with Stable Broadband Light Emissions

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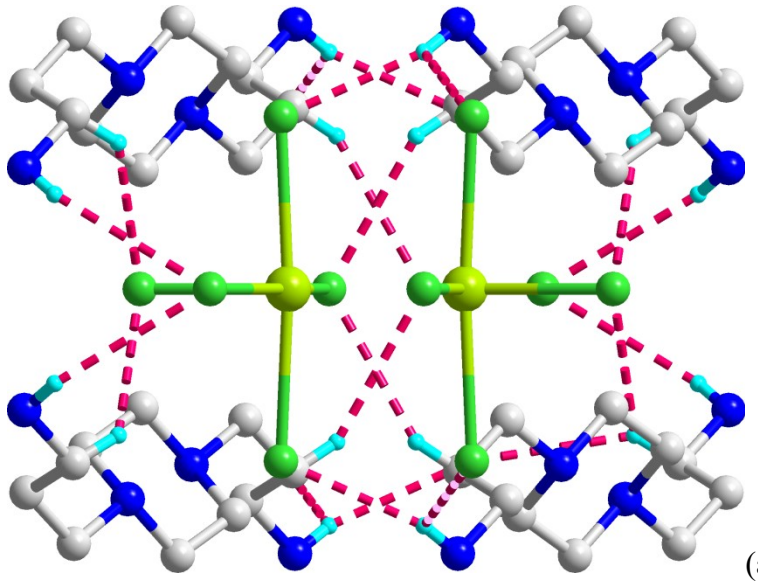
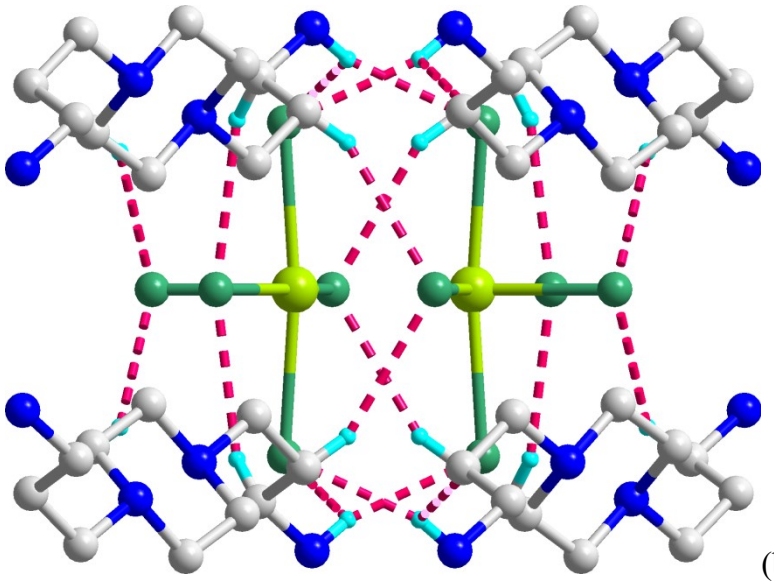
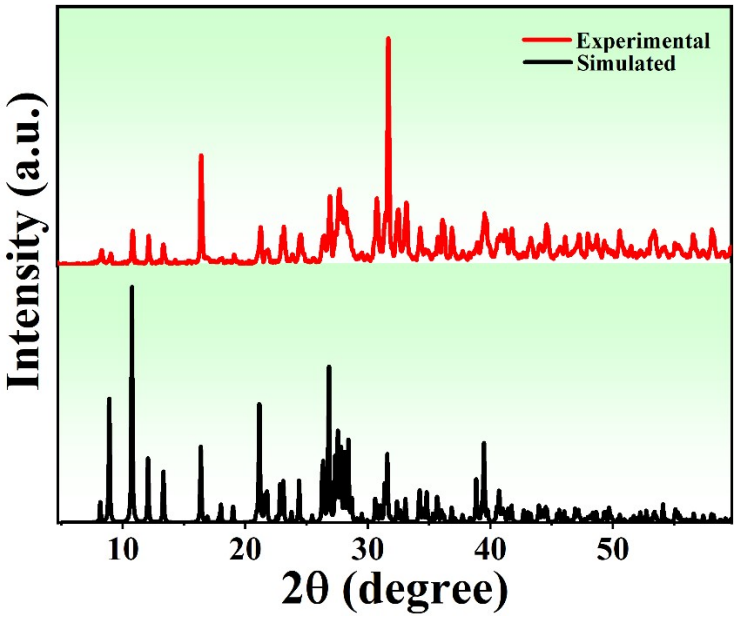


(a)

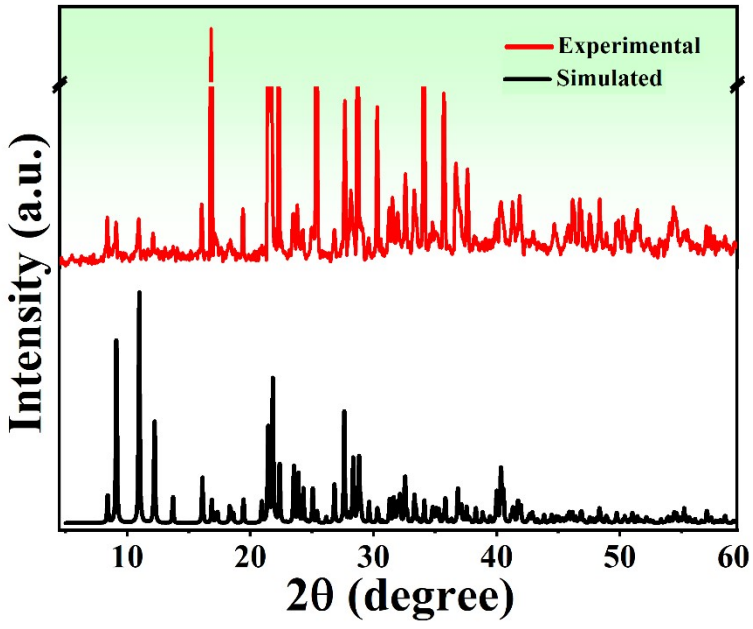


(b)

Figure S1. The hydrogen bonds between $[SnX_5]^{3-}$ and $[H4BAPP]^{4+}$ cations in two compounds.



(a)



(b)

Figure S2. The simulated and experimental XRD patterns of $[H_4BAPP]SnBr_5 \cdot Br$ (a) and $[H_4BAPP]SnCl_5 \cdot Cl \cdot H_2O$ (b).

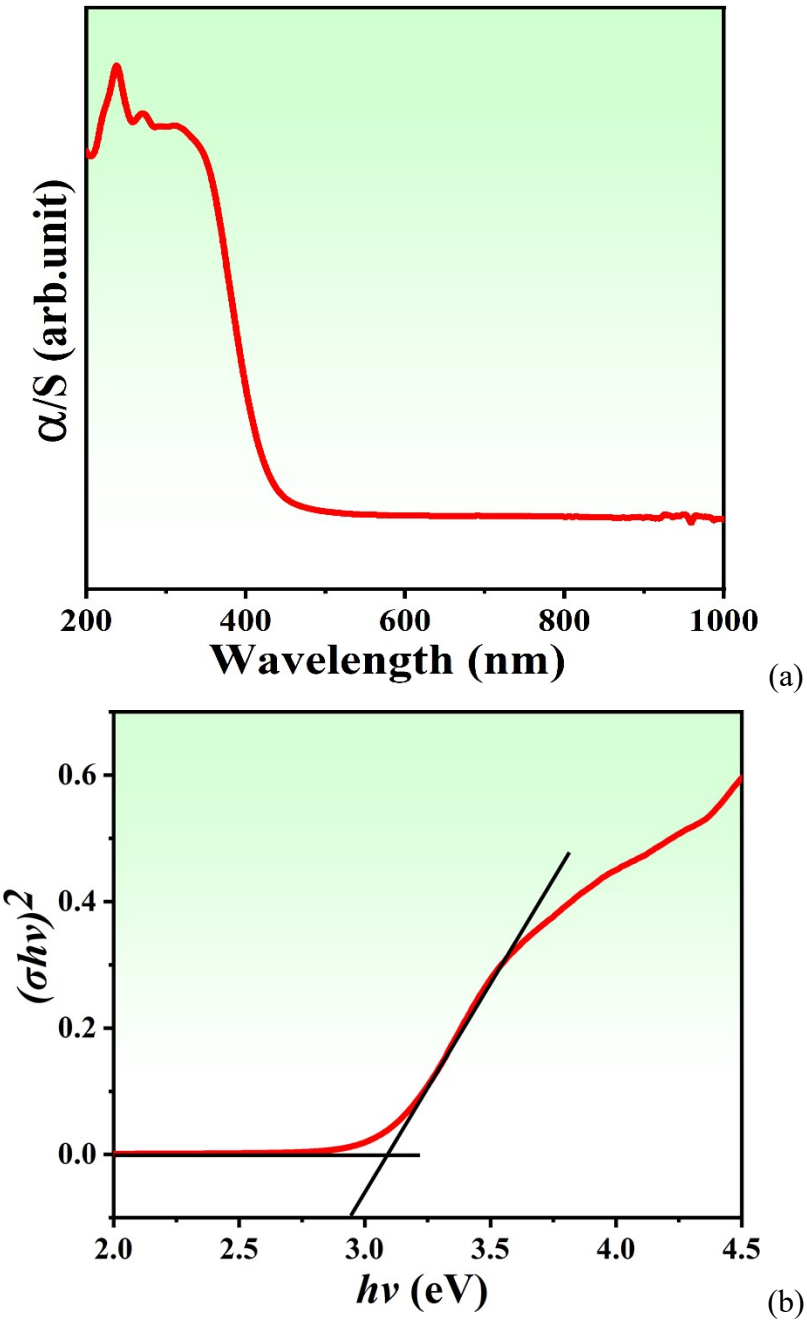
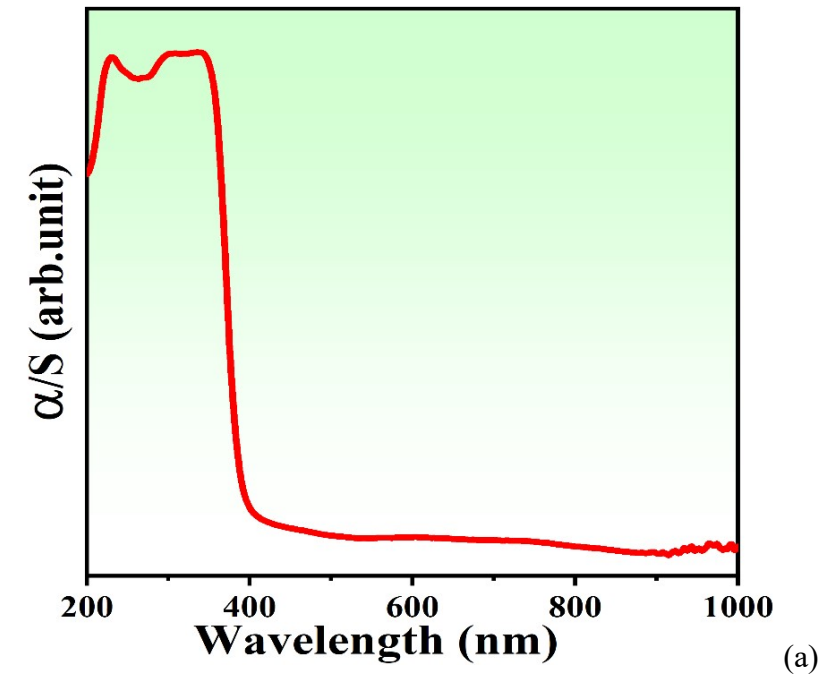
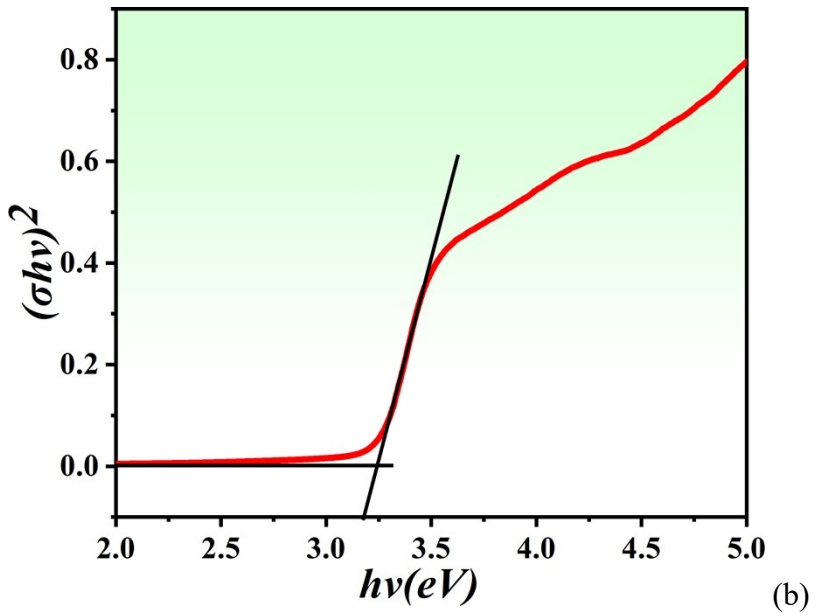


Figure S3. The solid state UV-vis adsorption spectra (a) and Tauc plot for band gap (b) of $[H_4BAPP]SnBr_5$.Br.

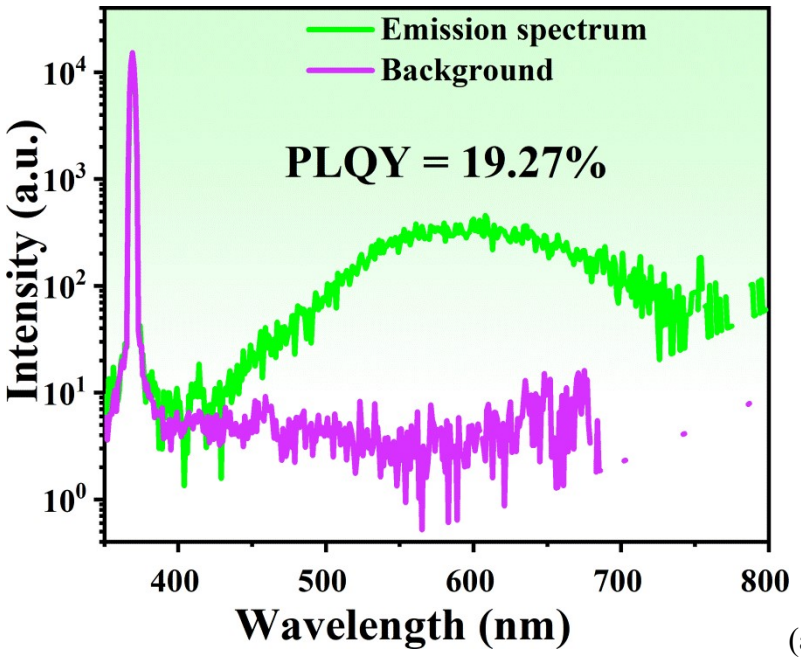


(a)

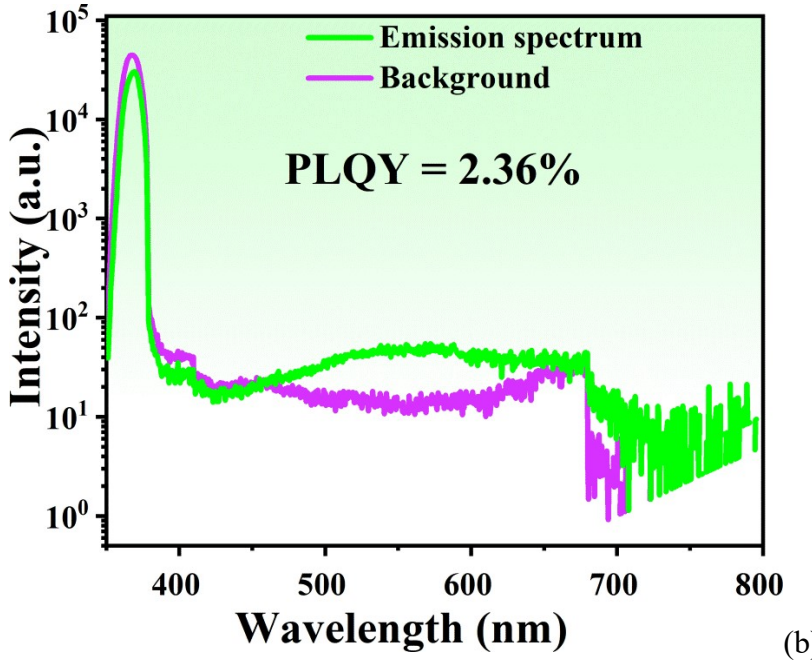


(b)

Figure S4. The solid state UV-vis adsorption spectra (a) and Tauc plot for band gap (b) of $[H_4BAPP]SnCl_5 \cdot Cl \cdot H_2O$.



(a)



(b)

Figure S5. The PLQYs of $[H_4BAPP]SnBr_5 \cdot Br$ (a) and $[H_4BAPP]SnCl_5 \cdot Cl \cdot H_2O$ (b).

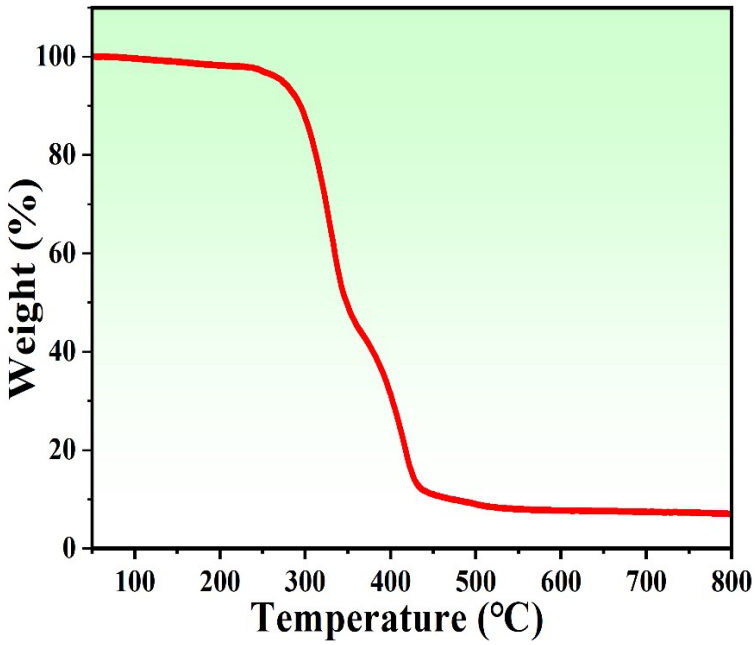


Figure S6. The thermogravimetric analyses (TGA) curve for $[H_4BAPP]SnBr_5 \cdot Br$.

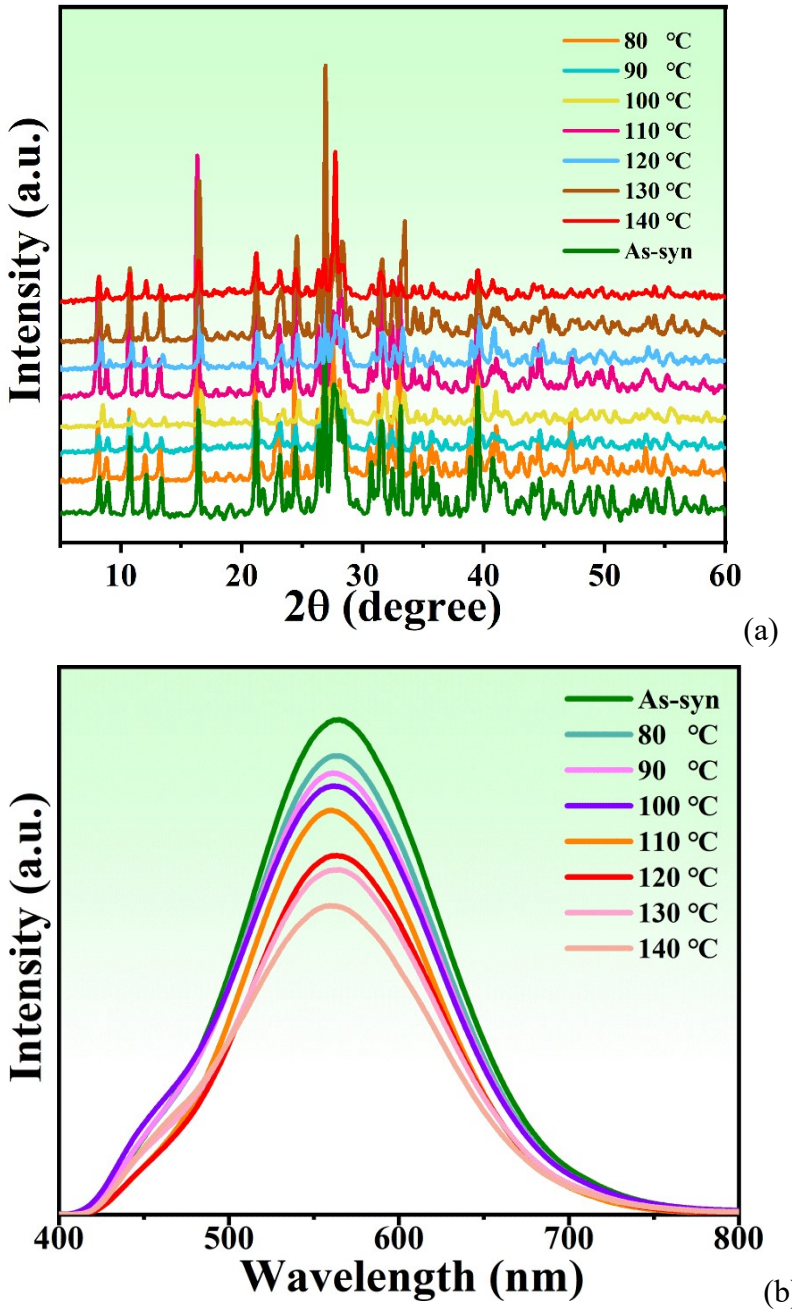


Figure S7. (a) The PXRD and (b) PL emission spectra of $[H_4BAPP]SnBr_5 \cdot Br$ at different temperature.

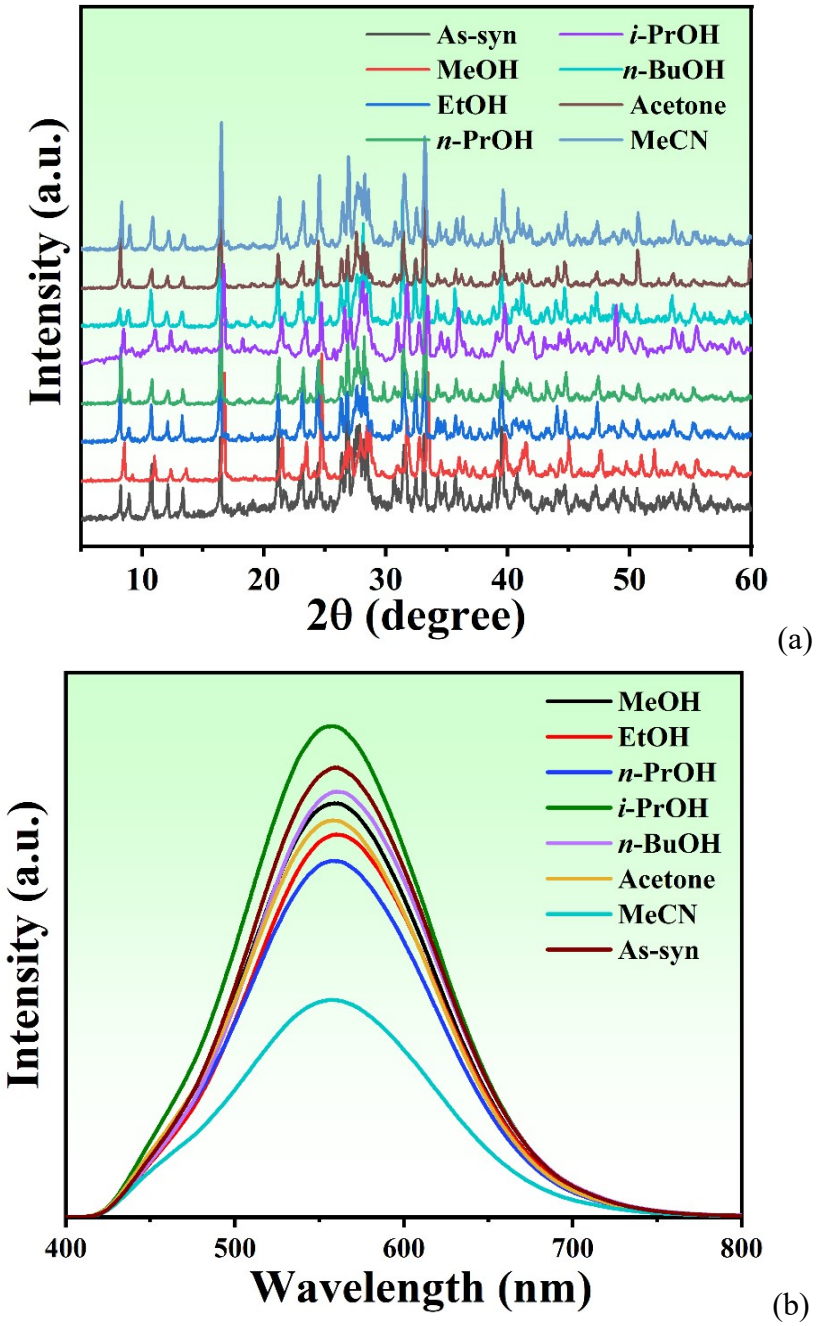
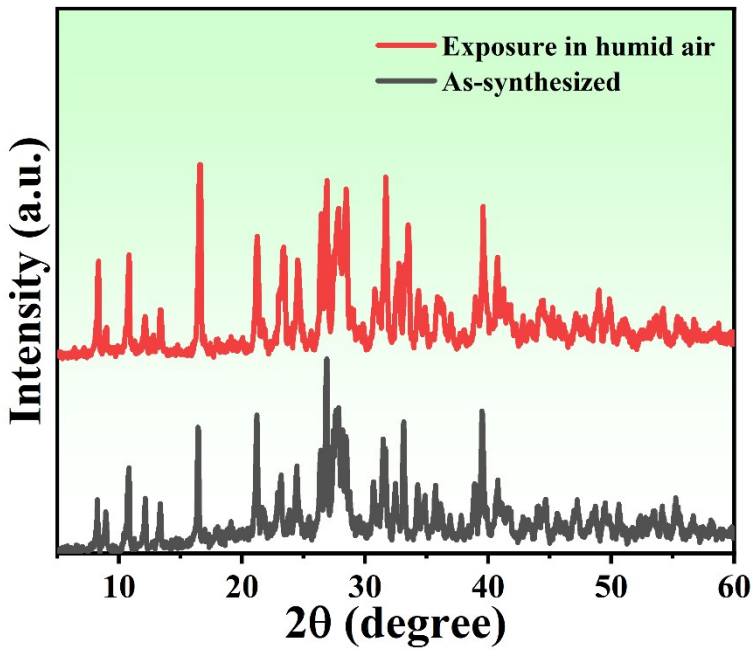
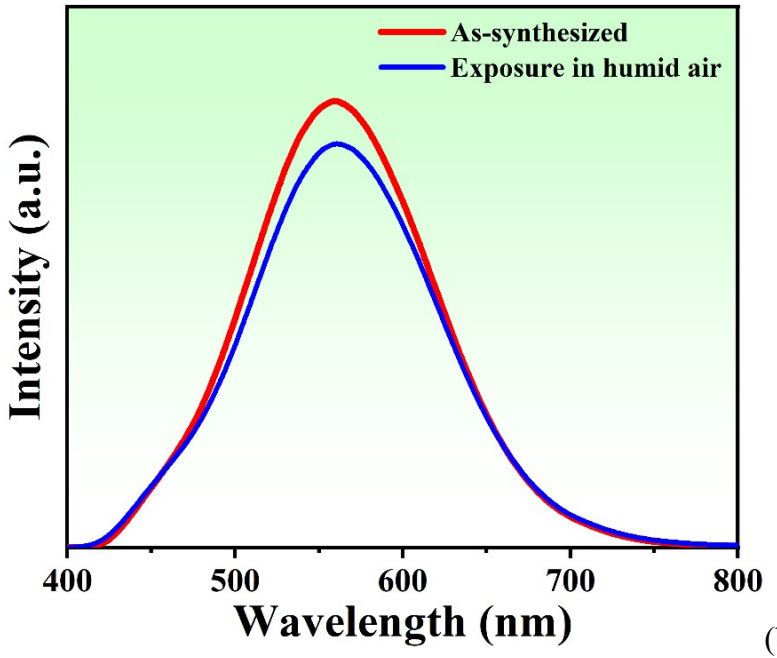


Figure S8. (a) The PXRD and (b) PL emission spectra of $[H_4BAPP]SnBr_5 \cdot Br$ after soaking in various organic solutions over one day.

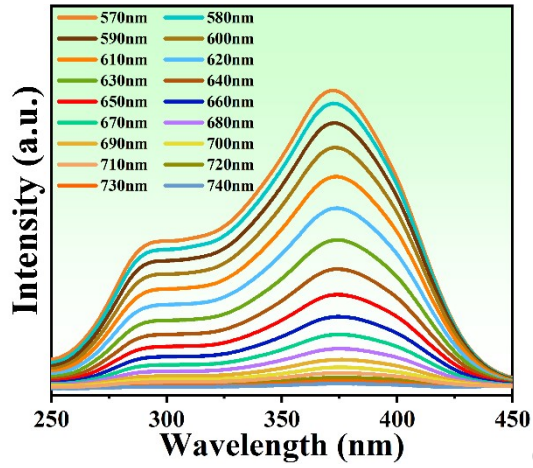


(a)

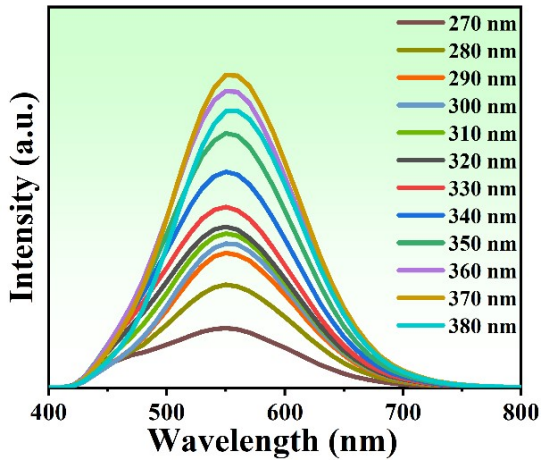


(b)

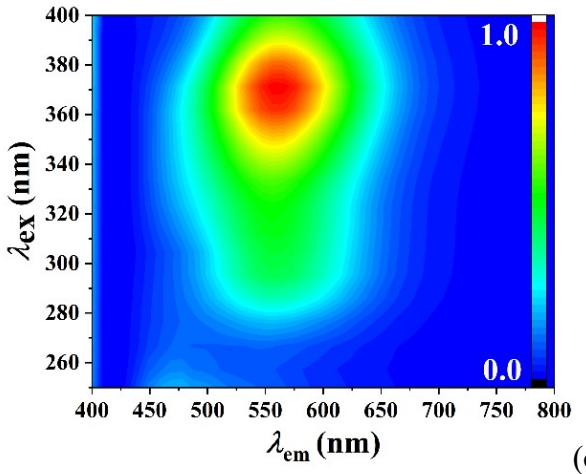
Figure S9. (a) The PXRD and (b) PL emission spectra of as-synthesized $[H_4BAPP]SnBr_5 \cdot Br$ crystals after exposure in humid air for 30 days.



(a)



(b)



(c)

Figure S10. The emission wavelength dependent PL excitation spectra (a), the excitation wavelength dependent PL emission spectra (b) and 3D consecutive PL excitation and emission correlation map of $[H_4BAPP]SnBr_5 \cdot Br$.

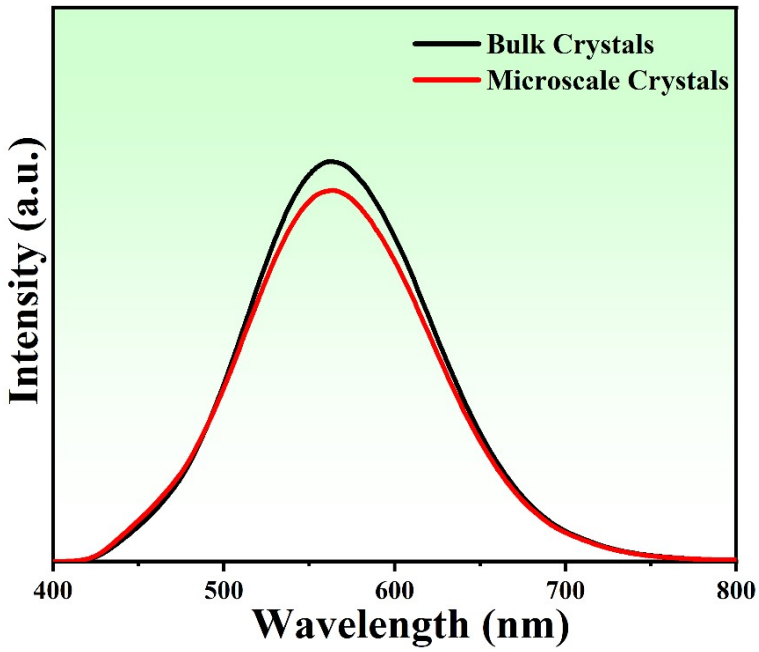


Figure S11. The bulk crystals and microscale crystals PL emission spectra of $[H_4BAPP]SnBr_5 \cdot Br$.

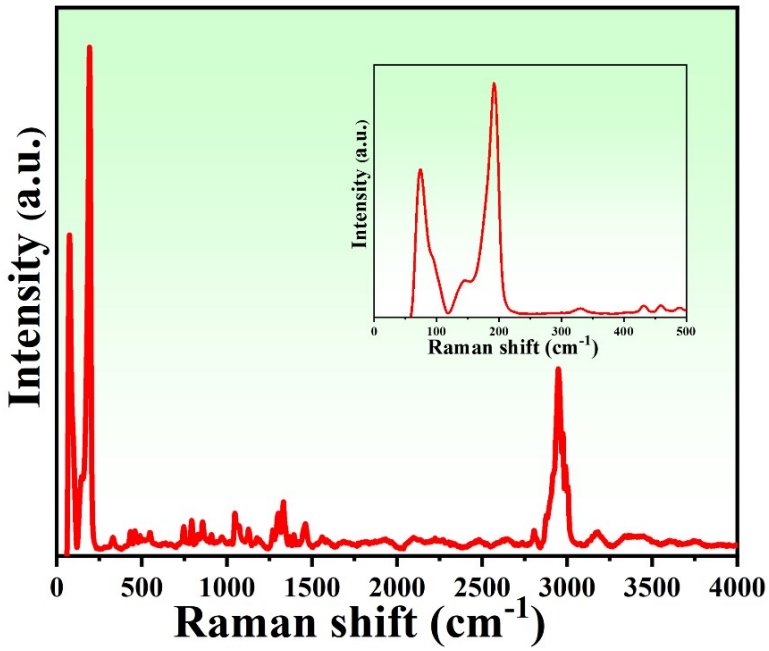


Figure S12. The Raman spectrum of $[H_4BAPP]SnBr_5 \cdot Br$ at 300 K.

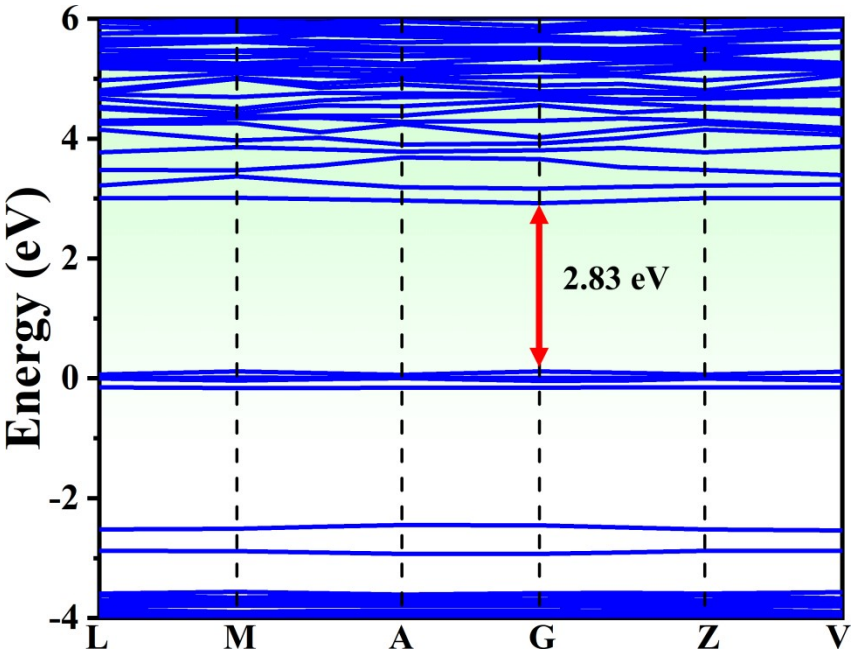


Figure S13. Band structure of $[H_4BAPP]SnCl_5 \cdot Cl \cdot H_2O$

Table S1. Crystal Data and Structural Refinements for $[H_4BAPP]SnBr_5 \cdot Br$ and $[H_4BAPP]SnCl_5 \cdot Cl \cdot H_2O$.

Compound	$[H_4BAPP]SnBr_5 \cdot Br$	$[H_4BAPP]SnCl_5 \cdot Cl \cdot H_2O$
chemical formula	$C_{10}H_{28}Br_6N_4Sn$	$C_{10}H_{28}Cl_6N_4OSn$
FW	802.51	551.75
Space group	*C2/m* (No. 12)	*C2/m* (No. 12)
a/Å	15.7684(6)	15.518(8)
*b*Å	13.2865(5)	12.908(7)
c/Å	11.4134(6)	11.136(8)
α/°	90	90
β/°	108.406(2)	109.40(2)
γ/°	90	90
V(Å^3)	2268.86(17)	2104(2)
Dcalcd (g·cm^{-3})	2.349	1.742
Temp (K)	293.15	293.15
μ (mm^{-1})	11.692	1.981
F (000)	1504.0	1104.0
Reflections collected	20010	23458
Unique reflections	2180	2729
GOF on F^2	1.040	1.067
[a]R_1,wR_2 ($I > 2\sigma(I)$)	0.0430/ 0.1202	0.0410/ 0.1089
[b]R_1,wR_2 (all data)	0.0485/ 0.1251	0.0467/ 0.1134

[a]$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b]$wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table S2. Selected bond lengths (Å) and bond angles (°) in $[H_4BAPP]SnBr_5 \cdot Br$.

Sn1-Br1	2.7818(13)	Sn1-Br2[1]	2.9696(7)
Sn1-Br2	2.9696(7)	Sn1-Br3	2.6765(12)
Sn1-Br5	3.1780(12)		
Br1-Sn1-Br2[1]	89.208(19)	Br1-Sn1-Br2	89.208(19)
Br2-Sn1-Br2[1]	174.51(4)	Br3-Sn1-Br1	87.49(4)
Br3-Sn1-Br2	87.341(18)	Br3-Sn1-Br2[1]	87.342(18)

[1]+X,-Y,+Z; [2]3/2-X,-1/2-Y,-2-Z

Table S3. Hydrogen bonds data for $[H_4BAPP]SnBr_5 \cdot Br$.

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N1-H1A···Br5	0.890	2.598	3.430	155.96
N1-H1B···Br2	0.890	2.705	3.478	145.79
N1-H1C···Br4	0.890	2.418	3.302	172.46
C1-H1D···Br5	0.970	3.097	3.957	148.55
C1-H1E···Br2	0.970	2.960	3.768	141.46
C1-H1E···Br3	0.970	2.981	3.716	133.48
N2-H2···Br2	0.980	2.463	3.312	144.75
N2-H2···Br3	0.980	3.129	3.807	127.52
C2-H2B···Br1	0.970	3.062	3.869	141.65
C3-H3A···Br1	0.970	3.003	3.911	156.30
C3-H3B···Br5	0.970	2.894	3.821	160.40
C4-H4A···Br1	0.970	3.114	4.007	153.66
C4-H4A···Br3	0.970	2.988	3.687	129.92
C4-H4B···Br4	0.970	2.906	3.625	131.79
C5-H5A···Br2	0.970	3.052	3.756	130.55
C5-H5B···Br3	0.970	3.057	3.617	118.13
C5-H5B···Br4	0.970	3.107	3.637	115.90

Table S4. Selected bond lengths (Å) and bond angles (°) in $[H_4BAPP]SnCl_5 \cdot Cl \cdot H_2O$.

Sn1-Cl1	2.677(2)	Sn1-Cl2[1]	2.8249(19)
Sn1-Cl2	2.8249(19)	Sn1-Cl3	2.5133(19)
Sn1-Cl5	3.0740(65)		
Cl1-Sn1-Cl2[1]	89.22(2)	Cl1-Sn1-Cl2	89.22(2)
Cl2-Sn1-Cl2[1]	172.32(4)	Cl3-Sn1-Cl1	87.36(7)
Cl3-Sn1-Cl2	86.21(2)	Cl3-Sn1-Cl2[1]	86.21(2)

[1]+X,-Y,+Z; [2]-1/2-X,1/2-Y,-Z

Table S5. Hydrogen bonds data for $[H_4BAPP]SnCl_5 \cdot Cl \cdot H_2O$.

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N1-H1A···Cl4	0.890	2.238	3.126	174.82
N1-H1B···Cl2	0.890	2.914	3.328	110.22
N1-H1C···O1	0.890	2.309	3.175	164.40
C1-H1D···Cl2	0.970	2.984	3.745	136.21
C1-H1D···Cl3	0.970	2.854	3.665	141.71
C1-H1E···Cl5	0.970	2.906	3.755	146.85
N2-H2···Cl2	0.980	2.286	3.155	147.27
C2-H2A···Cl1	0.970	2.912	3.740	143.85
C3-H3A···Cl1	0.970	2.879	3.869	155.41
C3-H3B···Cl5	0.970	2.851	3.693	145.81
C4-H4A···Cl4	0.970	2.815	3.528	131.01
C4-H4B···Cl1	0.970	2.939	3.834	153.99
C4-H4B···Cl3	0.970	2.894	3.596	130.05
C5-H5A···Cl2	0.970	2.955	3.653	129.76

Tabel S6. Summarized PLQYs for different samples after soaking in various organic solvents.

Sample	PLQY
As-synthesized	19.27%
EtOH	15.29%
n-PrOH	18.90%
i-PrOH	20.72%
Acetone	17.15%
MeCN	14.03%