Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Antimony Doping to Enhance Luminescence of Tin (IV)-Based Hybrid Metal Halides

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Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $(C_9H_{15}N_3)_2SnCl_8$ at 150.0 K with estimated standard deviations in parentheses.

Label	*x*	*y*	*z*	Occupancy	U_{eq}*
Sn(1)	0	5000	0	1	28(1)
Cl(1)	183(1)	6182(1)	1522(1)	1	39(1)
Cl(2)	2275(1)	4104(1)	957(1)	1	39(1)
Cl(3)	-1699(1)	3851(1)	777(1)	1	39(1)
Cl(4)	4401(1)	6125(1)	6242(1)	1	38(1)
N(1)	7455(2)	6239(2)	5399(2)	1	34(1)
N(2)	6511(2)	6552(2)	3559(2)	1	34(1)
N(3)	3924(2)	6549(2)	1825(2)	1	38(1)
C(1)	8596(2)	6086(2)	6282(2)	1	38(1)
C(2)	10081(2)	6108(2)	6189(2)	1	40(1)
C(3)	10408(2)	6309(2)	5158(2)	1	40(1)
C(4)	9257(2)	6466(2)	4276(2)	1	36(1)
C(5)	7724(2)	6428(2)	4393(2)	1	32(1)
C(6)	6734(2)	6540(2)	2438(2)	1	38(1)
C(7)	5373(2)	6018(2)	1706(2)	1	40(1)
C(8)	3724(2)	6532(2)	2982(2)	1	39(1)
C(9)	5078(2)	7057(2)	3690(2)	1	36(1)

*U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $(C_9H_{15}N_3)_2SnBr_8$ at 150.0 K with estimated standard deviations in parentheses.

Label	*x*	*y*	*z*	Occupancy	U_{eq}*
Sn(01)	10000	5000	10000	1	28(1)
Br(1)	7600(1)	5873(1)	8998(1)	1	36(1)
Br(2)	11669(1)	6206(1)	9133(1)	1	40(1)
Br(3)	9848(1)	3736(1)	8448(1)	1	38(1)
Br(4)	5813(1)	1091(1)	8809(1)	1	36(1)
N(1)	6069(4)	3475(3)	8159(3)	1	36(1)
N(2)	3576(4)	3385(3)	6474(3)	1	33(1)
N(3)	2710(4)	3764(2)	4683(3)	1	33(1)
C(1)	6246(5)	3504(3)	7024(3)	1	38(1)

C(2)	4975(4)	2944(3)	6349(3)	1	34(1)
C(3)	3366(5)	3373(3)	7577(3)	1	37(1)
C(4)	4629(5)	3931(3)	8283(3)	1	38(1)
C(5)	2430(4)	3550(3)	5648(3)	1	30(1)
C(6)	948(5)	3525(3)	5752(3)	1	36(1)
C(7)	-142(5)	3719(3)	4885(4)	1	40(1)
C(8)	209(5)	3950(3)	3903(4)	1	41(1)
C(9)	1647(5)	3962(3)	3820(3)	1	38(1)

*U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S3. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $(C_9H_{15}N_3)_2SnCl_8$ at 150.0 K with estimated standard deviations in parentheses.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn(1)	26(1)	31(1)	27(1)	0(1)	4(1)	-1(1)
Cl(1)	35(1)	46(1)	37(1)	-2(1)	8(1)	-12(1)
Cl(2)	32(1)	39(1)	42(1)	5(1)	1(1)	3(1)
Cl(3)	38(1)	43(1)	39(1)	-6(1)	9(1)	4(1)
Cl(4)	36(1)	39(1)	40(1)	-1(1)	8(1)	1(1)
N(1)	34(1)	36(1)	34(1)	1(1)	6(1)	1(1)
N(2)	31(1)	40(1)	31(1)	0(1)	6(1)	0(1)
N(3)	34(1)	40(1)	37(1)	-7(1)	0(1)	-1(1)
C(1)	48(1)	34(1)	31(1)	2(1)	3(1)	0(1)
C(2)	42(1)	37(1)	39(1)	3(1)	-2(1)	-2(1)
C(3)	33(1)	37(1)	48(1)	0(1)	3(1)	-4(1)
C(4)	36(1)	36(1)	36(1)	-1(1)	7(1)	-1(1)
C(5)	36(1)	27(1)	33(1)	-2(1)	4(1)	-1(1)
C(6)	35(1)	47(1)	33(1)	-1(1)	7(1)	0(1)
C(7)	41(1)	43(1)	34(1)	-1(1)	5(1)	-3(1)
C(8)	34(1)	45(1)	39(1)	-5(1)	7(1)	2(1)
C(9)	33(1)	41(1)	33(1)	2(1)	5(1)	0(1)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $(C_9H_{15}N_3)_2SnBr_8$ at 150.0 K with estimated standard deviations in parentheses.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn(01)	25(1)	30(1)	27(1)	0(1)	3(1)	0(1)
Br(1)	30(1)	35(1)	40(1)	4(1)	-1(1)	2(1)
Br(2)	38(1)	43(1)	39(1)	-7(1)	9(1)	6(1)
Br(3)	33(1)	45(1)	37(1)	0(1)	6(1)	-12(1)
Br(4)	34(1)	35(1)	39(1)	1(1)	7(1)	0(1)
N(1)	33(2)	36(2)	35(2)	-5(2)	0(2)	-1(2)
N(2)	30(2)	39(2)	30(2)	0(2)	3(2)	0(2)
N(3)	32(2)	35(2)	32(2)	-1(2)	4(2)	0(2)
C(1)	28(2)	44(2)	41(2)	-6(2)	5(2)	2(2)
C(2)	29(2)	37(2)	36(2)	2(2)	4(2)	3(2)
C(3)	30(2)	46(2)	34(2)	-3(2)	5(2)	2(2)
C(4)	38(2)	42(2)	33(2)	0(2)	3(2)	-2(2)
C(5)	32(2)	25(2)	31(2)	-2(2)	5(2)	-2(2)
C(6)	33(2)	36(2)	37(2)	-2(2)	7(2)	-2(2)
C(7)	28(2)	40(2)	50(3)	4(2)	2(2)	-5(2)
C(8)	41(3)	35(2)	40(2)	5(2)	-5(2)	-3(2)
C(9)	46(3)	35(2)	31(2)	1(2)	4(2)	0(2)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

Table S5. Bond lengths [Å] for $(C_9H_{15}N_3)_2SnCl_8$ at 150.0 K with estimated standard deviations in parentheses.

Label	Distances	Label	Distances
Sn(1)-Cl(1)	2.4136(4)	N(2)-C(9)	1.467(2)
Sn(1)-Cl(1)#1	2.4137(4)	N(3)-C(7)	1.491(2)
Sn(1)-Cl(2)#1	2.4291(4)	N(3)-C(8)	1.496(2)
Sn(1)-Cl(2)	2.4291(4)	C(1)-C(2)	1.350(3)
Sn(1)-Cl(3)#1	2.4431(4)	C(2)-C(3)	1.403(3)
Sn(1)-Cl(3)	2.4431(4)	C(3)-C(4)	1.367(2)
N(1)-C(1)	1.362(2)	C(4)-C(5)	1.402(2)
N(1)-C(5)	1.352(2)	C(6)-C(7)	1.523(2)
N(2)-C(5)	1.357(2)	C(8)-C(9)	1.507(2)

N(2)-C(6)	1.458(2)		

Symmetry transformations used to generate equivalent atoms.

Table S6. Bond lengths [Å] for $(C_9H_{15}N_3)_2SnBr_8$ at 150.0 K with estimated standard deviations in parentheses.

Label	Distances	Label	Distances
Sn(01)-Br(1)#1	2.6058(4)	N(2)-C(5)	1.363(5)
Sn(01)-Br(1)	2.6058(4)	N(3)-C(5)	1.344(5)
Sn(01)-Br(2)	2.6078(4)	N(3)-C(9)	1.355(5)
Sn(01)-Br(2)#1	2.6078(4)	C(1)-C(2)	1.509(5)
Sn(01)-Br(3)	2.5752(4)	C(3)-C(4)	1.520(6)
Sn(01)-Br(3)#1	2.5752(4)	C(5)-C(6)	1.403(6)
N(1)-C(1)	1.496(6)	C(6)-C(7)	1.371(6)
N(1)-C(4)	1.498(6)	C(7)-C(8)	1.394(7)
N(2)-C(2)	1.455(5)	C(8)-C(9)	1.355(7)
N(2)-C(3)	1.466(5)		

Symmetry transformations used to generate equivalent atoms.

Table S7. Bond angles [°] for $(C_9H_{15}N_3)_2SnCl_8$ at 150.0 K with estimated standard deviations in parentheses.

Label	Angles	Label	Angles
Cl(1)-Sn(1)-Cl(1)#1	180.000(16)	C(5)-N(2)-C(6)	120.26(14)
Cl(1)#1-Sn(1)-Cl(2)	90.954(15)	C(5)-N(2)-C(9)	122.85(14)
Cl(1)#1-Sn(1)-Cl(2)#1	89.047(15)	C(6)-N(2)-C(9)	113.51(13)
Cl(1)-Sn(1)-Cl(2)	89.046(15)	C(7)-N(3)-C(8)	111.09(13)
Cl(1)-Sn(1)-Cl(2)#1	90.953(15)	C(2)-C(1)-N(1)	120.87(16)
Cl(1)-Sn(1)-Cl(3)	90.632(15)	C(1)-C(2)-C(3)	117.87(16)
Cl(1)#1-Sn(1)-Cl(3)#1	90.632(15)	C(4)-C(3)-C(2)	120.98(17)
Cl(1)-Sn(1)-Cl(3)#1	89.368(15)	C(3)-C(4)-C(5)	120.03(17)
Cl(1)#1-Sn(1)-Cl(3)	89.368(15)	N(1)-C(5)-N(2)	118.77(15)
Cl(2)-Sn(1)-Cl(2)#1	180.0	N(1)-C(5)-C(4)	117.25(15)
Cl(2)-Sn(1)-Cl(3)#1	87.630(15)	N(2)-C(5)-C(4)	123.97(15)
Cl(2)#1-Sn(1)-Cl(3)	87.630(15)	N(2)-C(6)-C(7)	110.10(14)
Cl(2)#1-Sn(1)-Cl(3)#1	92.370(15)	N(3)-C(7)-C(6)	110.05(14)

Cl(2)-Sn(1)-Cl(3)	92.371(15)	N(3)-C(8)-C(9)	109.40(13)
Cl(3)-Sn(1)-Cl(3)#1	180.0	N(2)-C(9)-C(8)	110.54(14)
C(5)-N(1)-C(1)	123.00(15)		

Symmetry transformations used to generate equivalent atoms.

Table S8. Bond angles [°] for $(C_9H_{15}N_3)_2SnBr_8$ at 150.0 K with estimated standard deviations in parentheses.

Label	Angles	Label	Angles
Br(1)#1-Sn(01)-Br(1)	180.0	C(2)-N(2)-C(3)	113.0(3)
Br(1)#1-Sn(01)-Br(2)	87.670(14)	C(5)-N(2)-C(2)	123.5(3)
Br(1)-Sn(01)-Br(2)#1	87.672(14)	C(5)-N(2)-C(3)	121.5(4)
Br(1)-Sn(01)-Br(2)	92.329(14)	C(5)-N(3)-C(9)	123.6(4)
Br(1)#1-Sn(01)-Br(2)#1	92.330(14)	N(1)-C(1)-C(2)	109.0(3)
Br(2)#1-Sn(01)-Br(2)	180.0	N(2)-C(2)-C(1)	110.7(3)
Br(3)-Sn(01)-Br(1)#1	90.595(14)	N(2)-C(3)-C(4)	109.9(4)
Br(3)#1-Sn(01)-Br(1)#1	89.405(14)	N(1)-C(4)-C(3)	109.9(3)
Br(3)#1-Sn(01)-Br(1)	90.595(14)	N(2)-C(5)-C(6)	123.4(4)
Br(3)-Sn(01)-Br(1)	89.405(14)	N(3)-C(5)-N(2)	119.3(4)
Br(3)-Sn(01)-Br(2)	90.589(15)	N(3)-C(5)-C(6)	117.3(4)
Br(3)#1-Sn(01)-Br(2)#1	90.589(15)	C(7)-C(6)-C(5)	119.8(4)
Br(3)#1-Sn(01)-Br(2)	89.410(15)	C(6)-C(7)-C(8)	120.6(4)
Br(3)-Sn(01)-Br(2)#1	89.412(15)	C(9)-C(8)-C(7)	118.5(4)
Br(3)#1-Sn(01)-Br(3)	180.0	N(3)-C(9)-C(8)	120.2(4)
C(1)-N(1)-C(4)	111.2(3)		

Symmetry transformations used to generate equivalent atoms.

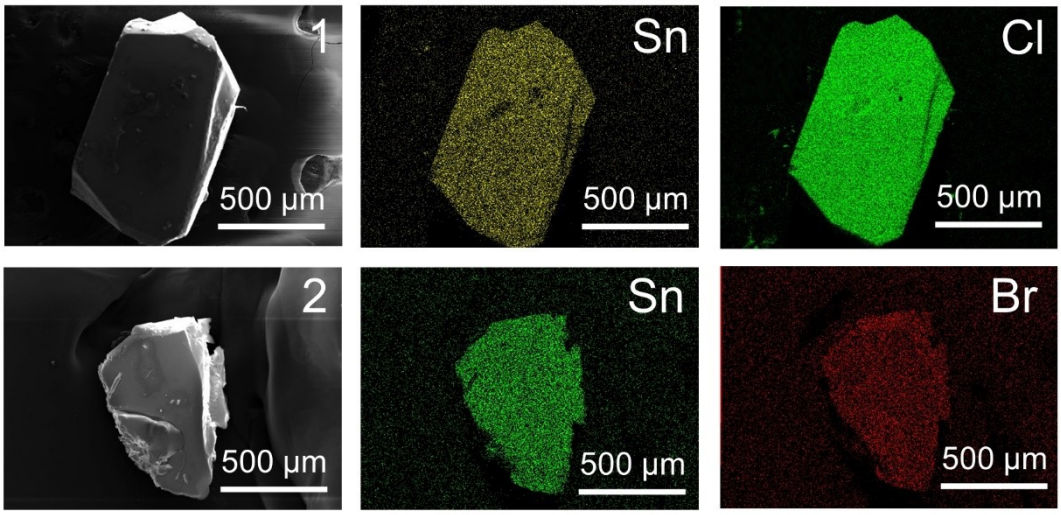

Figure S1. The scanning electron microscope (SEM) images and element maps of $(C_9H_{15}N_3)_2SnCl_8$ (1) and $(C_9H_{15}N_3)_2SnBr_8$ (2).

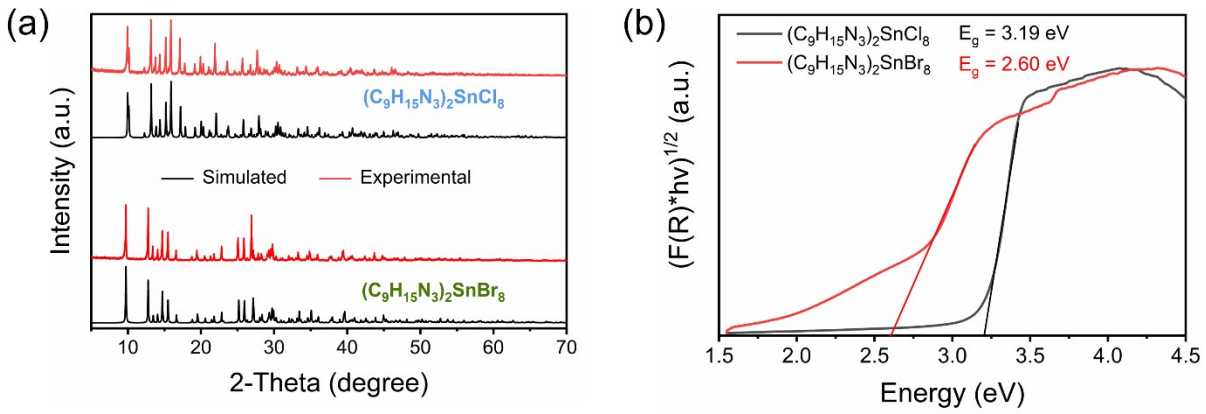

Figure S2. (a) Experimental PXRD and calculated PXRD pattern based on the obtained structure of $(C_9H_{15}N_3)_2SnCl_8$ and $(C_9H_{15}N_3)_2SnBr_8$. (b) The band gap of $(C_9H_{15}N_3)_2SnCl_8$ and $(C_9H_{15}N_3)_2SnBr_8$ determined from a Tauc plot.

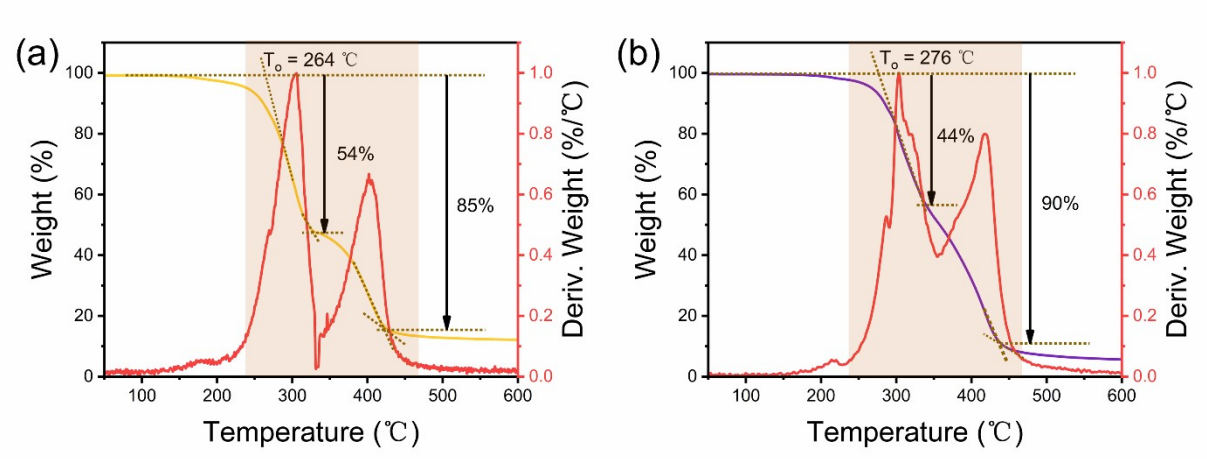

Figure S3. (a) and (b) TGA of $(C_9H_{15}N_3)_2SnCl_8$ $(C_9H_{15}N_3)_2SnBr_8$. T_o represents the onset decomposition temperature of the sample.

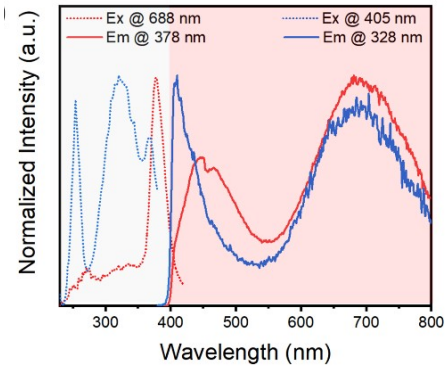

Figure S4. (a) Excitation and emission spectra of $(C_9H_{15}N_3)_2SnCl_8$.

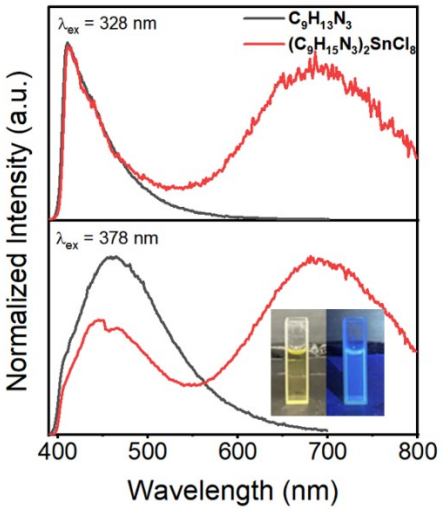

Figure S5. Normalized emission spectra of organic molecular and $(C_9H_{15}N_3)_2SnCl_8$ under the same excitation wavelength at room temperature. The inset is a photo of organic molecular under daylight (left) and 365 nm UV lamp (right).

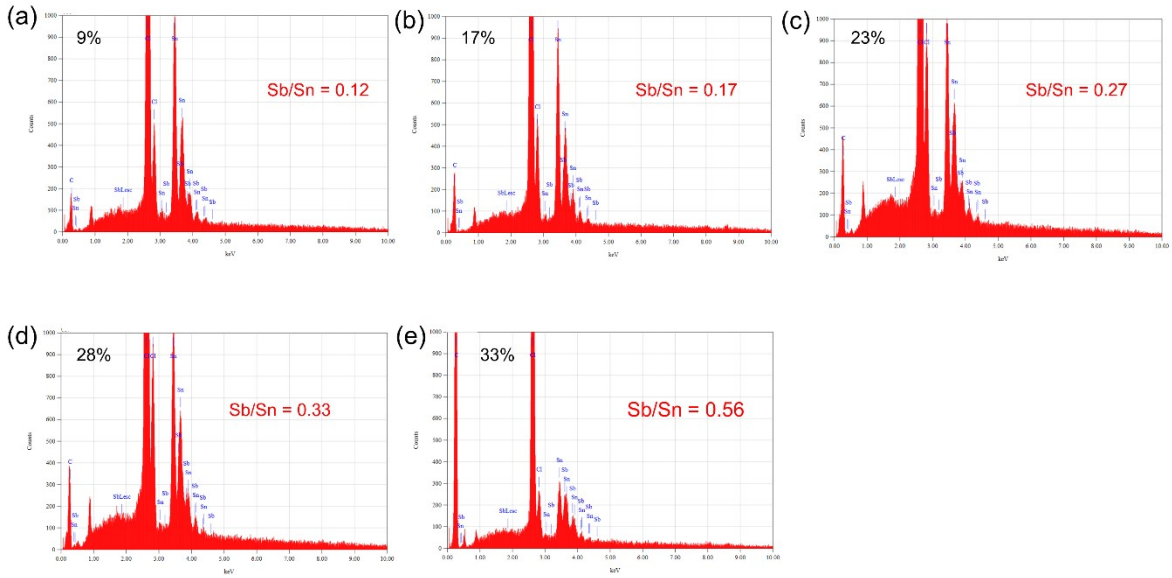

Figure S6. The EDS analysis of Sb^{3+}-doped $(C_9H_{15}N_3)_2SnCl_8$.

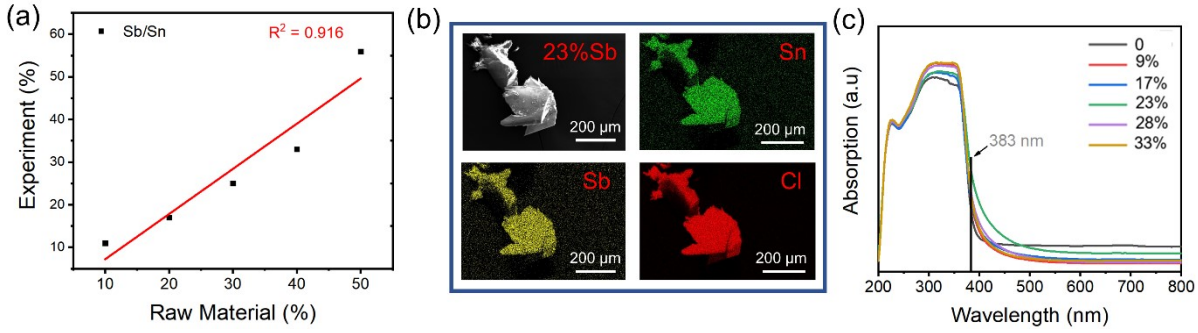

Figure S7. (a) Linear fitting of the metal cation ratio obtained by EDS to the feed ratio. (b) Elemental mapping of $(C_9H_{15}N_3)_2(Sn_{0.77}Sb_{0.23})Cl_8$. (c) Absorption spectra of $(C_9H_{15}N_3)_2SnCl_8$ with different doping levels.

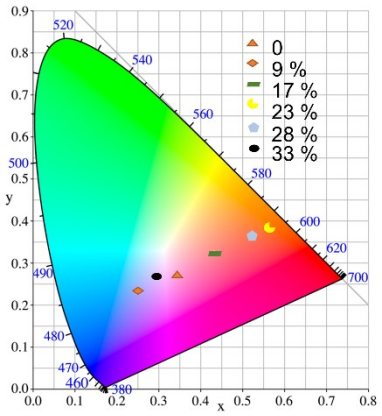

Figure S8. CIE color coordinates of Sb^{3+}-doped $(C_9H_{15}N_3)_2SnCl_8$.

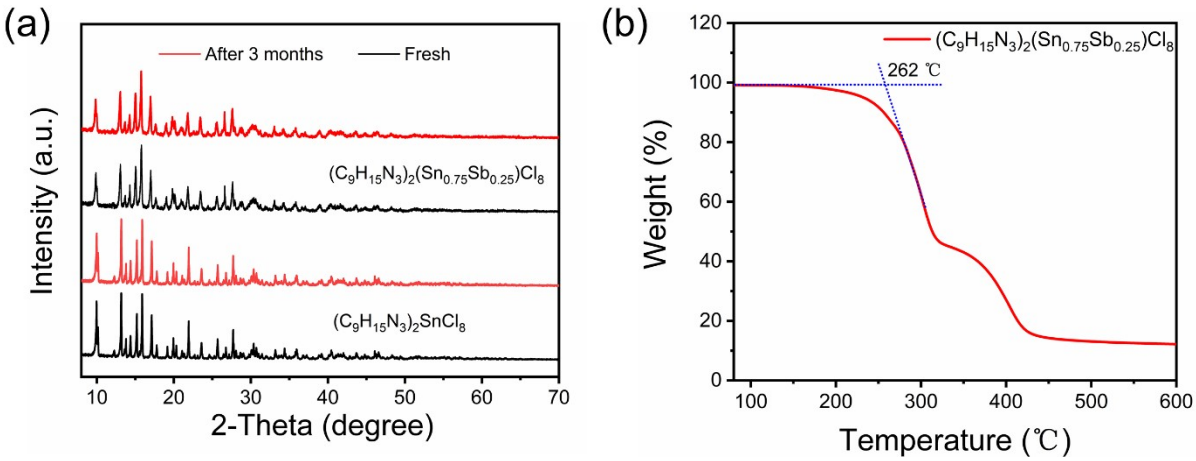

Figure S9. (a) PXRD patterns obtained from fresh and after storage in air for 3 months for $(C_9H_{15}N_3)_2SnCl_8$ and $(C_9H_{15}N_3)_2(Sn_{0.77}Sb_{0.23})Cl_8$. (b) TGA of $(C_9H_{15}N_3)_2(Sn_{0.77}Sb_{0.23})Cl_8$.

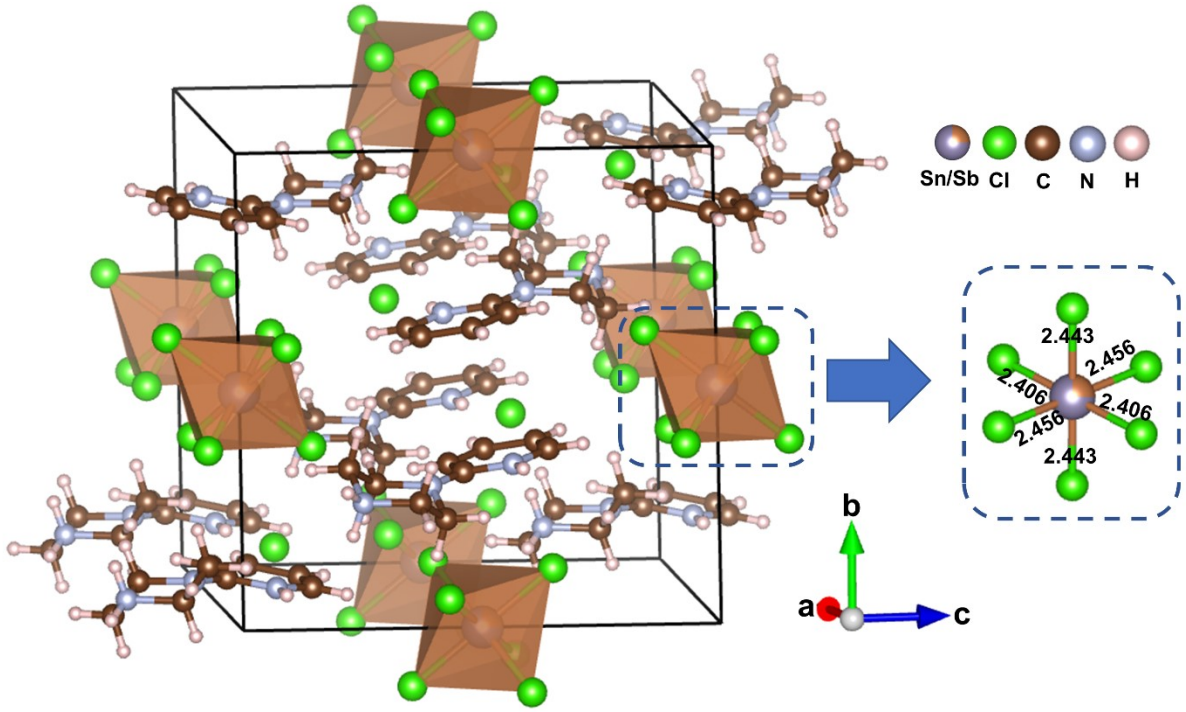

Figure S10. Crystal structure of $(C_9H_{15}N_3)_2(Sn_{0.75}Sb_{0.25})Cl_8$.

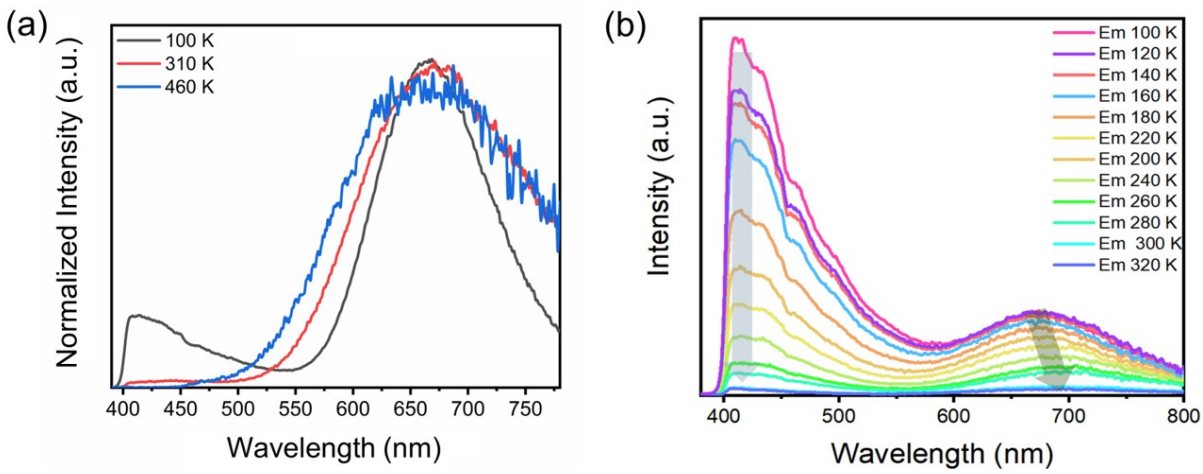

Figure S11. (a) Comparison of normalized PL peaks of $(C_9H_{15}N_3)_2(Sn_{0.77}Sb_{0.23})Cl_8$ at different temperatures. (b) Temperature dependence of the PL spectra of $(C_9H_{15}N_3)_2SnCl_8$.

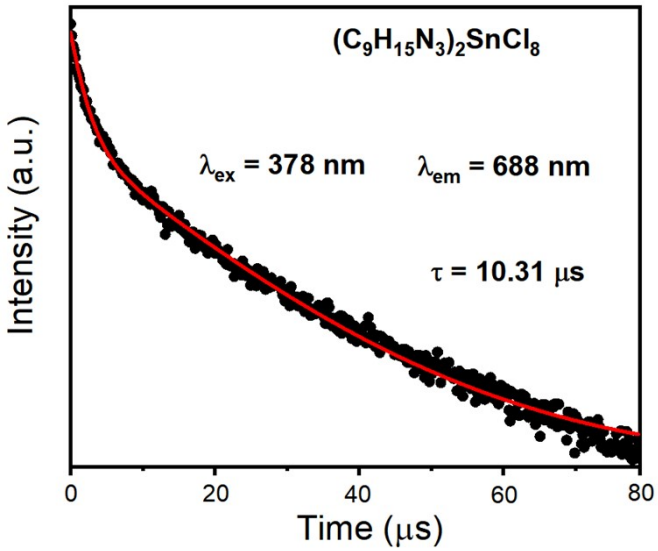

Figure S12. PL decay curves of $(C_9H_{15}N_3)_2SnCl_8$ at 100 K.