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Supporting Information

Zero-dimensional antimony halides with tunable photoluminescence via halogen ligand modulation

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Table S1 Single crystal X-ray diffraction data of $[AVIm]_3SbCl_6$ and $[AVIm]_3SbBr_6$.

Compound	$[AVIm]_3SbCl_6$	$[AVIm]_3SbBr_6$
Empirical formula	$C_{24}H_{33}Cl_6N_6Sb$	$C_{24}H_{33}Br_6N_6Sb$
Formula weight/g·mol^{-1}	740.01	1006.41
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	P -1
a/Å	22.051(3)	10.1511(14)
b/Å	11.9001(17)	12.3581(18)
c/Å	26.397(4)	21.957(3)
α/°	90	103.614(5)
β/°	109.599(6)	100.027(5)
γ/°	90	98.090(5)
Volume/Å3	6525.5(17)	2588.3(6)
Z	8	1
Density/ g·cm^{-3}	1.506	1.851
μ/mm^{-1}	11.421	14.623
F(000)	2976.0	1367.0
Theta range (data collection)/°	4.536 to 144.766	4.106 to 54.896
Reflections collected	83228	35036
Independent reflections	12853 [R_{int} = 0.0464, R_{sigma} = 0.0261]	11899 [R_{int} = 0.0583, R_{sigma} = 0.0540]
Data/restraints/parameters	12853/213/667	11899/85/468
Goodness-of-fit on F^2	1.048	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0321, wR_2 = 0.0883	R_1 = 0.0390, wR_2 = 0.0916
Final R indexes [all data]	R_1 = 0.0331, wR_2 = 0.0889	R_1 = 0.0513, wR_2 = 0.0982
Largest diff. peak/hole / e Å^{-3}	1.76/-0.97	0.99/-1.04

Table S2 Bond length and bond angle parameters of $[AVIm]_3SbCl_6$.

Atom	Atom	Length/Å	Atom	Atom	Atom	Angle/°
Sb1	Cl2	2.7401(9)	Cl2	Sb1	Cl10	98.94(2)
Sb1	Cl4	2.6198(8)	Cl4	Sb1	Cl2	88.74(3)
Sb1	Cl6	2.5733(8)	Cl4	Sb1	Cl8	177.08(2)
Sb1	Cl8	2.6876(8)	Cl4	Sb1	Cl10	92.74(3)
Sb1	Cl10	2.8855(8)	Cl6	Sb1	Cl2	171.18(3)
Sb1	Cl12	2.5114(8)	Cl6	Sb1	Cl4	88.75(3)
Sb2	Cl1	2.6824(8)	Cl6	Sb1	Cl8	88.41(3)
Sb2	Cl3	2.6548(8)	Cl6	Sb1	Cl10	89.62(2)
Sb2	Cl5	2.6799(8)	Cl8	Sb1	Cl2	94.17(3)
Sb2	Cl7	2.5671(8)	Cl8	Sb1	Cl10	86.58(3)
Sb2	Cl9	2.7453(9)	Cl12	Sb1	Cl2	85.82(3)
Sb2	Cl11	2.6125(8)	Cl12	Sb1	Cl4	89.37(3)
N1	C14	1.385(4)	Cl12	Sb1	Cl6	85.70(3)
N1	C22	1.439(4)	Cl12	Sb1	Cl8	91.08(3)
N1	C34	1.325(4)	Cl12	Sb1	Cl10	174.82(2)
N7	C26	1.373(5)	Cl1	Sb2	Cl9	88.72(2)
N7	C34	1.332(4)	Cl3	Sb2	Cl1	90.63(3)
N7	C46	1.465(5)	Cl3	Sb2	Cl5	88.98(3)
C14	C26	1.340(5)	Cl3	Sb2	Cl9	92.94(3)
C22	C40	1.298(5)	Cl5	Sb2	Cl1	179.38(2)
C23	C45	1.2772(10)	Cl5	Sb2	Cl9	90.81(3)
C45	C46	1.428(8)	Cl7	Sb2	Cl1	89.83(2)
N2	C9	1.386(5)	Cl7	Sb2	Cl3	85.42(3)
N2	C17	1.424(6)	Cl7	Sb2	Cl5	90.62(3)
N2	C38	1.320(5)	Cl7	Sb2	Cl9	177.80(3)
N11	C25	1.483(6)	Cl7	Sb2	Cl11	88.73(3)
N11	C33	1.381(6)	Cl11	Sb2	Cl1	88.82(3)
N11	C38	1.320(5)	Cl11	Sb2	Cl3	174.13(3)
C9	C33	1.321(7)	Cl11	Sb2	Cl5	91.62(3)
C17	C43	1.291(6)	Cl11	Sb2	Cl9	92.90(3)
C25	C35	1.507(6)	C14	N1	C22	126.5(3)
C35	C41	1.283(7)	C34	N1	C14	109.5(3)
N3	C8	1.312(4)	C34	N1	C22	124.0(3)
N3	C10	1.377(4)	C26	N7	C46	124.6(3)
N3	C31	1.476(4)	C34	N7	C26	109.1(3)
N4	C6	1.385(4)	C34	N7	C46	126.3(3)
N4	C8	1.343(4)	C26	C14	N1	106.4(3)
N4	C16	1.424(4)	C40	C22	N1	123.5(3)
C6	C10	1.345(5)	C14	C26	N7	107.5(3)
C11	C19	1.2778(10)	N1	C34	N7	107.6(3)
C16	C44	1.297(5)	C23	C45	C46	141.3(9)

C19	C31	1.447(6)	C45	C46	N7	111.3(4)
N5	C28	1.381(4)	C9	N2	C17	127.1(4)
N5	C30	1.322(4)	C38	N2	C9	109.0(4)
N5	C42	1.471(4)	C38	N2	C17	123.7(3)
N6	C12	1.390(4)	C33	N11	C25	126.2(4)
N6	C30	1.338(4)	C38	N11	C25	125.7(4)
N6	C48	1.419(5)	C38	N11	C33	107.5(4)
C3	C48	1.311(6)	C33	C9	N2	105.9(4)
C5	C15	1.310(7)	C43	C17	N2	123.1(5)
C12	C28	1.345(5)	N11	C25	C35	110.7(3)
C15	C42	1.475(6)	C9	C33	N11	108.8(4)
N8	C18	1.385(4)	C41	C35	C25	124.8(4)
N8	C20	1.337(4)	N2	C38	N11	108.8(3)
N8	C24	1.428(4)	C8	N3	C10	109.0(3)
N10	C4	1.384(4)	C8	N3	C31	124.7(3)
N10	C13	1.465(4)	C10	N3	C31	126.1(3)
N10	C20	1.321(4)	C6	N4	C16	128.4(3)
C2	C36	1.299(6)	C8	N4	C6	107.9(3)
C4	C18	1.339(5)	C8	N4	C16	123.7(3)
C7	C24	1.307(5)	C10	C6	N4	106.9(3)
C13	C36	1.493(6)	N3	C8	N4	108.9(3)
C36	H36	0.95	C6	C10	N3	107.3(3)
N9	C1	1.329(5)	C44	C16	N4	124.4(3)
N9	C29	1.368(5)	C11	C19	C31	125.7(6)
N9	C37	1.473(5)	C19	C31	N3	109.8(3)
N12	C1	1.332(5)	C28	N5	C42	126.2(3)
N12	C27	1.402(5)	C30	N5	C28	108.7(3)
N12	C32	1.390(5)	C30	N5	C42	125.1(3)
C21	C37	1.547(8)	C12	N6	C48	127.6(3)
C21	C47	1.2789(10)	C30	N6	C12	108.4(3)
C27	C39	1.328(6)	C30	N6	C48	123.9(3)
C29	C32	1.321(6)	C28	C12	N6	106.6(3)
			C5	C15	C42	123.3(4)
			C12	C28	N5	107.7(3)
			N5	C30	N6	108.6(3)
			N5	C42	C15	112.1(3)
			C3	C48	N6	123.2(3)
			C18	N8	C24	127.5(3)
			C20	N8	C18	108.2(3)
			C20	N8	C24	124.2(3)
			C4	N10	C13	125.9(3)
			C20	N10	C4	108.3(3)
			C20	N10	C13	125.8(3)
			C18	C4	N10	107.8(3)

N10	C13	C36	112.6(3)
C4	C18	N8	106.8(3)
N10	C20	N8	108.9(3)
C7	C24	N8	123.5(3)
C2	C36	C13	126.3(4)
C1	N9	C29	108.5(3)
C1	N9	C37	126.4(3)
C29	N9	C37	125.1(4)
C1	N12	C27	125.2(3)
C1	N12	C32	107.1(3)
C32	N12	C27	127.7(3)
N9	C1	N12	108.8(3)
C47	C21	C37	126.5(8)
C39	C27	N12	123.3(4)
C32	C29	N9	107.7(4)
C29	C32	N12	107.9(3)
N9	C37	C21	107.5(4)

Table S3 Bond length and bond angle parameters of $[AVIm]_3SbBr_6$.

Atom	Atom	Length/Å	Atom	Atom	Atom	Angle/°
Sb01	Br05	2.7822(4)	Br05	Sb01	Br05	180
Sb01	Br05	2.7822(4)	Br05	Sb01	Br03	89.247(14)
Sb01	Br03	2.8097(4)	Br05	Sb01	Br03	90.752(14)
Sb01	Br03	2.8097(4)	Br05	Sb01	Br03	90.752(14)
Sb01	Br04	2.8183(4)	Br05	Sb01	Br03	89.248(14)
Sb01	Br04	2.8183(4)	Br03	Sb01	Br03	180
Sb02	Br08	2.7698(5)	Br05	Sb01	Br04	90.742(14)
Sb02	Br0B	2.7753(5)	Br05	Sb01	Br04	89.258(14)
Sb02	Br0A	2.7821(5)	Br03	Sb01	Br04	92.257(13)
Sb02	Br06	2.8104(5)	Br03	Sb01	Br04	87.743(13)
Sb02	Br09	2.8400(5)	Br05	Sb01	Br04	89.259(14)
Sb02	Br07	2.8524(6)	Br05	Sb01	Br04	90.741(14)
N00C	C00O	1.334(5)	Br03	Sb01	Br04	87.744(13)
N00C	C00T	1.375(5)	Br03	Sb01	Br04	92.256(13)
N00C	C00X	1.427(6)	Br04	Sb01	Br04	180
N00D	C00L	1.317(6)	Br08	Sb02	Br0B	96.147(17)
N00D	C00J	1.356(6)	Br08	Sb02	Br0A	87.582(16)
N00D	C00Z	1.472(6)	Br0B	Sb02	Br0A	91.878(17)
N00E	C00N	1.302(5)	Br08	Sb02	Br06	89.087(15)
N00E	C00U	1.360(5)	Br0B	Sb02	Br06	87.628(16)
N00E	C00P	1.467(5)	Br0A	Sb02	Br06	176.562(17)
N00F	C00L	1.324(6)	Br08	Sb02	Br09	93.593(17)

N00F	C00M	1.369(6)	Br0B	Sb02	Br09	170.061(18)
N00F	C00W	1.426(6)	Br0A	Sb02	Br09	90.503(16)
N00G	C00N	1.311(5)	Br06	Sb02	Br09	90.557(15)
N00G	C010	1.383(6)	Br08	Sb02	Br07	176.635(15)
N00G	C013	1.430(6)	Br0B	Sb02	Br07	84.684(17)
N00H	C00R	1.319(6)	Br0A	Sb02	Br07	89.132(17)
N00H	C015	1.359(6)	Br06	Sb02	Br07	94.209(15)
N00H	C011	1.441(6)	Br09	Sb02	Br07	85.706(16)
N00I	C00O	1.321(6)	C00O	N00C	C00T	109.0(4)
N00I	C00S	1.393(6)	C00O	N00C	C00X	123.3(4)
N00I	C014	1.480(6)	C00T	N00C	C00X	127.6(4)
C00J	C00M	1.337(7)	C00L	N00D	C00J	108.1(4)
N00K	C00R	1.314(6)	C00L	N00D	C00Z	124.7(4)
N00K	C016	1.352(7)	C00J	N00D	C00Z	126.9(4)
N00K	C01B	1.464(7)	C00N	N00E	C00U	108.0(4)
C00P	C00Q	1.471(6)	C00N	N00E	C00P	127.2(4)
C00Q	C00V	1.273(7)	C00U	N00E	C00P	124.6(4)
C00S	C00T	1.339(7)	C00L	N00F	C00M	107.9(4)
C00U	C010	1.336(6)	C00L	N00F	C00W	122.8(4)
C00W	C017	1.283(8)	C00M	N00F	C00W	129.3(4)
C00X	C01C	1.286(7)	C00N	N00G	C010	107.7(4)
C00Y	C012	1.267(7)	C00N	N00G	C013	124.9(4)
C00Z	C012	1.483(7)	C010	N00G	C013	127.4(4)
C011	C01A	1.265(7)	C00R	N00H	C015	107.8(4)
C013	C018	1.288(7)	C00R	N00H	C011	127.3(4)
C014	C01G	1.399(10)	C015	N00H	C011	124.8(5)
C015	C016	1.332(8)	C00O	N00I	C00S	108.2(4)
C01B	C01E	1.434(10)	C00O	N00I	C014	126.3(4)
C01E	C01F	1.253(10)	C00S	N00I	C014	125.5(4)
C01G	C31A	1.025(18)	C00M	C00J	N00D	107.9(4)
C01G	C31	1.2496(10)	C00R	N00K	C016	108.0(4)
Sb01	Sb02	11.1144(5)	C00R	N00K	C01B	124.9(5)
Sb01	Sb01	10.2157(4)	C016	N00K	C01B	127.0(5)
Sb01	Sb02	9.6228(4)	N00D	C00L	N00F	109.2(4)
Sb01	Sb01	10.2157(4)	C00J	C00M	N00F	106.9(4)
Sb01	Sb01	17.0430(6)	N00E	C00N	N00G	110.1(4)
			N00I	C00O	N00C	108.5(4)
			N00E	C00P	C00Q	113.0(4)
			C00V	C00Q	C00P	124.4(5)
			C00T	C00S	N00I	107.4(4)
			C00S	C00T	N00C	106.9(4)
			C010	C00U	N00E	108.0(4)
			C017	C00W	N00F	123.5(5)
			C01C	C00X	N00C	122.9(4)

N00D	C00Z	C012	109.9(4)
C00U	C010	N00G	106.2(4)
C00Y	C012	C00Z	124.9(5)
C018	C013	N00G	124.2(5)
C01G	C014	N00I	112.8(6)
C015	C016	N00K	107.7(5)
C01E	C01B	N00K	113.0(6)
C01F	C01E	C01B	125.3(9)
C31A	C01G	C014	142.4(15)
C31	C01G	C014	148.1(12)

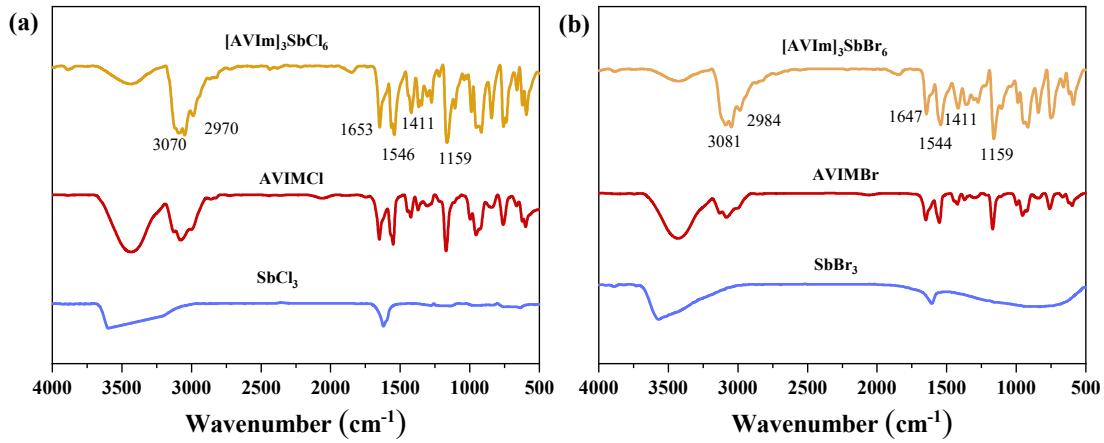

Fig. S1 FTIR spectra of $[AVIm]_3SbCl_6$, $[AVIm]_3SbBr_6$ and their raw materials.

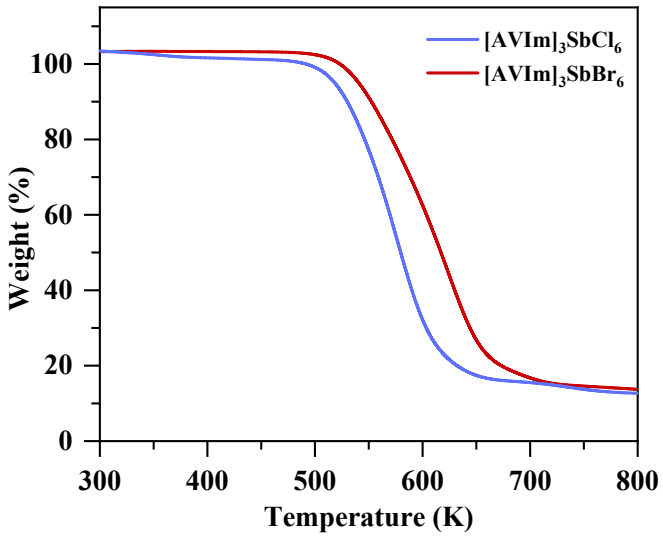

Fig. S2 TGA curves of $[AVIm]_3SbCl_6$ and $[AVIm]_3SbBr_6$.

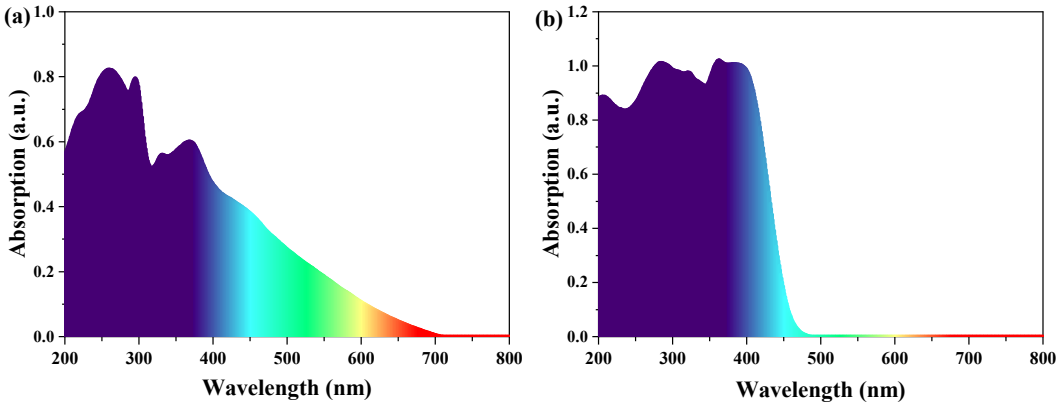

Fig. S3 UV-vis absorption spectra of (a) $[AVIm]_3SbCl_6$ and (b) $[AVIm]_3SbBr_6$.

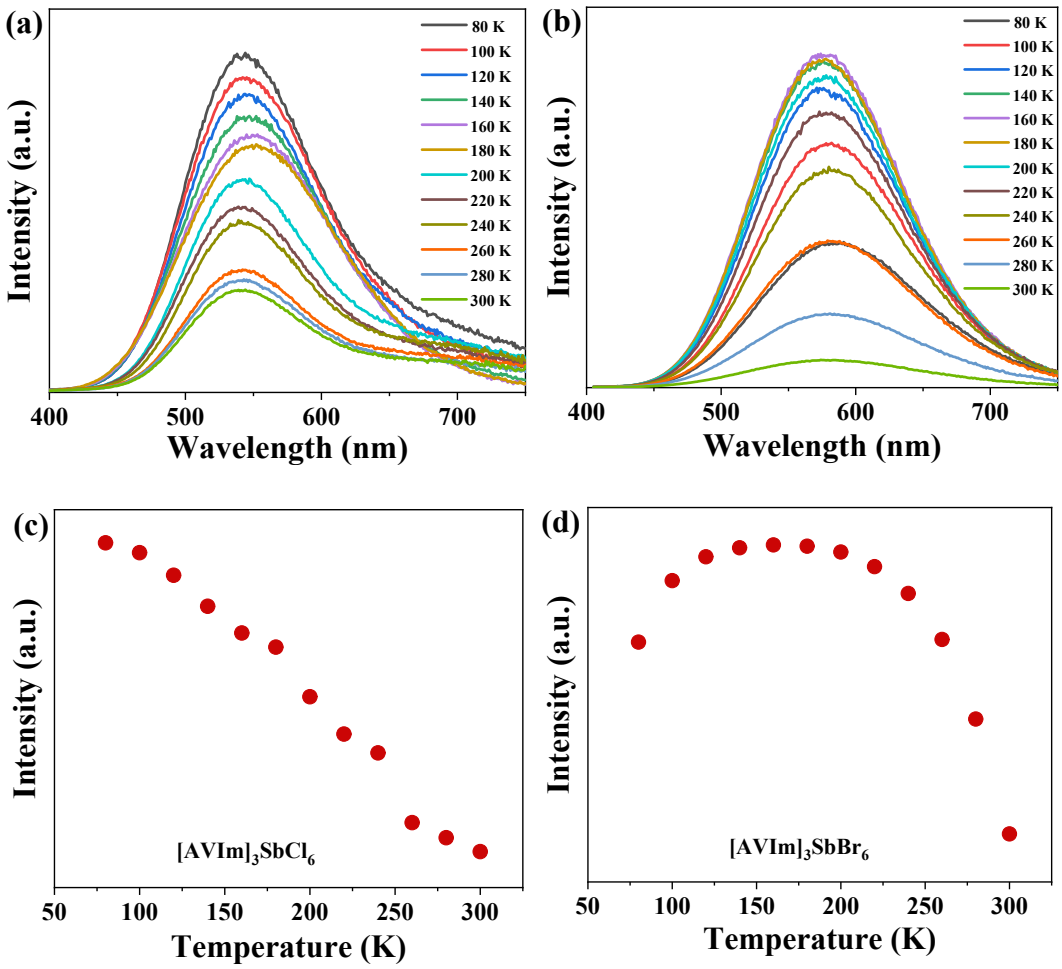

Fig. S4 Temperature-dependent emission spectra of (a) $[AVIm]_3SbCl_6$ and (b) $[AVIm]_3SbBr_6$ in the range of 80 – 300 K. Corresponding integrated emission intensity of (c) $[AVIm]_3SbCl_6$ and (d) $[AVIm]_3SbBr_6$ in the range of 80 – 300 K. The excitation wavelength was 365 nm for $[AVIm]_3SbCl_6$ and 395 nm for $[AVIm]_3SbBr_6$.