Electronic Supporting Information (ESI) for

Co-luminescence in a zero-dimensional organic–inorganic hybrid antimony halide with multiple coordination units

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Table S1. Crystal data and structure refinement for **1**.

Compound	$[Emim]_8[SbCl_6]_2[SbCl_5]$
Empirical formula	$C_{48}H_{88}N_{16}Cl_{17}Sb_3$
Formula Mass	1857.24
Crystal system	Tetragonal
Space group	*P*4/*n*
a/Å	25.1212(6)
b/Å	25.1212(6)
c/Å	12.0964(6)
α/°	90
β/°	90
γ/°	90
V/Å^3	7633.7(5)
Z	4
T/K	100(2)
λ/Å	0.71073
F(000)	3720
ρ_{calcd}/g cm^{-3}	1.616
μ/mm^{-1}	1.693
Measured refls.	31350
Independent refls.	11049
No. of parameters	487
R_{int}	0.0411
R_1 ($I > 2\sigma(I)$)[a]	0.0370
$wR(F^2)$ ($I > 2\sigma(I)$)[b]	0.0700
GOF	1.037
CCDC #	2051595

[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 (°) for **1**.

bond	lengths (Å)	bonds	angles (°)
Sb(1)–Cl(3)	2.5767(8)	Cl(3)–Sb(1)–Cl(1)	90.93(2)
Sb(1)–Cl(1)	2.6188(7)	Cl(3)–Sb(1)–Cl(5)	86.83(2)
Sb(1)–Cl(5)	2.6405(8)	Cl(1)–Sb(1)–Cl(5)	89.24(2)
Sb(1)–Cl(4)	2.6715(8)	Cl(3)–Sb(1)–Cl(4)	89.70(3)
Sb(1)–Cl(6)	2.6930(7)	Cl(1)–Sb(1)–Cl(4)	89.00(3)
Sb(1)–Cl(2)	2.7288(8)	Cl(5)–Sb(1)–Cl(4)	176.08(3)
Sb(2)–Cl(8)	2.3957(13)	Cl(3)–Sb(1)–Cl(6)	91.69(2)
Sb(2)–Cl(7)#1	2.6107(7)	Cl(1)–Sb(1)–Cl(6)	176.89(2)
Sb(2)–Cl(7)#2	2.6107(7)	Cl(5)–Sb(1)–Cl(6)	92.59(2)
Sb(2)–Cl(7)#3	2.6107(7)	Cl(4)–Sb(1)–Cl(6)	89.32(3)
Sb(2)–Cl(7)	2.6107(7)	Cl(3)–Sb(1)–Cl(2)	178.79(2)
Sb(3)–Cl(9)	2.4048(14)	Cl(1)–Sb(1)–Cl(2)	90.11(2)
Sb(3)–Cl(10)#2	2.6158(8)	Cl(5)–Sb(1)–Cl(2)	92.57(2)
Sb(3)–Cl(10)#3	2.6158(8)	Cl(4)–Sb(1)–Cl(2)	90.94(3)
Sb(3)–Cl(10)	2.6158(8)	Cl(6)–Sb(1)–Cl(2)	87.29(2)
Sb(3)–Cl(10)#1	2.6158(8)	Cl(8)–Sb(2)–Cl(7)#1	88.124(17)
		Cl(8)–Sb(2)–Cl(7)#2	88.124(17)
		Cl(7)#1–Sb(2)–Cl(7)#2	89.939(1)
		Cl(8)–Sb(2)–Cl(7)#3	88.124(17)
		Cl(7)#1–Sb(2)–Cl(7)#3	176.25(3)
		Cl(7)#2–Sb(2)–Cl(7)#3	89.938(2)
		Cl(8)–Sb(2)–Cl(7)	88.124(17)
		Cl(7)#1–Sb(2)–Cl(7)	89.939(2)
		Cl(7)#2–Sb(2)–Cl(7)	176.25(3)
		Cl(7)#3–Sb(2)–Cl(7)	89.939(1)
		Cl(9)–Sb(3)–Cl(10)#2	87.818(18)
		Cl(9)–Sb(3)–Cl(10)#3	87.818(18)
		Cl(10)#2–Sb(3)–Cl(10)#3	89.917(1)
		Cl(9)–Sb(3)–Cl(10)	87.818(18)
		Cl(10)#2–Sb(3)–Cl(10)	175.64(4)
		Cl(10)#3–Sb(3)–Cl(10)	89.915(2)
		Cl(9)–Sb(3)–Cl(10)#1	87.818(18)
		Cl(10)#2–Sb(3)–Cl(10)#1	89.919(2)
		Cl(10)#3–Sb(3)–Cl(10)#1	175.64(4)
		Cl(10)–Sb(3)–Cl(10)#1	89.917(1)

Symmetry transformations used to generate equivalent atoms: #1,-*y*+3/2,*x*,*z*; #2 -*x*+3/2,-*y*+3/2,*z* #3 *y*,-*x*+3/2,*z*

Table S3 Hydrogen bonding data for **1**.

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	<(DHA) (°)
C(1)–H(1A)···Cl(5)	0.95	2.77	3.689(3)	162.6
C(2)–H(2A)···Cl(2)#4	0.95	2.90	3.822(3)	164.1
C(3)–H(3A)···Cl(1)#5	0.95	2.71	3.540(3)	146.0
C(4)–H(4B)···Cl(1)#5	0.98	2.72	3.649(3)	157.4
C(4)–H(4C)···Cl(4)#6	0.98	2.78	3.695(3)	156.0
C(5)–H(5B)···Cl(6)	0.99	2.82	3.682(3)	146.3
C(8)–H(8A)···Cl(7)#3	0.95	2.81	3.664(3)	150.3
C(9)–H(9A)···Cl(6)#7	0.95	2.57	3.408(3)	147.3
C(10)–H(10A)···Cl(5)#3	0.98	2.71	3.653(4)	162.3
C(10)–H(10B)···Cl(2)#7	0.98	2.85	3.625(3)	136.1
C(10)–H(10C)···Cl(2)#3	0.98	2.81	3.406(4)	120.1
C(11)–H(11A)···Cl(7)	0.99	2.72	3.661(4)	158.2
C(11)–H(11B)···Cl(10)#1	0.99	2.77	3.596(3)	141.5
C(13)–H(13A)···Cl(1)#8	0.95	2.97	3.735(3)	138.8
C(13)–H(13A)···Cl(7)#8	0.95	2.87	3.474(3)	122.4
C(15)–H(15A)···Cl(4)#7	0.95	2.85	3.423(3)	119.7
C(15)–H(15A)···Cl(6)#7	0.95	2.81	3.654(3)	148.9
C(16)–H(16A)···Cl(1)#8	0.98	2.91	3.688(4)	136.5
C(16)–H(16B)···Cl(2)#8	0.98	2.72	3.493(3)	136.0
C(16)–H(16C)···Cl(2)#7	0.98	2.65	3.604(4)	163.5
C(17)–H(17A)···Cl(10)	0.99	2.86	3.441(3)	117.9
C(17)–H(17A)···Cl(10)#1	0.99	2.84	3.683(3)	143.3
C(20)–H(20A)···Cl(3)#7	0.95	2.76	3.645(4)	154.9
C(20)–H(20A)···Cl(6)#7	0.95	2.82	3.384(4)	118.9
C(21)–H(21A)···Cl(4)#6	0.95	2.57	3.406(4)	147.2
C(22)–H(22A)···Cl(5)	0.98	2.84	3.74(2)	152.8
C(22)–H(22B)···Cl(2)#4	0.98	2.79	3.519(15)	131.4
C(23)–H(23B)···Cl(3)#6	0.99	2.79	3.61(2)	139.7
C(24)–H(24C)···Cl(3)#7	0.98	2.98	3.867(13)	150.4
C(22B)–H(22D)···Cl(4)#7	0.98	2.83	3.81(3)	173.1
C(23B)–H(23C)···Cl(5)	0.99	2.89	3.68(3)	137.9
C(23B)–H(23D)···Cl(2)#4	0.99	2.85	3.466(14)	121.3
C(22C)–H(22H)···Cl(5)	0.98	2.79	3.70(5)	155.6
C(22C)–H(22I)···Cl(2)#4	0.98	2.82	3.69(4)	147.2
C(24C)–H(24G)···Cl(3)#6	0.98	2.99	3.46(2)	111.1
C(24C)–H(24H)···Cl(4)#7	0.98	2.52	3.45(3)	158.5

Symmetry transformations used to generate equivalent atoms:

#1 -*y*+3/2,*x*,*z*; #2 -*x*+3/2,-*y*+3/2,*z*; #3 *y*,-*x*+3/2,*z*; #4 -*x*+2,-*y*+1,-*z*+1; #5 *y*+1/2,-*x*+1,-*z*+1; #6 *x*,*y*,*z*+1; #7 -*y*+1,*x*-1/2,-*z*+1; #8 *y*,-*x*+3/2,*z*+1

Table S4 Element analysis of C, H and N for **1**.

Elements	C	H	N
Calculation	31.04	4.78	12.07
Found	30.40	4.80	11.77

Table S5 Summary of Sb···Sb distances and PLQYs for various hybrid chloroantimonates.

Compounds	**Two shortest Sb···Sb distances (Å)**		**PLQY (%)**	**Ref**
$Rb_7(SbCl_6)(Sb_2Cl_{10})$	4.527	4.532	3.8	1
$[Emim]_8[SbCl_6]_2[SbCl_5]$	5.932	6.164	11.2	This work
$(C_6N_2H_{16})_2SbCl_5$	4.337	7.465	25.3	2
$(Bmim)_2SbCl_5$	8.503	8.821	86.3	3
$(C_9NH_{20})_2SbCl_5$	8.229	8.756	98	4
$(TEBA)_2SbCl_5$	8.670	9.254	98	5
$(TTA)_2SbCl_5$	8.941	9.494	86	5
$(C@Cs)_2SbCl_5$	8.536	9.362	89	6
$(Bzmim)_2SbCl_5$	8.892	9.071	22.3	7
$(Bzmim)_3SbCl_6$	9.513	9.743	87.5	7
$(Ph_4P)_2SbCl_5$	10.006	10.015	87	8
$(C@Rb)_2SbCl_5$	10.397	10.468	75	6
$(PPN)_2SbCl_5$	11.042	12.191	98.1	9

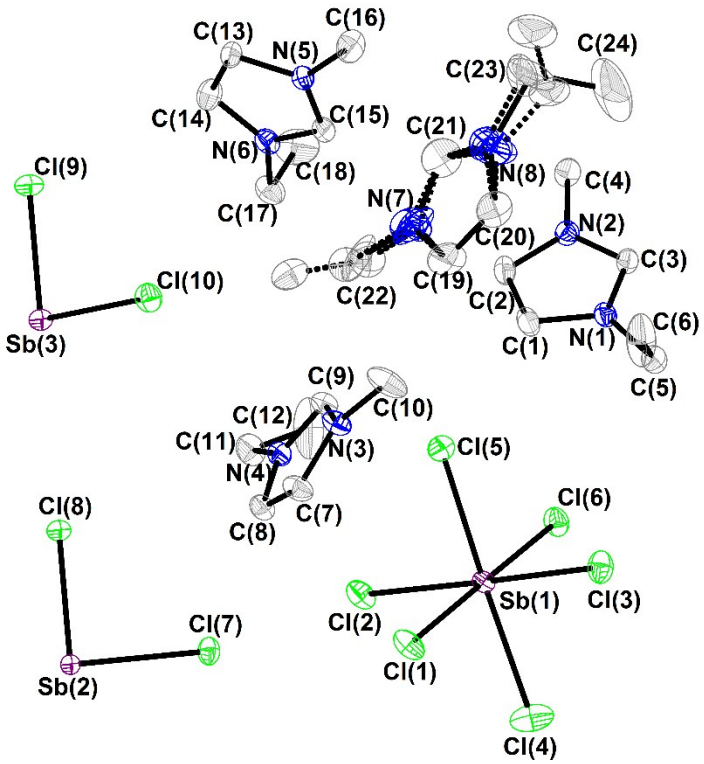

Fig. S1 *ORTEP* drawing (50% ellipsoid probability) of the asymmetric unit of **1**. Hydrogen atom are omitted for clarity.

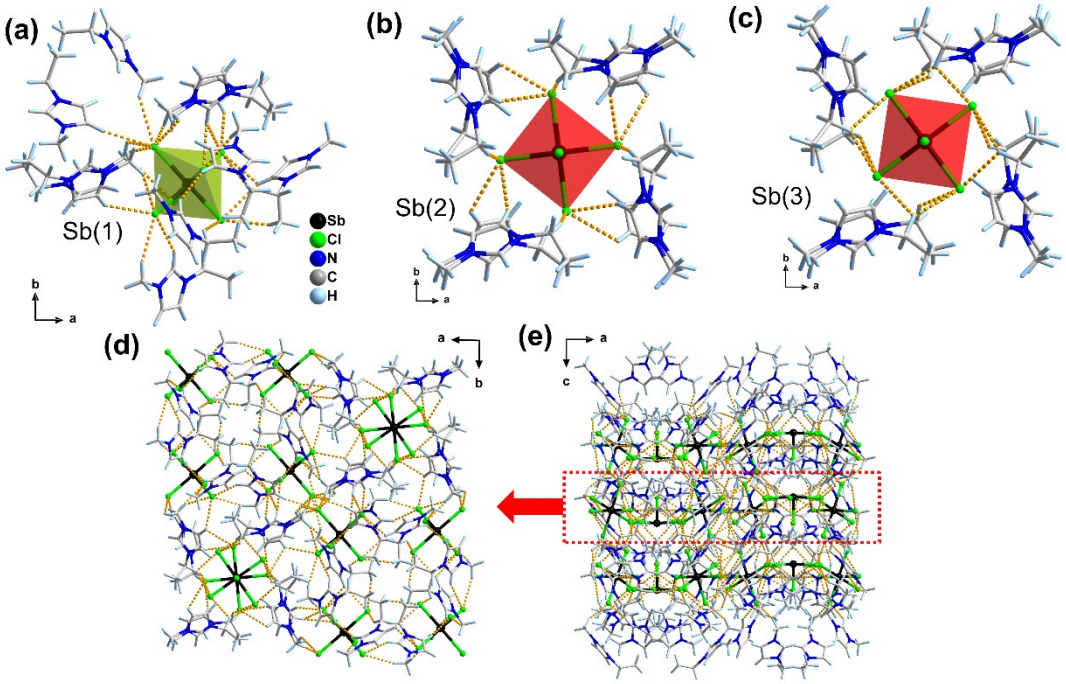

Fig. S2 Diagrams showing hydrogen bonds among the organic cations and $[Sb(1)Cl_6]^{3-}$ (a), $[Sb(2)Cl_5]^{2-}$ (b), and $[Sb(3)Cl_5]^{2-}$ (c) in **1**. (d) and (e) show the two- and three-dimensional supramolecular network, respectively, considering various hydrogen bonds in **1**.

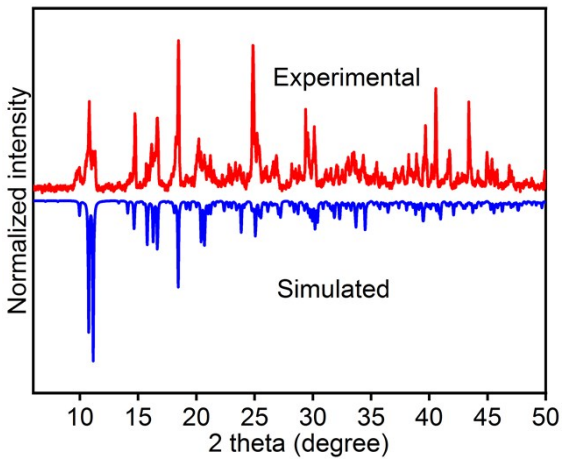

Fig. S3 PXRD patterns of **1**.

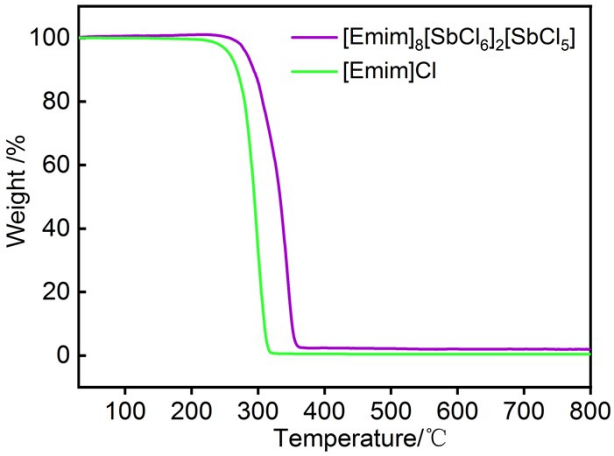

Fig. S4 TG curves for **1** and [Emim]Cl.

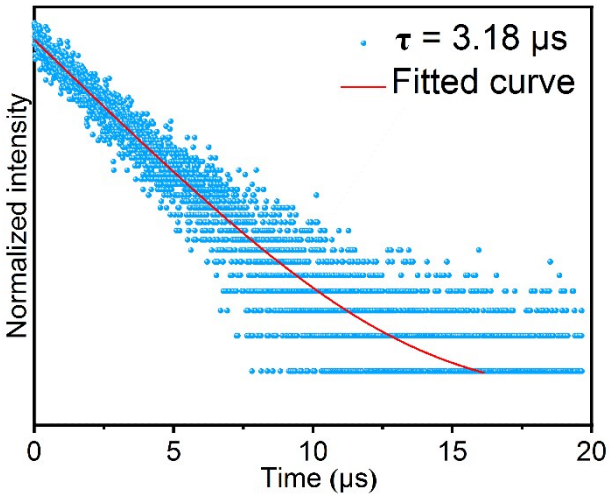

Fig. S5 PL lifetime curve and its fitted curve for **1** measured at 77K.

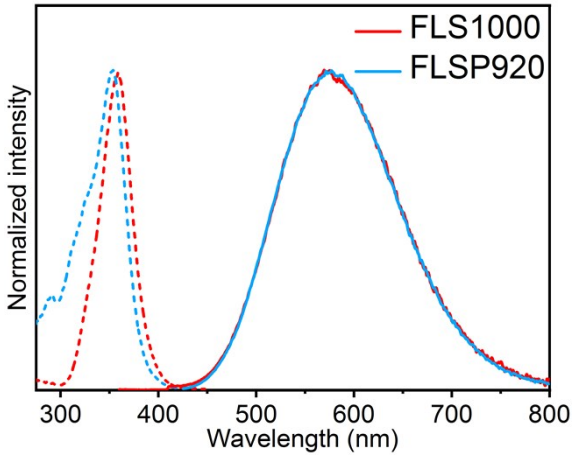

Fig. S6 The PLE and PL of **1** measured on FLSP920 and FLS1000 fluorescence spectrometer.

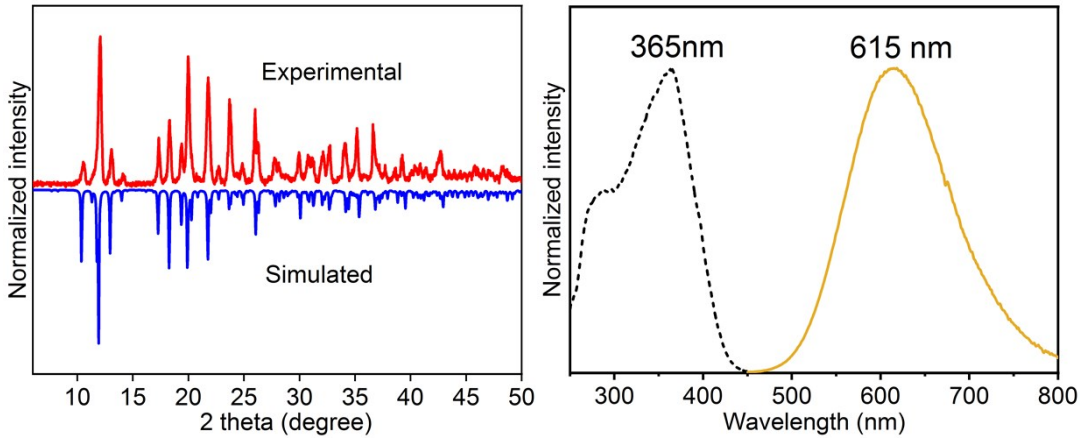

Fig. S7 PXRD patterns of $[Bmim]_2SbCl_5$ (left) and its PLE and PL spectra measured on FLSP920 (right).

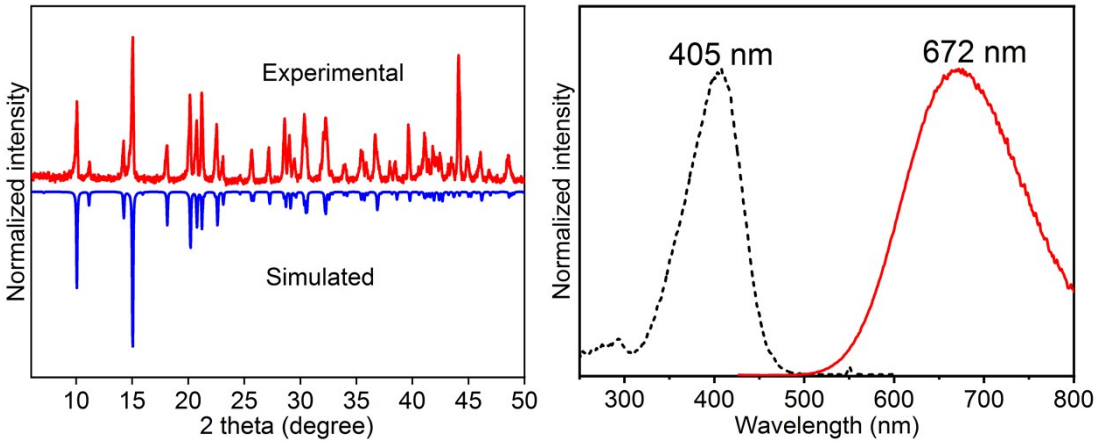

Fig. S8 PXRD patterns of $[Bzmim]_2SbCl_5$ (left) and its PLE and PL spectra measured on FLSP920 (right).

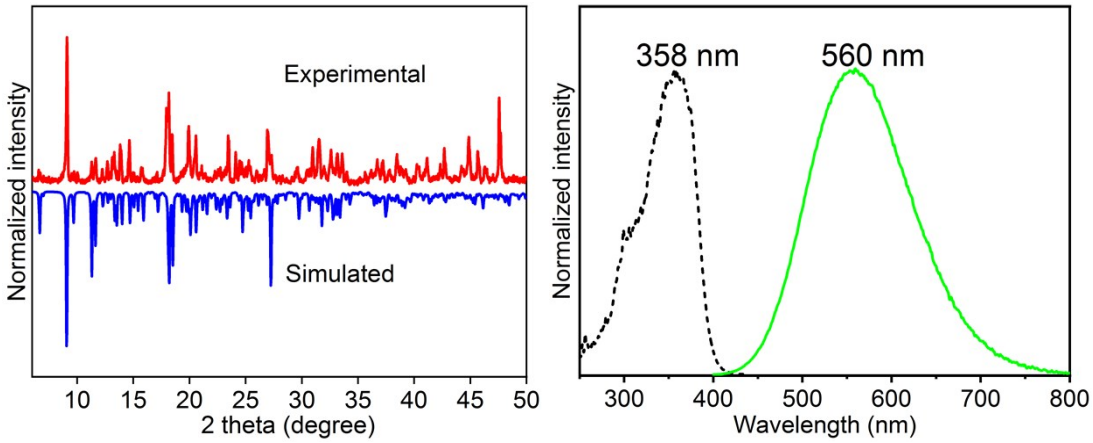

Fig. S9 PXRD patterns of $[Bzmim]_3SbCl_6$ (left) and its PLE and PL spectra measured on FLSP920 (right).

References

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