Supporting Information for

Modulating organic functional groups in stimuli-responsive luminescent antimony chlorides

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Table S1. Crystal data and structure refinement for compound **1**, **2** and **3**.

	1	**2**	**3**
CCDC number	2341218	2344297	2341219
Empirical formula	$C_{24}H_{39}N_6Cl_6SbO_6$	$C_{36}H_{51}Cl_6N_{12}O_{12}Sb$	$C_{18}H_{27}N_6O_6Cl_6Sb$
Formula weight	842.06	1178.34	757.90
Temperature/K	100(2)	100(2)	100(2)
Wavelength/Å	1.54178	1.54178	1.54178
Crystal system	orthorhombic	trigonal	monoclinic
Space group	*Pbca*	$R\bar{3}$	$P2_1/c$
a/Å	20.4908(3)	21.8818(4)	20.7233(11)
b/Å	16.2409(3)	21.8818(4)	8.7393(3)
c/Å	21.6024(4)	8.6170(3)	17.6064(9)
α/°	90	90	90
β/°	90	90	114.637(6)
γ/°	90	120	90
Volume/Å^3	7189.0(2)	3573.16(18)	2898.4(3)
Z	8	3	4
ρ_{calc} g/cm^3	1.556	1.643	1.737
Absorption coefficient/mm^{-1}	1.258	0.987	1.549
F(000)	3408.0	1800.0	1512.0
Crystal size/mm^3	0.25 × 0.15 × 0.04	0.25 × 0.15 × 0.04	0.25 × 0.15 × 0.04
Theta range for data collection /°	6.584-50.046	7.398-57.458	6.904-54.202
Reflections collected/ unique	35961/6345 [R_{int} = 0.0610]	6917/1902 [R_{int} = 0.0431]	35961/6345 [R_{int} = 0.0610]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6345/1068/505	1902/1/106	6242/3/349
Goodness-of-fit on F^2	1.410	1.006	1.065
Final *R* indexes [$I >= 2\sigma(I)$]	R_1 = 0.1047, wR_2 = 0.2321	R_1 = 0.0304, wR_2 = 0.0662	R_1 = 0.0274, wR_2 = 0.0554
Final *R* indexes [all data]	R_1 = 0.1191, wR_2 = 0.2381	R_1 = 0.0412, wR2 = 0.0726	R_1 = 0.0373, wR_2 = 0.0616
Largest diff. peak and hole	1.12/-1.29	0.47/-0.39	0.62/-0.43

[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 length (Å) and bond angle (°) for **1**, **2** and **3**.

1			
Sb(1)-Cl(4)	2.549(3)	Sb(1)-Cl(5)	2.717(4)
Sb(1)-Cl(2)	2.580(3)	Sb(1)-Cl(3)	2.744(3)
Sb(1)-Cl(6)	2.592(3)	Sb(1)-Cl(1)	2.809(4)
Cl(4)-Sb(1)-Cl(2)	88.66(10)	Cl(6)-Sb(1)-Cl(3)	176.96(11)
Cl(4)-Sb(1)-Cl(6)	86.24(11)	Cl(5)-Sb(1)-Cl(3)	90.53(11)
Cl(2)-Sb(1)-Cl(6)	91.80(10)	Cl(4)-Sb(1)-Cl(1)	172.91(11)
Cl(4)-Sb(1)-Cl(5)	90.02(11)	Cl(2)-Sb(1)-Cl(1)	90.13(11)
Cl(2)-Sb(1)-Cl(5)	178.66(11)	Cl(6)-Sb(1)-Cl(1)	86.82(11)
Cl(6)-Sb(1)-Cl(5)	88.30(11)	Cl(5)-Sb(1)-Cl(1)	91.21(11)
Cl(4)-Sb(1)-Cl(3)	90.96(10)	Cl(3)-Sb(1)-Cl(1)	96.01(11)
Cl(2)-Sb(1)-Cl(3)	89.30(10)		

Symmetry transformations used to generate equivalent atoms: N.A. for **1.**

2			
Sb(1)-Cl(1)	2.6487(5)		
Cl(1)#1-Sb(1)-Cl(1)#2	88.327(17)	Cl(1)#3-Sb(1)-Cl(1)#5	88.327(17)
Cl(1)#1-Sb(1)-Cl(1)#3	88.327(17)	Cl(1)#4-Sb(1)-Cl(1)#5	88.326(17)
Cl(1)#2-Sb(1)-Cl(1)#3	91.673(17)	Cl(1)#1-Sb(1)-Cl(1)	91.673(17)
Cl(1)#1-Sb(1)-Cl(1)#4	180.0	Cl(1)#2-Sb(1)-Cl(1)	88.326(17)
Cl(1)#2-Sb(1)-Cl(1)#4	91.673(17)	Cl(1)#3-Sb(1)-Cl(1)	180.0
Cl(1)#3-Sb(1)-Cl(1)#4	91.674(17)	Cl(1)#4-Sb(1)-Cl(1)	88.326(17)
Cl(1)#1-Sb(1)-Cl(1)#5	91.674(17)	Cl(1)#5-Sb(1)-Cl(1)	91.674(17)
Cl(1)#2-Sb(1)-Cl(1)#5	180.00(2)		

Symmetry transformations used to generate equivalent atoms: N.A. for **2**

3			
Sb(1)-Cl(1)	2.5430(6)	Sb(1)-Cl(4)	2.5866(6)
Sb(1)-Cl(2)	2.4050(6)	Sb(1)-Cl(5)	2.7379(6)
Sb(1)-Cl(3)	2.6540(6)	Sb(1)-Cl(6)	3.3245(7)
Cl(2)-Sb(1)-Cl(1)	90.55(2)	Cl(4)-Sb(1)-Cl(5)	97.56(2)
Cl(2)-Sb(1)-Cl(4)	85.55(2)	Cl(3)-Sb(1)-Cl(5)	83.743(19)
Cl(1)-Sb(1)-Cl(4)	91.01(2)	Cl(2)-Sb(1)-Cl(6)	174.710(19)
Cl(2)-Sb(1)-Cl(3)	87.61(2)	Cl(1)-Sb(1)-Cl(6)	91.83(2)
Cl(1)-Sb(1)-Cl(3)	87.57(2)	Cl(4)-Sb(1)-Cl(6)	89.685(19)
Cl(4)-Sb(1)-Cl(3)	173.00(2)	Cl(3)-Sb(1)-Cl(6)	97.210(18)
Cl(2)-Sb(1)-Cl(5)	88.67(2)	Cl(5)-Sb(1)-Cl(6)	89.692(19)
Cl(1)-Sb(1)-Cl(5)	171.30(2)		

Symmetry transformations used to generate equivalent atoms: N.A. for **3**.

Table S3. Hydrogen bonds data for **1**, **2** and **3**.

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
1				
C(1)-H(1A)···Cl(3)	0.95	2.92	3.703(14)	140.3
C(2)-H(2A)···Cl(2)#1	0.95	2.67	3.502(13)	146.3
C(3)-H(3A)···Cl(1)#2	0.95	2.89	3.450(18)	119.0
C(3)-H(3A)···Cl(5)#2	0.95	2.71	3.534(14)	144.9
C(4)-H(4A)···Cl(5)#2	0.98	2.85	3.712(17)	147.3
C(4)-H(4C)···Cl(5)	0.98	2.71	3.65(2)	159.4
C(5)-H(5A)···Cl(6)#2	0.99	2.90	3.554(14)	124.7
C(5)-H(5B)···Cl(3)#1	0.99	2.80	3.546(13)	133.0
C(7)-H(7B)···O(5B)#3	0.99	2.42	2.93(3)	111.7
C(9)-H(9A)···Cl(1)#4	0.95	2.83	3.558(13)	134.3
C(10)-H(10A)···Cl(4)#5	0.95	2.64	3.566(14)	164.5
C(11)-H(11A)···Cl(2)	0.95	2.69	3.376(14)	129.7
C(11)-H(11A)···Cl(6)	0.95	2.76	3.548(13)	141.3
C(12)-H(12A)···Cl(6)	0.98	2.87	3.769(15)	153.0
C(13)-H(13A)···Cl(3)#5	0.99	2.72	3.647(14)	155.2
C(13)-H(13B)···Cl(2)	0.99	2.96	3.774(14)	140.7
C(13)-H(13B)···Cl(4)	0.99	2.92	3.641(14)	130.2
C(15)-H(15A)···O(5B)#5	0.99	2.63	3.59(3)	163.8
C(15)-H(15B)···Cl(1)#6	0.99	2.84	3.757(15)	153.6
C(17)-H(17A)···Cl(3)#7	0.95	2.79	3.72(3)	169.3
C(18)-H(18A)···Cl(1)#7	0.95	2.56	3.26(2)	130.4
C(19)-H(19C)···Cl(5)	0.95	2.44	3.24(2)	142.5
C(21)-H(21A)···Cl(5)	0.99	2.59	3.41(3)	140.1
C(17B)-H(17B)···Cl(3)#7	0.95	2.68	3.32(3)	124.7
C(19B)-H(19A)···Cl(5)	0.95	2.86	3.67(4)	145.0
C(19B)-H(19A)···O(3)#1	0.95	2.52	3.21(4)	129.0
C(20B)-H(20F)···O(3)#1	0.98	2.29	3.21(4)	156.1
C(23B)-H(23C)···N(3)#8	0.99	2.68	3.38(4)	127.9
C(24B)-H(24E)···N(1)#2	0.98	2.59	3.52(4)	156.7
Symmetry transformations used to generate equivalent atoms:				
#1 1/2-*x*, 1/2+*y*, +*z*; #2 1-*x*, 1-*y*, 1-*z*; #3 +*x*, 3/2-*y*, -1/2+*z*; #4 1-*x*, -*y*, 1-*z*; #5 1/2-*x*, -1/2+*y*, +*z*; #6 -1/2+*x*, 1/2-*y*, 1-*z*; #7 +*x*, 1/2-*y*, 1/2+*z*; #8 1-*x*, 1/2+*y*, 3/2-*z*				

2				
O(1)-H(1)···O(11)	0.817(10)	1.648(14)	2.459(3)	171(6)
C(2)-H(2A)···O(22)	0.95	2.43	3.154(3)	132.4
C(3)-H(3A)···Cl(1)	0.95	2.94	3.391(2)	110.5
C(3)-H(3A)···Cl(1)#3	0.95	2.70	3.563(2)	150.9
C(4)-H(4A)···Cl(1)#4	0.98	2.83	3.600(2)	135.5
C(5)-H(5A)···Cl(1)	0.99	2.95	3.747(2)	138.0
C(5)-H(5A)···Cl(1)#5	0.99	2.83	3.508(2)	126.4
C(5)-H(5B)···O(2)#6	0.99	2.33	3.291(3)	163.3
Symmetry transformations used to generate equivalent atoms:				
#1 2/3-*x*, 1/3-*y*, 4/3-*z*; #2 2/3-*y*, 1/3+*x*-*y*, -2/3+*z*; #3 +*y*-*x*, -*x*, +*z*; #4 +*y*, -*x*+*y*, -*z*; #5 +*y*, -*x*+*y*,1-*z*; #6 1/3+*y*-*x*, 2/3-*x*, -1/3+*z*				
3				
O(1)-H(1)···O(2)#1	0.818(10)	1.841(10)	2.659(3)	178(3)
C(1)-H(1A)···Cl(1)#2	0.95	2.93	3.484(3)	118.4
C(2)-H(2A)···Cl(2)#3	0.95	2.71	3.533(3)	145.9
C(3)-H(3A)···Cl(1)	0.95	2.72	3.565(3)	148.9
C(4)-H(4A)···Cl(1)	0.98	2.86	3.738(3)	149.4
C(4)-H(4B)···Cl(2)#4	0.98	2.89	3.573(3)	127.5
C(4)-H(4B)···Cl(4)#4	0.98	2.79	3.703(3)	155.0
C(4)-H(4C)···Cl(4)#2	0.98	2.76	3.674(3)	154.6
C(5)-H(5A)···Cl(1)#3	0.99	2.93	3.593(3)	125.5
C(5)-H(5A)···Cl(3)#3	0.99	2.63	3.539(3)	153.3
C(5)-H(5B)···Cl(4)	0.99	2.74	3.423(3)	126.9
O(3)-H(3)···Cl(6)	0.818(10)	2.322(15)	3.0977(19)	159(3)
C(7)-H(7A)···Cl(5)#5	0.95	2.93	3.532(3)	122.7
C(8)-H(8A)···O(6)#6	0.95	2.43	3.223(3)	140.7
C(9)-H(9A)···Cl(5)#3	0.95	2.68	3.531(3)	150.1
C(10)-H(10C)···O(5)#3	0.98	2.54	3.153(3)	120.8
C(11)-H(11A)···O(4)#5	0.99	2.45	3.298(3)	143.2
C(11)-H(11B)···Cl(3)#3	0.99	2.89	3.421(3)	114.5
O(5)-H(5)···Cl(6)	0.816(10)	2.205(15)	2.997(2)	164(4)
C(13)-H(13A)···Cl(5)#7	0.95	2.81	3.582(3)	138.7
C(14)-H(14A)···Cl(1)#3	0.95	2.86	3.598(2)	135.2
C(14)-H(14A)···O(4)#7	0.95	2.49	3.163(3)	127.8
C(15)-H(15A)···Cl(2)#4	0.95	2.71	3.386(3)	128.4
C(15)-H(15A)···Cl(3)#4	0.95	2.82	3.646(3)	146.6
C(16)-H(16B)···Cl(4)#7	0.98	2.99	3.721(3)	132.6
C(16)-H(16C)···Cl(5)#7	0.98	2.94	3.661(3)	131.2
C(17)-H(17A)···Cl(3)	0.99	2.79	3.691(3)	151.0
C(17)-H(17B)···Cl(5)#4	0.99	2.77	3.424(3)	123.8
Symmetry transformations used to generate equivalent atoms:				
#1 -*x*, -*y*, 1-*z*; #2 -*x*, 1/2+*y*, 1/2-*z*; #3 +*x*, 1/2-*y*, 1/2+*z*; #4 +*x*, 1+*y*, +*z*; #5 1-*x*, 1/2+*y*, 3/2-*z*; #61-*x*, 1-*y*, 1-*z*; #7 +*x*, 1/2-*y*, -1/2+*z*				

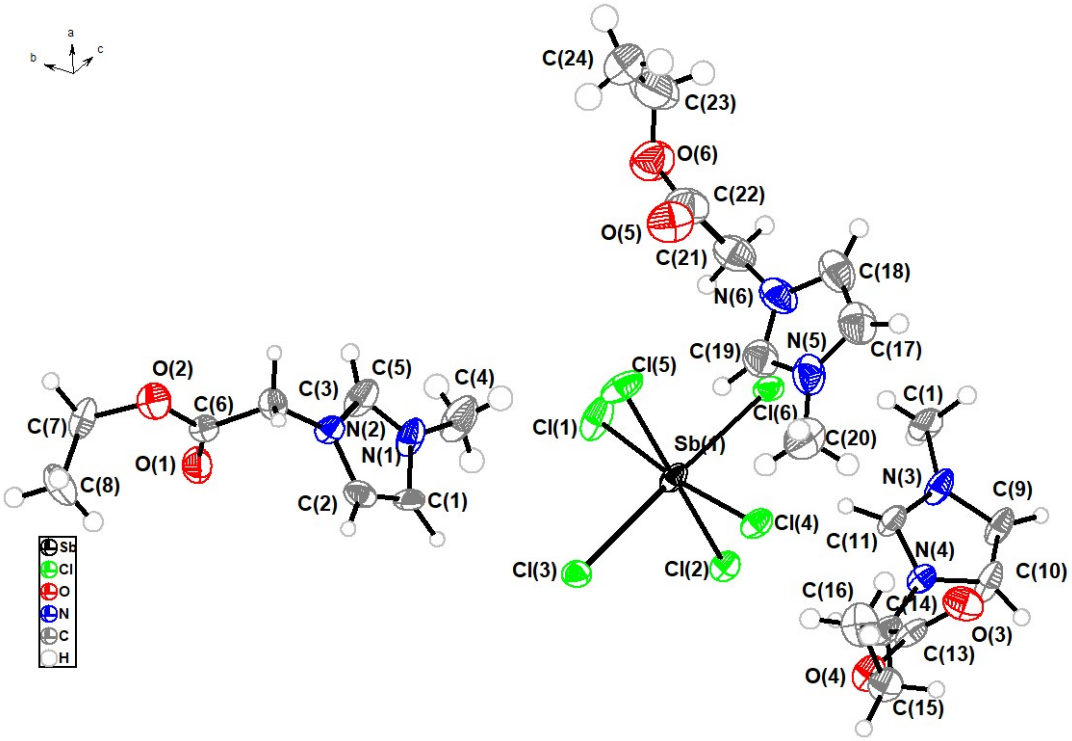

Figure S1. *ORTEP* drawing (50% ellipsoid probability) of the asymmetric unit of **1**.

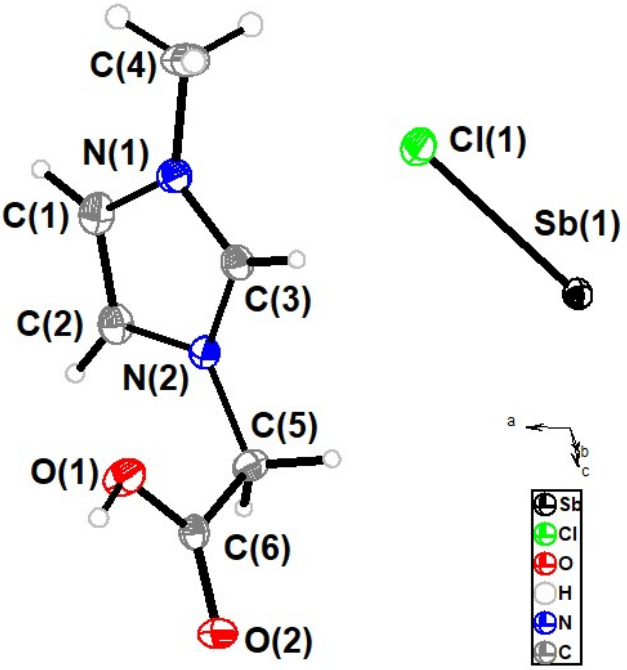

Figure S2. *ORTEP* drawing (50% ellipsoid probability) of the asymmetric unit of **2**.

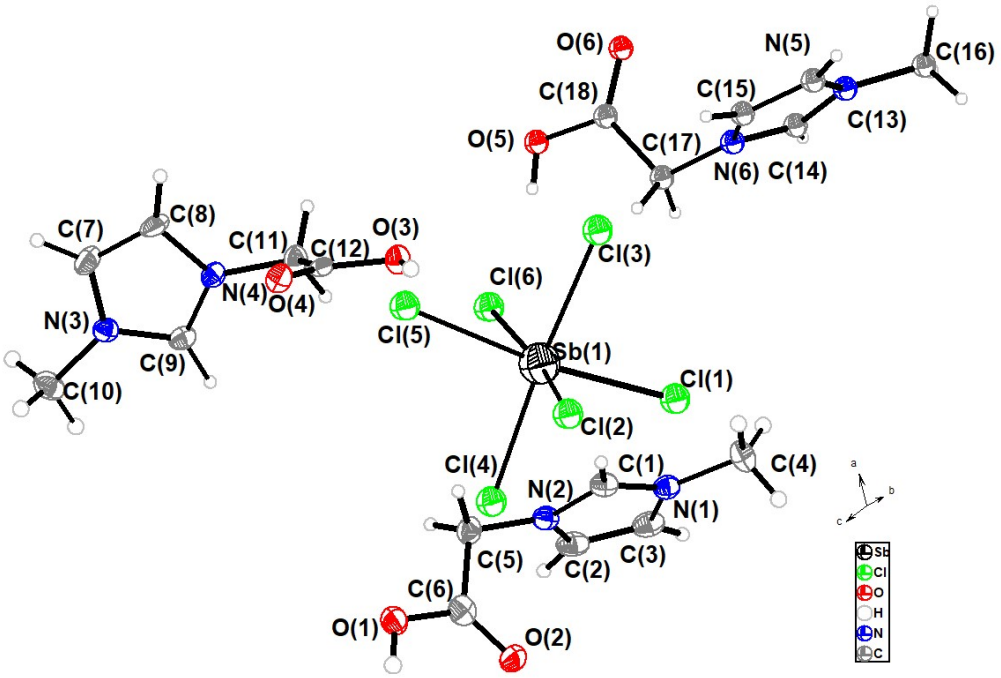

Figure S3. *ORTEP* drawing (50% ellipsoid probability) of the asymmetric unit of **3**.

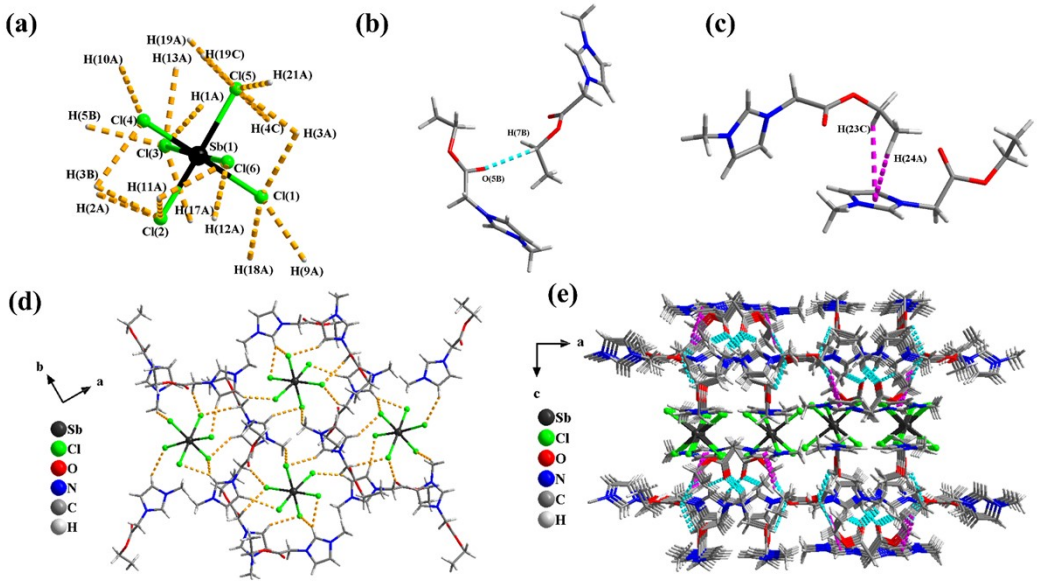

Figure S4. (a) The hydrogen bonds around each $[SbCl_6]^{3-}$ anion in **1**; (b) C-O···H bond in **1**; (c) cation-π interaction in **1**; (d) a two-dimensional anion layer formed by hydrogen bonds C-H···Cl observed along the *c*-axis; (e) the packing diagram observed along the *b*-axis. The purple and cyan dashed lines represent the cation-π interaction and the C-O···H bond, respectively, connecting the anion and cation layers.

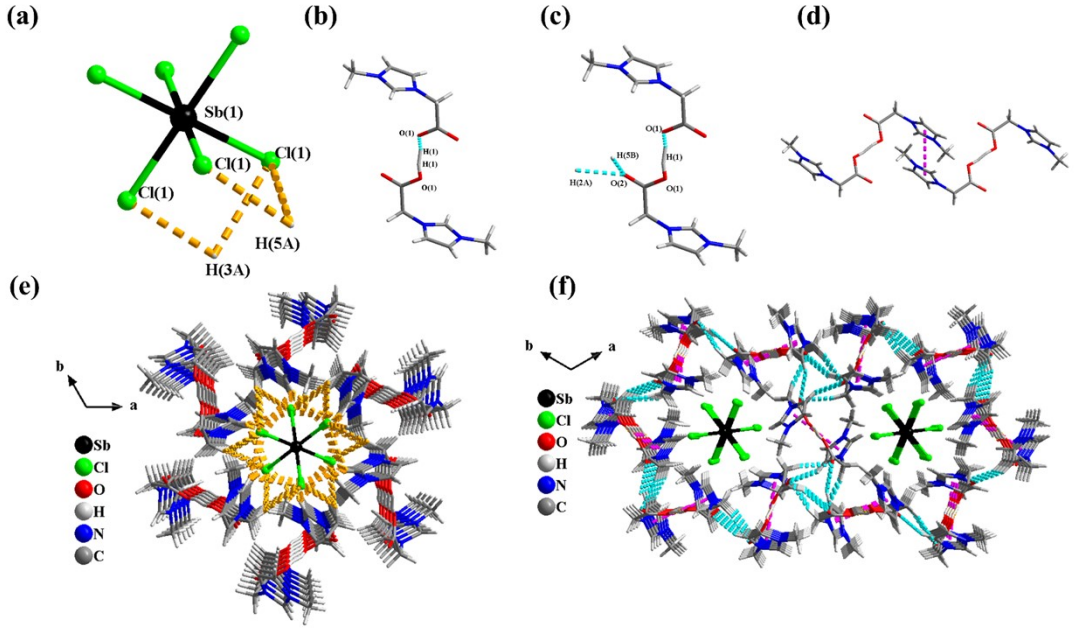

Figure S5. (a) The hydrogen bonds around each $[SbCl_6]^{3-}$ anion in **2**; (b) the two organic in in **2** share one H(1); (c) C-O···H bond in **2**; (d) π···π interaction in **2**; (e) a one-dimensional tubular structure formed by hydrogen bond C-H···Cl view along the *c*-axis; (f) the packing diagram view along the *c*-axis. The purple and cyan dotted lines represent the π···π interaction and C-O···H bond, respectively.

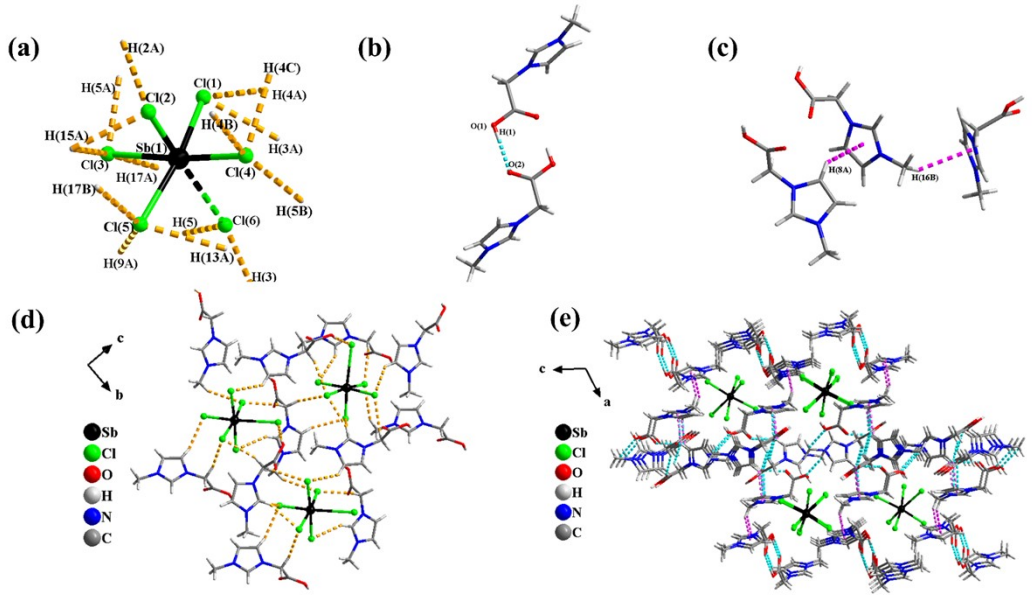

Figure S6. (a) The hydrogen bonds around each $[SbCl_6]^{3-}$ anion in **3**; (b) C-O···H bond in **3**; (c) cation-π interaction in **3**; (d) a two-dimensional anion layer formed by hydrogen bonds C-H···Cl viewed along the *a*-axis; (e) the packing diagram viewed along the *b*-axis. The purple and cyan dashed lines represent the cation-π interaction and the C-O···H bond, respectively.

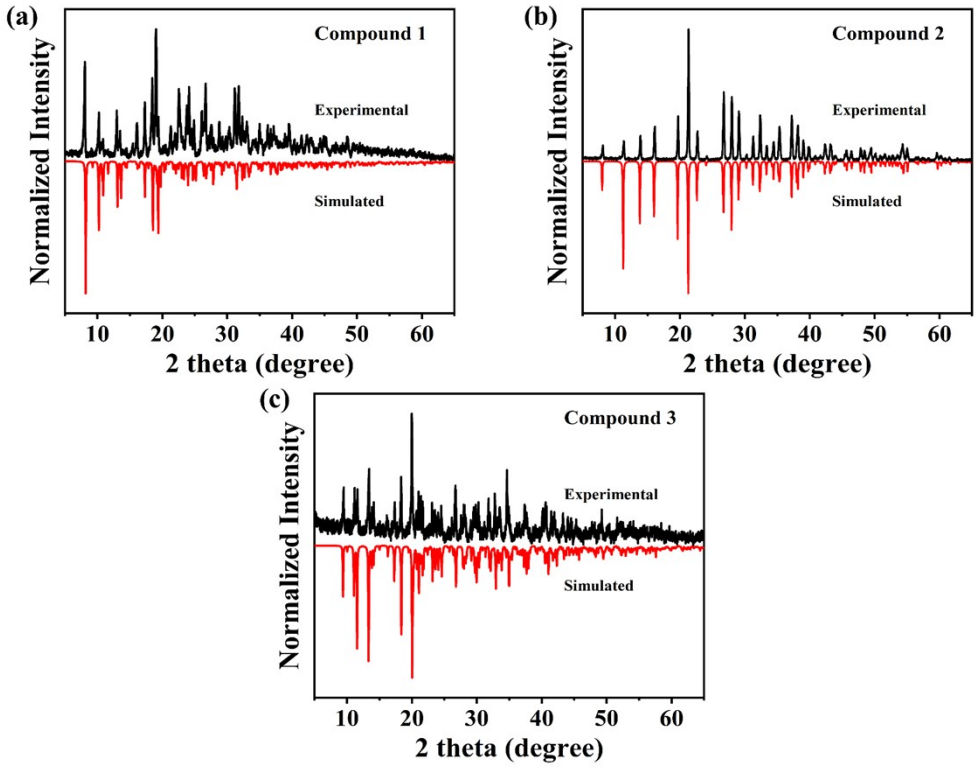

Figure S7. Experimental and simulated PXRD patterns of **1, 2**, and **3**.

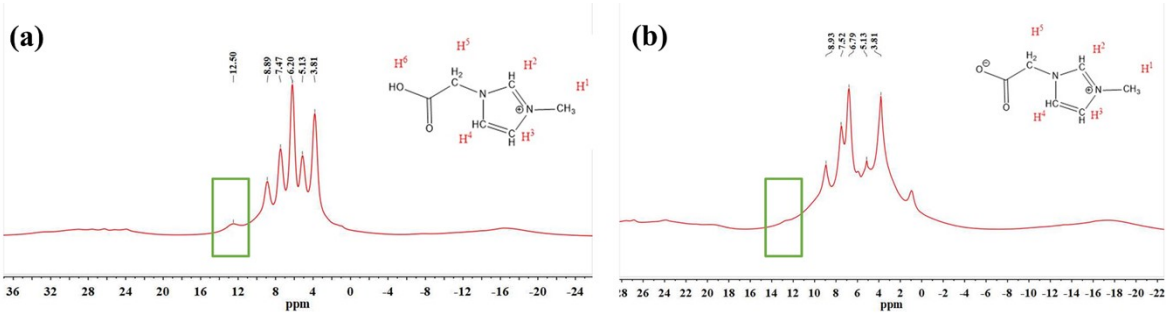

Figure S8. 1HNMR of **3** (a) and **3**→**2** (b).

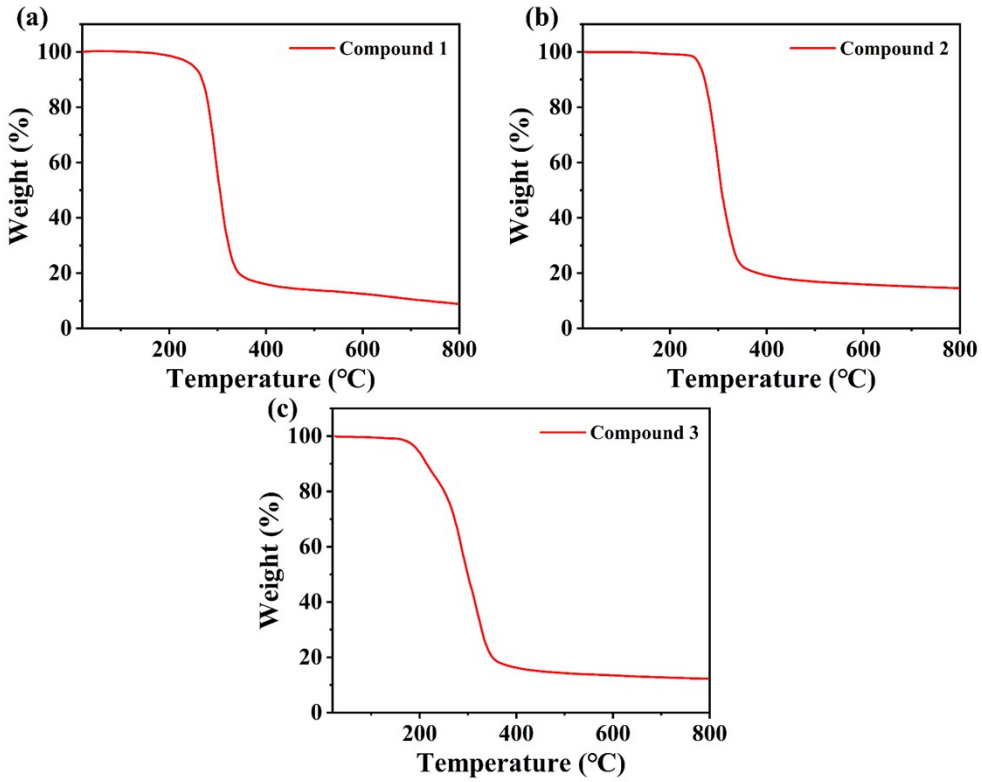

Figure S9. Thermogravimetric curves for **1**, **2**, and **3**.

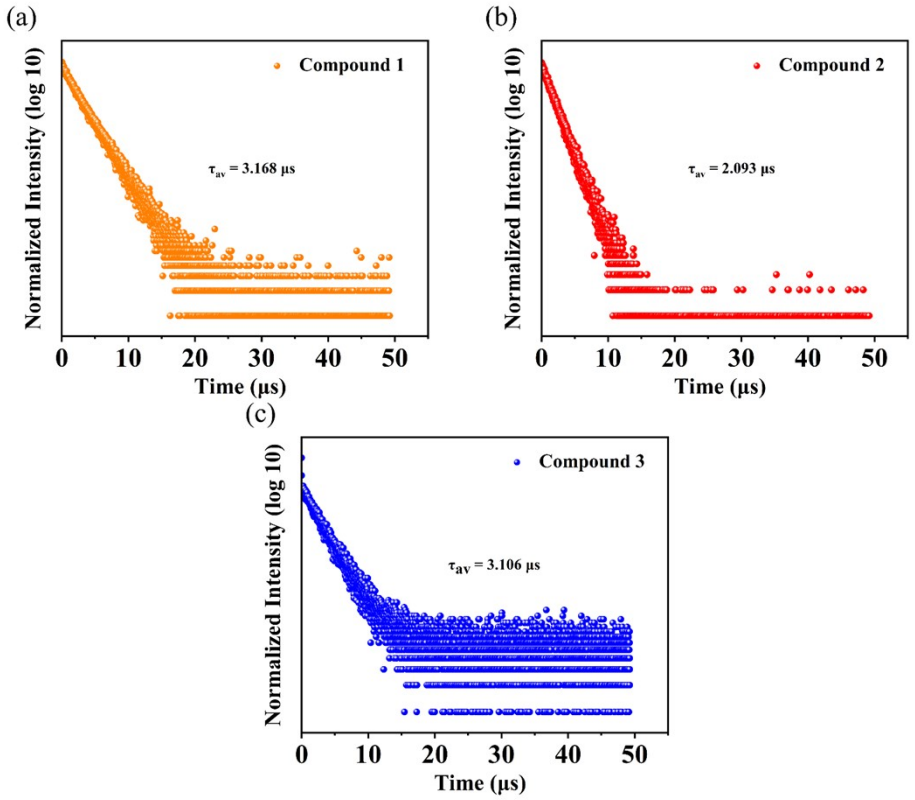

Figure S10. The PL decay spectra at 300K for **1**, **2**, and **3**.

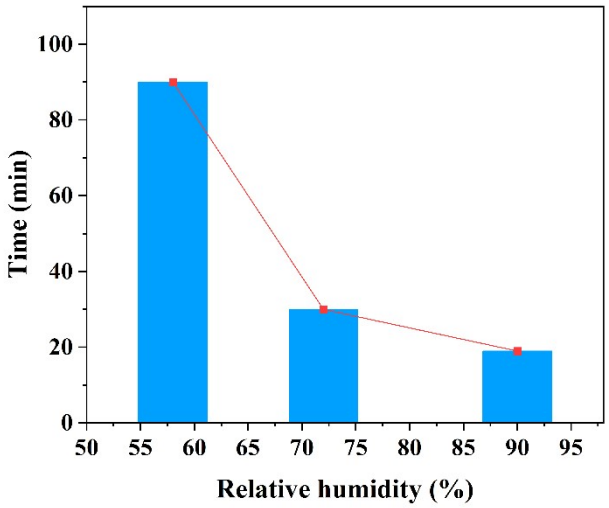

Figure S11. Comparison of transition time at 90% RH, 72% RH, and 58% RH.

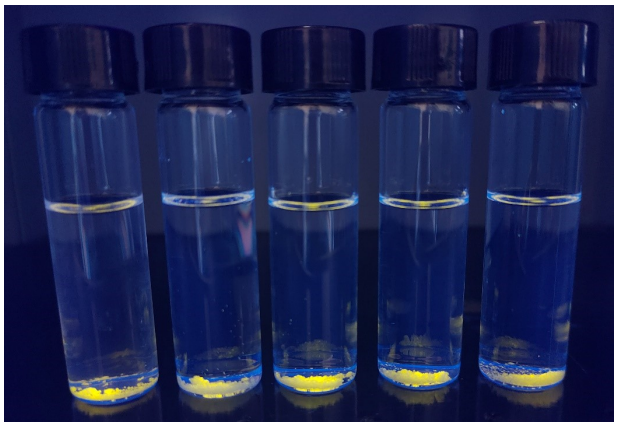

Figure S12. Images for the sample of **3** being immersed in anhydrous solvents for 6 hours. From left to right: acetonitrile, toluene, ethyl acetate, isopropanol, and tetrahydrofuran.

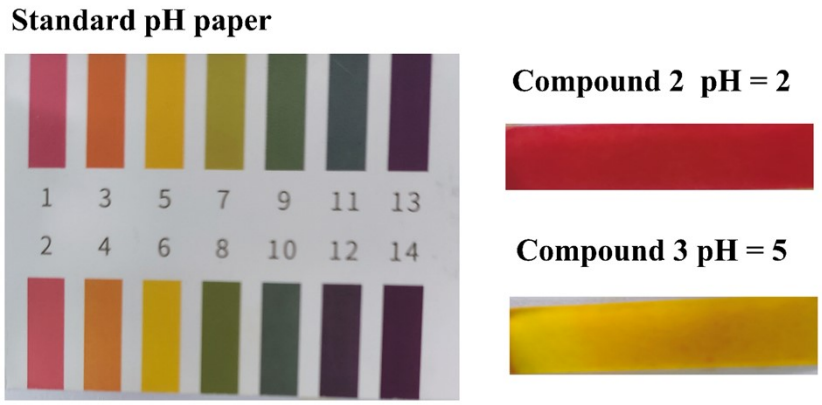

Figure S13. In acetonitrile solution, the pH value of the solution was 5 when the compound was yellow-green-emission **3** and was 2 when it was converted to green-emission **2**.

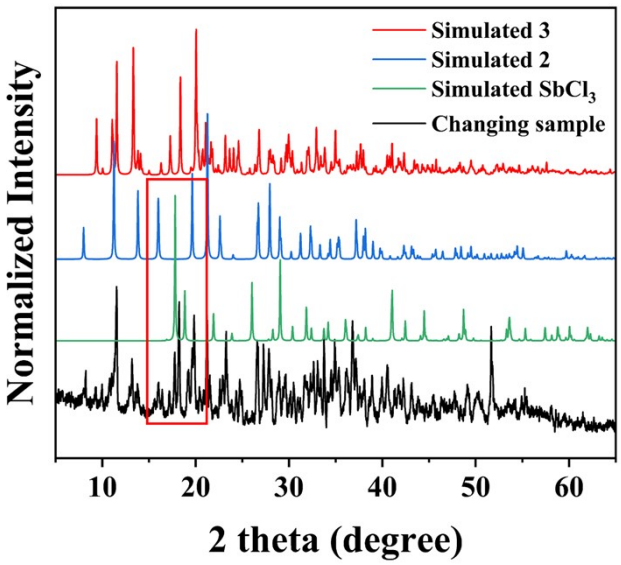

Figure S14. PXRD diagram showing that $SbCl_3$ was released during the conversion of **3** to **2**.

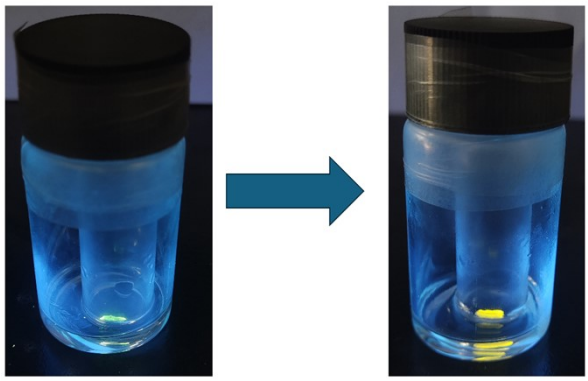

Figure S15. The process photograph of converting **2** to **3** by fumigation with $SbCl_3$ and HCl.