Supporting Information for:

A deep-red-emission antimony(III) chloride with dual-cations: Extremely large Stokes shift due to high [$SbCl_6$] distortion

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1. Materials

Antimony(III) chloride ($SbCl_3$, 99%) was purchased from Adamas Reagent Co., Ltd. 1-Pentyl-3-methylimidazolium chloride ([C_5mim]Cl, 99%) and N-methylimidazolium chloride ([Mim]Cl, 98%) were purchased from Lanzhou GreenChem ILs, LICP, CAS (Lanzhou, China). All reagents were used without further purification.

2. Synthesis

*[C_5mim][Mim]$_2$[$SbCl_6$] (**1**):* 1 mmol $SbCl_3$ (0.2281 g), 1 mmol [C_5mim]Cl (0.2027 g) and 2 mmol [Mim]Cl (0.2371 g) were put into a 20 mL glass bottle, which was sealed with a plastic cover and heated at 120 °C for 3 h. After cooling to RT, bulk-like colourless and transparent crystals were obtained. The yield was calculated to be near 100% based on Sb. Note that no additional organic solvents are needed to be added to this reaction system, while the ionic liquid acted as both the template and reactive solvent. Elemental analysis (EA) calculated for [C_5mim][Mim]$_2$[$SbCl_6$]: C, 31.22%; N, 12.85%; H, 4.78%; experimental: C, 31.39%; N, 12.41%; H, 5.04%.

*[Bzmim]$_3$[$SbCl_6$] (**2**) and [$H_{0.5}$COOmim]$_6$[$SbCl_6$] (**3**):* **2** and **3** were synthesized according to references.[1, 2]

3. Single Crystal X-ray diffraction (SCXRD)

A suitable crystal of **1** was selected under an optical microscope for the measurement of single-crystal X-ray diffraction (SCXRD). Data were measured and collected on a Supernova CCD diffractometer *via* using graphite-monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å) at 100 K. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX-2018 program package.[3] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms connected to all C atoms were located at geometrically calculated positions. CCDC No. 2110407 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

4. Characterization methods

The experimental powder X-ray diffraction (PXRD) pattern was measured by Rigaku Miniflex-II diffractometer by utilizing Cu$K\alpha$ radiation (λ = 1.54178 Å) in the angular range of 2θ = 5 - 30°. The simulated PXRD patterns were calculated by using the single crystal X-ray structural data at RT *via* Mercury software.[4] Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 449F3 instrument with a heating rate of 10 K min^{-1} under a dry N_2 atmosphere. Photoluminescence excitation (PLE), photoluminescence (PL) spectra and PL decay spectra were measured on FLS1000 UV/V/NIR fluorescence spectrometer.

5. Theoretical calculations

Compounds **1** was calculated by using CASTEP in Material Studio software.[5, 6] The exchange-correlation interactions were described by Perdew-Burke-Ernzerhof-General Gradient Approximation (PBE-GGA).[7] For all of the calculations, the qualities were selected as “fine”, and the SCF tolerance is set as 10^{-6} eV/atom. We used 5×5×7 Monkhorst-Pack grid to the Brillouin-zone integrations. However, for the LUMO and HOMO of two compounds, the Brillouin zone was sampled by using Gamma points. The other sets were the default for all calculations.

6. Other Data

Table S1. Crystal data and structure refinement for $[C_5mim][Mim]_2[SbCl_6]$ (**1**) at 100 K.

	1
Empirical formula	$C_{17}H_{31}Cl_6N_6Sb$
Formula weight	653.93
Temperature/K	100(2)
Wavelength/Å	0.71073
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.9017(5)
b/Å	16.1484(9)
c/Å	17.2408(9)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2756.7(3)
Z	4
ρ_{calc} g/cm^3	1.576
Absorption coefficient/mm^{-1}	1.599
F(000)	1312
Crystal size/mm^3	0.300×0.150×0.100
Theta range for data collection /°	2.363-30.173
Limiting indices	$-13 \le h \le 13$, $-22 \le k \le 21$, $-22 \le l \le 22$
Reflections collected/ unique	18508/6626 [R_{int} = 0.0497]
Completeness to theta	25.242, 100.0 %
Absorption correction	Semi-empirical from equivalents
Max. transmission	1.00000
Min. transmission	0.51719
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6626/0/282
Goodness-of-fit on F^2	1.007
Final R indexes [$I >= 2\sigma(I)$]	R_1 = 0.0362, wR_2 = 0.0823
Final R indexes [all data]	R_1 = 0.0409, wR_2 = 0.0865
Largest diff. peak and hole/e Å^{-3}	1.041/-2.768

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

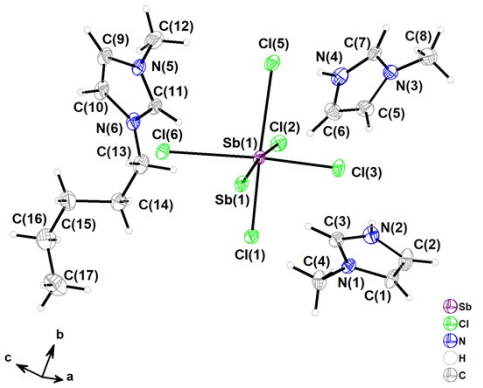

Figure S1. *ORTEP* drawing (50% ellipsoid probability) of the asymmetric unit of **1** at 100 K.

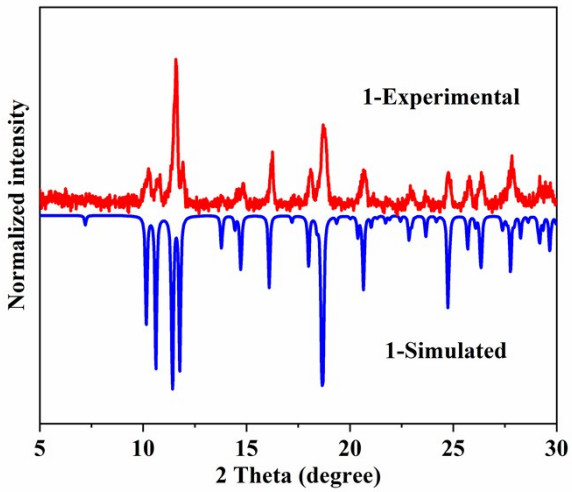

Figure S2. The simulated and experimental PXRD patterns of **1**.

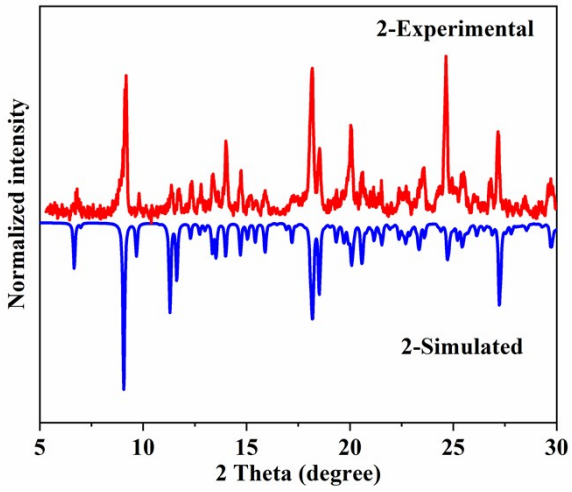

Figure S3. The simulated and experimental PXRD patterns of **2**.

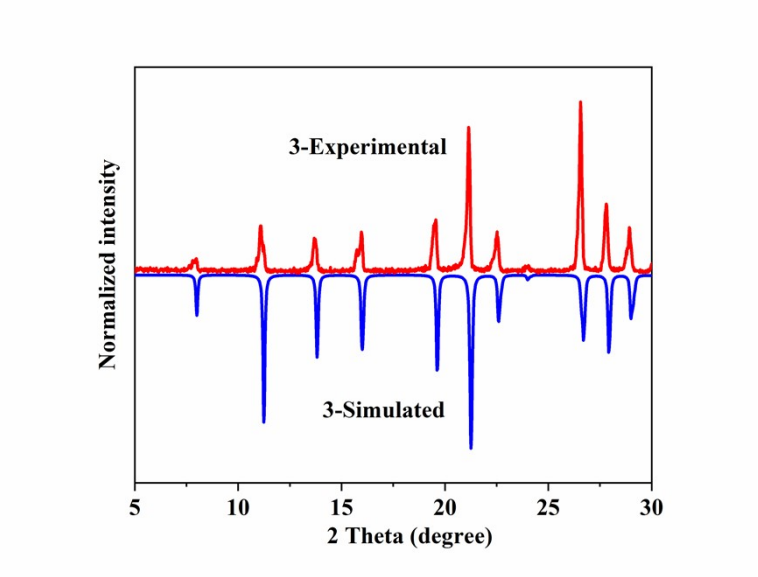

Figure S4. The simulated and experimental PXRD patterns of **3**.

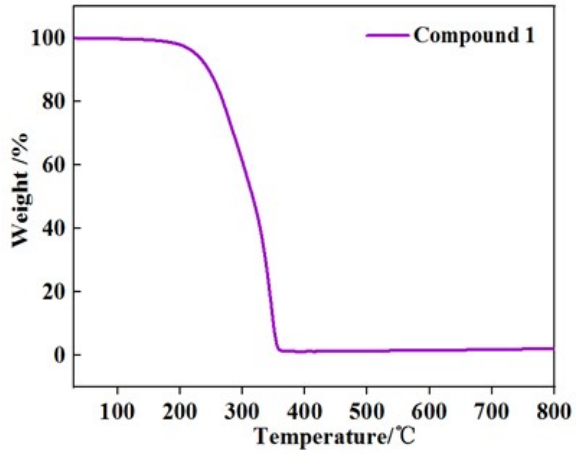

Figure S5. Thermogravimetric (TG) curve of **1**.

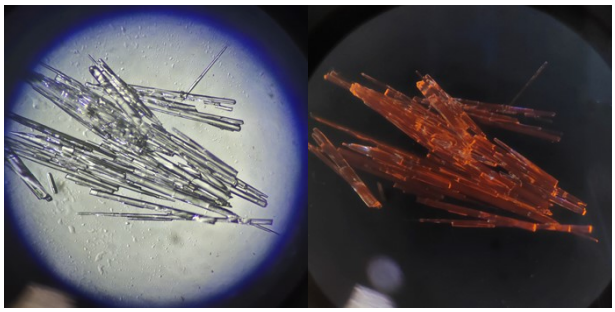

Figure S6. Photographs of crystals of **1** under natural light (left) and 365 UV irradiation (right).

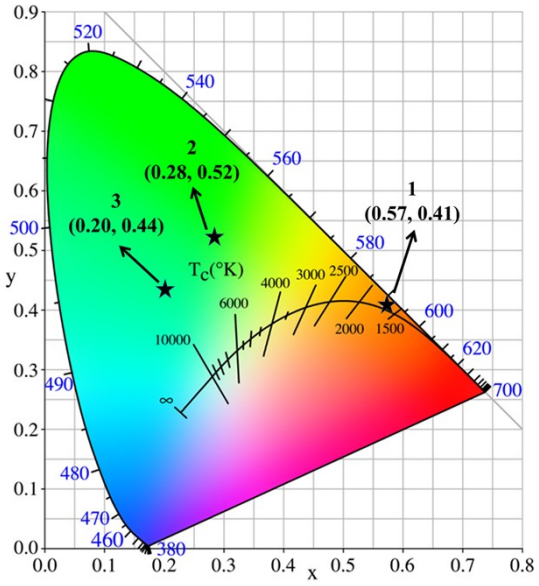

Figure S7. The Commission Internationale del'Eclairage (CIE) (1931) chromaticity coordinates of **1**-**3** at RT.

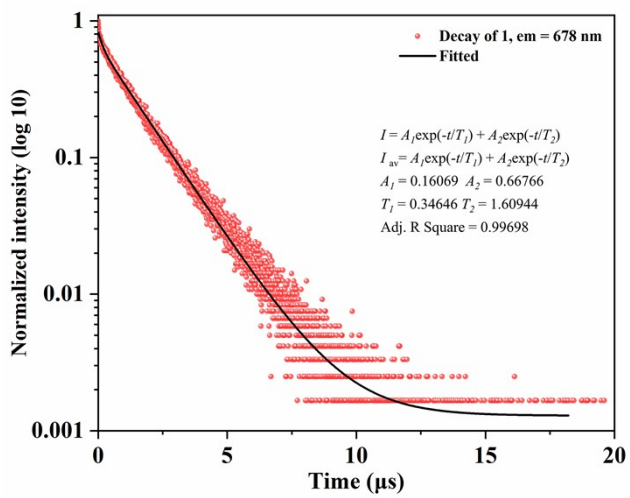

Figure S8. Time-resolved PL decay curves of **1** under 375 nm excitation at RT. The lifetime of **1** can be fitted well *via* bi-exponential function of $I = A_1\exp(-t/T_1) + A_2\exp(-t/T_2)$, and the average lifetime can be obtained by $I_{av} = A_1\exp(-t/T_1) + A_2\exp(-t/T_2)$. The average lifetime of **1** is calculated as 1.53 μs.

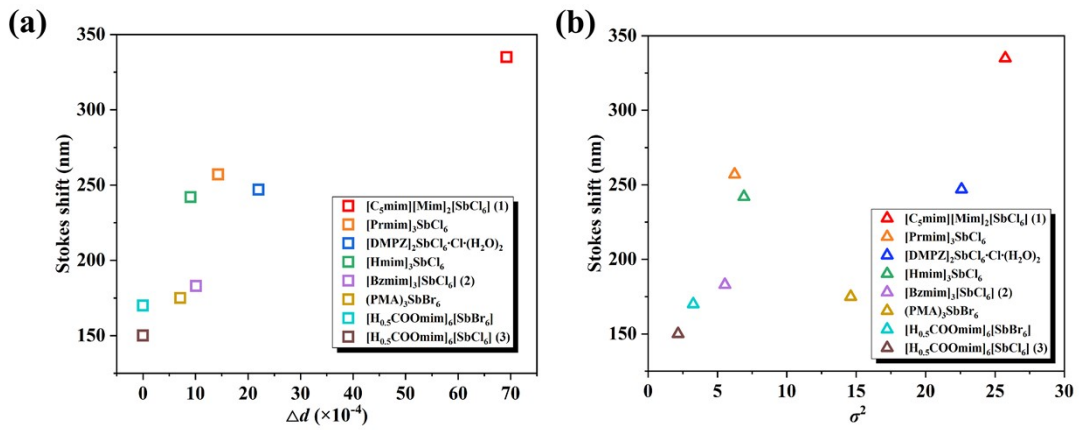

Figure S9. The relationship between Stokes shift and distortion level of Δd (**a**) and σ^2 (**b**) for [SbX_6]-based 0D OIMHs (X = Cl, Br). PMA = phenylmethylammonium; Hmim = 1-hexyl-3-methylimidazolium; Prmim = 1-propyl-3-methylimidazolium; DMPZ = N,N-dimethylpiperazine.

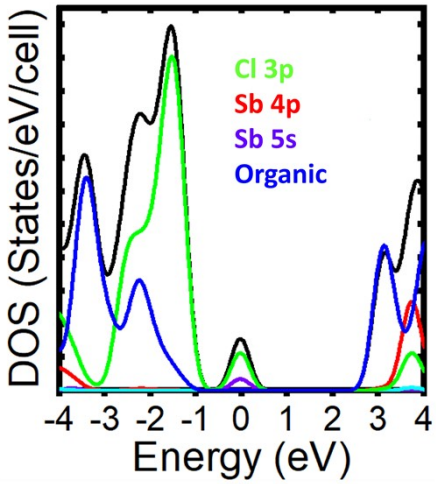

Figure S10. The orbital-resolved density of states (DOS) for **1**.

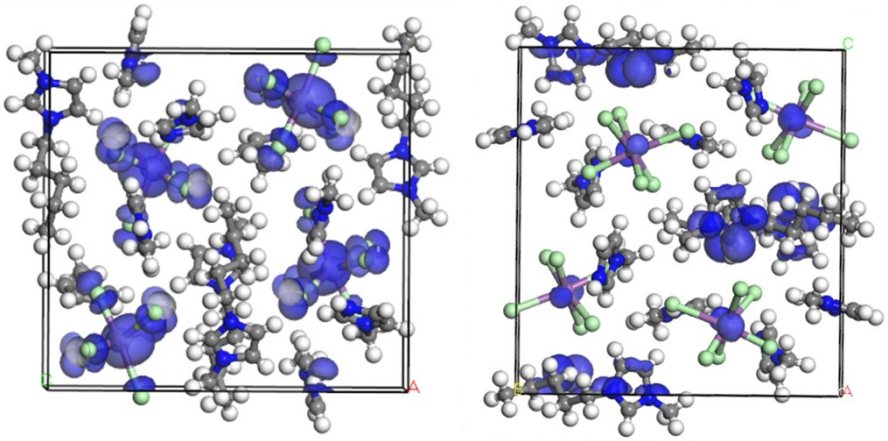

Figure S11. The molecular orbitals of **1** showing the highest occupied molecular orbital (left, HOMO) and the lowest occupied molecular orbital (right, LUMO).

Table S2. Selected bond lengths (Å) and bond angles (°) for $[C_5mim][Mim]_2[SbCl_6]$ (**1**).

Sb(1)-Cl(3)	2.4529(13)
Sb(1)-Cl(1)	2.4703(12)
Sb(1)-Cl(2)	2.4900(13)
Sb(1)-Cl(4)	2.8525(13)
Sb(1)-Cl(5)	2.9086(13)
Sb(1)-Cl(6)	2.9806(13)
Cl(3)-Sb(1)-Cl(1)	91.15(4)
Cl(3)-Sb(1)-Cl(2)	90.16(4)
Cl(1)-Sb(1)-Cl(2)	87.20(4)
Cl(3)-Sb(1)-Cl(4)	86.79(4)
Cl(1)-Sb(1)-Cl(4)	86.88(4)
Cl(2)-Sb(1)-Cl(4)	173.29(4)
Cl(3)-Sb(1)-Cl(5)	88.06(4)
Cl(1)-Sb(1)-Cl(5)	174.24(4)
Cl(2)-Sb(1)-Cl(5)	87.09(4)
Cl(4)-Sb(1)-Cl(5)	98.77(4)
Cl(3)-Sb(1)-Cl(6)	176.09(4)
Cl(1)-Sb(1)-Cl(6)	85.09(4)
Cl(2)-Sb(1)-Cl(6)	90.74(4)
Cl(4)-Sb(1)-Cl(6)	91.91(4)
Cl(5)-Sb(1)-Cl(6)	95.79(4)

Table S3. Hydrogen bonds for $[C_5mim][Mim]_2[SbCl_6]$ (**1**).

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N(2)-H(2)···Cl(6)#1	0.75(7)	2.46(7)	3.191(5)	168(7)
C(1)-H(1A)···Cl(1)#2	0.95	2.97	3.672(5)	131.7
C(1)-H(1A)···Cl(2)#2	0.95	2.97	3.786(6)	145.2
C(1)-H(1A)···Cl(3)#2	0.95	2.88	3.598(5)	133
C(2)-H(2B)···Cl(1)#1	0.95	2.79	3.385(6)	121.3
C(3)-H(3A)···Cl(4)	0.95	2.7	3.515(6)	143.9
C(4)-H(4C)···Cl(1)	0.98	2.87	3.399(6)	115.1
C(4)-H(4C)···Cl(4)	0.98	2.98	3.838(6)	146.6
N(4)-H(4)···Cl(5)	0.93(7)	2.16(7)	3.086(5)	176(6)
C(5)-H(5A)···Cl(6)#1	0.95	2.58	3.505(6)	164.3
C(6)-H(6A)···Cl(4)	0.95	2.72	3.634(6)	162.8
C(7)-H(7A)···Cl(4)#3	0.95	2.63	3.530(6)	159.2
C(8)-H(8A)···Cl(2)#1	0.98	2.86	3.725(6)	148.4
C(8)-H(8C)···Cl(6)#3	0.98	2.66	3.615(7)	163.4
C(9)-H(9A)···Cl(5)#4	0.95	2.74	3.560(5)	145.6
C(11)-H(11A)···Cl(4)	0.95	2.71	3.497(5)	140.3
C(12)-H(12A)···Cl(3)#4	0.98	2.78	3.719(7)	160.2
C(12)-H(12C)···Cl(5)	0.98	2.73	3.698(7)	168

C(13)-H(13A)···Cl(6)#5	0.99	2.74	3.688(6)	160.6
C(13)-H(13B)···Cl(4)	0.99	2.73	3.517(6)	137.2

Symmetry transformations used to generate equivalent atoms: #1 *x*+1, *y*, *z* #2 *x*+1/2, -*y*+1/2, -*z* #3 -*x*+1, *y*+1/2, -*z*+1/2 #4 -*x*+1/2, -*y* +1, *z* +1/2 #5 *x* +1/2, -*y* +1/2, -*z* +1

Table S4. Selected bond lengths (Å) and bond angles (°) for $[Bzmim]_3[SbCl_6]$ (**2**).

Sb(1)-Cl(5)	2.498(2)
Sb(1)-Cl(3)	2.6383(19)
Sb(1)-Cl(4)	2.643(2)
Sb(1)-Cl(2)	2.659(3)
Sb(1)-Cl(1)	2.660(2)
Sb(1)-Cl(6)	2.868(3)
Sb(2)-Cl(7)	2.549(2)
Sb(2)-Cl(12)	2.582(2)
Sb(2)-Cl(10)	2.646(2)
Sb(2)-Cl(8)	2.667(2)
Sb(2)-Cl(11)	2.715(2)
Sb(2)-Cl(9)	2.816(3)
Cl(5)-Sb(1)-Cl(3)	87.90(8)
Cl(5)-Sb(1)-Cl(4)	91.04(8)
Cl(3)-Sb(1)-Cl(4)	89.29(8)
Cl(5)-Sb(1)-Cl(2)	88.14(7)
Cl(3)-Sb(1)-Cl(2)	91.93(8)
Cl(4)-Sb(1)-Cl(2)	178.51(9)
Cl(5)-Sb(1)-Cl(1)	87.61(7)
Cl(3)-Sb(1)-Cl(1)	174.23(9)
Cl(4)-Sb(1)-Cl(1)	87.18(8)
Cl(2)-Sb(1)-Cl(1)	91.54(8)
Cl(5)-Sb(1)-Cl(6)	176.07(8)
Cl(3)-Sb(1)-Cl(6)	94.07(7)
Cl(4)-Sb(1)-Cl(6)	92.39(7)
Cl(2)-Sb(1)-Cl(6)	88.39(8)
Cl(1)-Sb(1)-Cl(6)	90.64(7)
Cl(7)-Sb(2)-Cl(12)	88.45(8)
Cl(7)-Sb(2)-Cl(10)	90.45(7)
Cl(12)-Sb(2)-Cl(10)	91.40(7)
Cl(7)-Sb(2)-Cl(8)	87.03(7)
Cl(12)-Sb(2)-Cl(8)	92.58(7)
Cl(10)-Sb(2)-Cl(8)	175.23(7)
Cl(7)-Sb(2)-Cl(11)	91.54(7)
Cl(12)-Sb(2)-Cl(11)	179.59(7)
Cl(10)-Sb(2)-Cl(11)	89.01(7)
Cl(8)-Sb(2)-Cl(11)	87.01(7)

Cl(7)-Sb(2)-Cl(9)	176.59(8)
Cl(12)-Sb(2)-Cl(9)	89.79(7)
Cl(10)-Sb(2)-Cl(9)	92.52(7)
Cl(8)-Sb(2)-Cl(9)	90.13(7)
Cl(11)-Sb(2)-Cl(9)	90.20(8)

Symmetry transformations used to generate equivalent atoms: #1 -*x*+1, -*y*, *z* #2 *y*+1/2, -*x*+1/2, -*z*+1/2 #3 -*y*+1/2, *x*-1/2, -*z*+1/2 #4 -*y*+1, *x*, -*z*+1 #5 *y*, -*x*+1, -*z*+1 #6 -*x*+1, -*y*+1, *z*

Table S5. Hydrogen bonds for $[Bzmim]_3[SbCl_6]$ (**2**).

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
C(1)-H(1A)···Cl(9)#1	0.95	2.89	3.651(10)	137.5
C(1)-H(1A)···Cl(10)#1	0.95	2.81	3.528(11)	133.6
C(2)-H(2A)···Cl(11)#1	0.95	2.86	3.544(11)	129.6
C(3)-H(3A)···Cl(1)	0.95	2.82	3.479(10)	127.5
C(3)-H(3A)···Cl(6)	0.95	2.73	3.509(9)	139.5
C(4)-H(4A)···Cl(2)	0.98	2.89	3.724(12)	142.9
C(12)-H(12A)···Cl(7)#2	0.95	2.96	3.648(10)	130.0
C(14)-H(14A)···Cl(8)#3	0.95	2.57	3.450(9)	154.9
C(15)-H(15A)···Cl(9)#3	0.98	2.93	3.866(9)	161.0
C(15)-H(15B)···Cl(11)#2	0.98	2.67	3.628(10)	167.5
C(16)-H(16B)···Cl(1)	0.99	2.97	3.684(11)	129.6
C(16)-H(16B)···Cl(5)	0.99	2.63	3.400(10)	135.1
C(24)-H(24A)···Cl(7)#3	0.95	2.82	3.716(9)	157.3
C(25)-H(25A)···Cl(1)	0.95	2.80	3.622(9)	145.8
C(25)-H(25A)···Cl(5)	0.95	2.90	3.403(8)	114.0
C(26)-H(26A)···Cl(2)	0.98	2.88	3.828(9)	162.9
C(26)-H(26A)···Cl(5)	0.98	2.96	3.426(9)	110.4
C(26)-H(26C)···Cl(6)#4	0.98	2.63	3.603(10)	173.1
C(27)-H(27A)···Cl(8)#3	0.99	2.92	3.634(10)	129.7
C(27)-H(27A)···Cl(12)#3	0.99	2.87	3.710(9)	143.1
C(27)-H(27B)···Cl(1)	0.99	2.89	3.756(9)	146.2
C(34)-H(34A)···Cl(10)#5	0.95	2.76	3.690(9)	166.1
C(35)-H(35A)···Cl(4)	0.95	2.90	3.773(10)	153.8
C(36)-H(36A)···Cl(9)	0.95	2.77	3.523(9)	136.3
C(37)-H(37A)···Cl(10)	0.98	2.69	3.607(10)	156.0
C(37)-H(37C)···Cl(5)	0.98	2.90	3.365(9)	110.2
C(38)-H(38A)···Cl(9)	0.99	2.80	3.701(10)	151.0
C(38)-H(38B)···Cl(11)#5	0.99	2.63	3.568(8)	157.3
C(45)-H(45A)···Cl(3)#6	0.95	2.70	3.564(12)	150.9
C(46)-H(46A)···Cl(6)#6	0.95	2.65	3.370(10)	132.5
C(47)-H(47A)···Cl(8)#3	0.95	2.91	3.585(11)	129.2
C(47)-H(47A)···Cl(11)#3	0.95	2.58	3.366(10)	140.7
C(48)-H(48A)···Cl(9)#3	0.98	2.88	3.845(12)	169.8
C(58)-H(58A)···Cl(6)#4	0.95	2.94	3.680(9)	135.6

C(59)-H(59A)···Cl(3)#4	0.98	2.85	3.801(10)	163.3
C(59)-H(59B)···Cl(7)	0.98	2.66	3.637(9)	175.2
C(60)-H(60A)···Cl(6)#4	0.99	2.68	3.625(9)	160.6
C(60)-H(60B)···Cl(2)	0.99	2.64	3.610(10)	166.3

Symmetry transformations used to generate equivalent atoms: #1 -*x*+1, *y*+1/2, -*z*+1 #2 *x*+1, *y*, *z*-1 #3 *x*, *y*, *z*-1 #4 *x*-1, *y*, *z* #5 *x*+1, *y*, *z* #6 -*x*+1, *y*-1/2, -*z*+1

Table S6. Selected bond lengths (Å) and bond angles (°) for $[H_{0.5}COOmim]_6[SbCl_6]$ (**3**).

Cl(1)-Sb(1)	2.7194(13)
Cl(1)-Sb(1)-Cl(1)#1	180.0
Cl(1)-Sb(1)-Cl(1)#2	88.87(4)
Cl(1)#1-Sb(1)-Cl(1)#2	91.13(4)
Cl(1)-Sb(1)-Cl(1)#3	91.13(4)
Cl(1)#1-Sb(1)-Cl(1)#3	88.87(4)
Cl(1)#2-Sb(1)-Cl(1)#3	180.0
Cl(1)-Sb(1)-Cl(1)#4	91.12(4)
Cl(1)#1-Sb(1)-Cl(1)#4	88.88(4)
Cl(1)#2-Sb(1)-Cl(1)#4	88.88(4)
Cl(1)#3-Sb(1)-Cl(1)#4	91.13(4)
Cl(1)-Sb(1)-Cl(1)#5	88.87(4)
Cl(1)#1-Sb(1)-Cl(1)#5	91.12(4)
Cl(1)#2-Sb(1)-Cl(1)#5	91.12(4)
Cl(1)#3-Sb(1)-Cl(1)#5	88.87(4)
Cl(1)#4-Sb(1)-Cl(1)#5	180.00(4)

Symmetry transformations used to generate equivalent atoms: #1 1-*y*, 1+*x*-*y*, *z* #2 -*x*+*y*, 1-*x*, *z* #3 2/3-*x*, 4/3-*y*, 4/3-*z* #4 -1/3+*y*, 1/3-*x*+*y*, 4/3-*z* #5 2/3+*x*-*y*, 1/3+*x*, 4/3-*z*

Table S7. Hydrogen bonds for $[H_{0.5}COOmim]_6[SbCl_6]$ (**3**).

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(1)-H(1D)···O(1)	0.84	1.66	2.454(9)	156
O(1)-H(1E)···O(1)	0.84	1.66	2.454(9)	156
C(3)-H(3)···O(2)	0.95	2.48	3.210(11)	134
C(4)-H(4)···Cl(1)	0.95	2.78	3.627(8)	149
C(5)-H(5B)···O(2)	0.99	2.33	3.290(10)	164

Symmetry transformations used to generate equivalent atoms: #1 -*x*+*y*, 1-*x*, *z*, #2 4/3-*x*, 5/3-*y*, 5/3-*z*, #3 5/3-*y* ,4/3+*x*-*y*, -2/3+*z*, #4 1/3-*x*+*y*, 5/3-*x*, -1/3+*z*

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