Electronic Supplementary Material (ESI) for CrystEngComm.

Band gap modulation of organic-inorganic Sb(III) halide by molecular design

Yan-Ning Wang, Liang Tong, Min-Wan, Jing-Yuan Liu, Si-Yu Ye, Abraham Mensah, Jun-Yi Li, Li-Zhuang Chen**

School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, People's Republic of China.

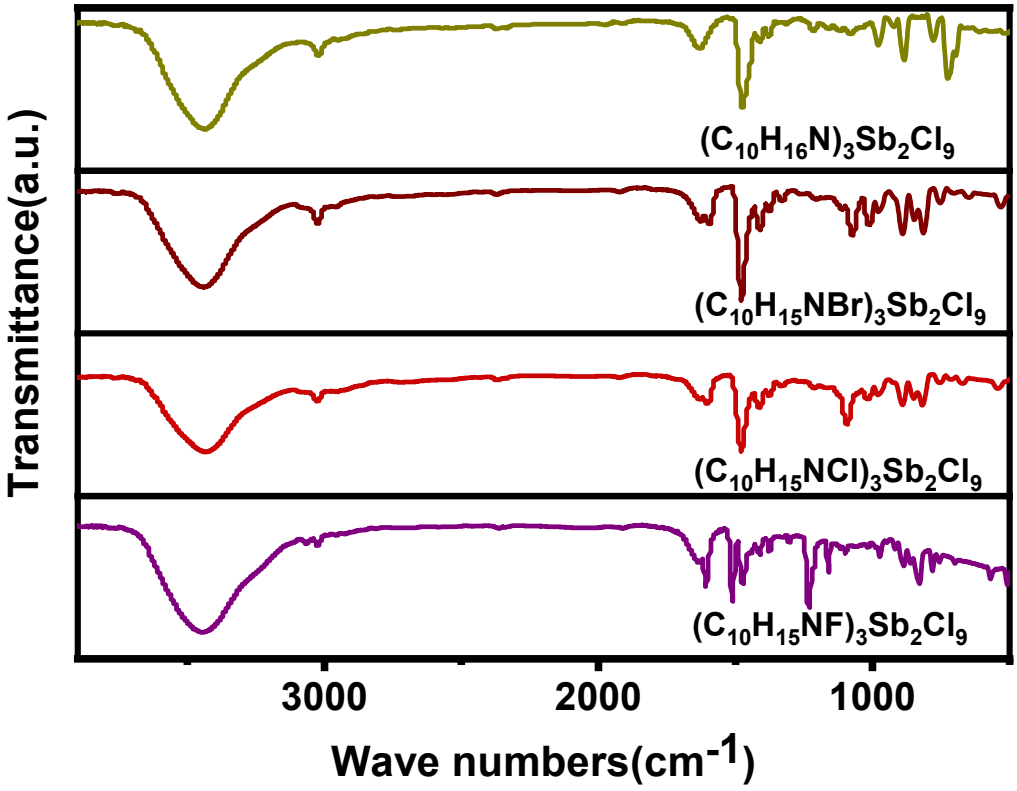

Fig. S1. Infraed spectrum of compound **1**-**4**.

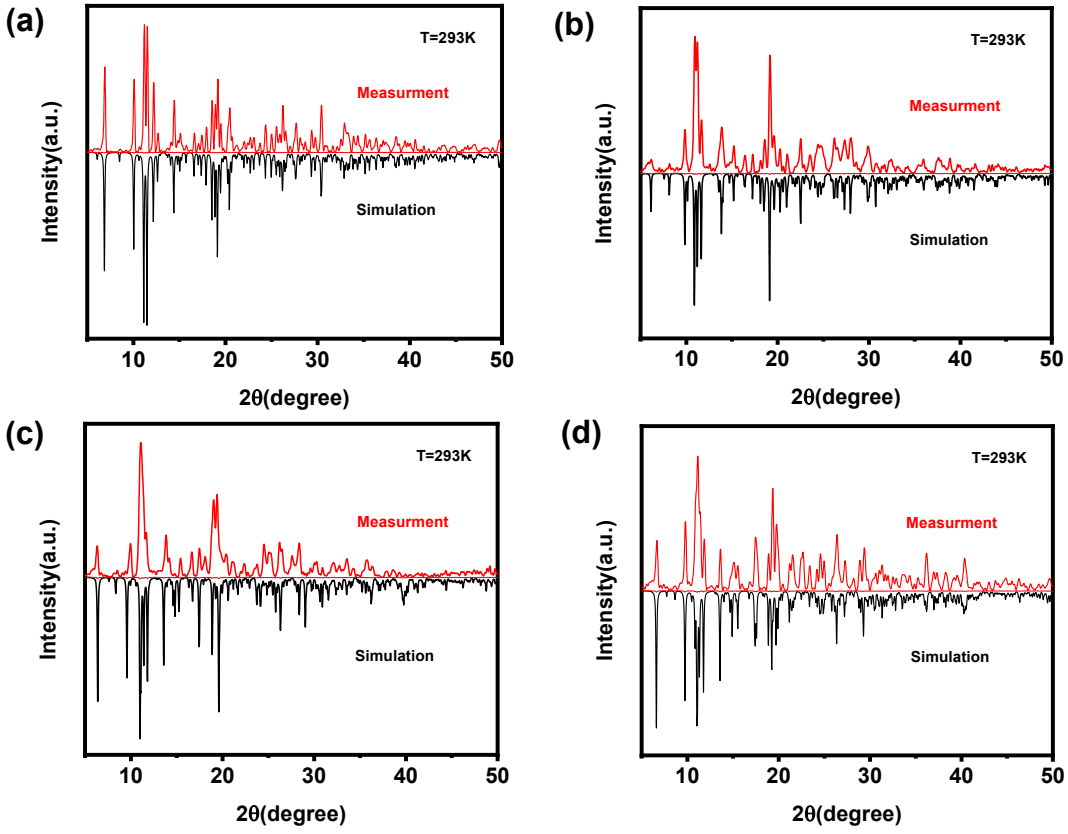

Fig. S2. Powder X-ray diffraction (PXRD) of compound **1** (a), **2** (b), **3** (c) and **4** (d).

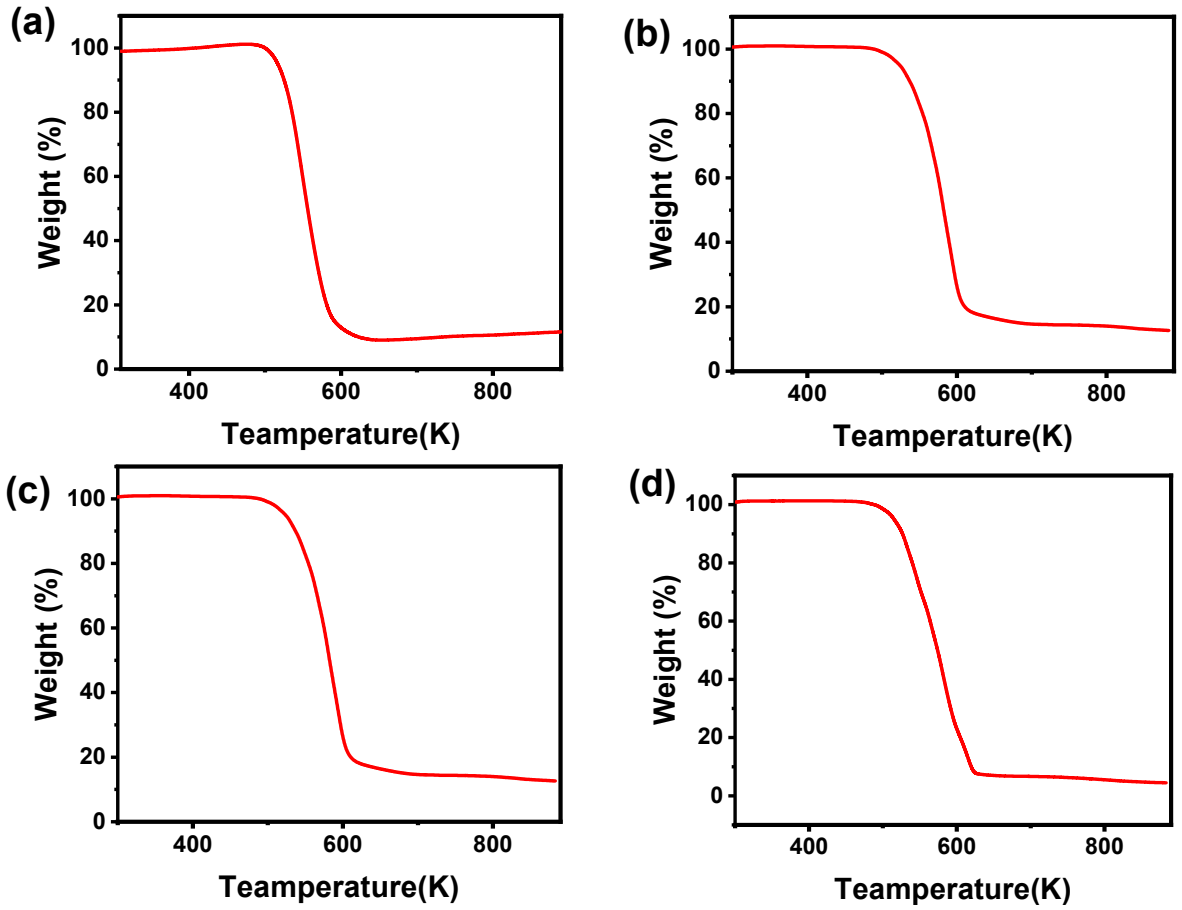

Fig. S3 The TG curves for **1-4** (a-d), indicating that the four compounds are stable at least up to 500K.

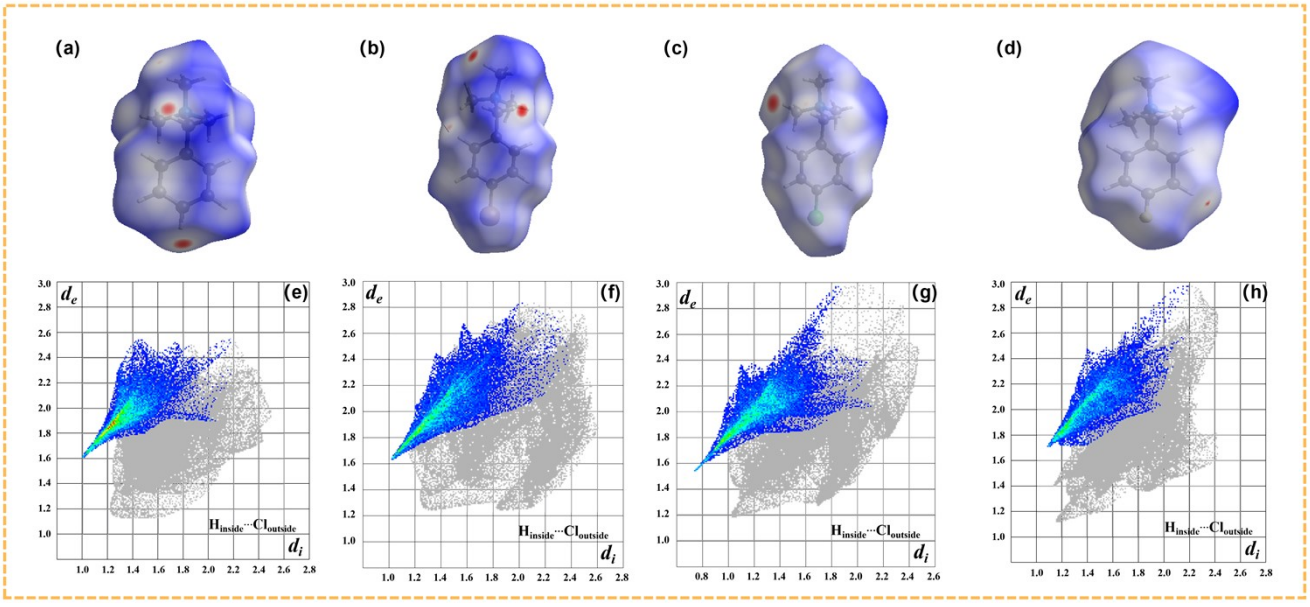

Fig. S4 The Hirshfeld dnorm surface of **1-4** (a-d) and 2D fingerprint plot of **1-4** (e-h).

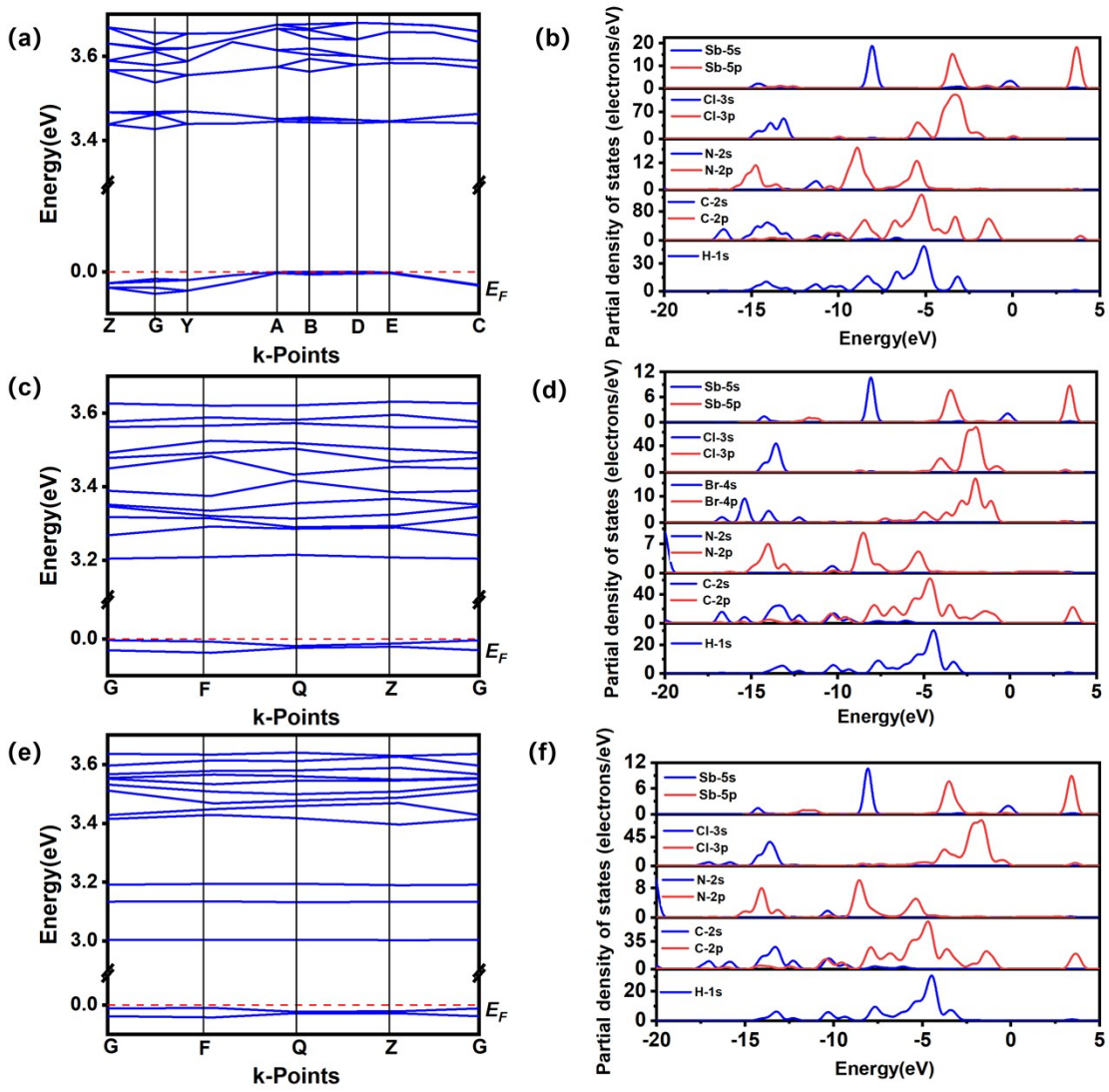

Fig. S5. Calculated band structure of compound **1** (a), **2** (c), **3** (e) and Partial density of states (PDOS) of compound **1** (b), **2** (d), **3** (f).

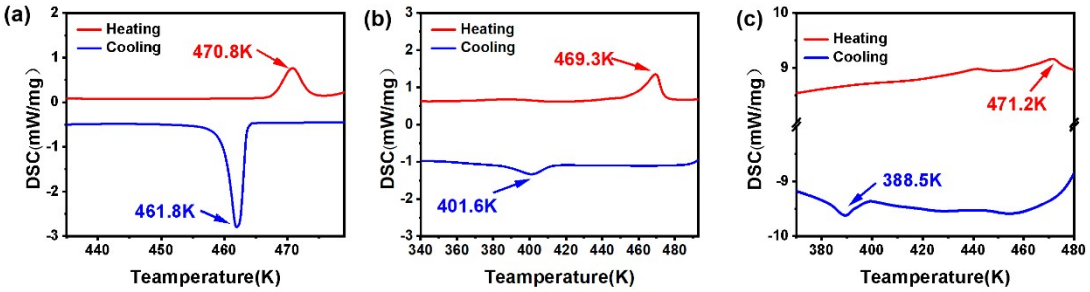

Fig. S6. DSC of compound **1** (a), **3** (b) and **4** (c).

Table S1. Crystal data of compound **1-4**.

	$(C_{10}H_{16}N)_3Sb_2Cl_9$	$(C_{10}H_{15}NBr)_3Sb_2Cl_9$	$(C_{10}H_{15}NCl)_3Sb_2Cl_9$	$(C_{10}H_{15}NF)_3Sb_2Cl_9$
T (K)	293	293	293	293
Empirical formula	$C_{30}H_{48}Cl_9N_3Sb_2$	$C_{30}H_{45}Br_3Cl_9N_3Sb_2$	$C_{30}H_{45}Cl_{12}N_3Sb_2$	$C_{30}H_{45}Cl_9F_3N_3Sb_2$
Formula weight	1013.26	1249.97	1116.59	1067.24
Crystal system	monoclinic	triclinic	triclinic	triclinic
Space group	$P2_1/c$	P-1	P-1	P-1
a (Å)	9.2809(9)	9.3055(3)	9.1074(10)	9.275(2)
b (Å)	25.774(3)	14.9937(6)	14.2404(16)	13.826(3)
c (Å)	17.6172(18)	18.0441(7)	18.540(2)	18.274(4)
α (°)	90.00	84.989(3)	84.512(9)	83.423(5)
β (°)	92.2610(10)	86.538(3)	89.419(9)	89.796(6)
γ (°)	90.00	74.258(2)	77.186(8)	76.621(5)
Volume ($Å^3$)	4210.8(7)	2412.13(16)	2333.8(5)	2264.1(9)
Z	4	2	2	2
D_c (g/cm^{-3})	1.598	1.721	1.589	1.565
M (mm^{-1})	1.879	4.127	1.869	1.760
F (000)	2016.0	1212.0	1104.0	1056.0
2θ range [°]	2.8 to 52	5.024 to 50.054	5.98 to 51.36	2.24 to 52.74
Collected reflections	27639	29777	15117	16879
Unique reflections	8251	8475	8736	9192
R_1, wR_2 [I>=2σ (I)]	0.0485, 0.1448	0.1008, 0.3214	0.0995, 0.2704	0.0898, 0.2772
R_1, wR_2 [all data]	0.0576, 0.1524	0.1368, 0.3504	0.1601, 0.3082	0.1152, 0.3029
GOF	1.065	1.334	1.039	1.058
Largest peak and hole ($e/Å^3$)	2.01 and -0.90	8.03 and -1.11	2.70 and -1.89	3.54 and -1.34

Table S2. Hydrogen bonds at 293 K for **1**.

D—H…A	D—H	H···A	D···A	＜DHA
C2AA—H2AA…Cl10	0.97(7)	2.79(2)	3.646(7)	148(5)
C0AA—H0AA…Cl7	0.93(10)	2.78(2)	3.658(10)	157(6)
C8—H8…Cl2	0.93(10)	2.75(2)	3.572(10)	148(7)
C11—H11A…Cl10	0.96(9)	2.78(2)	3.598(9)	144(5)
C9AA—H9AB…Cl10	0.961(17)	2.83(2)	3.296(17)	111(10)
C19—H19A…Cl7	0.970(7)	2.79(2)	3.728(8)	163(5)

Table S3. Hydrogen bonds at 293 K for **2**.

D—H…A	D—H	H…A	D…A	<DHA
C0AA—H0AA…Cl20	0.98(3)	2.80(4)	3.64(3)	144(14)
C17—H17A…Cl10	0.989(16)	2.76(6)	3.584(17)	142(10)
C20—H20B…Cl8	0.980(17)	2.82(6)	3.538(19)	130(13)
C21—H21B…Cl9	0.98(2)	2.80(5)	3.48(2)	127(11)
C21—H21C…Cl10	0.978(18)	2.633(4)	3.57(2)	160(14)
C24—H24A…Cl10	0.98(3)	2.78(6)	3.72(3)	162(13)
C25—H25B…Cl11	0.98(3)	2.82(5)	3.76(3)	160(15)

Table S4. Hydrogen bonds at 293 K for **3**.

D—H…A	D—H	H…A	D…A	<DHA
C23—H23A…Cl10	0.96(18)	2.79(5)	3.719(18)	162(9)
C81—H81A…Cl6	0.96(3)	2.74(5)	3.47(3)	133(13)
C81—H81B…Cl11	0.96(2)	2.61(4)	3.54(3)	163(16)

Table S5. Hydrogen bonds at 293 K for **4**.

D—H…A	D—H	H…A	D…A	<DHA
C27—H27B…Cl10	0.961(16)	2.81(4)	3.762(16)	172(9)

Table S6. Selected bond angles [°] for compound **1** at 293 K

Cl2-Sb1-Cl5	86.41(7)	C3-N1-C11	108.6(6)
Cl2-Sb1-Cl6	89.00(7)	C9-N1-C2AA	111.0(6)
Cl2-Sb1-Cl10	92.10(7)	C11-N1-C2AA	108.9(6)
Cl6-Sb1-Cl5	175.31(6)	C11-N1-C9	107.8(6)
Cl10-Sb1-Cl5	91.18(6)	C4-C2AA-N1	115.1(5)
Cl10-Sb1-Cl6	89.93(6)	C7-C4-C2AA	120.8(7)
Cl7-Sb2-Cl3	175.02(5)	C10-C4-C2AA	120.3(7)
Cl8-Sb2-Cl3	88.74(5)	C10-C4-C7	118.8(8)
Cl8-Sb2-Cl7	93.07(6)	C8-C9AA-C7	120.2(9)
Cl8-Sb2-Cl9	89.23(6)	C10-C6-C8	120.0(9)

Cl9-Sb2-Cl3	95.24(6)	C8AA-C7-C4	120.4(8)
Cl9-Sb2-Cl7	89.43(6)	C8AA -C8-C6	119.7(9)
C14-N0AA-C19	110.8(6)	C4-C10-C6	120.9(9)
C15-N0AA-C14	108.3(6)	C3AA-N2-C5	110.6(10)
C15-N0AA-C19	111.6(5)	C3AA-N2-C7AA	104.2(10)
C15-N0AA-C22	108.7(6)	C3AA-N2-C9AA	104.6(11)
C22-N0AA-C14	109.4(6)	C5-N2-C7AA	112.1(11)
C22-N0AA-C19	107.9(6)	C5-N2-C9AA	111.8(9)
C17-C13-C18	118.3(8)	C9AA-N2-C7AA	112.9(12)
C17-C13-C19	122.0(7)	C0AA-C1-C1AA	117.1(9)
C18-C13-C19	119.7(7)	C0AA-C1-C5	124.3(10)
C20-C16-C21	120.5(10)	C1AA-C1-C5	118.6(10)
C13-C17-C20	120.7(9)	C6AA-C0AA-C1	121.6(10)
C21-C18-C13	121.1(9)	C4AA-C1AA-C1	119.6(9)
C13-C19-N0AA	114.7(5)	N2-C5-C1	116.9(8)
C16-C20-C17	119.3(10)	C6AA-C5AA-C4AA	121.1(11)
C18-C21-C16	120.2(10)	C5AA-C6AA-C0AA	121.1(10)
C3-N1-C2AA	111.3(6)	C5AA-C4AA-C1AA	119.3(10)
C3-N1-C9	109.2(6)		

Table S7. Selected bond angles [°] for compound **2** at 293 K

Cl1-Sb1 -Cl8	90.85(12)	C3-N12-C14	109.3(10)
Cl1-Sb1 -Cl2	92.22(17)	C3-N12-C1	110.7(12)
Cl1-Sb1-Cl12	88.65(15)	C3-N12-C2	108.6(12)
Cl2-Sb1 -Cl8	93.65(14)	C15-C14-N12	118.5(11)
Cl2-Sb1-Cl12	89.32(17)	C18-C15-C14	122.3(16)
Cl12-Sb1-Cl8	177.01(15)	C18-C15-C19	115.7(17)

Cl9-Sb2 -Cl3	88.51(12)	C19-C15-C14	121.9(15)
Cl9-Sb2 -Cl10	88.83(14)	C15-C18-6	121.1(18)
Cl10-Sb2-Cl3	177.02(13)	C5-C4-C19	117(2)
Cl11-Sb2-Cl3	88.44(12)	C15-C19-C4	124.2(18)
Cl11-Sb2-Cl9	94.58(17)	C4-C5-Br4	118.7(15)
Cl11-Sb2-Cl10	90.43(15)	C6-C5-C4	122.2(18)
C40 -C10-C56	116.7(15)	C6-C5-Br4	119.0(15)
C40 -C10-C17	124.3(14)	C5-C6-C18	119.7(18)
C56-C10-C17	119.1(14)	C7-N1-C0AA	112.9(15)
C40 -C13-C30	123.6(18)	C21-N1-C7	106.6(14)
C13-C30-Br6	122.4(13)	C21-N1-C0AA	108.6(18)
C55-C30-Br6	118.0(13)	C25-N1-C7	117.6(19)
C55-C30-C13	119.1(17)	C25 -N1-C21	101.1(16)
C13 -C40-C10	122.2(15)	C25 -N1-C0AA	109.1(18)
C30-C55-C56	116.8(16)	C8-C7-N1	115.1(14)
C10-C56-C55	121.2(15)	C7-C8-C9	125.5(19)
C20 -N14-C17	112.8(12)	C16-C8-C7	121(2)
C20-N14-C24	107.3(18)	C16-C8-C9	113(2)
C23-N14-C17	109.1(14)	C11-C9-C8	130(2)
C23-N14-C20	108.4(15)	C8-C16-C22	123(2)
C23-N14-C24	111.0(17)	C9-C11-C12	114(2)
C24-N14-C17	108.2(14)	C11-C12-Br7	120.7(18)
C10-C17-N14	114.5(12)	C11-C12-C22	124(2)
C14 -N12-C1	109.1(12)	C22-C12-Br7	114.9(17)
C2-N12-C14	112.5(12)	C16 -C22-C12	116(2)
C2-N12-C1	106.6(13)		

Table S8. Selected bond angles [°] for compound **3** at 293 K

Cl5-Sb1 -Cl10	178.94(14)	C41-C20-C18	117.4(15)
Cl7-Sb1-Cl5	90.07(13)	C41-C24-C30	119.8(16)
Cl7-Sb1-Cl10	89.01(15)	C38-C29-54	120.6(19)
Cl8-Sb1-Cl5	90.68(14)	C24 -C30-Cl1	120.3(15)
Cl8-Sb1-Cl7	93.27(16)	C46 -C30-Cl1	120.1(18)
Cl8-Sb1-Cl10	88.84(14)	C46-C30-C24	119.4(16)
Cl6-Sb2-Cl3	87.68(13)	C29-C38-Cl2	119.9(13)
Cl6-Sb2-Cl11	89.56(14)	C29-C38-C42	118.3(16)
Cl9-Sb2 -Cl3	90.50(14)	C42 -C38-Cl2	120.4(13)
Cl9-Sb2 -Cl6	95.69(15)	C24-C41-C20	118.7(16)
Cl9-Sb2-Cl11	92.02(16)	C38-C42-C15	121.0(16)
Cl11-Sb2-Cl3	176.44(13)	C12 -C46-C30	119.9(19)
C18-N7-C17	108.8(11)	C29-C54-C19	120.9(19)
C18-N7-C23	109.8(11)	N11-C70-C19	113.6(14)
C18 -N7-C34	112.7(11)	C26-C8-C44	120(2)
C23-N7-C17	107.5(11)	C50-N14-C67	111.0(19)
C23 -N7-C34	107.9(13)	C50-N14-C81	107.4(17)
C34 -N7-C17	110.1(12)	C67-N14-C81	105.3(19)
C31 -N11-C32	106.8(15)	C76-N14-C50	115.4(17)
C31-N11-C70	109.5(14)	C76 -N14-C67	107.6(18)
C31-N11-C7	107.5(16)	C76-N14-C81	109.7(17)
C70 -N11-C32	113.1(13)	C8-C26-C76	124(2)
C7-N11-C32	110.3(15)	C8-C26-C4	112(2)
C7-N11-C70	109.5(14)	C4-C26-C76	123(2)
C20-C12-C46	121.5(17)	C44-C35-Cl12	123(2)
C19 -C15-C42	117.8(16)	C44-C35-C52	121(3)
N7-C18-C20	116.3(12)	C52 -C35-Cl12	116(2)

C15 -C19-C54	120.5(17)	C35-C44-C8	123(3)
C15-C19-C70	116.8(16)	C4-C52-C35	115(2)
C54-C19-C70	122.3(16)	N14-C76-C26	113.9(18)
C12-C20-C18	122.0(15)	C52-C4-C26	127(2)
C12-C20-C41	120.4(14)		

Table S9. Selected bond angles [°] for compound **4** at 293 K

Cl9-Sb2-Cl8	91.22(12)	C13-C31-C79	120.1(15)
Cl9-Sb2-Cl1	96.01(14)	C47-C44-C12	120.5(16)
Cl1-Sb2-Cl8	92.02(13)	C44-C47-F21	119.6(18)
C41--N17-C43	106.1(15)	C44-C47--C79	120.8(15)
C41-N17-C19	106.4(16)	C47-C79-C31	119.0(16)
C43-N17-C77	111.3(15)	C26-N5-C10	109.3(10)
C19-N17-C43	113.0(17)	C49-N5-C10	110.0(12)
C19-N17-C77	112.0(16)	C49-N5-C26	110.7(13)
F53-C38-C64	119(3)	C1-N5-C10	107.8(11)
C2-C38-F53	118(3)	C1-N5-C26	106.6(13)
C2-C38-C64	123(3)	C1-N5-C49	112.3(12)
C73-C48-C64	125(2)	C20-C9-C10	121.3(13)
C73-C54-C2	124(2)	C28-C9-C10	120.4(13)
C38-C64-C48	114(3)	C28-C9-C20	118.3(14)
C48-C73-C54	115(2)	C9-C10-N5	114.9(11)
C48-C73-C77	124(2)	C36-C20-C9	121.9(14)
C54-C73-C77	120(2)	C9-C28-C30	120.8(14)
C73-C77-N17	116.8(16)	C63-C30-C28	118.6(15)
C15-N4-C11	108.9(10)	C20-C36-C63	119.5(15)

C27-N4-C11	109.9(11)	F14-C63-C36	119.9(15)
C27-N4-C15	111.8(10)	C30-C63-F14	119.5(16)
C33-N4-C11	109.5(11)	C30-C63-C36	120.5(16)
C33-N4-C15	110.7(10)	C38-C2-C54	118(3)