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Supplementary Information

On structural factors determining the nature of the fluorescent properties of OIHMs based on 8-hydroxyquinoline

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Table of content

1. Synthesis details

bis(8-hydroxyquinolinium) tetrachloridomercurate(II) synthesis (HgCl(1))

The compound was obtained from the filtrate solution which was left after removing crystals of *8-hydroxyquinolinium μ-chlorido-dichloridomercurate(II) dihydrate*. After two months new yellow crystals grew from this filtrate. Yield: 42%.

8-hydroxyquinolinium μ-chlorido-dichloridomercurate(II) dihydrate synthesis (HgCl(2))

The 8-hydroxyquinoline powder (1 mmol; 0.1452 g) was dissolved in a 5 ml of methanol. Solid mercury(II) chloride (0.5 mmol; 0.1358 g) was dissolved in 5 ml of 37% HCl. The acidic halide solution was added to 10 ml of water and the solution was stirred for about 10 minutes. To this solution, a methanolic ligand solution was added dropwise. The reaction mixture was stirred for 30 minutes. Immediately yellow crystals grew. A batch of crystals was filtered off and dried in an air atmosphere. Yield: 36%.

bis(8-hydroxyquinolinium) tetrabromidomercurate(II) synthesis (HgBr)

The 8-hydroxyquinoline powder (1.05 mmol; 0.1525 g) was dissolved in a 5 ml of methanol. Solid mercury(II) bromide (0,525 mmol; 0.1892 g) was dissolved in 5 ml of 40% HBr. The acidic halide solution was added to 10 ml of water and the solution was stirred for about 10 minutes. To this solution, a methanolic ligand solution was added dropwise. The reaction mixture was stirred for 30 minutes. The yellow solution was left to crystallize. After three months yellow crystals grew. A batch of crystals was filtered off and dried in an air atmosphere. Yield: 64%.

8-hydroxyquinolinium μ-chlorido-dichloridoleadate(II) synthesis (PbCl)

The 8-hydroxyquinoline powder (1.02 mmol; 0.1481 g) was dissolved in a 5 ml of methanol. Solid lead(II) chloride (0.51 mmol; 0.1418 g) was dissolved in 10 ml of 37% HCl. To this solution, a methanolic ligand solution was added dropwise. The reaction mixture was stirred for 30 minutes. The yellow solution was left to crystallize. After two days yellow crystals grew. A batch of crystals was filtered off and dried in an air atmosphere. Yield: 74%.

8-hydroxyquinolinium μ-bromido-dibromidoleadate(II) synthesis (PbBr)

The 8-hydroxyquinoline powder (1.06 mmol; 0.1539 g) was dissolved in a 5 ml of methanol. Solid lead(II) bromide (0,53 mmol; 0.1945 g) was dissolved in 10 ml of 40% HBr. To this solution, a methanolic ligand solution was added dropwise. The reaction mixture was stirred for 30 minutes. Immediately yellow precipitate appeared. The precipitate was filtered off, and the yellow solution was left to crystallize. After two months yellow crystals were obtained. A batch of crystals was filtered off and dried in an air atmosphere. Yield: 69%.

bis(8-hydroxyquinolinium) tetrachloridocobaltate(II) synthesis (CoCl)

The 8-hydroxyquinoline powder (1 mmol; 0.1452 g) was dissolved in a 5 ml of methanol. Solid cobalt(II) chloride hexahydrate (0.5 mmol; 0.1190 g) was dissolved in 5 ml of 37% HCl. The acidic halide solution was added to 9.5

ml of water and the solution was stirred for about 10 minutes. To this solution, a methanolic ligand solution was added dropwise. The reaction mixture was stirred for 30 minutes. The green solution was left to crystallize. After three months green crystals were obtained. A batch of crystals was filtered off and dried in an air atmosphere. Yield: 45%.

bis(8-hydroxyquinolinium) tetrachloridozincate(II)synthesis (ZnCl)

The 8-hydroxyquinoline powder (1.05 mmol; 0.1524 g) was dissolved in a 5 ml of methanol. Solid zinc(II) chloride (0.525 mmol; 0.0716 g) was dissolved in 5 ml of 37% HCl. The acidic halide solution was added to 10 ml of water and the solution was stirred for about 10 minutes. To this solution, a methanolic ligand solution was added dropwise. The reaction mixture was stirred for 30 minutes. The yellow solution was left to crystallize. After one-month yellow crystals were obtained. A batch of crystals was filtered off and dried in an air atmosphere. Yield: 62%.

bis(8-hydroxyquinolinium) tetrabromidocobaltate(II) synthesis (CoBr)

The 8-hydroxyquinoline powder (1.01 mmol; 0.1466 g) was dissolved in a 5 ml of methanol. Solid cobalt(II) bromide (0.505 mmol; 0.1104 g) was dissolved in 5 ml of 40% HBr. The acidic halide solution ws added to 10 ml of water and the solution was stirred for about 10 minutes. To this solution, a methanolic ligand solution was added dropwise. The reaction mixture was stirred for 30 minutes. The orange solution was left to crystallize. After five months orange crystals were obtained. A batch of crystals was filtered off and dried in an air atmosphere. Yield: 43%.

bis(8-hydroxyquinolinium) tetrabromidozincate(II) synthesis (ZnBr)

The 8-hydroxyquinoline powder (1.012 mmol; 0.1469 g) was dissolved in a 5 ml of methanol. Solid zinc(II) bromide (0.506 mmol; 0.1140 g) was dissolved in 5 ml of 40% HBr. The acidic halide solution was added to 10 ml of water and the solution was stirred for about 10 minutes. To this solution, a methanolic ligand solution was added dropwise. The reaction mixture was stirred for 30 minutes. The yellow solution was left to crystallize. After three months yellow crystals were obtained. A batch of crystals was filtered off and dried in an air atmosphere. Yield: 54%.

bis(8-hydroxyquinolinium) tetrabromidocadmate(II) synthesis (CdBr)

The 8-hydroxyquinoline powder (1 mmol; 0.1452 g) was dissolved in a 5 ml of methanol. Solid cadmium(II) bromide (0.5 mmol; 0.1361 g) was dissolved in 5 ml of 40% HBr. The acidic halide solution was added to 10 ml of water and the solution was stirred for about 10 minutes. To this solution, a methanolic ligand solution was added dropwise. The reaction mixture was stirred for 30 minutes. The yellow solution was left to crystallize. After three months yellow crystals were obtained. A batch of crystals was filtered off and dried in an air atmosphere. Yield: 56%

bis(8-hydroxyquinolinium) tetrachloridocadmate(II) synthesis (CdCl)

The 8-hydroxyquinoline powder (1.04 mmol; 0.1510 g) was dissolved in a 5 ml of methanol. Solid cadmium(II) chloride (0.520 mmol; 0.095 g) was dissolved in 5 ml of 37% HCl. The acidic halide solution was added to 10 ml of water and the solution was stirred for about 10 minutes. To this solution, a methanolic ligand solution was added dropwise. The reaction mixture was stirred for 30 minutes. The yellow solution was left to crystallize. After one-month yellow crystals were obtained. A batch of crystals was filtered off and dried in an air atmosphere. Yield: 57%

bis(8-hydroxyquinolinium) tetrachloridoferrate(III) chloride (FeCl)

The 8-hydroxyquinoline powder (1.07 mmol; 0.1553 g) was dissolved in a 5 ml of methanol. Solid iron(III) chloride hexahydrate (0.535 mmol; 0.1446 g) was dissolved in 5 ml of 37% HCl. The acidic halide solution was added to 10 ml of water and the solution was stirred for about 10 minutes. To this solution, a methanolic ligand solution was added dropwise. The reaction mixture was stirred for 30 minutes. The yellow solution was left to crystallize. After two weeks yellow crystals were obtained. A batch of crystals was filtered off and dried in an air atmosphere. Yield: 66%.

bis(8-hydroxyquinolinium) tetrabromidoferrate(III) bromide (FeBr)

The 8-hydroxyquinoline powder (1.05 mmol; 0.1525 g) was dissolved in a 5 ml of methanol. Solid iron(III) bromide (0,525 mmol; 0.1552 g) was dissolved in 5 ml of 40% HBr. The acidic halide solution was added to 10 ml of water and the solution was stirred for about 10 minutes. To this solution, a methanolic ligand solution was added dropwise. The reaction mixture was stirred for 30 minutes. Immediately red-brown precipitate appeared. The precipitate was filtered off, and the red solution was left to crystallize. After six weeks red crystals were obtained. A batch of crystals was filtered off and dried in an air atmosphere. Yield: 51%.

bis(8-hydroxyquinolinium) tetrachloridocopperate(II) (CuCl)

The 8-hydroxyquinoline powder (1.06 mmol; 0.1539 g) was dissolved in a 5 ml of methanol. Solid copper(II) chloride dihydrate (0.530 mmol; 0.0903 g) was dissolved in 5 ml of 37% HCl. The acidic halide solution was added to 10 ml of water and the solution was stirred for about 10 minutes. To this solution, a methanolic ligand solution was added dropwise. The reaction mixture was stirred for 30 minutes. The green-yellow solution was left to crystallize. After two months green-yellow crystals were obtained. A batch of crystals was filtered off and dried in an air atmosphere. Yield: 60%.

tetrakis(8-hydroxyquinolinium)heksachloridobismuthate(III) chloride dihydrate (BiCl)

The 8-hydroxyquinoline powder (1.03 mmol; 0.1488 g) was dissolved in a 5 ml of methanol. Solid bismuth(III) chloride (0.513 mmol; 0.1618 g) was dissolved in 5 ml of 37% HCl. To this solution, a methanolic ligand solution was added dropwise. The reaction mixture was stirred for 30 minutes. The yellow solution was left to crystallize.

After one-month yellow crystals were obtained. A batch of crystals was filtered off and dried in an air atmosphere. Yield: 53%.

8-hydroxyquinolinium chloride (8hqHCl)

The 8-hydroxyquinoline powder (1.2 mmol; 0.1742 g) was dissolved in a 5 ml of methanol. To this solution, 5 ml of 37% hydrochloric acid was added dropwise. The reaction mixture was stirred for 30 minutes. The yellow solution was left to crystallize. After one-month transparent, yellow crystals were obtained. A batch of crystals was filtered off and dried in an air atmosphere. Yield: 72%.

8-hydroxyquinolinium bromide (8hqHBr)

The 8-hydroxyquinoline powder (1.1 mmol; 0.1597 g) was dissolved in a 5 ml of methanol. To this solution, 5 ml of 40% hydrobromic acid was added dropwise. The reaction mixture was stirred for 30 minutes. The yellow solution was left to crystallize. After three months yellow crystals were obtained. A batch of crystals was filtered off and dried in an air atmosphere. Yield: 66%.

bis(8-hydroxyquinolinium)heksachloridotinnate(IV) dihydrate (SnCl(1))

The compound was obtained from the filtrate solution which was left after removing crystals of *8-hydroxyquinolinium tetrachlorido-(quinolin-8-olato-κ2-N, O) tinnate(IV) hydrate*. After one month new yellow crystals grew from this filtrate. Yield: 32%.

8-hydroxyquinolinium tetrachlorido-(quinolin-8-olato-κ2-N, O) tinnate(IV) hydrate (SnCl(2))

The 8-hydroxyquinoline powder (1.02 mmol; 0.1481 g) was dissolved in a 5 ml of methanol. Liquid, anhydrous tin(IV) chloride (0.510 mmol; 0.1329 g) was dissolved in 5 ml of 37% HCl. To this solution, a methanolic ligand solution was added dropwise. The reaction mixture was stirred for 30 minutes. Immediately after mixing, yellow crystals grew. A batch of crystals was filtered off and dried in an air atmosphere. Yield: 46%.

bis(8-hydroxyquinolinium)heksabromidotinnate(IV) dihydrate (SnBr)

The 8-hydroxyquinoline powder (1.12 mmol; 0.1626 g) was dissolved in a 5 ml of methanol. Solid tin(IV) bromide (0.560 mmol; 0.2455 g) was dissolved in 8 ml of 40% HBr. To this solution, a methanolic ligand solution was added dropwise. The reaction mixture was stirred for 30 minutes. The yellow solution was left to crystallize. After one month yellow crystals were obtained. A batch of crystals was filtered off and dried in an air atmosphere. Yield: 67%.

2. Supplemental tables

Table S1. Crystal data and structure refinement details for the studied compounds.

Compound	**FeCl**	**FerBr**	**CoCl**	**CoBr**	**CuCl**	**ZnCl**	**CdCl**
Empirical formula	$C_{18}H_{16}Cl_5N_2O_2Fe$	$C_{18}H_{16}Br_5N_2O_2Fe$	$C_{18}H_{16}Cl_4N_2O_2Co$	$C_{18}H_{16}Br_4N_2O_2Co$	$C_{18}H_{16}Cl_4N_2O_2Cu$	$C_{18}H_{16}Cl_4N_2O_2Zn$	$C_{18}H_{16}Cl_4N_2O_2Cd$
Formula weight	525.43	747.73	493.06	670.90	497.67	499.50	546.53
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1	*P*-1	*C2/c*	*P2/n*	*P*-1	*C2/c*	*C2/c*
Radiation	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Cu Kα (1.54184 Å)	Cu Kα (1.54184 Å)	Mo Kα (0.71073 Å)
Unit cell dimensions							
a (Å)	7.4707(2)	7.68190(10)	15.2078(7)	17.0128(6)	9.54840(10)	15.1939(2)	15.2834(6)
b (Å)	10.1801(2)	10.4227(2)	8.0042(4)	7.1435(2)	10.74010(10)	7.99590(10)	8.2421(4)
c (Å)	14.1377(4)	14.4180(3)	16.6991(8)	17.1911(7)	10.78680(10)	16.6547(2)	16.5244(7)
α (°)	86.275(2)	86.456(2)	90.00	90.00	98.6680(10)	90.00	90
β (°)	86.472(2)	85.113(2)	91.133(4)	90.158(3)	113.4250(10)	91.0690(10)	91.322(4)
γ (°)	84.890(2)	85.066(2)	90.00	90.00	99.3670(10)	90.00	90
Volume (Å^3)	1066.99(5)	1144.21(4)	2032.32(17)	2089.24(13)	972.727(18)	2023.01(4)	2080.98(16)
Z	2	2	4	4	2	4	4
Calculated density (Mg/m^3)	1.635	2.170	1.611	2.133	1.699	1.640	1.744
Absorption coefficient (mm^{-1})	1.350	9.406	1.386	8.488	6.788	6.690	1.579
F(000)	530	710	996	1284	502	1008	1080
Min. and max. transmission	0.364 and 1.000	0.237 and 0.789	0.943 and 1.000	0.310 and 0.777	0.676 and 0.993	0.653 and 0.887	0.868 and 1.000
θ Range for data collection (°)	3.622 to 25.020	2.360 to 25.023	3.589 to 25.023	2.851 to 32.202	4.296 to 66.590	5.313 to 66.569	2.666 to 25.024
Index ranges	-8 ≤ h ≤ 8 -11 ≤ k ≤ 12 -16 ≤ l ≤ 16	-9 ≤ h ≤ 9 -12 ≤ k ≤ 12 -17 ≤ l ≤ 17	-17 ≤ h ≤ 17 -9 ≤ k ≤ 9 -19 ≤ l ≤ 19	-25 ≤ h ≤ 25 -10 ≤ k ≤ 10 -25 ≤ l ≤ 25	-11≤ h ≤10 -12 ≤ k ≤12 -12 ≤ l≤12	-18 ≤ h ≤ 17 -9 ≤ k ≤ 7 -19 ≤ l ≤ 19	-18≤ h ≤ 18 -9≤ k ≤9 -19≤ l ≤19
Reflections collected / unique	22440 / 3754	28566 / 4033	8765 / 1784	57774 / 7751	25526 / 3448	9647 / 1790	7746 / 1840
R_{int}	0.0233	0.0238	0.0354	0.0948	0.0349	0.0261	0.0322
Completeness (%)	99.7	99.9	99.3	99.9	100.0	100.0	99.9
Data / restraints / parameters	3754 / 0/ 255	4033 / 0 / 255	1784 / 0/ 124	7751 / 0 / 248	3448 / 0 / 246	1790 / 0 / 124	1840 / 0 /124
Goodness-of-fit on F^2	1.069	1.041	1.040	1.097	1.044	1.085	1.031
Final *R* indices [$I>2\sigma(I)$]	$R1$ = 0.0247 $wR2$ = 0.0627	$R1$ = 0.0159 $wR2$ = 0.0381	$R1$ = 0.0241 $wR2$ = 0.0557	$R1$ = 0.0805 $wR2$ = 0.2159	$R1$ = 0.0258 $wR2$ = 0.0681	$R1$ = 0.0197 $wR2$ = 0.0536	$R1$ = 0.0184, $wR2$ = 0.0397
R indices (all data)	$R1$ = 0.0253 $wR2$ = 0.0630	$R1$ = 0.0175, $wR2$ = 0.0386	$R1$ = 0.0309 $wR2$ = 0.0580	$R1$ = 0.1064, $wR2$ = 0.2344	$R1$ = 0.0297 $wR2$ = 0.0701	$R1$ = 0.0208, $wR2$ = 00.0542	$R1$ = 0.0231, $wR2$ = 0.0410
Largest diff. peak and hole (e·Å^{-3})	1.329 and -0.566	1.660 and -0.240	0.425 and -0.209	2.652 and -2.208	0.938 and -0.404	0.261 and -0.325	0.300 and -0.322

Table S1. *continued*

Compound	**CdBr**	**HgCl(1)**	**HgCl(2)**	**HgBr**	**SnCl(1)**	**SnCl(2)**	**SnBr**
Empirical formula	$C_{18}H_{16}Br_4N_2O_2Cd$	$C_{18}H_{16}Cl_4N_2O_2Hg$	$C_9H_{12}Cl_3N_1O_3Hg$	$C_{18}H_{16}Br_4N_2O_2Hg$	$C_{18}H_{20}Cl_6N_2O_4Sn$	$C_{18}H_{16}Cl_4N_2O_3Sn$	$C_{18}H_{16}Br_6N_2O_4Sn$
Formula weight	724.37	634.72	489.14	812.56	659.75	568.82	926.51
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Triclinic
Space group	*C2/c*	*C2/c*	*P2₁/n*	*P2/n*	*P*-1	*Pbca*	*P*-1
Radiation	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
Unit cell dimensions							
a (Å)	15.7785(6)	15.2852(2)	13.7376(4)	17.0829(8)	7.2163(3)	7.8652(4)	7.4143(3)
b (Å)	8.5996(3)	8.25560(10)	4.3663(2)	7.2297(3)	9.5228(4)	16.7617(7)	9.8360(4)
c (Å)	16.6373(7)	16.5412(2)	22.5270(8)	17.2934(8)	9.5411(4)	31.4221(15)	9.5667(3)
α (°)	90.00	90.00	90.00	90.00	83.177(3)	90.00	83.836(3)
β (°)	92.280(4)	91.3170(10)	95.846(3)	90.388(4)	71.049(4)	90.00	72.170(3)
γ (°)	90.00	90.00	90.00	90.00	79.945(3)	90.00	79.668(4)
Volume (Å^3)	2255.71(15)	2086.76(4)	1344.20(9)	2135.76(17)	609.24(5)	4142.5(3)	652.37(4)
Z	4	4	4	4	1	8	1
Calculated density (Mg/m^3)	2.133	2.020	2.417	2.527	1.798	1.824	2.358
Absorption coefficient (mm^{-1})	8.069	7.904	12.009	14.706	1.734	1.772	10.193
F(000)	1368	1208	912	1496	326	2240	434
Min. and max. transmission	0.710 to 1.000	0.316 and 0.948	0.041 and 0.798	0.462 and 0.706	0.817 and 0.966	0.684 and 1.000	0.164 and 1.000
θ Range for data collection (°)	3.611 to 25.021	3.589 to 25.019	3.637 to 25.011	3.674 to 25.027	3.455 to 25.008	3.555 to 25.025	2.921 to 25.028
Index ranges	-18 ≤ h ≤ 18 -10 ≤ k ≤ 10 -19 ≤ l ≤ 19	-18 ≤ h ≤ 18 -9 ≤ k ≤ 9 -19 ≤ l ≤ 19	-16≤ h ≤16 -5≤ k ≤5 -26≤ l ≤ 26	-20≤ h ≤ 20 -8≤ k ≤ 8 -20 ≤ l ≤ 20	-8 ≤ h ≤ 8 -11 ≤ k ≤ 11 -11 ≤ l ≤ 11	-8 ≤ h ≤ 9 -19 ≤ k ≤ 18 -37 ≤ l ≤ 37	-8≤ h ≤ 8 -11≤ k ≤11 -11≤ l ≤11
Reflections collected / unique	8130 / 1988	31143 / 1842	14421 / 2373	12595 / 3745	31869 / 4468	23321 / 3651	16086 / 2299
R_{int}	0.0296	0.0288	0.0330	0.0531	0.0517	0.0296	0.0401
Completeness (%)	99.7	99.7	99.7	99.0	99.7	99.7	99.9
Data / restraints / parameters	1988 / 0 / 124	1842 / 0/ 124	2373 / 0 / 155	3745 / 0 / 247	4468 / 0 / 144	3651 / 0 / 254	2299 / 0 / 143
Goodness-of-fit on F^2	1.029	1.120	1.046	1.037	1.108	1.043	1.067
Final *R* indices [$I>2\sigma(I)$]	$R1$ = 0.0173 $wR2$ = 0.0381	$R1$ = 0.0082 $wR2$ = 0.0215	$R1$ = 0.0144 $wR2$ = 0.0338	$R1$ = 0.0359, $wR2$ = 0.0858	$R1$ = 0.0393 $wR2$ = 0.1162	$R1$ = 0.0197 $wR2$ = 0.0403	$R1$ = 0.0161, $wR2$ = 0.0408
R indices (all data)	$R1$ = 0.0225, $wR2$ = 0.0394	$R1$ = 0.0082 $wR2$ = 0.0215	$R1$ = 0.0159 $wR2$ = 0.0342	$R1$ = 0.0456, $wR2$ = 0.0898	$R1$ = 0.0433, $wR2$ = 0.1179	$R1$ = 0.0226, $wR2$ = 0.0411	$R1$ = 0.0176, $wR2$ = 0.0414
Largest diff. peak and hole (e·Å^{-3})	0.619 and -0.418	0.319 and -0.169	0.637 and -0.724	2.752 and -2.026	1.217 and -0.694	0.308 and -0.306	0.537 and -0.442

Table S1. *continued*

Compound	**PbCl**	**PbBr**	**BiCl**	**8hqHCl**	**8hqHBr**
Empirical formula	$C_9H_8Cl_3N_1O_1Pb$	$C_9H_8Br_3N_1O_1Pb$	$C_{36}H_{36}Cl_7N_4O_6Bi$	$C_9H_{10}Cl_1N_1O_2$	$C_9H_{10}Br_1N_1O_2$
Formula weight	459.70	593.08	1077.82	199.63	244.09
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	P-1	$P2_1/c$	$P2_1/c$
Radiation	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Cu Kα (1.54184 Å)
Unit cell dimensions					
a (Å)	3.9550(2)	4.06310(10)	8.35930(10)	7.7734(4)	7.72230(10)
b (Å)	20.7707(7)	21.2351(7)	13.0386(2)	8.0302(4)	8.3116(2)
c (Å)	14.0139(5)	14.5111(5)	18.9457(3)	15.1465(8)	15.3112(3)
α (°)	90.00	90.00	76.3850(10)	90	90
β (°)	95.449(3)	97.763(4)	83.6190(10)	99.036(5)	101.017(2)
γ (°)	90.00	90.00	84.6520(10)	90	90
Volume (Å^3)	1146.01(8)	1240.55(7)	1989.69(5)	933.74(8)	964.63(3)
Z	4	4	2	4	4
Calculated density (Mg/m^3)	2.664	3.175	1.799	1.420	1.681
Absorption coefficient (mm^{-1})	15.391	23.235	4.951	0.374	5.555
F(000)	840	1056	1060	416	488
Min. and max. transmission	0.094 and 1.000	0.149 and 0.947	0.379 and 1.000	0.756 and 1.000	0.632 and 0.823
θ Range for data collection (°)	3.285 to 25.027	3.422 to 32.025	3.463 to 25.026	3.672 to 25.027	5.837 to 66.587
Index ranges	-4≤ h ≤ 4 -24≤ k ≤24 -16≤ l ≤16	-4≤ h ≤ 4 -24≤ k ≤25 -17≤ l ≤17	-9 ≤ h ≤ 9 -15 ≤ k ≤ 15 -21 ≤ l ≤ 22	-9≤ h ≤ 9 -9≤ k ≤9 -18≤ l ≤17	-9≤ h ≤ 9 -9≤ k ≤7 -14≤ l ≤18
Reflections collected / unique	12411 / 2025	18634 / 2184	41842 / 7009	9932 / 1649	12671 / 3521
R_{int}	0.0428	0.0324	0.0287	0.0500	0.0535
Completeness (%)	99.8	99.7	99.7	99.8	99.8
Data / restraints / parameters	2025 /0/ 137	2184 / 0 / 137	7009 / 0 / 491	1649 / 0 / 119	3521 / 0 / 120
Goodness-of-fit on F^2	1.043	1.038	1.064	1.073	1.114
Final R indices [I>2σ(I)]	R1 = 0.0167 wR2 = 0.0388	R1 = 0.0118, wR2 = 0.0273	R1 = 0.0132 wR2 = 0.0327	R1 = 0.0557, wR2 = 0.1378	R1 = 0.0275, wR2 = 0.0904
R indices (all data)	R1 = 0.0200 wR2 = 0.0396	R1 = 0.0135, wR2 = 0.0277	R1 = 0.0140, wR2 = 0.0328	R1 = 0.0600, wR2 = 0.1403	R1 = 0.0292, wR2 = 0.0922
Largest diff. peak and hole (e·Å^{-3})	1.128 and -0.635	0.572 and -0.397	0.580 and -0.302	1.298 and -0.549	0.333 and -0.410

Table S2. Structural data of the coordination polyhedra in the studied compounds.

i—j	d_{ij} [Å]	i—j—k	a_{ijk} [°]	i—j—k	a_{ijk} [°]
FeCl					
Fe1—Cl1	2.1944(5)	Cl1—Fe1—Cl2	108.30(2)	Cl2—Fe1—Cl4	111.09(2)
Fe1—Cl2	2.2083(6)	Cl1—Fe1—Cl3	108.54(2)	Cl3—Fe1—Cl4	111.61(2)
Fe1—Cl3	2.1990(6)	Cl1—Fe1—Cl4	108.21(2)		
Fe1—Cl4	2.1998(6)	Cl2—Fe1—Cl3	108.99(2)		
FerBr					
Fe1—Br1	2.3352(4)	Br1—Fe1—Br2	108.342(14)	Br2—Fe1—Br4	110.945(15)
Fe1—Br2	2.3484(4)	Br1—Fe1—Br3	108.276(15)	Br3—Fe1—Br4	112.125(15)
Fe1—Br3	2.3367(4)	Br1—Fe1—Br4	107.842(14)		
Fe1—Br4	2.3411(4)	Br2—Fe1—Br3	109.197(15)		
CoCl					
Co1—Cl1	2.2762(5)	Cl1—Co1—Cl1^{vi}	104.65(3)	Cl2—Co1—Cl1^{i}	112.687(19)
Co1—Cl2	2.2868(5)	Cl1—Co1—Cl2	107.564(18)	Cl2—Co1— Cl2^{i}	111.56(3)
		Cl1—Co1—Cl2 ^{vi}	112.689(19)	Cl1^{i}—Co1—Cl2^{i}	107.562(18)
CoBr					
Co1—Br1	2.4092(16)	Br1—Co1—Br1^{ii}	109.45(10)	Br11—Co11—Br11^{iii}	106.19(11)
Co1—Br2	2.4125(17)	Br1—Co1—Br2	109.30(4)	Br11—Co11—Br12	110.69(4)
Co11—Br11	2.4206(18)	Br1—Co1—Br2^{ii}	109.16(5)	Br11—Co11—Br12^{iii}	111.66(4)
Co11—Br12	2.4224(18)	Br2—Co1—Br1^{ii}	109.16(5)	Br12—Co11—Br11^{iii}	111.66(4)
		Br2 —Co1—Br2^{ii}	110.45(10)	Br12—Co11—Br12ii^{i}	106.04(11)
		Br1^{ii}—Co1—Br2^{ii}	109.30(4)	Br11^{iii} —Co11—Br12^{iii}	110.69(4)
CuCl					
Cu1—Cl1	2.2574(6)	Cl1—Cu1—Cl2	93.53(2)	Cl2—Cu1—Cl4	146.01(2)
Cu1—Cl2	2.2967(6)	Cl1—Cu1—Cl3	144.77(2)	Cl3—Cu1—Cl4	96.74(2)
Cu1—Cl3	2.2282(6)	Cl1—Cu1—Cl4	96.19(2)		
Cu1—Cl4	2.2542(6)	Cl2—Cu1—Cl3	93.77(2)		
ZnCl					
Zn1—Cl1	2.2720(4)	Cl1—Zn1—Cl1 ^{vi}	104.77(2)	Cl1—Zn1—Cl2^{i}	112.426(14)
Zn1—Cl2	2.2792(4)	Cl1—Zn1—Cl2	107.893(13)	Cl2—Zn1—Cl2^{i}	111.31(2)
		Cl1—Zn1—Cl2^{vi}	112.425(14)	Cl1^{i} —Zn1—Cl2^{i}	107.891(13)
CdCl					
Cd1—Cl1	2.4605(5)	Cl1—Cd1—Cl1^{vi}	102.14(3)	Cl2—Cd1—Cl1^{i}	114.684(17)
Cd1—Cl2	2.4634(5)	Cl1—Cd1—Cl2	105.716(17)	Cl2—Cd1—Cl2^{i}	113.56(3)
		Cl1—Cd1—Cl2^{vi}	114.685(17)	Cl1^{i} —Cd1—Cl2^{i}	105.716(17)
CdBr					
Cd1—Br1	2.5938(3)	Br1—Co1—Br1^{vi}	101.945(16)	Br2—Cd1—Br1^{i}	115.488(9)
Cd1—Br2	2.5937(3)	Br1—Cd1—Br2	105.806(8)	Br2—Cd1—Br2^{i}	112.171(15)
		Br1—Cd1—Br2^{vi}	115.487(9)	Br1^{i}—Co1—Br2^{i}	105.805(8)
HgCl(1)					
Hg1—Cl1	2.4968(4)	Cl1—Hg1—Cl1^{vi}	100.811(17)	Cl2—Hg1—Cl1^{i}	115.681(12)
Hg1—Cl2	2.4844(4)	Cl1—Hg1—Cl2	105.020(12)	Cl2—Hg1—Cl2^{i}	114.187(17)
		Cl1—Hg1—Cl2^{vi}	115.680(12)	Cl2^{i}—Hg1—Cl1^{i}	105.019(12)
HgCl(2)					
Hg1—Cl1	2.3336(7)	Cl1—Hg1—Cl2	170.10(2)	Cl2—Hg1—Cl3^{vi}	92.27(2)
Hg1—Cl2	2.3600(7)	Cl1—Hg1—Cl3	96.23(2)	Cl3—Hg1—Cl2^{iv}	86.99(3)
Hg1—Cl3	2.8881(7)	Cl1—Hg1—Cl2^{iv}	90.61(2)	Cl3—Hg1—Cl2^{v}	171.12(3)
Hg1—Cl2^{iv}	3.2501(7)	Cl1—Hg1—Cl2^{v}	88.91(2)	Cl3—Hg1—Cl3^{vi}	98.24(3)
Hg1—Cl2^{v}	3.1702(7)	Cl1—Hg1—Cl3^{vi}	94.34(2)	Cl2^{iv}—Hg1—Cl2^{v}	85.71(5)
Hg1—Cl3^{vi}	2.8874(7)	Cl2—Hg1—Cl3	90.10(2)	Cl2^{iv}—Hg1—Cl3^{vi}	172.35(5)
		Cl2—Hg1—Cl2^{iv}	82.10(2)	Cl2^{v}—Hg1—Cl3^{vi}	88.56(4)
		Cl2—Hg1—Cl2^{v}	83.89(3)		
HgBr					
Hg1—Br1	2.6128(7)	Br1—Hg1—Br1^{ii}	109.42(3)	Br11—Hg11—Br11^{iii}	104.54(4)
Hg1—Br2	2.6021(7)	Br1—Hg1—Br2	109.24(2)	Br11—Hg11—Br12	111.61(2)
Hg11—Br11	2.6203(7)	Br1—Hg1— Br2^{ii}	109.18(2)	Br11—Hg11—Br12 ^{iii}	112.00(2)
Hg11—Br12	2.6247(8)	Br2—Hg1—Br1^{ii}	109.18(2)	Br12—Hg11— Br11^{iii}	112.00(2)
		Br2—Hg1—Br2^{ii}	110.57(4)	Br12—Hg11—Br12^{iii}	105.26(4)
		Br1^{ii}—Hg1—Br2^{ii}	109.24(2)	Br11^{iii} —Hg11—Br12^{iii}	111.60(2)
SnCl(1)					
Sn1—Cl1	2.4404(14)	Cl1—Sn1—Cl2	90.66(5)	Cl2—Sn1—Cl3 ^{xii}	90.10(5)
Sn1—Cl2	2.4249(14)	Cl1—Sn1—Cl3	89.75(5)	Cl3—Sn1—Cl1 ^{xii}	90.25(5)
Sn1—Cl3	2.4343(14)	Cl1—Sn1—Cl1^{vii}	180.00	Cl3—Sn1—Cl2^{vii}	90.10(5)

i—j	d_{ij} [Å]	i—j—k	a_{ijk} [°]	i—j—k	a_{ijk} [°]
		Cl1—Sn1—Cl2^{vii}	89.34(5)	Cl3—Sn1—Cl3^{vii}	180.00
		Cl1—Sn1—Cl3^{vii}	90.25(5)	Cl1^{vii} —Sn1—Cl2^{vii}	90.66(5)
		Cl2—Sn1—Cl3	89.91(5)	Cl1^{vii} —Sn1—Cl3^{vii}	89.75(5)
		Cl2—Sn1—Cl1^{vii}	89.35(5)	Cl2^{vii} —Sn1—Cl3^{vii}	89.90(5)
		Cl2—Sn1—Cl2^{vii}	180.00		
SnCl(2)					
Sn1—N1	2.2058(18)	N1—Sn1—O1	78.18(6)	O1—Sn1—Cl4	93.22(4)
Sn1—O1	2.0942(14)	N1—Sn1—Cl1	89.70(5)	Cl1—Sn1—Cl2	91.98(2)
Sn1—Cl1	2.4233(6)	N1—Sn1—Cl2	92.17(5)	Cl1—Sn1—Cl3	176.035(18)
Sn1—Cl2	2.3895(5)	N1—Sn1—Cl3	87.04(5)	Cl1—Sn1—Cl4	92.01(2)
Sn1—Cl3	2.4311(6)	N1—Sn1—Cl4	171.13(5)	Cl2—Sn1—Cl3	90.394(19)
Sn1—Cl4	2.3916(5)	O1—Sn1—Cl1	87.06(4)	Cl2—Sn1—Cl4	96.463(19)
		O1—Sn1—Cl2	170.30(4)	Cl3—Sn1—Cl4	90.87(2)
		O1—Sn1—Cl3	90.07(4)		
SnBr					
Sn1—Br1	2.6148(3)	Br1—Sn1—Br2	90.195(8)	Br2—Sn1—Br3^{vii}	89.422(9)
Sn1—Br2	2.5886(2)	Br1—Sn1—Br3	89.468(9)	Br3—Sn1—Br1^{vii}	90.532(9)
Sn1—Br3	2.5973(3)	Br1—Sn1—Br1^{vii}	180.0	Br3—Sn1—Br2^{vii}	89.422(9)
		Br1—Sn1—Br2^{vii}	89.805(8)	Br3—Sn1—Br3^{vii}	180.0
		Br1—Sn1—Br3^{vii}	90.533(9)	Br1^{x}—Sn1—Br2^{vii}	90.194(8)
		Br2—Sn1—Br3	90.578(9)	Br1^{x}—Sn1—Br3^{vii}	89.468(9)
		Br2—Sn1—Br1^{vii}	89.806(8)	Br2^{x}—Sn1—Br3^{vii}	90.578(9)
		Br2—Sn1—Br2^{vii}	180.0		
PbCl					
Pb1—Cl1	2.9227(9)	Cl1—Pb1—Cl2	90.15(3)	Cl3—Pb1— Cl1^{viii}	127.17(2)
Pb1—Cl2	2.9133(9)	Cl1—Pb1—Cl3	75.11(2)	Cl3—Pb1— Cl1^{ix}	139.15(3)
Pb1—Cl3	3.0343(9)	Cl1—Pb1—Cl1^{viii}	84.60(2)	Cl3—Pb1— Cl2^{viii}	126.54(2)
Pb1—Cl1^{viii}	2.9536(9)	Cl1—Pb1—Cl1^{ix}	74.08(3)	Cl3—Pb1—Cl3^{viii}	80.67(2)
Pb1—Cl1^{ix}	2.9289(9)	Cl1—Pb1—Cl2^{viii}	155.02(2)	Cl1^{viii}—Pb1—Cl1^{ix}	75.45(3)
Pb1—Cl2^{viii}	2.9267(9)	Cl1—Pb1—Cl3^{viii}	127.33(2)	Cl1^{viii}—Pb1—Cl2^{viii}	89.29(2)
Pb1—Cl3^{viii}	3.0759(10)	Cl2—Pb1—Cl3	74.21(2)	Cl1^{viii}—Pb1—Cl3^{viii}	74.05(2)
		Cl2—Pb1—Cl1^{viii}	155.11(2)	Cl1^{ix}—Pb1—Cl2^{viii}	80.94(2)
		Cl2—Pb1—Cl1^{ix}	79.71(3)	Cl1^{ix}—Pb1—Cl3^{viii}	139.96(2)
		Cl2—Pb1—Cl2^{viii}	85.25(2)	Cl2^{viii}—Pb1—Cl3^{viii}	73.40(3)
		Cl2—Pb1—Cl3^{viii}	126.86(3)		
PbBr					
Pb1—Br1	3.0761(3)	Br1—Pb1—Br2	90.487(8)	Br3—Pb1—Br1^{viii}	126.168(8)
Pb1—Br2	3.0774(3)	Br1—Pb1—Br3	73.781(7)	Br3—Pb1—Br1^{ix}	137.831(8)
Pb1—Br3	3.2315(3)	Br1—Pb1—Br1^{viii}	83.288(7)	Br3—Pb1—Br2^{viii}	126.856(8)
Pb1—Br1^{viii}	3.0382(3)	Br1—Pb1—Br1^{ix}	75.254(8)	Br3—Pb1—Br3^{viii}	79.341(7)
Pb1—Br1^{ix}	3.0856(3)	Br1—Pb1— Br2^{viii}	155.013(7)	Br1^{viii}—Pb1—Br1^{ix}	76.941(8)
Pb1—Br2^{viii}	3.0308(3)	Br1—Pb1—Br3^{viii}	125.491(8)	Br1^{viii}—Pb1—Br2^{viii}	92.106(8)
Pb1—Br3^{viii}	3.1321(3)	Br2—Pb1—Br3	74.270(8)	Br1^{viii} —Pb1—Br3^{viii}	75.738(8)
		Br2 —Pb1—Br1^{viii}	155.045(7)	Br1^{ix}—Pb1—Br2^{viii}	79.777(8)
		Br2—Pb1—Br1^{ix}	78.104(8)	Br1^{ix}—Pb1—Br3^{viii}	142.701(8)
		Br2 —Pb1—Br2^{viii}	83.389(7)	Br2^{viii}—Pb1—Br3^{viii}	76.367(8)
		Br2—Pb1—Br3^{viii}	126.257(8)		
BiCl					
Bi1—Cl1	2.5979(5)	Cl1—Bi1—Cl2	92.558(17)	Cl2—Bi1—Cl6	87.845(15)
Bi1—Cl2	2.6900(5)	Cl1—Bi1—Cl3	173.797(14)	Cl3—Bi1—Cl4	87.778(14)
Bi1—Cl3	2.9822(5)	Cl1—Bi1—Cl4	89.450(16)	Cl3—Bi1—Cl5	83.700(13)
Bi1—Cl4	2.7331(5)	Cl1—Bi1—Cl5	90.805(15)	Cl3—Bi1—Cl6	93.309(13)
Bi1—Cl5	2.6863(4)	Cl1—Bi1—Cl6	92.307(15)	Cl4—Bi1—Cl5	91.036(15)
Bi1—Cl6	2.7150(5)	Cl2—Bi1—Cl3	90.284(15)	Cl4—Bi1—Cl6	91.454(15)
		Cl2—Bi1—Cl4	177.899(16)	Cl5—Bi1—Cl6	176.031(14)
		Cl2—Bi1—Cl5	89.558(15)		

Symmetry transformations used to generate equivalent atoms: (i) –x+1, y, -z+0.5; (ii) –x+0.5, y, -z+0.5; (iii) -x+1.5, y, -z+0.5; (iv) -x+1.5, y+0.5, -z+1.5; (v) -x+1.5, y-0.5,-z+1.5; (vi) x, y-1, z; (vii) –x+1, -y, -z+1; (viii) x+1, y , z; (ix) –x+1, -y+1, -z

Table S3. Stacking interactions in the studied compounds.

Each ring is indicated by one atom, which belongs solely to this ring. The α is a dihedral angle between planes I and J, β is an angle between Cg(I)-Cg(J) vector and normal to plane I, d_p is a perpendicular distance of Cg(I) on ring J plane.

R(I)•••R(J)	d(Cg•••Cg) [Å]	α [°]	β [°]	d_p[Å]
FeCl				
N1•••N11	4.1582(12)	3.69(10)	36.0	3.3852(8)
N1•••C18	3.7117(12)	1.70(10)	23.5	3.3702(8)
C8•••N11	3.7355(12)	3.33(10)	27.1	3.3997(9)
C8•••C18	3.5892(13)	1.65(10)	19.0	3.3705(9)
N1•••C18^{i}	4.1685(12)	1.70(10)	35.2	3.4382(8)
C8•••C18^{i}	4.5109(13)	1.65(10)	41.7	3.4380(9)
FerBr				
N1•••N11	4.1848(12)	2.70(11)	36.0	3.4054(9)
N1•••C18	3.7285(13)	1.54(11)	23.5	3.3838(9)
C8•••N11	3.7538(13)	2.91(11)	26.8	3.3931(9)
C8•••C18	3.5958(13)	1.82(11)	18.8	3.3782(9)
N1•••C18^{i}	4.3850(13)	1.54(11)	38.7	3.4421(9)
C8•••C18^{i}	4.8082(13)	1.82(11)	45.5	3.4478(9)
CoCl				
N1•••N1^{ii}	3.8002(12)	0.02(10)	28.4	3.3443(9)
N1•••C8^{ii}	3.6353(12)	0.54(10)	22.7	3.3424(9)
CoBr				
N1•••C8^{iii}	3.706(6)	2.1(5)	26.2	3.267(4)
C8•••C8^{iii}	3.565(6)	0.0(5)	22.0	3.306(5)
C8•••C8^{iv}	4.129(6)	0.0(5)	34.6	3.398(5)
N11•••C18^{v}	3.553(6)	2.3(5)	25.1	3.195(5)
C18•••C18^{v}	3.590(6)	0.0(5)	25.7	3.235(4)
C18•••C18^{vi}	4.052(6)	0.0(5)	35.7	3.290(4)
CuCl				
N1•••C8^{vii}	3.5916(11)	1.37(10)	23.3	3.3279(8)
C8•••C8^{vii}	3.9500(14)	0.00(10)	33.4	3.2985(9)
C8•••N11^{iv}	3.8499(13)	7.72(10)	23.0	3.3604(8)
C8•••C18^{iv}	3.5768(12)	6.91(10)	18.7	3.3747(8)
N11•••C18^{viii}	3.6889(12)	1.15(10)	27.3	3.2990(9)
C18•••C18^{viii}	3.4623(13)	0.00(10)	17.9	3.2941(8)
ZnCl				
N1•••N1^{ii}	3.7964(9)	0.00(7)	28.4	3.3380(6)
N1•••C8^{ii}	3.6296(9)	0.51(7)	22.8	3.3357(6)
CdCl				
N1•••N1^{ii}	3.7696(12)	0.00(11)	27.4	3.3458(9)
N1•••C8^{ii}	3.7003(13)	1.02(11)	24.6	3.3443(9)
CdBr				
N1•••N1^{ii}	3.7084(15)	0.02(12)	25.5	3.3476(10)
N1•••C8^{ii}	3.7989(15)	0.98(12)	27.6	3.3445(10)
HgCl(1)				
N1•••N1^{ii}	3.7694(9)	0.02(7)	27.6	3.3416(6)
N1•••C8^{ii}	3.6997(9)	0.88(7)	24.8	3.3403(6)
HgCl(2)				
N1•••N1^{ix}	4.3664(15)	0.00(12)	40.6	3.3133(11)
N1•••C8^{ix}	3.4295(16)	0.23(13)	15.4	3.3071(11)
C8•••C8^{ix}	4.3664(16)	0.00(13)	40.8	3.3065(11)
HgBr				
N1•••C8^{iii}	3.694(4)	1.0(3)	26.3	3.283(3)
C8•••C8^{iii}	3.566(4)	0.0(3)	22.4	3.298(3)
C8•••C8^{iv}	4.276(4)	0.0(3)	37.0	3.416(3)
N11•••C18^{v}	3.576(4)	2.1(3)	25.4	3.214(3)
C18•••C18^{v}	3.603(4)	0.0(3)	25.8	3.244(3)
C18•••C18^{vi}	4.196(4)	0.0(3)	38.1	3.302(3)
SnCl(1)				
N1•••N1^{x}	3.484(4)	0.0(3)	15.1	3.364(3)
N1•••C8^{x}	3.681(4)	0.7(3)	24.5	3.368(3)
N1•••C8^{xi}	3.634(4)	0.7(3)	22.7	3.368(3)
C8•••C8^{xi}	3.781(4)	0.0(3)	27.5	3.353(3)

SnCl(2)				
N1•••N1^{iii}	4.0942(13)	0.00(10)	32.4	3.4585(9)
N1•••C8^{iii}	3.8416(12)	2.02(10)	25.6	3.4131(9)
N11•••C18^{xii}	4.1920(13)	16.45(11)	32.7	2.7611(9)
C18•••C18^{xii}	4.0300(14)	13.72(11)	30.7	3.2558(9)
C18•••N11^{xiii}	4.1921(13)	16.45(11)	48.8	3.5285(9)
C18•••C18^{xiii}	4.0300(14)	13.72(11)	36.1	3.4660(9)
SnBr				
N1•••N1^{x}	3.4769(17)	0.00(14)	12.1	3.4000(12)
N1•••C8^{x}	3.7906(17)	0.52(14)	26.7	3.3999(12)
N1•••C8^{xi}	3.7592(17)	0.52(14)	25.1	3.4166(12)
C8•••C8^{xi}	3.8463(17)	0.00(14)	27.5	3.4103(12)
PbCl				
N1•••N1^{i}	3.955(2)	0.02(19)	31.2	3.3825(16)
N1•••C8^{i}	3.811(2)	0.59(19)	27.6	3.3752(16)
C8•••C8^{i}	3.955(2)	0.03(19)	31.8	3.3612(17)
PbBr				
N1•••N1^{i}	4.0630(17)	0.02(14)	31.9	3.4507(12)
N1•••C8^{i}	3.9487(17)	0.26(14)	28.8	3.4536(12)
C8•••C8^{i}	4.0632(17)	0.03(14)	31.7	3.4561(12)
BiCl				
N1•••N11^{iii}	4.4349(11)	9.05(9)	39.8	3.1272(8)
N1•••C18^{iii}	3.6716(11)	6.91(9)	23.8	3.1646(8)
C8•••N11^{iii}	3.9322(12)	7.42(10)	32.1	3.4552(9)
C8•••C18^{iii}	3.4756(12)	4.79(10)	14.8	3.4129(9)
C8•••N31^{iv}	4.5325(12)	5.43(10)	45.7	3.2381(9)
N11•••N11^{xiv}	4.1467(11)	0.03(9)	36.1	3.3514(8)
N11•••C18^{xiv}	4.0164(12)	3.04(9)	32.3	3.2766(8)
N21•••N21^{xv}	4.8966(12)	0.00(9)	47.9	3.2833(8)
N21•••C28^{xv}	4.6304(12)	1.86(10)	44.4	3.2155(8)
N21•••N31^{v}	4.3330(11)	7.72(10)	42.8	3.4418(8)
N21•••C38^{v}	3.7459(11)	5.60(9)	23.3	3.3635(8)
C28•••N31^{v}	3.8351(12)	6.38(10)	33.1	3.4126(9)
C28•••C38^{v}	3.5472(12)	3.91(9)	15.0	3.4079(9)
8hqHCl				
N1•••C8^{iii}	3.8001(18)	0.79(15)	27.6	3.3550(12)
C8•••C8^{iii}	3.5671(18)	0.00(15)	19.2	3.3680(13)
8hqHBr				
N1•••C8^{iii}	3.8293(13)	0.78(11)	28.0	3.3594(9)
C8•••C8^{iii}	3.5609(14)	0.00(11)	18.6	3.3743(10)

Symmetry transformations used to generate equivalent atoms: (i) x+1, y, z; (ii) -x+0.5, -y+0.5, -z+1; (iii) –x+1, -y+1, -z+1; (iv) –x+1, -y+2, -z+1; (v) –x+1, -y+2, -z; (vi) –x+1, -y+1, -z; (vii) -x+2, -y+1, -z; (viii) –x, -y, -z+1; (ix) x, y-1, z; (x) -x+2, -y+1, -z+2; (xi) -x+1, -y+1, -z+2; (xii) x-0.5, y, -z+1.5; (xiii) x+0.5, y, -z+1.5; (xiv) –x, -y+1, -z+1; (xv) –x, -y+2, -z; (xvi) –x+1, -y, -z+1

Table S4. Hydrogen bond in the studied compounds.

D-H•••A	d(D—H) [Å]	d(H•••A) [Å]	d(D•••A) [Å]	<(DHA) [°]	G_d^a(n)
FeCl					
N1—H1N•••Cl99^{i}	0.79	2.46	3.1333(17)	143.8	D(2)
O1—H1O•••Cl99	0.84	2.30	3.1169(16)	164.4	D(2)
N11—H11N•••Cl99^{ii}	0.81	2.41	3.1577(18)	152.8	D(2)
O11—H11O•••Cl99	0.84	2.24	3.0693(15)	167.2	D(2)
FerBr					
N1—H1N•••Br99^{i}	0.82	2.53	3.2652(19)	149.7	D(2)
O1—H1O•••Br99	0.84	2.44	3.2530(16)	163.1	D(2)
N11—H11N•••Br99^{ii}	0.85	2.53	3.2621(19)	145.1	D(2)
O11—H11O•••Br99	0.84	2.40	3.2235(16)	168.2	D(2)
CoCl					
N1—H1N•••Cl1	0.95	2.26	3.0985(17)	147.0	D(2) [D_2^2(5)]
O1—H1O•••Cl2^{iii}	0.84	2.25	3.0922(16)	179.4	D(2) [D_2^2(5)]
CoBr					
N1—H1N•••Br12^{iv}	0.90	2.74	3.407(10)	132.4	D(2) [D_2^2(5)]
O1—H1O•••Br2	0.84	2.42	3.259(9)	178.7	D(2) [D_2^2(5)]

D-H•••A	d(D—H) [Å]	d(H•••A) [Å]	d(D•••A) [Å]	<(DHA) [°]	$G_d^a(n)$
N11—H11N•••Br11	0.87	2.48	3.254(10)	147.6	D(2) [$D_2^2(5)$]
O11—H11O•••Br1	0.84	2.44	3.265(7)	166.7	D(2) [$D_2^2(5)$]
CuCl					
N1—H1N•••Cl2^{v}	0.96	2.38	3.1737(18)	139.4	D(2)
O1—H1O•••Cl2	0.84	2.26	3.092(2)	173.5	D(2)
N11—H11N•••Cl4^{vi}	0.95	2.40	3.268(2)	152.2	D(2)
O11—H11O•••Cl1	0.84	2.23	3.0742(18)	178.9	D(2)
ZnCl					
N1—H1N•••Cl1	0.94	2.23	3.0868(13)	150.2	D(2) [$D_2^2(5)$]
O1—H1O•••Cl2^{iii}	0.84	2.26	3.0973(12)	178.0	D(2) [$D_2^2(5)$]
CdCl					
N1—H1N•••Cl1	0.91	2.25	3.0812(17)	152.7	D(2) [$D_2^2(5)$]
O1—H1O•••Cl2^{iii}	0.84	2.26	3.0960(16)	177.1	D(2) [$D_2^2(5)$]
CdBr					
N1—H1N•••Br1	0.87	2.40	3.237(2)	161.6	D(2) [$D_2^2(5)$]
O1—H1O•••Br2^{iii}	0.84	2.43	3.2708(18)	178.1	D(2) [$D_2^2(5)$]
HgCl(1)					
N1—H1N•••Cl1	0.84	2.33	3.0854(13)	150.0	D(2) [$D_2^2(5)$]
O1—H1O•••Cl2^{iii}	0.84	2.26	3.1032(12)	177.2	D(2) [$D_2^2(5)$]
HgCl(2)					
N1—H1N•••O99	0.90	1.89	2.747(3)	159.1	D(2)
O1—H1O•••O98	0.84	1.79	2.633(3)	176.1	D(2)
O98—H98O•••Cl3^{vii}	0.90	2.45	3.210(2)	141.5	D(2)
O98—H98P•••Cl2^{vii}	0.93	2.78	3.474(2)	132.3	D(2)
O98—H98P•••Cl3^{viii}	0.93	2.67	3.367(2)	132.9	D(2)
O99—H99O•••O99^{viii}	0.95	1.85	2.763(3)	161.9	C(2)
O99—H99P•••Cl3	0.90	2.27	3.119(2)	157.7	D(2)
HgBr					
N1—H1N•••Br12^{iv}	0.84	2.70	3.420(5)	145.2	D(2) [$D_2^2(5)$]
O1—H1O•••Br2	0.84	2.48	3.256(5)	153.1	D(2) [$D_2^2(5)$]
N11—H11N•••Br11	0.85	2.52	3.295(5)	151.5	D(2) [$D_2^2(5)$]
O11—H11O•••Br1	0.84	2.43	3.269(5)	175.9	D(2) [$D_2^2(5)$]
SnCl(1)					
N1—H1N•••O99^{v}	0.88	2.00	2.857(7)	165.0	D(2)
O1—H1O•••O99	0.84	1.86	2.693(7)	174.3	D(2)
O99—H99O•••Cl2^{ix}	0.91	2.62	3.357(5)	138.9	D(2) [$D_2^2(5)$]
O99—H99O•••Cl3^{ix}	0.91	2.74	3.489(5)	141.4	D(2) [$D_2^2(5)$]
O99—H99B•••Cl1	0.89	2.56	3.275(6)	137.9	D(2) [$D_2^2(5)$]
O99—H99B•••Cl3^{vi}	0.89	2.61	3.323(5)	138.2	D(2) [$D_2^2(5)$]
SnCl(2)					
N11—H11N•••O99	0.83	1.92	2.737(2)	169.9	D(2)
O11—H11O•••O1	0.84	1.93	2.724(2)	157.3	D(2)
O99—H99O•••Cl3	0.79	2.47	3.2376(18)	165.1	D(2)
O99—H99P•••Cl4^{x}	0.90	2.48	3.1927(19)	136.8	D(2)
SnBr					
N1—H1N•••O99^{v}	0.95	1.94	2.842(3)	159.7	D(2)
O1—H1O•••O99	0.84	1.89	2.725(3)	175.3	D(2)
O99—H99O•••Br2^{ix}	0.85	2.95	3.602(3)	134.7	D(2) [$D_2^2(5)$]
O99—H99O•••Br3^{ix}	0.85	2.80	3.529(2)	144.8	D(2) [$D_2^2(5)$]
O99—H99B•••Br1	0.89	2.57	3.428(2)	159.8	D(2) [$D_2^2(5)$]
O99—H99B•••Br3^{vi}	0.89	2.96	3.415(2)	113.6	D(2) [$D_2^2(5)$]
PbCl					
N1—H1N•••Cl2^{xi}	0.80	2.48	3.173(3)	145.8	D(2) [$D_2^2(5)$]
O1—H1O•••Cl3	0.84	2.27	3.098(3)	171.8	D(2) [$D_2^2(5)$]
PbBr					
N1—H1N•••Br2^{xi}	0.89	2.52	3.292(2)	145.6	D(2) [$D_2^2(5)$]
O1—H1O•••Br3	0.84	2.42	3.260(2)	174.4	D(2) [$D_2^2(5)$]
BiCl					
N1—H1N•••Cl99^{xii}	0.88	2.43	3.1742(18)	142	D(2)
O1—H1O•••O99	0.84	1.82	2.652(2)	174	D(2)
N11—H11N•••Cl3^{xiii}	0.88	2.41	3.1825(17)	147	D(2)
O11—H11O•••Cl99	0.84	2.27	3.1118(17)	178	D(2)
N21—H21N•••Cl3^{xiii}	0.88	2.42	3.1674(17)	142	D(2)
O21—H21O•••O98	0.84	1.85	2.688(2)	176	D(2)

D-H•••A	d(D—H) [Å]	d(H•••A) [Å]	d(D•••A) [Å]	<(DHA) [°]	$G_d^a(n)$
N31—H31N•••Cl99^{xii}	0.88	2.36	3.1518(17)	150	D(2)
O31—H31O•••Cl3^{xiv}	0.84	2.30	3.1419(17)	175	D(2)
O98—H98O•••Cl3^{xv}	0.77	2.45	3.1937(16)	164	D(2)
O98—H98P•••Cl4^{xvi}	0.90	2.34	3.1893(16)	158	D(2)
O99—H99O•••Cl99^{xvii}	0.97	2.17	3.1119(17)	165	D(2)
O99—H99P•••Cl2^{xviii}	0.97	2.65	3.3619(17)	131	D(2)
8hqHCl					
N1—H1N•••Cl1	0.91	2.27	3.107(3)	153.3	D(2)
O1—H1O•••O99	0.84	1.76	2.596(3)	173.9	D(2)
O99—H99O•••Cl1^{xiii}	0.85	2.27	3.114(3)	171.5	D(2)
O99—H99P•••Cl1^{xix}	0.91	2.27	3.159(2)	165.6	D(2)
8hqHBr					
N1—H1N•••Br1	0.90	2.44	3.2360(18)	148.1	D(2)
O1—H1O•••O99	0.84	1.76	2.600(2)	177.0	D(2)
O99—H99O•••Br1^{xiv}	0.79	2.46	3.2435(16)	167.5	D(2)
O99—H99P•••Br1^{xv}	0.89	2.42	3.2873(16)	166.0	D(2)

Symmetry transformations used to generate equivalent atoms: (i) -x, -y+1, -z+1; (ii) -x, -y, -z+1; (iii) x, -y+1, z+0.5; (iv) x-0.5, -y+1, z+0.5; (v) -x+2, -y+1, -z+1; (vi) -x+1, -y, -z+1; (vii) –x+0.5, y+1.5, -z+1.5; (viii) –x+0.5, y+0.5, -z+1.5; (ix) x+1, y, z; (x) x-0.5, y, -z+1.5; (xi) x+0.5, -y+0.5, z+0.5; (xii) x+1, y+1, z; (xiii) x-1, y, z; (xiv) x, y+1, z; (xv) -x+1, -y+1, -z; (xvi) -x, -y+1, -z; (xvii) -x+1, -y+1, -z+1; (xviii) -x+2, -y+2, -z+1; (xix) -x+1, y-0.5, -z+1.5;

Table S5. Vibrational frequencies (cm^{-1}) and their assignment for the studied compounds.

Vibrations symbols: w – weak, m – medium, s – strong, b - broadened ν – stretching, δ – bending, σ – scissoring, ρ – rocking, τ – twisting, ω – wagging, T – torsional α – in plane, γ – out of plane, as – asymmetric, s – symmetric, ar – aromatic ring.

PbCl	PbBr	HgCl(1)	HgCl(2)	HgBr	8hqHCl	8hqHBr	8hq	Assignment
3451sb	3464sb	3477s	3464s	3460sb	3387sb	3391sb		ν OH
						3318s		
1631s	1629s	1632s	1633s	1633s	1631s	1632s	1638s	ν CO, ν_s CC, ν_{as} ring, δ COH
1603s	1602s	1605s	1605s	1603s	1604s	1606s		ν_s CC,ν_s CN, δ NH
1587m	1588m	1592w	1592w	1592w	1591s	1592s	1593w	ν CN, ν_s CC, νCH
							1580s	ν CC, ν CN, ν CH
1553s	1551s	1553s	1554s	1552s	1551s	1552s		ν CC, τ CH
							1510s	δ OH, δ CH, ν CC
1490m	1488m	1490m	1491m	1491m	1500m	1499m	1499s	ν_s CC,ν_s CN, δ CH
1470w	1470w	1471w	1471w	1471w	1472m	1471m	1473s	α δ OH
							1434m	δ OH
1421w	1420w	1418s	1418s	1417s				ν CC, δ OH, ν CH
1414m	1413m						1410s	ν CC, δ OH, ν CH
1397s	1396s	1401s	1400s	1400s	1400s	1400s	1399m	ν CO, δ OH
1371m	1369m	1377w	1376w	1375w	1381s	1380s	1380s	γ OH, δ CH, ν CC, ν_{as} ring
	1321s				1316s	1317s		ν CN
1295s	1296s	1300s	1300s	1299s	1300s	1297s		ν CN
1273m	1280m	1285m	1287m	1284m			1286s	ν CO, ν CN, ν_{as} ring
					1269s	1271s	1274s	ν CO, ν CN, ν_{as} ring
							1244m	ν CO, ν CN, ν_{as} ring
1226w	1223w	1224w	1225w	1223w	1220m	1218m	1223s	ν CO, ν CH
1201m	1200m	1200m	1201m	1200m	1205m	1202m	1205s	ν CC, νCH
1169w	1167w	1168w	1168w	1167w			1165m	δ CH
1142w	1141w	1141w	1141w	1140w	1134w	1134w	1139m	δ CH, δ OH
1094s	1093s	1093s	1093s	1093s	1099s	1097s	1094m	δ CH, ν_s CN, $\nu_s$ring, δ OH
1057m	1057m	1057w	1058w	1058w	1059m	1058m	1059m	γ CH, ν CC
998w	996m	997w	997w		999w	998m		δ CH
	985w	983w	983w	983w			974m	ω CH
905w	905w	905w	905m	905w		907w		ω CH
887s	886s	889s	888s	888s	881m	886m	897m	γ OH, γCH
821s	821s	818s	817s	818s	821s	822s	817s	ν_s CN, γ CH, ω CH, $\nu_s$ring, ν_{as}ring,
		809s	808s	808s			807m	ν CC
802s	801s	801s	800s	801s	802m	802w		ν CC
780s	777s	773s	772s	773m	784m	782w	782m	γ CH
756s	755s	758s	758s	759s	756s	754s		γ CH
							741s	ν_{as} ring, T_s ring, T OH
712m	712m	711m	710m	710m	712s	711m	711s	γ CH
								ν CN
620w	618s	614w	612mb	615mb	623m	622m	637s	γ CH
		598mb	609mb	600mb				γ CH
575wb	573w	573m	574m	574m	578m	574m	574m	δ ring, T ring
536w	537m	538m	538m	537m	541m	542w	544m	δ ring, α CO, T ring
489w	488m	487w	488w	487w	488m	488m	490m	ν CC, ω CO
480w	479w	477w			474w	473w		ν CC, ω CO
471w	468w	468w	470w	468w			471m	γ CO
							464m	γ CO, T ring
	457w			457w		458w		γ CO
408m	407s	406m	406s	406m	413s	410m	423m	δ ring

Table S5. *continued*

CoCl	FeCl	CuCl	ZnCl	CdCl	SnCl(1)	SnCl(2)	BiCl	Assignment
3378sb	3461sb	3378s	3444s	3451sb	3434sb	3515sb	3435sb	ν OH
3314s						3461sb		ν OH
1633s	1631s	1633s	1632s	1631s	1638sb	1634s	1631s	ν CO, ν_s CC, ν_{as} ring, δ COH
1605s	1602m	1602s	1604s	1602s	1607m	1606s	1599s	ν_s CC, ν_s CN, δ NH
1592s	1592m	1592s	1591s	1592s		1592s		ν_s CC, ν_s CN, ν CH
					1579w			ν CC, ν CN, ν CH
1552s	1550s	1552s	1554s	1552s		1558s	1551s	ν CC, τ CH
		1514w	1513w			1519w		δ OH, δ CH, ν CC
1499m	1498m	1493m	1491m	1492m	1499s	1499m	1496m	ν_s CC, ν_s CN, δ CH
1472m	1470w	1472m	1472w	1472m	1465s	1465m	1470m	α δ OH
					1430w			δ OH
1424w	1418w	1418s	1419s	1420s		1423s	1416s	ν CC, δ OH, ν CH
1400s	1397s	1399s	1401s	1399s	1394m	1401s	1397s	ν CO, δ OH
1381m	1376m	1380m	1377w	1377m	1375s	1375m	1377m	γ OH, δ CH, ν CC,ν_{as} ring
1316s					1323s			ν CN
1300s	1297s	1300s	1299s	1301s		1309s	1301s	ν CN
			1284m			1294m	1281m	ν CO, ν CN, ν_{as} ring
1270s	1269w	1271s	1270m	1268m	1268m	1274m	1264m	ν CO, ν CN, ν_{as} ring
					1232m			ν CO, ν CN, ν_{as} ring
1220m	1219w	1220m	1226w	1221m			1217m	ν CO, ν CH
1204m	1198w	1204m	1202m	1202m		1205m		ν CC, ν CH
		1172w				1172w	1192m	δ CH
1136w	1141w	1138w	1143w	1147w		1144m	1144m	δ CH, δ OH
1099s	1094s	1093s	1093s	1094s	1107s	1098s	1093s	δ CH, ν_s CN, ν_s ring, δ OH
1058m	1058w	1058w	1058w	1058m		1062w	1059m	γ CH, ν CC
998w		998w	998w	996w		998w		δ CH
	990w		984w			985w	987w	ω CH
		977w					968w	ω CH
904w	907w		905w	907w				ω CH
885m	886m	888s	886m	886m	881w	887w	887m	γ OH, γCH
822s	822s	823s	819s	819s	827s	825s	816s	ν_s CN, γ CH, ω CH, $\nu_s$ring, νasring,
		804s	809s					ν CC
802w	801w	801s	801m	802m	805m	802m	801m	ν CC
783w	780w	766s	776w	775m	786m	785m	773m	γ CH
755s	759s	756s	758s	757s	752s	761m	761s	γ CH
					745s	747w		ν_{as} ring, T_s ring, T OH
711m	711w	711m	711w	712m		711w	711m	γ CH
			633w		645w			ν CN
623w	617w	616mb	611mb	615w		618w	615m	γ CH
576w	576w	574m	574m	576m		577m	577m	δ ring,T ring
540m	537w	538m	538m	538m	538m	539w	539w	δ ring, α CO, T ring
488m	485m	488m	489m	488m		490w	490m	νCC, ωCO
	470w		470w	470w	475w		466w	γ CO
	464w			455w	444w		460w	γ CO, T ring
	441w			438w	432w			γ CO
413m	419m			413m	418w	411m		δ ring
	409m	405m	408m		406w		404m	δ ring

Table S5. *continued*

CoBr	FeBr	ZnBr	CdBr	SnBr	Assignment
3411sb	3461sb	3455s	3461s	3508sb	νOH
3314sb				3451sb	νOH
1633s	1628s	1635s	1634s	1634s	ν CO, ν_s CC, ν_{as} ring, δ COH
1605s	1599s	1605s	1606s	1604s	ν_s CC, ν_s CN, δ NH
1592s	1591s	1593s	1591m	1591s	ν CN, ν_s CC, ν CH
1552s	1548s	1554s	1552s	1556s	ν CC, τ CH
1497w	1494m	1490m	1492w		ν_s CC, ν_s CN, δ CH
1471m	1471w	1471w	1471w	1472w	α δ OH
	1417s	1418s	1418m	1421s	ν CC, δ OH, ν CH
1401s	1394s	1401s	1401s	1401s	ν CO, δ OH
1382s	1371m	1374w	1376w	1374w	γ OH, δ CH, ν CC, ν_{as} ring
1317s					ν CN
1298s	1296s	1299s	1300s	1308s	ν CN
	1282s	1282m	1284w	1289m	ν CO, ν CN,ν_{as} ring
1270s	1269m			1273w	ν CO, ν CN,ν_{as} ring
1239w					ν CO, ν CN,ν_{as} ring
1218s	1218w	1225w	1223w		ν CO, ν CH
1202m	1195w	1201m	1200w	1204w	ν CC, νCH
	1174w	1167w		1170w	δ CH
1136w	1141w	1142w	1140w	1142m	δ CH, δ OH
1098s	1092s	1093s	1093s	1097s	δ CH, ν_s CN, ν_s ring, δ OH
1058m	1056w	1057w	1059w	1062w	γ CH, ν CC
997m				997w	δ CH
	986w	984w	984w		ω CH
				933	ω CH
906w	903w	903w	904w		ω CH
887m	885m	890m	889m	887w	γ OH, γ CH
823s	821s	818s	819m	824s	ν_s CN, γ CH, ω CH, ν_s ring, ν_{as} ring,
		809s	809m		
802w	800m	801s	802m	801m	N CC
783w				783w	ω CH
	777m	776m	773m		
754s	759s	759s	759s	763m	γ CH
711m	710w	711m	710w	712m	γ CH
621m	617w			617m	γ CH
		606mb	602wb	594wb	γ CH
574m	575m	574m	574m	575m	δ ring, T ring
542w	535m	537m	538w	539w	δ ring, α CO, T ring
488w	485m	487m	487w	489w	νCC, ωCO
472w			474w		γ CO
459w	458w	461w	462w	464w	γ CO, T ring
420w	423w				γ CO
410m		415m	417m	419w	δ ring
	403w	409m	408m	407w	δ ring

Table S6. The most important electronic transitions for the compounds containing the open-shell coordination centers. H letter indicates HOMO, L - LUMO, α – α orbitals, β - β orbitals, and +/-(number) represents subsequent orbitals below HOMO and above LUMO, respectively.

λmax (nm)										**The most important orbitals involved in electronic transitions**	**Character of transition**
Experimental					Calculated						
FeCl	CoCl	CuCl	FeBr	CoBr	FeCl	CoCl	CuCl	FeBr	CoBr		
										(FeCl) αH-16→αL+5	(FeCl) n(Cl)π(8hq)→π*(8hq)
										(CoCl) βH-14→βL+2	(CoCl) π(8hq)d(Co)→ π*(8hq)
					225.13	224.54		232.28	231.05	(FeBr) βH-17→ βL+3	(FeBr) σ(Fe-Br)→ n(Br)π*(8hq)d(Fe)
										(CoBr) αH-26→αL+6	(CoBr) n(8hq-OH)π(8hq)→π*(8hq)
										(FeCl) βH-18→βL+1	(FeCl) n(Cl)d(Fe)→ π*(8hq)
					228.16	225.81		233.74		(CoCl) βH-19→βL+1	(CoCl) σ(Co-Cl)π(8hq)→ π*(8hq)
										(FeBr) β H-11→ β L+7	(FeBr) n(8hq-OH)π(8hq)→ π*(8hq)
										(FeCl) βH-12→βL+5	
										(CoCl) βH-14→βL+2	
					232.36	228.18	210.72	241.97		(CuCl) βH-21→βL+1	(FeCl, CuCl, FeBr) π(8hq)→π*(8hq)
										(FeBr) αH-16→ αL+7	(CoCl) π(8hq)d(Co)→ π*(8hq)
										(FeCl) αH-12→αL+5	(FeCl) n(8hq-OH)n(Cl)π(8hq)d(Fe)→π*(8hq)
										(CoCl) αH-16→αL+3	(CoCl) σ(Co-Cl)→ n(Cl)d(Co)
					234.21	231.23	226.55	244.56		(CuCl) αH-1→αL+9	(CuCl) n(Cl)d(Cu)→ π*(8hq)
										(FeBr) αH-18→ αL+1	(FeBr) π(8hq)→π*(8hq)
										(FeCl) αH-19→αL	(FeCl) π(8hq)→ π*(8hq)
										(CoCl) βH-18→βL+5	(CoCl, FeBr) n(Cl, Br)d(Co, Fe)→ n(Cl,
					237.01	232.86	226.78	248.08		(CuCl) αH-1→αL+9	Br)d(Co,Fe)
										(FeBr) βH-19→βL+6	(CuCl) n(Cl)d(Cu)→ π*(8hq)
										(FeCl) βH→βL+14	(FeCl) n(Cl-)π(8hq)→π*(8hq)
										(CoCl) αH-12→αL+4	(CoCl) π(8hq)→ π*(8hq)d(Co)
					242.95	240.56	233.41	251.64		(CuCl) βH-9→βL+5	(CuCl) n(Cl)π(8hq)d(Cu)→ π*(8hq)
										(FeBr) αH-17→ αL+4	(FeBr) σ(Fe-Br)→n(Br)d(Fe)
										(FeCl) βH-12→βL+3	
										(CoCl) βH-11→βL+2	(FeCl) n(Cl)d(Fe)→n(Cl)d(Fe)
					285.29	260.26	235.17	259.27	258.64	(CuCl) αH-21→αL	(CoCl, FeBr) n(Cl, Br)d(Co, Fe)→ π*(8hq)
										(FeBr) βH-7→ β L+8	(CuCl) σ(Cu-Cl)π(8hq)→n(Cl)π*(8hq)d(Cu)
										(CoBr) βH-24→βL+6	(CoBr) σ(Co-Br)n(Br)d(Co)→π*(8hq)
										(CoCl) αH→αL+10	
						275.32	257.42		276.73	(CuCl) αH-10→αL+3	(CoCl, CuCl) n(Cl)π(8hq)d(Co, Cu)→ π*(8hq)
										(CoBr) αH-36→αL+2	(CoBr) σ(Co-Br)→n(Br)d(Co)
						300.86				(CoCl) αH-10→αL+3	(CoCl) σ(Co-Cl)→ n(Cl)d(Co)
										(FeCl) αH-10→αL+1	(FeCl, CuCl) n(Cl)d(Fe, Cu)→π*(8hq)
318	323	336	313	322	316.36	324.18	296.93	294.18	323.13	(CoCl) αH-16→αL	(CoCl) σ(Co-Cl)→ n(Cl)π*(8hq)d(Co)
										(CuCl) βH-4→βL+5	(FeBr, CoBr) n(Br)d(Fe,Co)→ n(Br)d(Fe,Co)

λmax (nm)										The most important orbitals involved in electronic transitions	Character of transition
Experimental					Calculated						
FeCl	CoCl	CuCl	FeBr	CoBr	FeCl	CoCl	CuCl	FeBr	CoBr		
										(FeBr) αH-21→ αL+3 (CoBr) βH-42→βL+1	
					333.73	339.08	301.16	311.22		(FeCl) βH-3→βL+5 (CoCl) βH-12→βL (CuCl) βH-8→βL+4 (FeBr) αH-10→ αL+2	(FeCl, FeBr) n(Cl, Br)d(Fe)→π*(8hq) (CoCl) π(8hq)→ π*(8hq) (CuCl) σ(Cu-Cl)n(Cl)d(Cu)→ n(Cl)d(Cu)π*(8hq)
					377.36		346.24	312.72	363.8	(FeCl) βH-7→βL+3 (CuCl) βH-13→βL+1 (FeBr) βH-14→βL+3 (CoBr) βH-29→βL+2	(FeCl, CoBr) n(Cl,Br)d(Fe,Co)→n(Cl,Br)d(Fe, Co) (CuCl) σ(Cu-Cl)π(8hq→ π*(8hq) (FeBr) n(Br)d(Fe)→n(Br)π*(8hq)d(Fe)
					396.92			315.35		(FeCl) βH-5→βL+4 (FeBr) βH-12→βL+5	(FeCl) n(Cl)d(Fe)→n(Cl)d(Fe) (FeBr) n(Br)d(Fe)→n(Br)π*(8hq)d(Fe)
420	412	411	375	406	418.1	411.92	412.27	359.81		(FeCl, CoCl) βH-6→βL+1 (CuCl) αH-5→αL+2 (FeBr) αH-14→αL+4	(FeCl, CuCl) n(Cl)d(Fe, Cu)→π*(8hq) (CoCl) n(Cl)π(8hq)→ π*(8hq) (FeBr) σ(Fe-Br)→ n(Br)d(Fe)
								370.96		(FeBr) αH-14→ αL+3	(FeBr) σ(Fe-Br)→ n(Br)d(Fe)
								375.03	392.8	(FeBr) βH-7→ βL+6 (CoBr) βH-42→βL+1	(FeBr, CoBr) n(Br)d(Fe, Co) →n(Br)d(Fe, Co)
								376.34		(FeBr) αH-2→ αL+5	(FeBr) n(Br)d(Fe) → π*(8hq)d(Fe)
								402.01		(FeBr) αH-10→ αL+1	(FeBr) n(Br)d(Fe) →π*(8hq)
537	520	502	460	549	510.04	496.13	500.53	452.33		(FeCl) βH-3→βL+1 (CoCl) αH→αL+5 (CuCl) αH→αL+4 (FeBr) β H-4→ βL+2	(FeCl) n(Cl)d(Fe)→π*(8hq) (CoCl) π(8hq)→ π*(8hq) (CuCl) n(Cl)π(8hq)d(Cu)→ π*(8hq) (FeBr) n(Br)n(8hq-OH)d(Fe)→ π*(8hq)
						505.34	506.53	464.17		(CoCl) αH-10→αL (CuCl) αH-9→αL (FeBr) αH-15→ αL	(CoCl) σ(Co-Cl)→ n(Cl)π*(8hq)d(Co) (CuCl) σ(Cu-Cl)n(Cl)d(Cu)→ n(Cl)π*(8hq)d(Cu) (FeBr) π (8hq)→π*(8hq)
						516.94		466.02		(CoCl) βH-4→βL (FeBr) βH-3→βL+3	(CoCl) n(Cl)d(Co)→ π*(8hq) (FeBr) n(Br)d(Fe)→ n(Br)π*(8hq)d(Fe)
619	624	576	542	661	618.63	625.77	579.45	540.05	673.1	(FeCl) βH-3→βL+6 (CoCl) αH-4→αL+1 (CuCl) αH-9→αL (FeBr) αH-8→ αL+3 (CoBr)βH-6→βL+4	(FeCl, FeBr) n(Cl, Br)d(Fe)→n(Cl,Br)d(Fe) (CoCl) n(Cl)d(Co)→ π*(8hq)d(Co) (CuCl) σ(Cu-Cl)n(Cl)d(Cu)→ n(Cl)π*(8hq)d(Cu) (CoBr) d(Co)n(Br)→π*(8hq)
						647.73		541.7		(CoCl) αH-7→αL	(CoCl) σ(Co-Cl)n(Cl)d(Co)→ n(Cl)π*(8hq)d(Co)
								565.62		(FeBr) αH-8→αL+1	(FeBr) π(8hq)→π*(8hq)

λmax (nm)										The most important orbitals involved in electronic transitions	Character of transition
Experimental					Calculated						
FeCl	CoCl	CuCl	FeBr	CoBr	FeCl	CoCl	CuCl	FeBr	CoBr		
693	694	720	632	734	690.95	671.8	739.69	630.41		(FeCl) βH→βL+3 (CoCl) αH-3→αL+1 (CuCl) αH-6→αL+1 (FeBr) αH-3→αL+1	(FeCl) n(Cl-)π(8hq)→n(Cl)d(Fe) (CoCl, CuCl) n(Cl)d(Co, Cu)→ π*(8hq)d(Co, Cu) (FeBr) n(Br)d(Fe)→ π*(8hq)
								636.82		(FeBr) βH-3→ βL+1	(FeBr) n(Br)d(Fe)→ π*(8hq)
			716					728.98		(FeBr) βH→ βL+6	(FeBr) n(Br)d(Fe)→ n(Br)d(Fe)
753	788	795	795		729.16	768.17	796.52	795.18		(FeCl) αH-3→αL (CoCl) αH→αL+4 (CuCl) βH→βL+1 (FeBr) αH→αL+1	(FeCl, CuCl) n(Cl)d(Fe, Cu)→ π*(8hq) (CoCl) π*(8hq)→π*(8hq)d(Co) (FeBr) n(Br)d(Fe)→π*(8hq)
					761.28	810.63				(FeCl) αH-1→αL+1 (CoCl) αH-5→αL	(FeCl) n(Cl-)→ π*(8hq) (CoCl)n(Cl)d(Co)→ π*(8hq)n(Cl)d(Co)

Used abbreviations: d – d orbital, n – non-bonding orbital, σ - σ orbital, π - π orbital, * - an antibonding orbital.

Table S7. The most important electronic transitions for the chloride compounds containing the closed-shell coordination centers. H letter indicates HOMO, L - LUMO, α – α orbitals, β - β orbitals, and +/-(number) represents subsequent orbitals below HOMO and above LUMO, respectively.

λmax (nm)																The most important orbitals involved in electronic transitions	Character of transition
Experimental								Calculated									
ZnCl	CdCl	SnCl(2)	SnCl(1)	HgCl(1)	HgCl(2)	PbCl	BiCl	ZnCl	CdCl	SnCl(2)	SnCl(1)	HgCl(1)	HgCl(2)	PbCl	BiCl		
248	250	250	238	250	239	270	238	219.26	225.31	228.05		209.73		229.08		(ZnCl) H-22→L (CdCl) H-10→L+6 (SnCl(2)) H-22→L+4 (HgCl(1)) H-6 → L+9 (PbCl)H-41→L	(ZnCl, PbCl) π(8hq) → n(Cl)π*(8hq) (CdCl) σ(8hq-NH)n(Cl)d(Cd)→σ*(8hq) (SnCl(2)) n(Cl)n(8hq-OH)n(H_2O)→ π/π*(8hq) (HgCl(1)) n(Cl)→ complex(8hq)
								225.57	225.98	246.02		221.23		246.49		(ZnCl) H-16 →L+1 (CdCl) H-11→L+4 (SnCl(2))H-14→L+5 (HgCl(1)) H-16→L (PbCl) H-30→L+5	(ZnCl) d(Zn) → π (8hq-OH-ring)π*(8hq-N-ring) (CdCl) σ(Cd-Cl)π(8hq1)→ π*(8hq2)

λmax (nm)																	The most important orbitals involved in electronic transitions	Character of transition
Experimental								Calculated										
ZnCl	CdCl	SnCl(2)	SnCl(1)	HgCl(1)	HgCl(2)	PbCl	BiCl	ZnCl	CdCl	SnCl(2)	SnCl(1)	HgCl(1)	HgCl(2)	PbCl	BiCl			
																		(SnCl(2), PbCl) n(Cl)→ π/π*(8hq) (HgCl(1)) π(8hq)→n(Cl)π*(8hq)
								226.76	228.15	281.07		227.94	222.9 *223.34 230.67	273.19	241.83	(ZnCl) H-11→L+4 (CdCl, HgCl(1)) H-14→L+2 (SnCl(2)), BiCl) H-28→L+1 (PbCl) H-19→L+11 (HgCl(2)) H-34→L+3 *(HgCl(2)) H-6→L+13 (HgCl(2)) H-24→L+7	(ZnCl, CdCl, HgCl(1), HgCl(2)) π(8hq) →π*(8hq) (SnCl(2)) π(8hq)→π/π*(8hq) (PbCl) n(Cl)d(Pb)→σ*(Pb-Cl) (BiCl) n(8hq-OH)π(8hq)→ π/π*(8hq) *(HgCl(2)) n(Cl)→ σ*(Hg-Cl)
								229.88	242.62		213.21	231.19 242.55			284.83	(ZnCl, HgCl(1)) H-14→L+2 (CdCl, HgCl(1)) H-13→L+3 (BiCl) H-30→L (SnCl(1)) H-20→L+3	(ZnCl, CdCl, SnCl(1), HgCl(1)) π(8hq)→π*(8hq) (BiCl) π(8hq)→σ*(Bi-Cl)π /π*(8hq)
								243.92	273.05				231.21			(ZnCl) H-12→L+3 (HgCl(2)) H-19 → L+7	(ZnCl) σ(Zn-Cl)→ π*(8hq) (HgCl(2)) n(Cl)→π*(8hq)
								274.21			227.13	274.08	274.84			(ZnCl) H-15→L (SnCl(1)) H-24→L (HgCl(2)) H → L+10	(ZnCl) π(8hq) → n(Cl)π*(8hq) (SnCl(1)) π(8hq)→ n(Cl)n(8hq-OH)π/π*(8hq) (HgCl(2)) n(Cl)→n(Hg)
313	335	333	339	319	308	353	329	294.67	303.91	339.42	339.8	301.77	344.51	356.92	313.96	(ZnCl, HgCl) H-14→L+1 (CdCl) H-7→L+5 (HgCl(2)) H-30→L (SnCl(2)) H-1→L+5 (SnCl(1)) H-19→L+1 (PbCl) H-11→L+10 (BiCl) H-10→L+9	(ZnCl, SnCl(2), SnCl(1)) π(8hq)→π/π*(8hq) (CdCl) n(Cl)d(Cd)→π*(8hq) (HgCl(1) π(8hq) →π*(8hq) (HgCl(2)) n(Cl)d(Hg) → n(Cl) (PbCl) n(Cl)→σ*(Pb-Cl) (BiCl) n(Cl)→ π*(8hq)
								344.92	344.64	340.93		311.37			353.25	(ZnCl) H-12→L+1 (CdCl) H-13→L+1	(ZnCl) σ(Zn-Cl) → π (8hq-OH-ring) /π*(8hq-N-ring)

λmax (nm)																	The most important orbitals involved in electronic transitions	Character of transition
Experimental								Calculated										
ZnCl	CdCl	SnCl(2)	SnCl(1)	HgCl(1)	HgCl(2)	PbCl	BiCl	ZnCl	CdCl	SnCl(2)	SnCl(1)	HgCl(1)	HgCl(2)	PbCl	BiCl			
																	(SnCl(2)) H-24→L+1 (BiCl) H-23→L (HgCl) H-7→L+5	(CdCl, SnCl(2)) π(8hq) → π/π*(8hq) (HgCl) n(Cl) → π*(8hq) (BiCl) σ(Bi-Cl)n(Cl)→π /π*(8hq)σ*(Bi-Cl)
372	421	418	423	365	360	407	417	402.95	423.12	379.27	390.47	356.83	353.45	395.76	414.93		(ZnCl) H-11→L+1 (CdCl) H-8→L+2 (SnCl(2)) H-1→L+4 (SnCl(1)) H-19→L (BiCl) H-10→L+5 (PbCl) H-11→L+7 (HgCl(1)) H-13→L+1 (HgCl(2)) H-31→ L+1	(ZnCl) π(8hq) → π (8hq-OH-ring) /π*(8hq-N-ring) (CdCl) n(Cl)d(Cd)→π*(8hq) (SnCl(2)) π(8hq) → π/π*(8hq) (SnCl(1)) π(8hq)→n(Cl)n(8hq-OH)π/π*(8hq) (PbCl) n(Cl)→σ*(Pb-Cl) (HgCl(1)) π(8hq)→π*(8hq) (HgCl(2)) σ(Hg-Cl)→n(Cl) (BiCl) n(Cl)→π*(8hq)
									428.61	383.75				425.71			(CdCl) H-11→L (SnCl(2)) H→L+5 (PbCl) H→L+12	(CdCl) σ(Cd-Cl)π(8hq)→n(Cl)π/π*(8hq) (SnCl(2)) n(Cl)π(8hq)→π/π*(8hq) (PbCl) n(Cl)π(8hq)→π*(8hq)
										427.87							(SnCl(2)) H-16→L	(SnCl(2)) n(Cl)π(8hq)→π/π*(8hq)
427	510	512	520	428	407	504	513	430.1	502.94	491.71	478.84	426.85	444.14	523.31	533.38		(ZnCl) H-11→L (CdCl) H-7→L+2 (SnCl(2)) H→L+3 (SnCl(1)) H-14→L (HgCl(1)) H-11→L+1 (HgCl(2)) H-32→L	(ZnCl) π(8hq) → n(Cl)π*(8hq) (CdCl) n(Cl)d(Cd)→π*(8hq) (SnCl(2)) n(Cl)π(8Hq)→π*(8hq) (SnCl(1)) π(8hq)→n(Cl)n(8hq-OH)π/π*(8hq) (HgCl(1)) σ(Hg-Cl)π(8hq)→π*(8hq) (HgCl(2)) σ(Hg-Cl)→ n(Cl)
										511.72		435.31					(SnCl(2)) H-6→L (HgCl(1)) H-11→L	(SnCl(2)) n(Cl)→π/π*(8hq) (HgCl(1)) σ(Hg-Cl)π(8hq)→n(Cl)π*(8hq)
490	596	576	600	507	502	600	579	503.77	600.75			470.5	526.49	634.8			(ZnCl) H-5→L+3 (CdCl) H-4→L+2 (HgCl(1)) H-7→L+3	(ZnCl, CdCl) n(Cl)d(Zn,Cd) → π*(8hq) (HgCl(1)) n(Cl) →π*(8hq)

λmax (nm)																The most important orbitals involved in electronic transitions	Character of transition
Experimental								Calculated									
ZnCl	CdCl	SnCl(2)	SnCl(1)	HgCl(1)	HgCl(2)	PbCl	BiCl	ZnCl	CdCl	SnCl(2)	SnCl(1)	HgCl(1)	HgCl(2)	PbCl	BiCl		
																(PbCl) H-15→L (HgCl(2)) H-22→L	(HgCl(2)) σ(Hg-Cl)n(Cl)→n(Cl) (PbCl) n(Cl) →n(Cl)π*(8hq)
													539.7			(HgCl(2)) H-22→L+1	(HgCl(2)) σ(Hg-Cl)n(Cl)→n(Cl)
542	681	644			623	691	643	579.77	700.77				631.94	672.58		(ZnCl) H-5→L+2 (CdCl) H-9→L+1 (PbCl) H-1→L+7 (HgCl(2)) H-22→L+1	(ZnCl) n(Cl)d(Zn) → π*(8hq) (CdCl) n(Cl)d(Cd) →π/ π*(8hq) (PbCl) n(Cl)→σ*(Pb-Cl) (HgCl(2))σ(Hg-Cl)n(Cl)→n(Cl)
680		756	737		683	771	719	695.06					676.89	759.78	691.6	(ZnCl) H-9→L (PbCl) H→L+6 (BiCl) H-14→L (HgCl(2)) H-21+L	(ZnCl) n(Cl)d(Zn) →n(Cl)π*(8hq) (PbCl) n(Cl)π(8hq) →π*(8hq) (BiCl) n(Cl)→σ*(Bi-Cl)π /π*(8hq) (HgCl(2)) n(Cl)→n(Cl)
767								728.03								(ZnCl) H-8→L	(ZnCl) n(Cl)d(Zn) →n(Cl)π*(8hq)

Used abbreviations: d – d orbital, n – non-bonding orbital, σ - σ orbital, π - π orbital, poly – orbital belonging to inorganic polymer chain, stack – orbital associated with the 8Hq stacked system,* - an antibonding orbital.

Table S8. The most important electronic transitions for the bromide compounds containing the close-shell coordination centers. H letter indicates HOMO, L - LUMO, α – α orbitals, β - β orbitals, and +/-(number) represents subsequent orbitals below HOMO and above LUMO, respectively.

λmax (nm)										The most important orbitals involved in electronic transitions	Character of transition
Experimental					Calculated						
CdBr	ZnBr	SnBr	HgBr	PbBr	CdBr	ZnBr	SnBr	HgBr	PbBr		
241	244	229	238	225	223.22	209.47	228.52	226.32	227.24	(CdBr) H-14 → L+2 (ZnBr) H-17 → L (SnBr) H-23→ L (HgBr) H-17→L (PbBr) H-14 → L+15	(CdBr) π(8hq)→π*(8hq) (ZnBr) π(8hq)→ π /π*(8hq) (SnBr) n(8hq-OH)n(8hq-N)π(8hq)→ n(Br)n(8hq-OH)π*(8hq) (HgBr) π(8hq)→n(Br)π*(8hq) (PbBr) n(Br)→complex(8hq)
					228.74	215.18	229.2	229.07		(CdBr) H-8 → L+7	(CdBr) n(Br)→σ*(8hq-OH)

λmax (nm)										The most important orbitals involved in electronic transitions	Character of transition
Experimental					Calculated						
CdBr	ZnBr	SnBr	HgBr	PbBr	CdBr	ZnBr	SnBr	HgBr	PbBr		
										(ZnBr) H-3 → L+12 (SnBr) H-14→L+4 (HgBr) H-11→L+4	(ZnBr) n(Br)d(Zn)→ π*(8hq) (SnBr) n(8hq-OH)π(8hq)→ n(8hq-OH)π*(8hq) (HgBr) π(8hq)→π*(8hq)
					229.52	223.30	231.7	230.81		(CdBr) H-15 → L+1 (ZnBr) H-14 → L+1 (SnBr) H-18→L+3 (HgBr) H-6→L+10	(CdBr) π(8hq)→π*(8hq) (ZnBr) n(8hq-OH)π(8hq)→ π*(8hq)n(Br) (SnBr) n(8hq-OH)n(8hq-N)π(8hq)→ π*(8hq) (HgBr) n(Br)d(Hg)→σ*(8hq)
					245.3	229.61	238	236.67		(CdBr) H-13 → L+3 (ZnBr) H-3 → L+10 (SnBr) H-22 → L (HgBr) H-2 → L+11	(CdBr) π(8hq)→π*(8hq) (ZnBr) n(Br)d(Zn)→ π*(8hq) (SnBr) n(8hq-OH)π(8hq)→ n(8hq-OH)π*(8hq) (HgBr) n(Br)d(Hg)→σ*(8hq)
					272.04	245.19	260.1	253.64		(CdBr) H-15 → L+1 (ZnBr) H-12 → L+3 (SnBr) H → L+11 (HgBr) H-12→L+3	(CdBr, HgBr) π(8hq)→π*(8hq) (ZnBr) π(8hq)n(8hq-N)→π*(8hq) (SnBr) n(Br)→n(H_2O-OH)π*(8hq)
					296.79	252.97		254.44	254.2	(CdBr) H-14 → L (ZnBr) H-5 → L+7 (HgBr) H-12→L+3 (PbBr) H-14 → L+10	(CdBr) π(8hq)→n(Br)π/π*(8hq) (ZnBr) n(Br)d(Zn)n(8hq-N)→π*(8hq) (HgBr) π(8hq)→π*(8hq) (PbBr) n(Br)π(8hq)→σ*(Pb-Br)
					301.6	253.70		275.07		(CdBr) H-1 → L+7 (ZnBr) H-3 → L+8 (HgBr) H-14 → L+1	(CdBr) n(Br)→σ*(8hq-OH) (ZnBr) n(Br)d(Zn)→π*(8hq) (HgBr) π(8hq)→π/π*(8hq)
338	324	315	324	298	348.75	308.01	314.41	355.44	267.92	(CdBr, HgBr) H-13 → L+1 (ZnBr) H-15→L (SnBr) H-7→L+7 (PbBr) H-36 → L+1	(CdBr, PbBr) π(8hq)→π*(8hq) (ZnBr) π(8hq)n(8hq-OH)→π/π*(8hq) (SnBr) n(Br)→ σ*(Sn-Br) (HgBr) σ(Hg-Br)→ π/π*(8hq)
					353.91	317.37	320.95		303.29	(CdBr) H-4→L+5 (ZnBr) H-11→L+1 (SnBr) H-6→L+7 (PbBr) H-23 → L+3	(CdBr) n(Br)→π*(8hq) (ZnBr) π(8hq)→π*(8hq)n(Br) (SnBr, PbBr) n(Br)→ σ*(Sn,Pb-Br)
					367.81	327.09	351.64			(CdBr) H-13→L	(CdBr) π(8hq)→n(Br)π/π*(8hq)

λmax (nm)										The most important orbitals involved in electronic transitions	Character of transition
Experimental					Calculated						
CdBr	ZnBr	SnBr	HgBr	PbBr	CdBr	ZnBr	SnBr	HgBr	PbBr		
										(ZnBr) H-4→L+5	(ZnBr) n(Br)d(Zn)→π*(8hq)
										(SnBr) H-18→L+1	(SnBr) n(8hq-OH)n(8hq-N)π(8hq)→n(8hq-OH)π/π*(8hq)
					409.92	331.90				(CdBr) H-11→L+1	(CdBr) σ(Cd-Br)π(8hq)→π*(8hq)
										(ZnBr) H-10→L+3	(ZnBr) σ(Zn-Br)n(Br)→π*(8hq)
										(CdBr) H-11→L	(CdBr) σ(Cd-Br)π(8hq)→ n(Br)π/π*(8hq)
					434.05	412.79	395.98		438.11	(ZnBr) H-6→L+3	(ZnBr) n(Br)d(Zn)n(8hq-N)→π*(8hq)
										(SnBr) H-15→L	(SnBr) σ(Sn-Br)n(Br)n(H_2O-OH)→ n(8hq-OH)π*(8hq)
421	426	416	411	411						(PbBr) H-10→L+5	(PbBr) n(Br)→ σ*(Pb-Br)π*(8hq)
										(CdBr) H-6→L+3	
					491.91	454.95	410.7	413.57		(ZnBr) H-4→L+3	(CdBr, HgBr) n(Br)→π*(8hq)
										(SnBr) H-14→L+1	(ZnBr) n(Br)d(Zn)→π*(8hq)
										(HgBr) H-9→L+3	(SnBr) n(8hq-OH)π(8hq) →π/ π*(8hq)n(8hq-OH)
										(CdBr) H-6→L+2	(CdBr) n(Br)→π*(8hq)
										(ZnBr) H-5→L+2	(ZnBr) n(Br)d(Zn)n(8hq-N)→π*(8hq)
					533.42	563.86	480.15	464.98	488.43	(SnBr) H-14→L	(SnBr) n(8hq-OH)π(8hq)→ n(8hq-OH)π*(8hq)
										(HgBr) H-11→L	(HgBr) π(8hq)→ n(Br)π*(8hq)
539	513	521	535	503						(PbBr) H-10→L+4	(PbBr) n(Br) → σ*(Pb-Br)π*(8hq)
										(SnBr) H-5→L+3	(SnBr) n(Br)→π*(8hq)
							518.73	522.05	520.38	(HgBr) H-6→L+3	(HgBr) n(Br)d(Hg)→ π*(8hq)
										(PbBr) H→L+12	(PbBr) n(Br)π(8hq) →π*(8hq)
							525.96			(SnBr) H-4→L+3	(SnBr) n(Br)→π*(8hq)
											(CdBr) n(Br)→π*(8hq)
										(CdBr, HgBr) H-4 → L+2	(ZnBr) n(Br)d(Zn)→π*(8hq)
631	623	632	641	622	623.93	592.49	628.54	674.59	590.66	(ZnBr) H-4→L+2	(SnBr) n(Br)→ n(8hq-OH)π /π*(8hq)
										(SnBr) H-11→L+1	(HgBr) n(Br)d(Hg)→π*(8hq)
										(PbBr) H-4 → L+8	(PbBr) n(Br) → σ*(Pb-Br)π*(8hq)
										(CdBr) H-10 → L	(CdBr) n(Br)→ n(Br)π/π*(8hq)
										(ZnBr) H-4→L+1	(ZnBr) n(Br)d(Zn)→ π*(8hq)n(Br)
705	727	700	701	716	732.73	751.04	708.17	680.03	727.40	(SnBr) H-12→L	(SnBr) n(Br)n(H_2O)→ n(8hq-OH)π*(8hq)
										(HgBr) H-10→L+1	(HgBr) σ(Hg-Br)d(Hg)→ π/π*(8hq)
										(PbBr) H-1 → L+10	(PbBr) n(Br)→σ*(Pb-Br)

Used abbreviations: d – d orbital, n – non-bonding orbital, σ - σ orbital, π - π orbital, * - an antibonding orbital.

3. Supplemental figures

XRPD pattern (Figure S1)

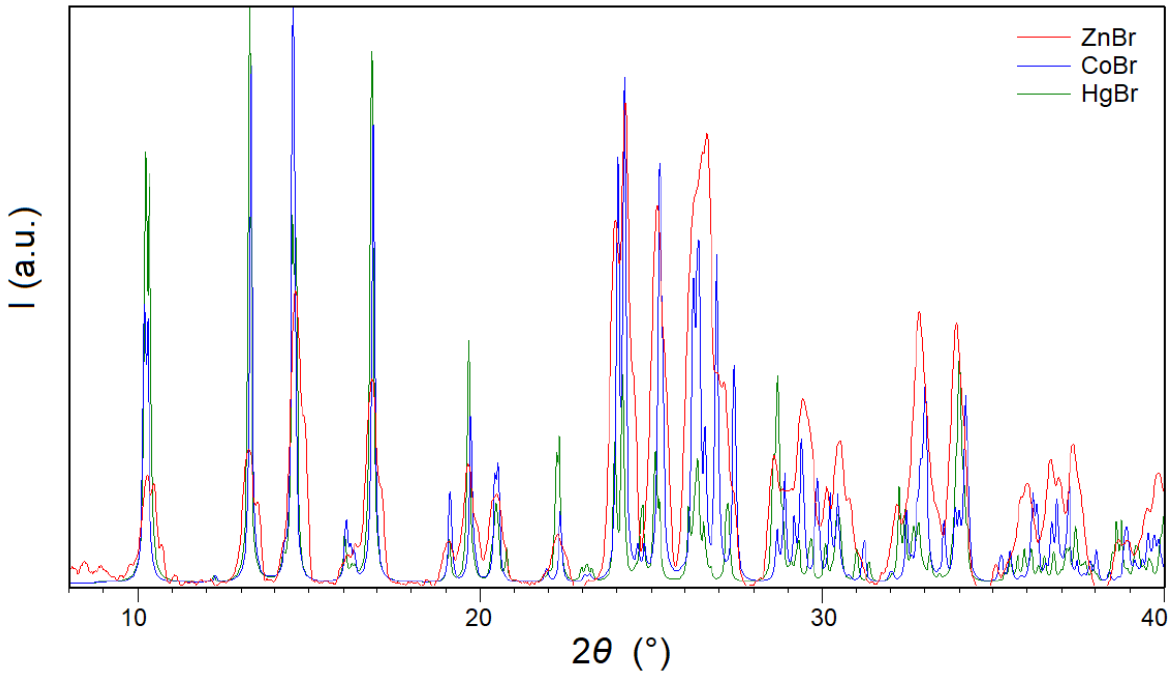


Figure S1. Experimental XRPD pattern of ZnBr (red) and theoretical XRPD patterns of CoBr (blue) and HgBr (green) generated in Mercury 2022.1.0 software based on CIF files of these compounds.

Molecular structures and intermolecular interactions (Figure S2-S18)

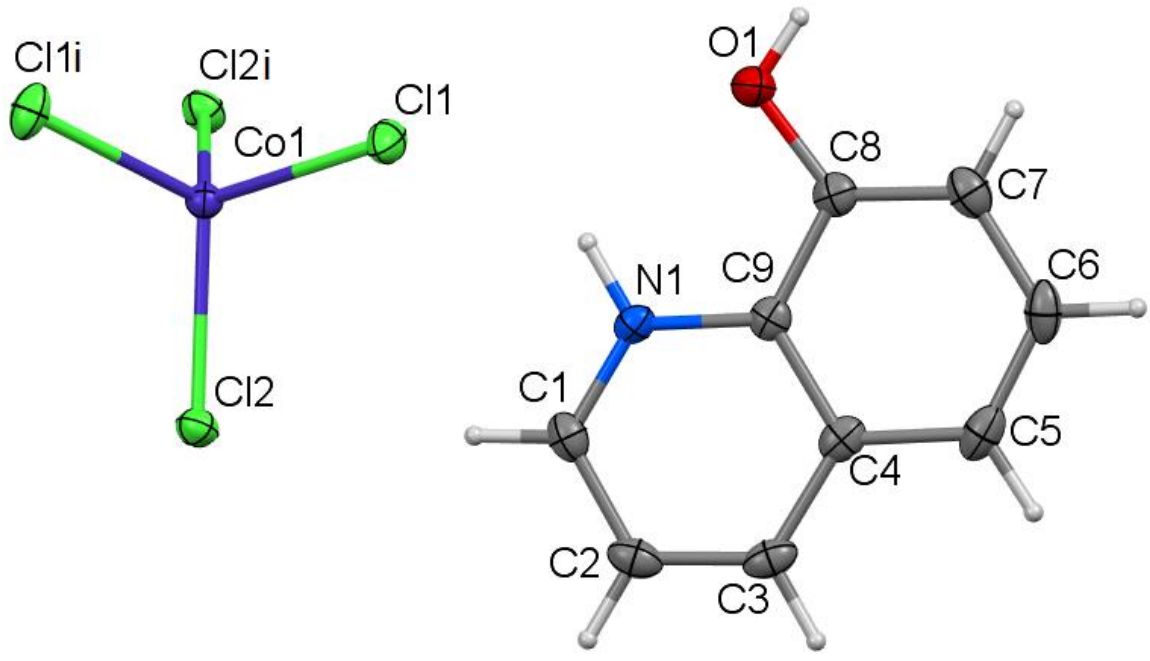


Figure S2. Molecular structure of CoCl. The equivalent atoms were generated according to symmetry transformations: (i) -x+1, y, -z+0.5.

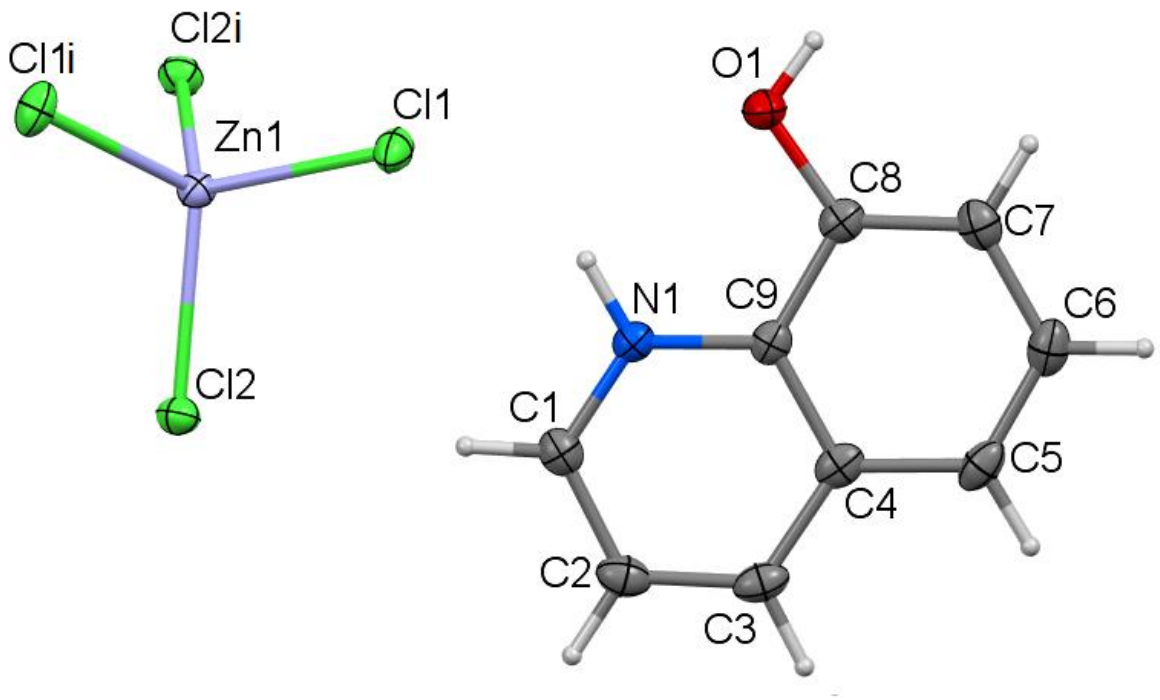


Figure S3. Molecular structure of ZnCl. The equivalent atoms were generated according to symmetry transformations: (i) -x+1, y, -z+0.5.

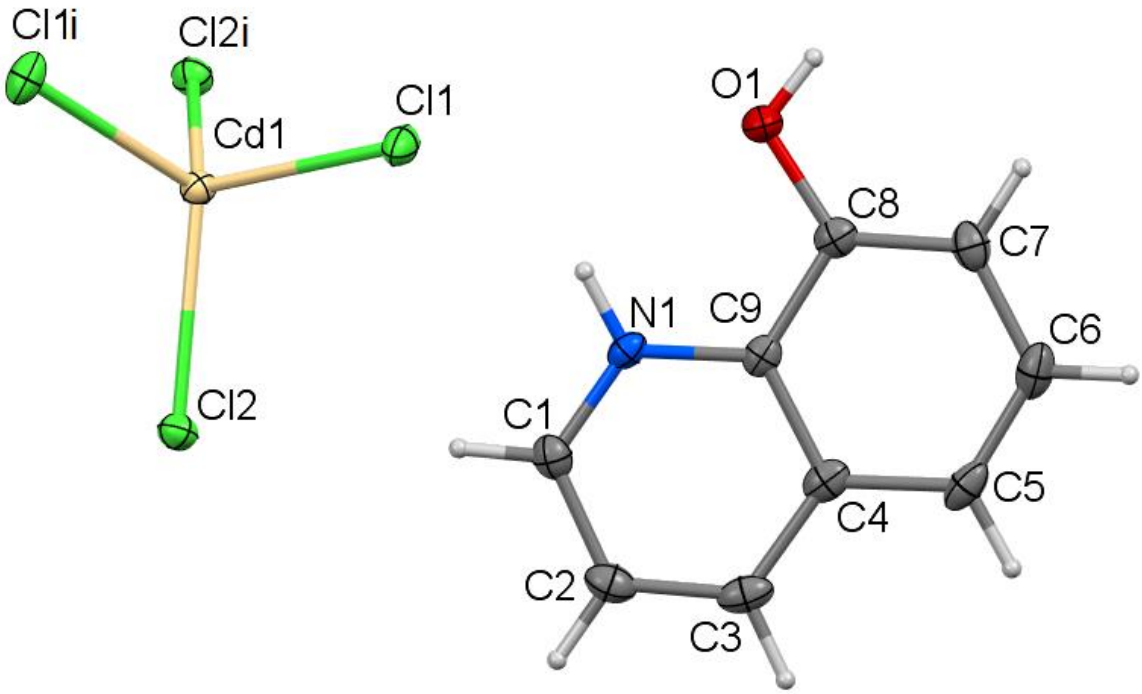


Figure S4. Molecular structure of CdCl. The equivalent atoms were generated according to symmetry transformations: (i) -x+1, y, -z+0.5.

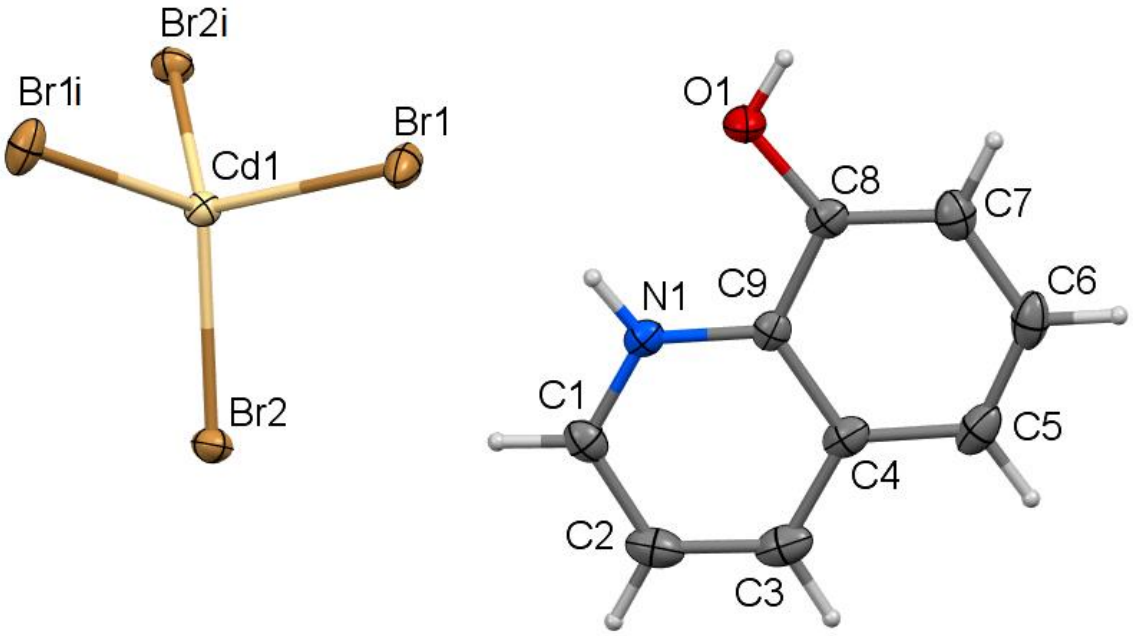


Figure S5. Molecular structure of CdBr. The equivalent atoms were generated according to symmetry transformations: (i) -x+1, y, -z+0.5.

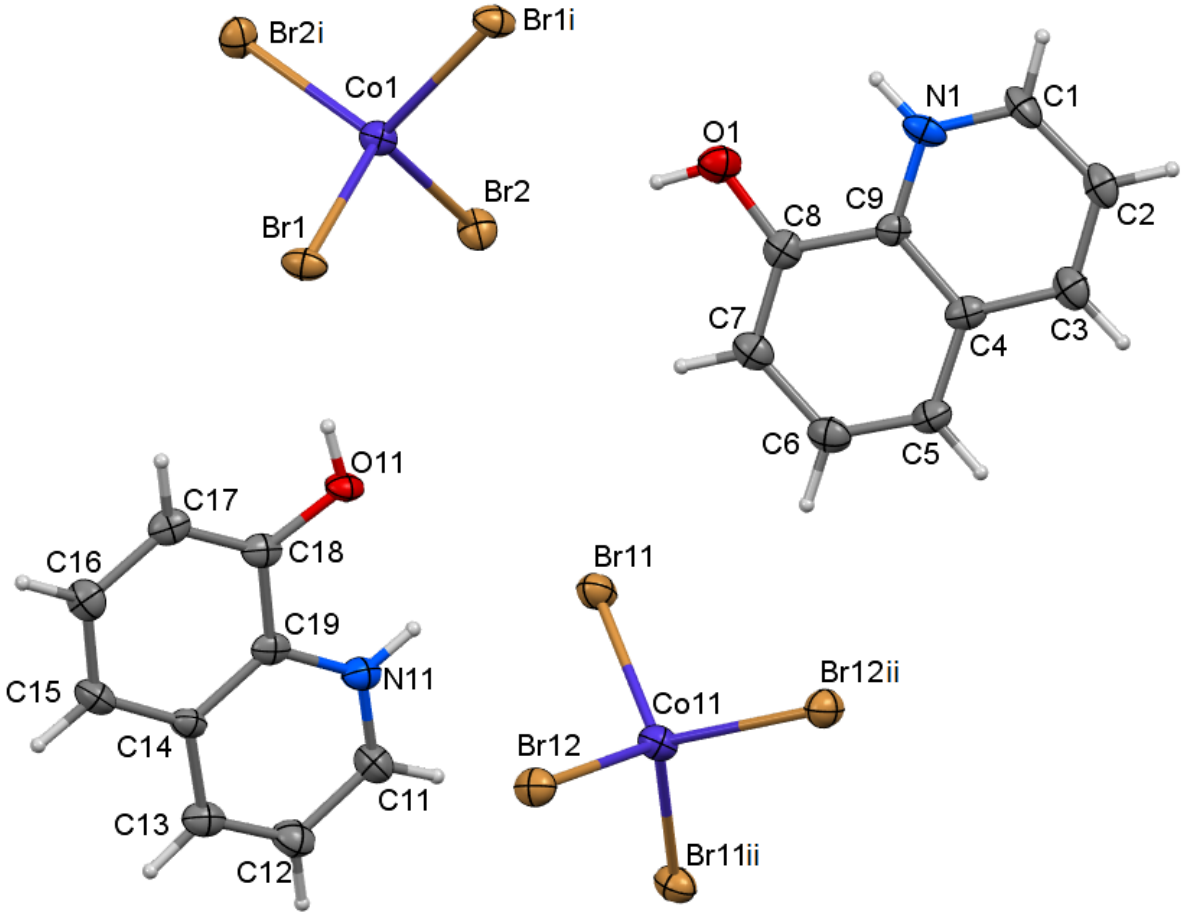


Figure S6. Molecular structure of CoBr. The equivalent atoms were generated according to symmetry transformations: (i) -x+0.5, y, -z+0.5; (ii) -x+1.5, y, -z+0.5

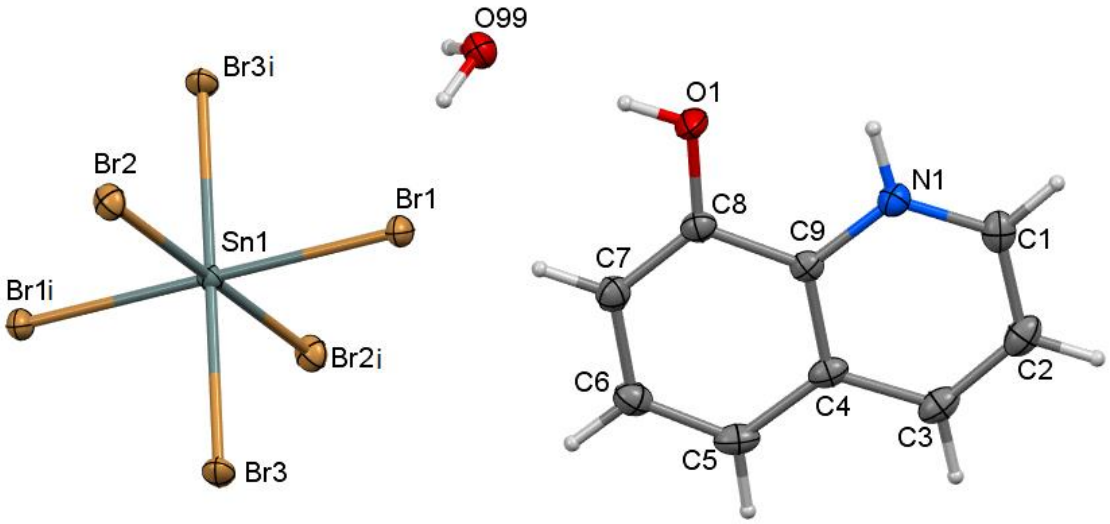


Figure S7. Molecular structure of SnBr. The equivalent atoms were generated according to symmetry transformations: (i) -x+1, -y, -z+1.

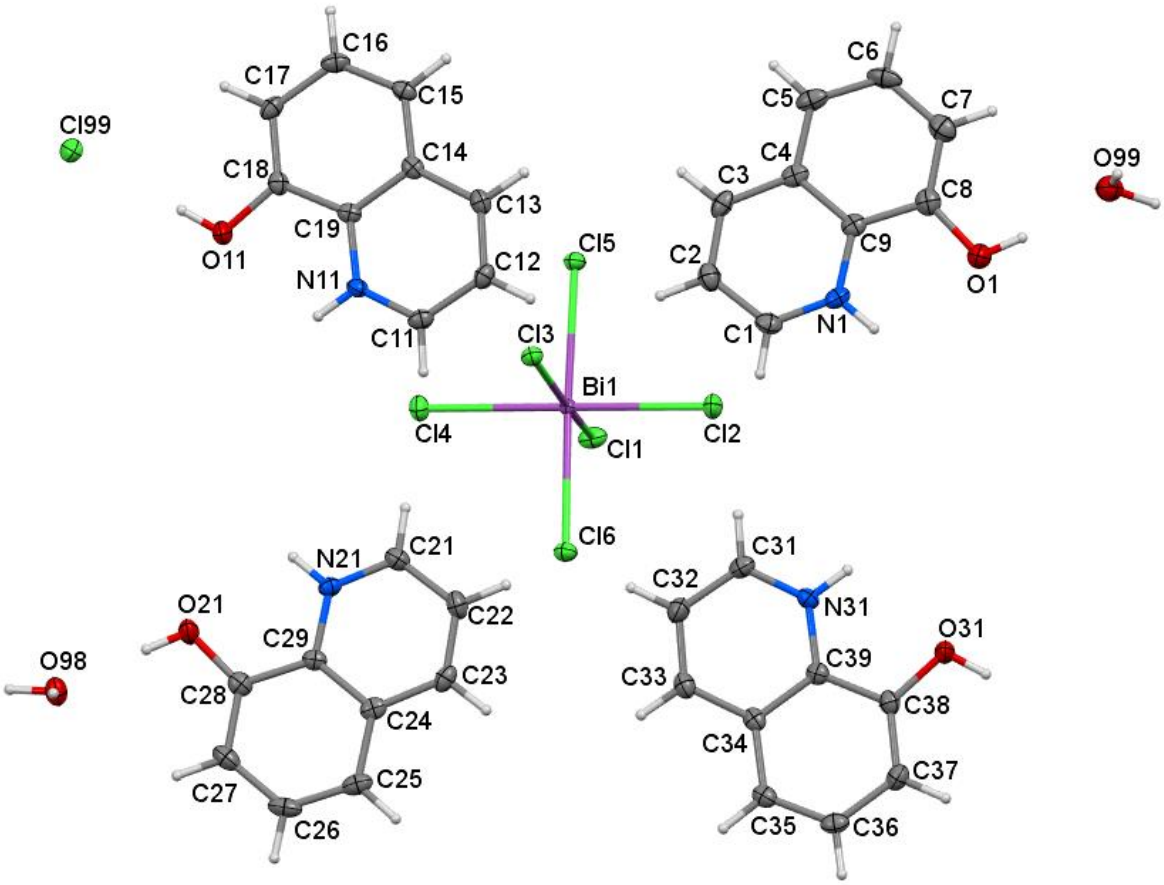


Figure S8. Molecular structure of BiCl.

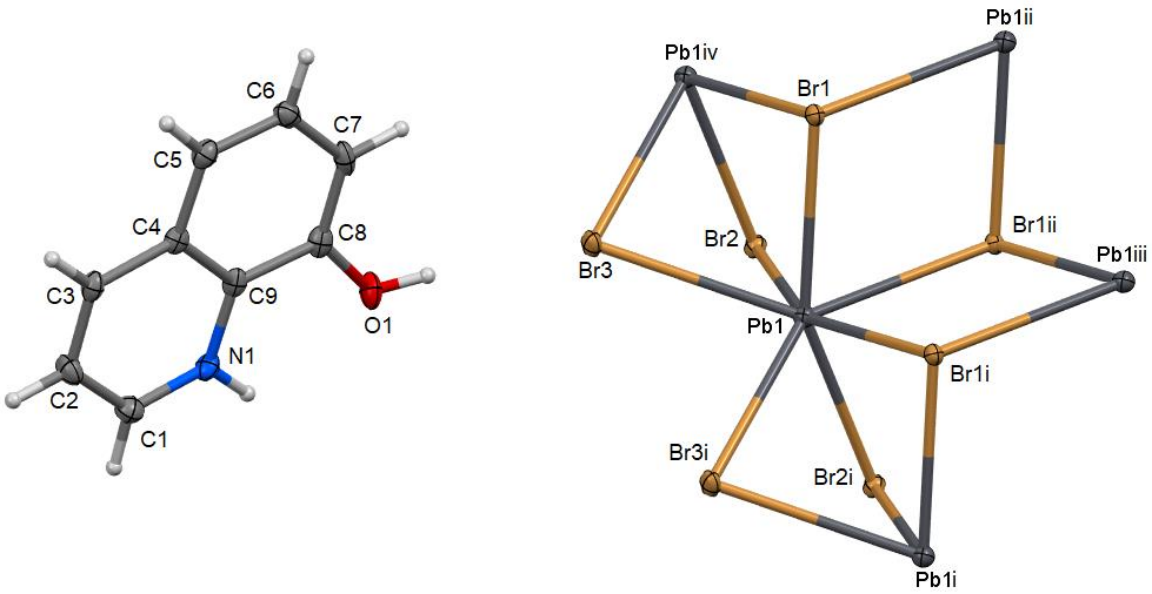


Figure S9. Molecular structure of PbBr. The equivalent atoms were generated according to symmetry transformations: (i) x+1, y, z; (ii) -x+1, -y+1, -z; (iii) -x+2, -y+1, -z; (iv) x-1, y, z

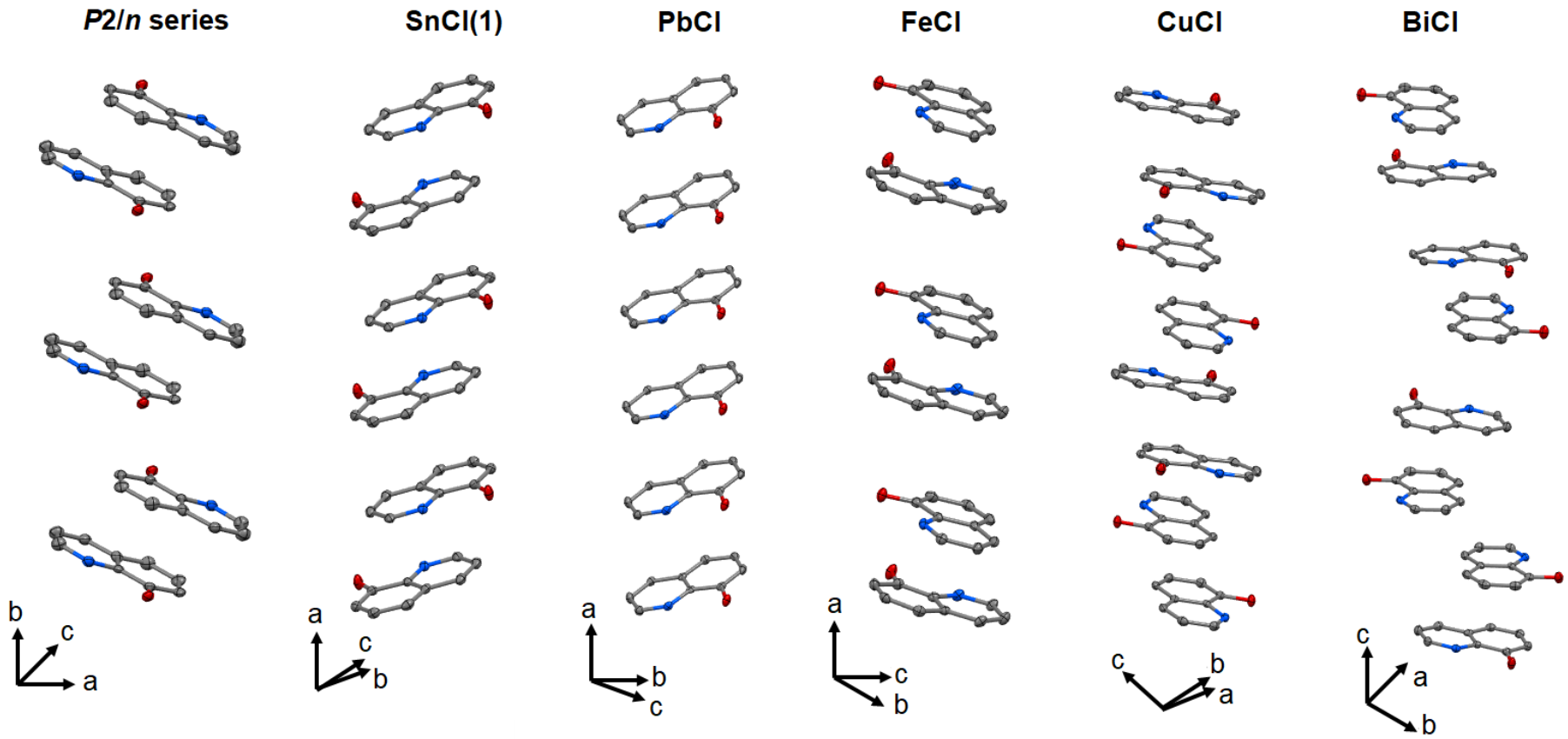


Figure S10. 8hqH^{+} stacks assembled according to different motifs of π-π interactions in the studied compounds.

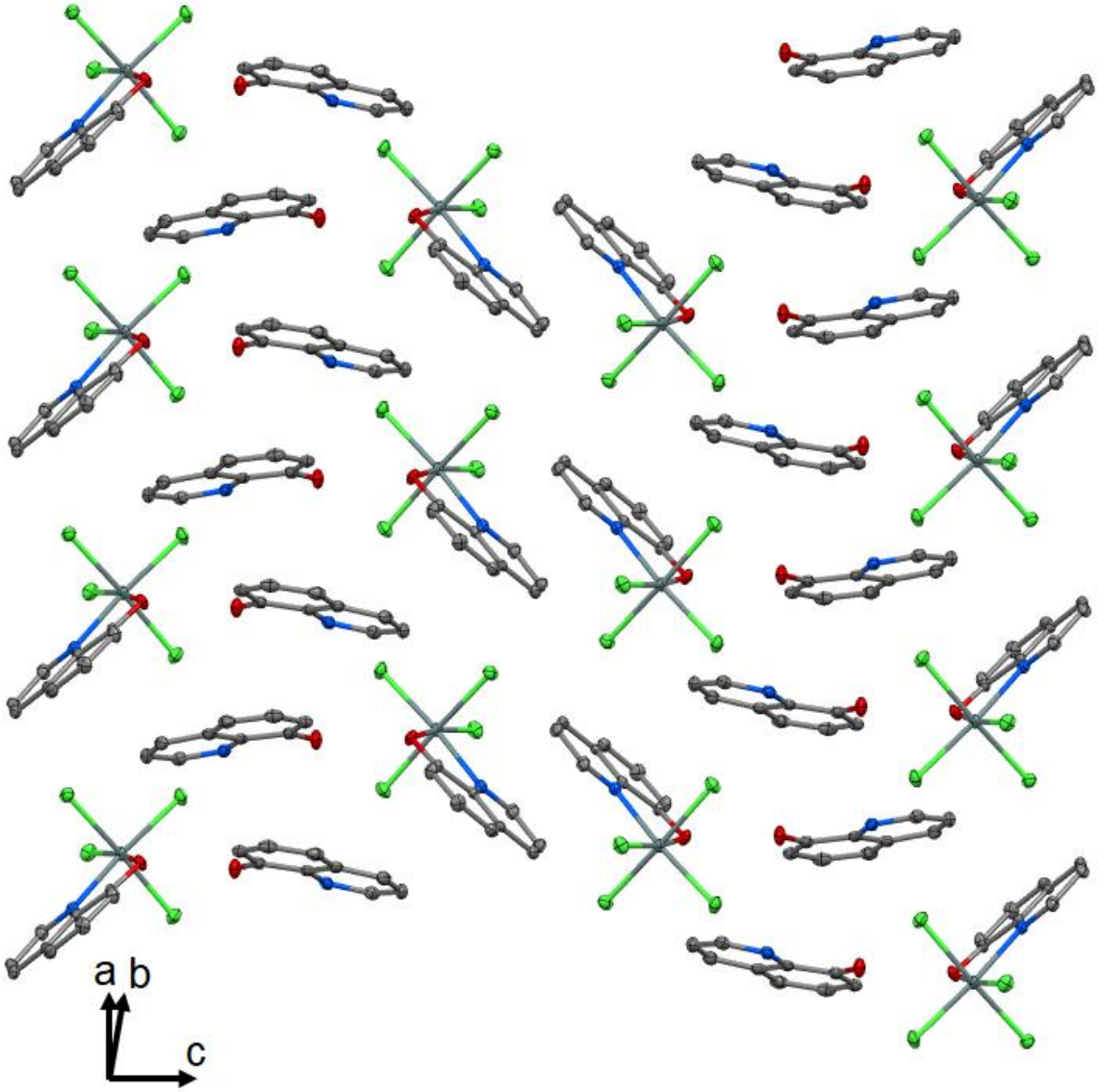


Figure S11. Molecular packing in SnCl(2) showing π-π interactions.

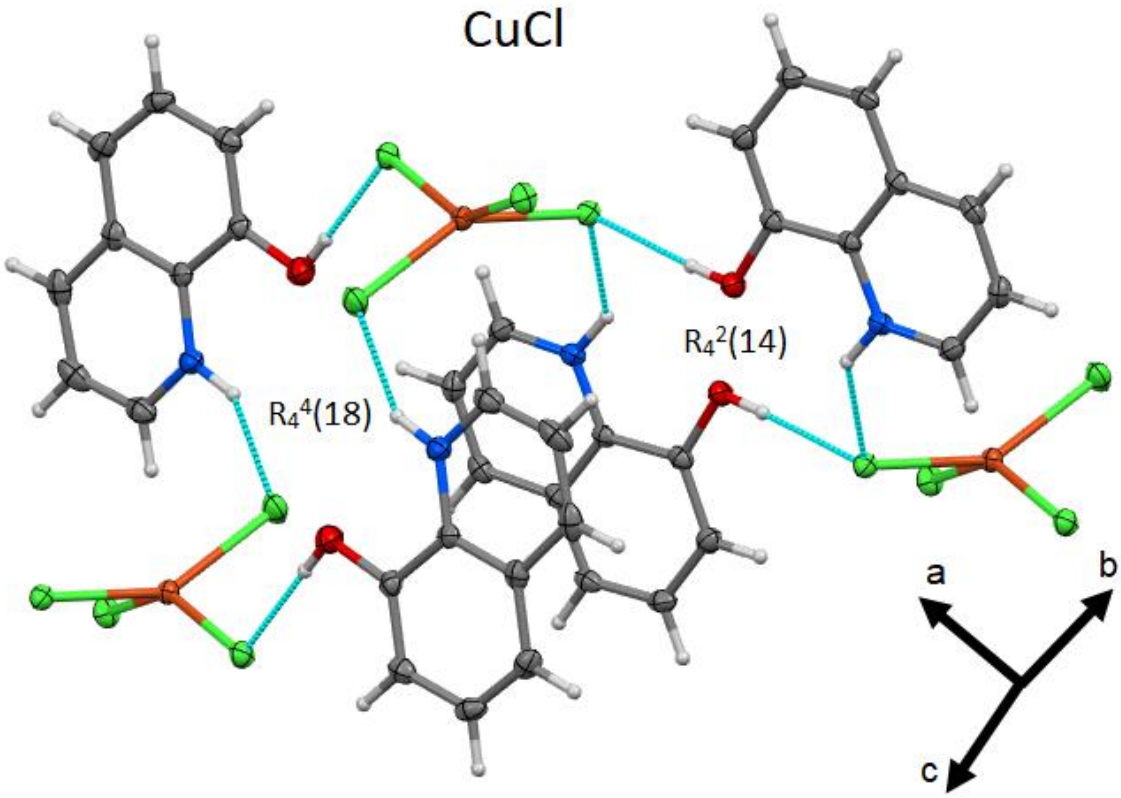


Figure S12. H-bond ring motifs in the structure of CuCl

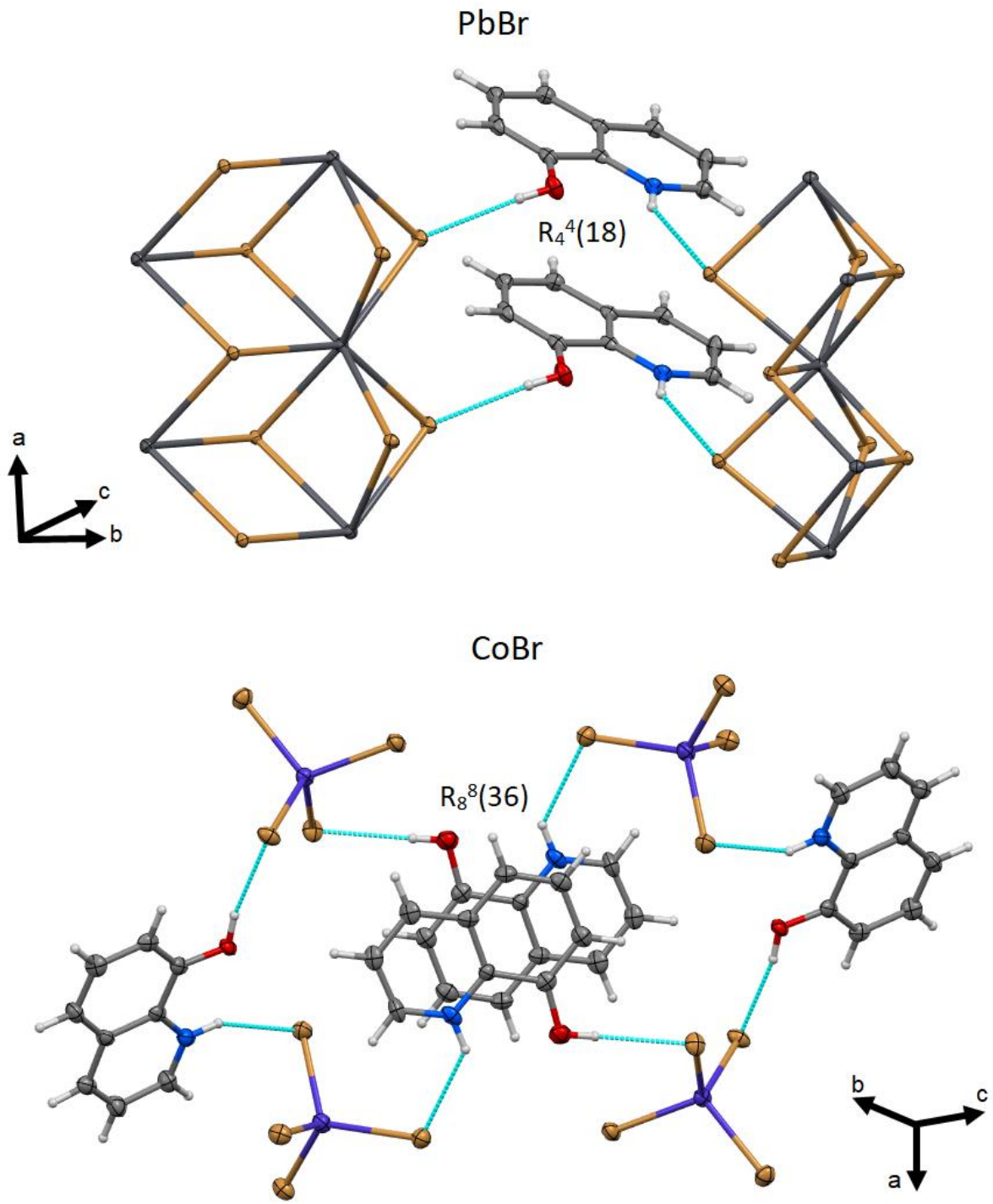


Figure S13. H-bond ring motifs in the structure of PbBr and CoBr

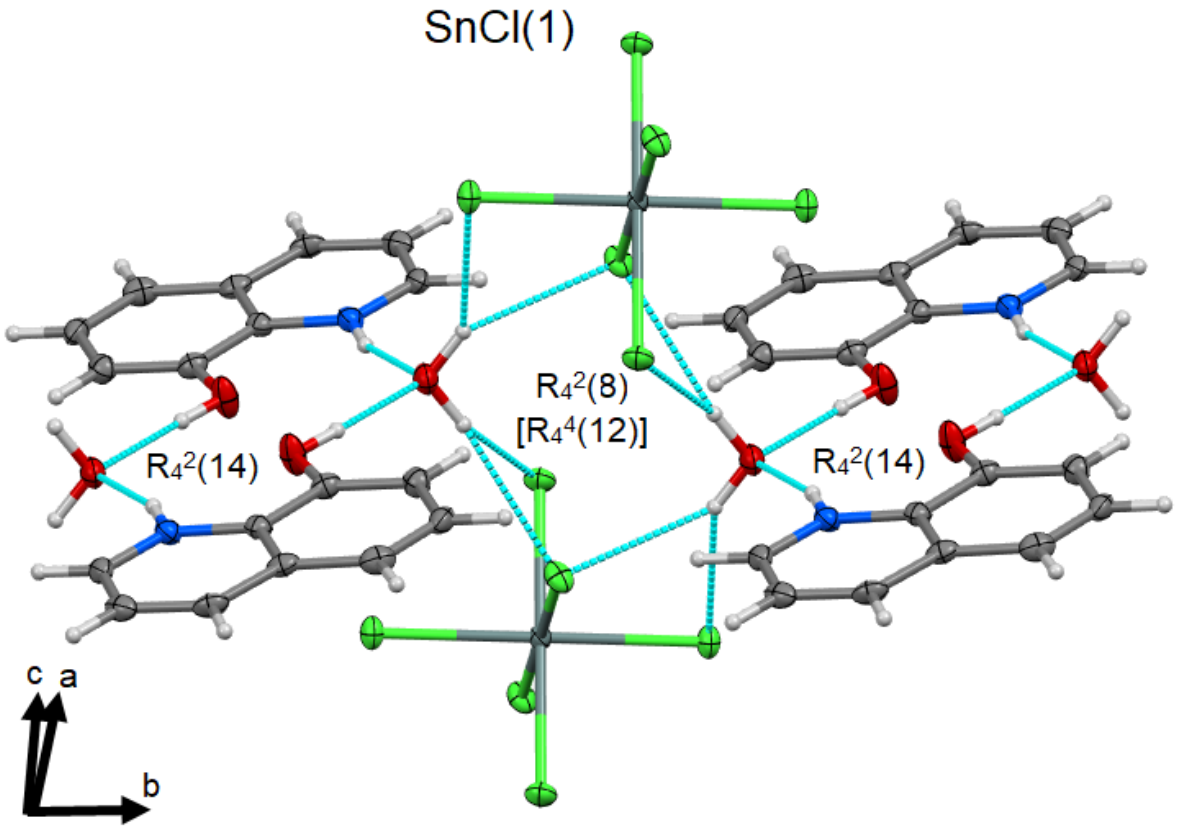


Figure S14. H-bond ring motifs in the structure of SnCl(1).

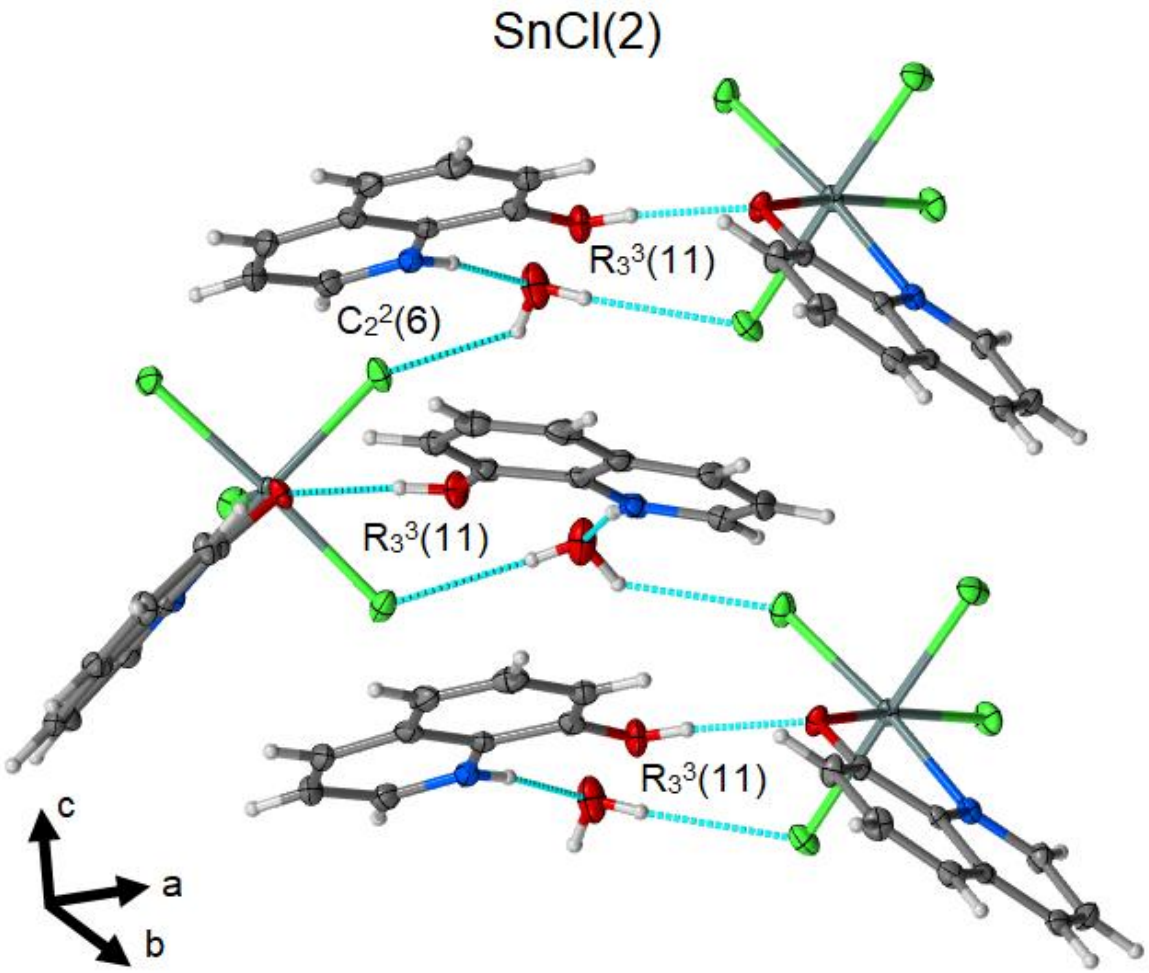


Figure S15. H-bond motifs in the structure of SnCl(2)

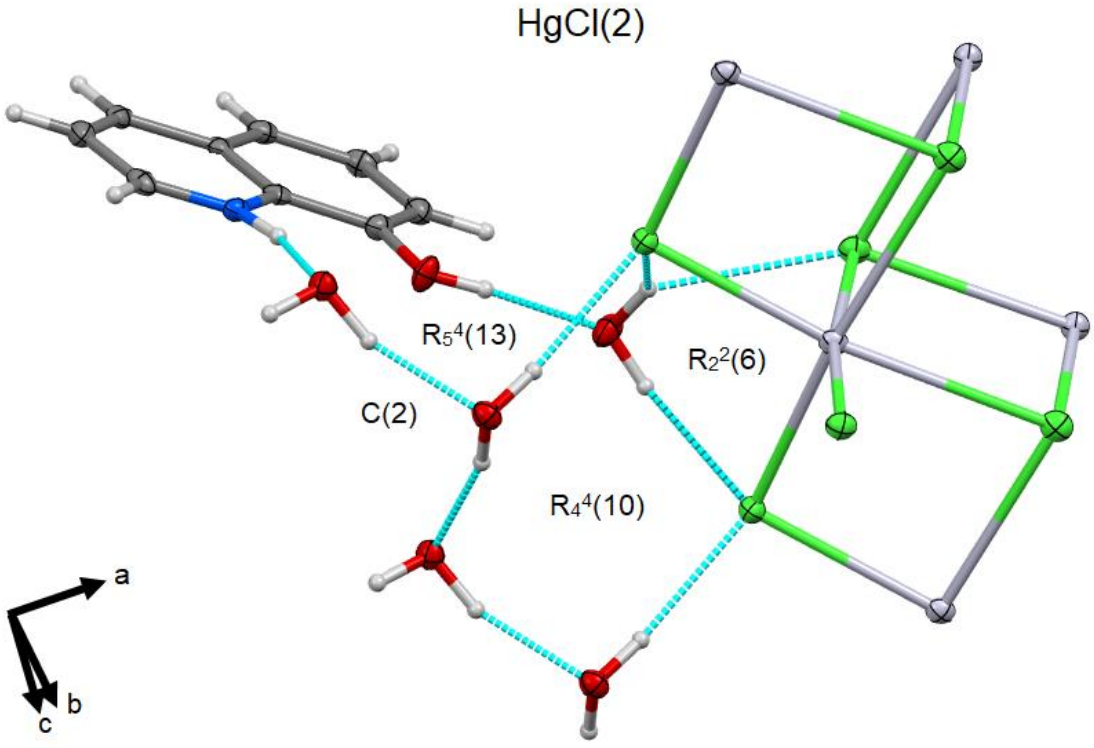


Figure S16. H-bond motifs in the structure of HgCl(2)

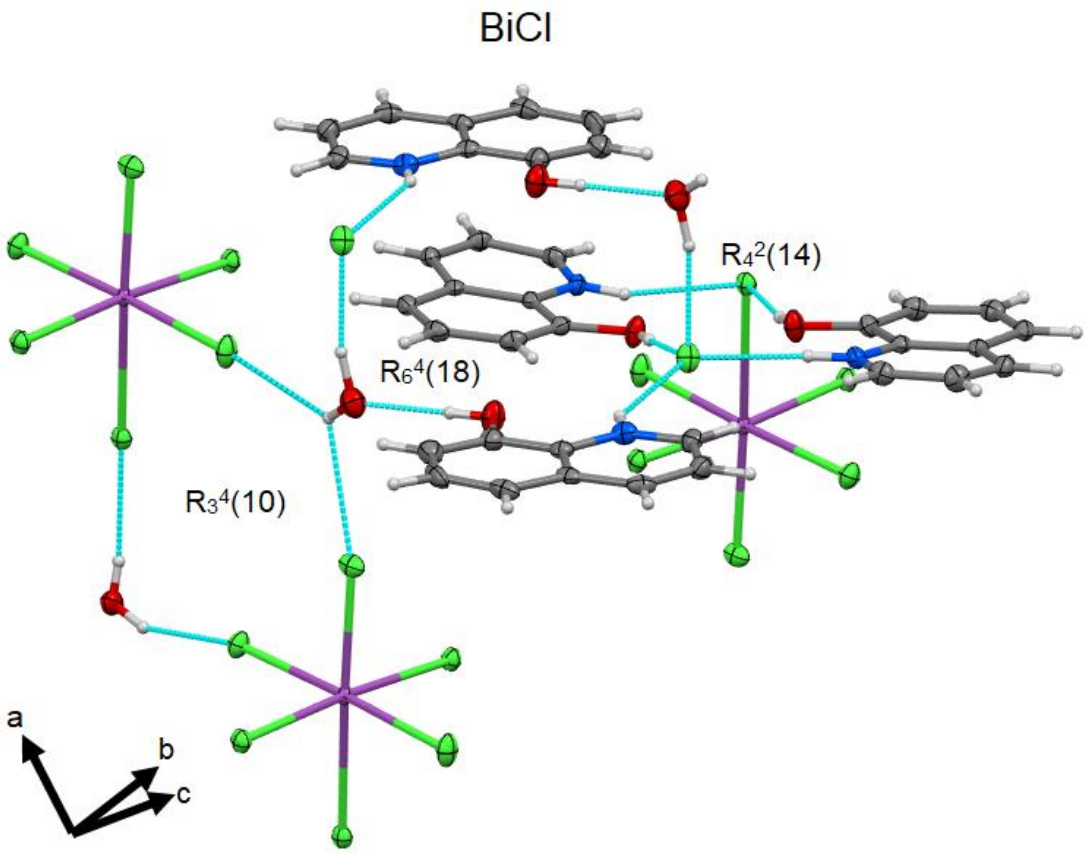


Figure S17. H-bond ring motifs in the structure of BiCl

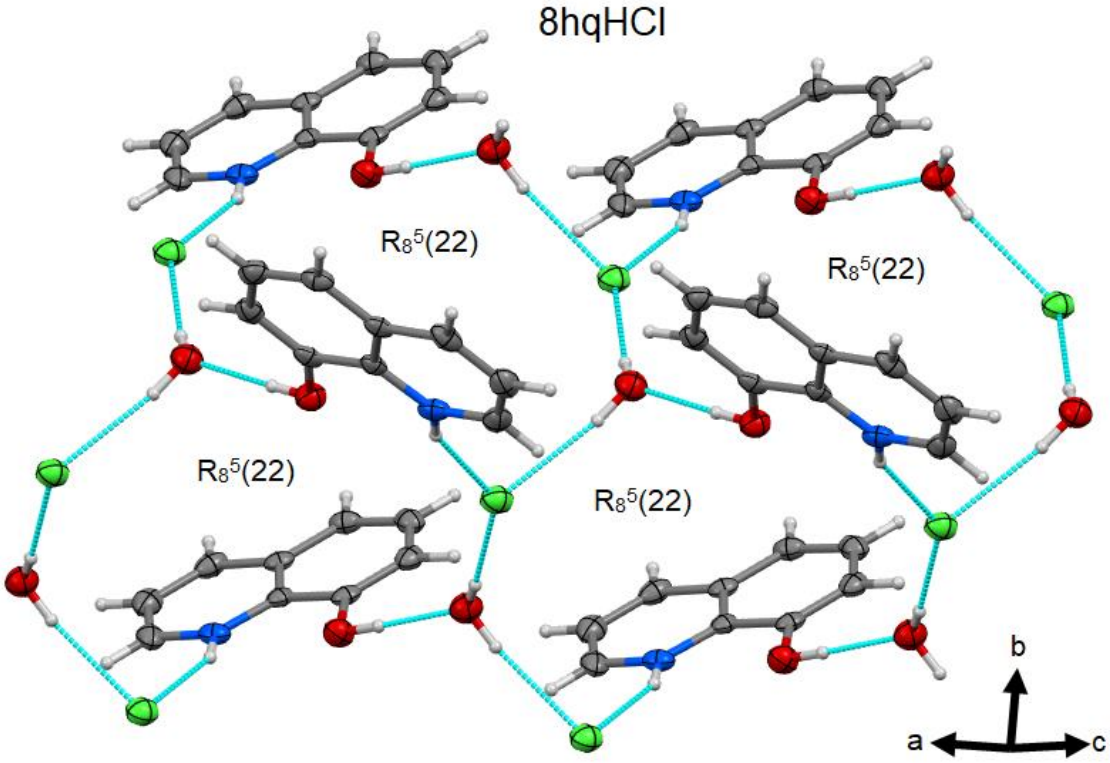


Figure S18. H-bond ring motifs in the structure of 8hqHCl

UV-Vis spectra (Figure S19-S38)

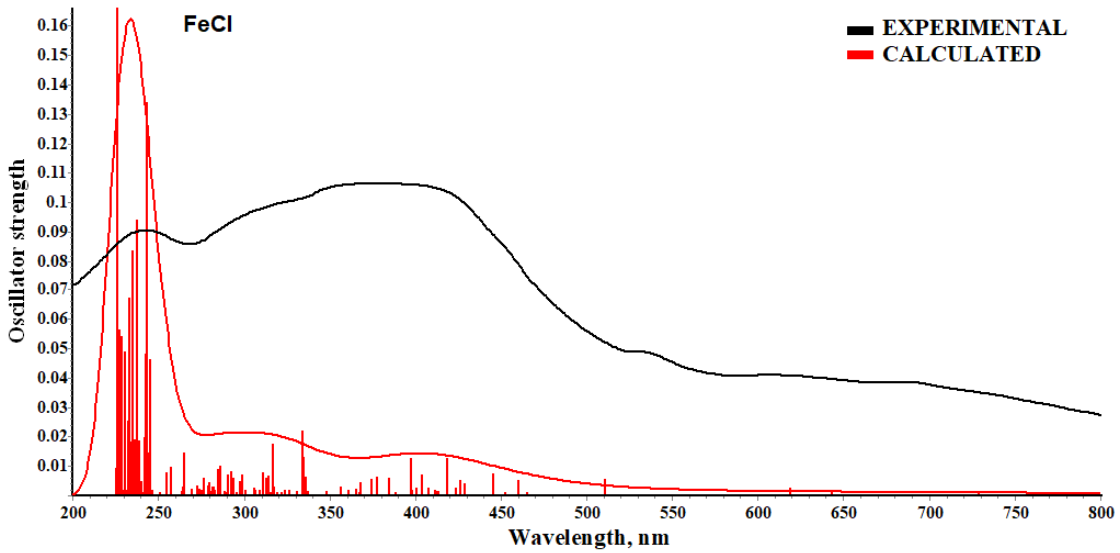


Figure S19. Experimental (black) and calculated (red) UV-Vis spectra of FeCl**.** The most important oscillator strengths are shown as vertical red lines.

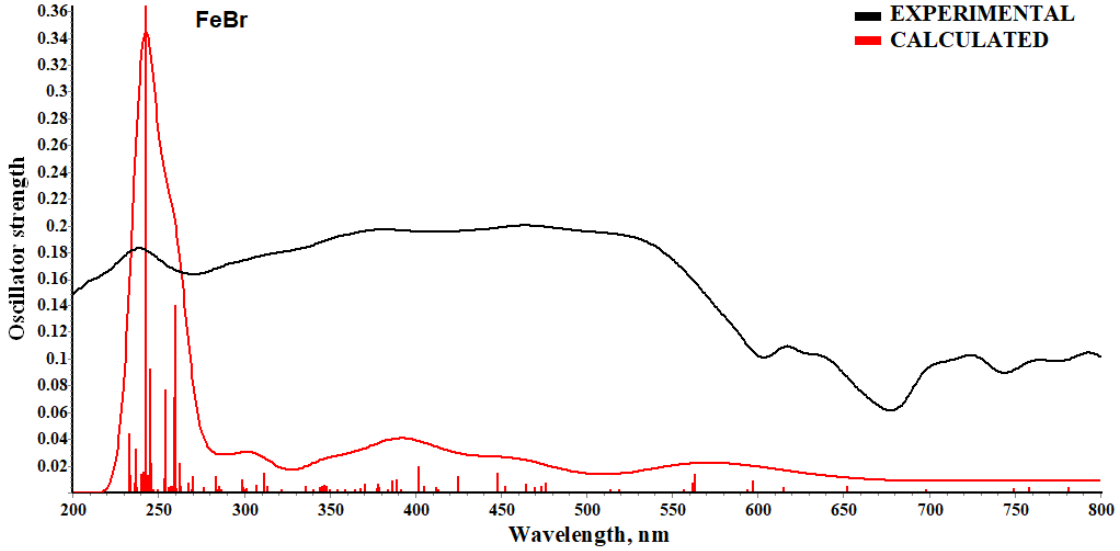


Figure S20. Experimental (black) and calculated (red) UV-Vis spectra of FeBr**.** The most important oscillator strengths are shown as vertical red lines.

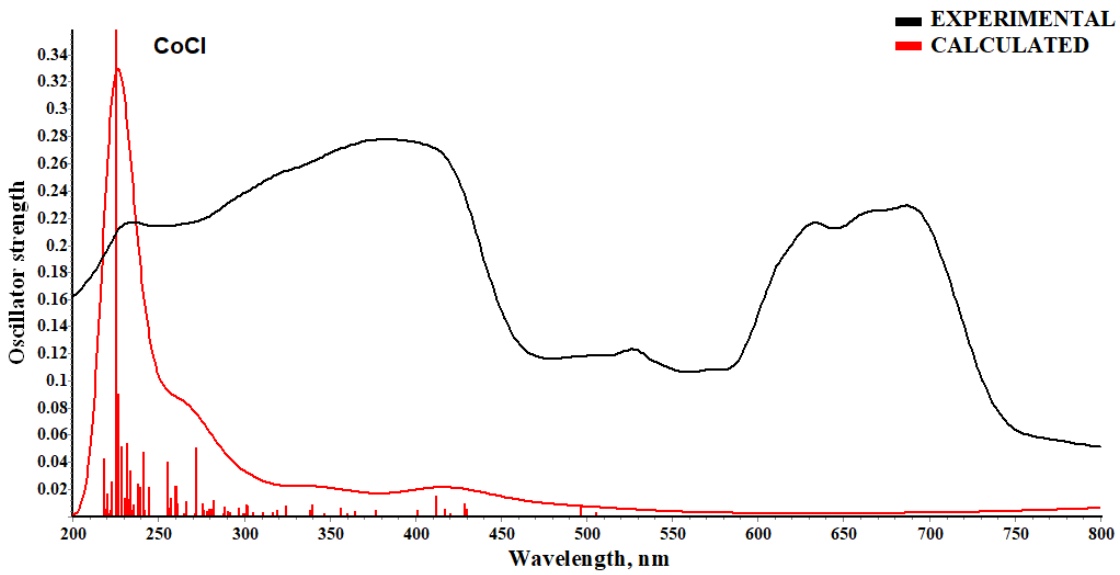


Figure S21. Experimental (black) and calculated (red) UV-Vis spectra of CoCl**.** The most important oscillator strengths are shown as vertical red lines.

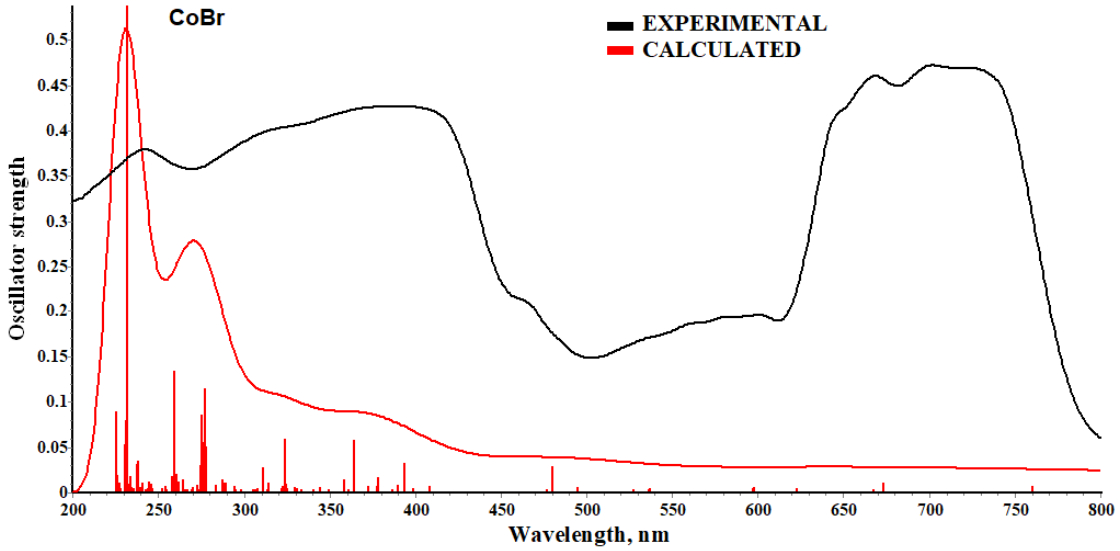


Figure S22. Experimental (black) and calculated (red) UV-Vis spectra of CoBr**.** The most important oscillator strengths are shown as vertical red lines.

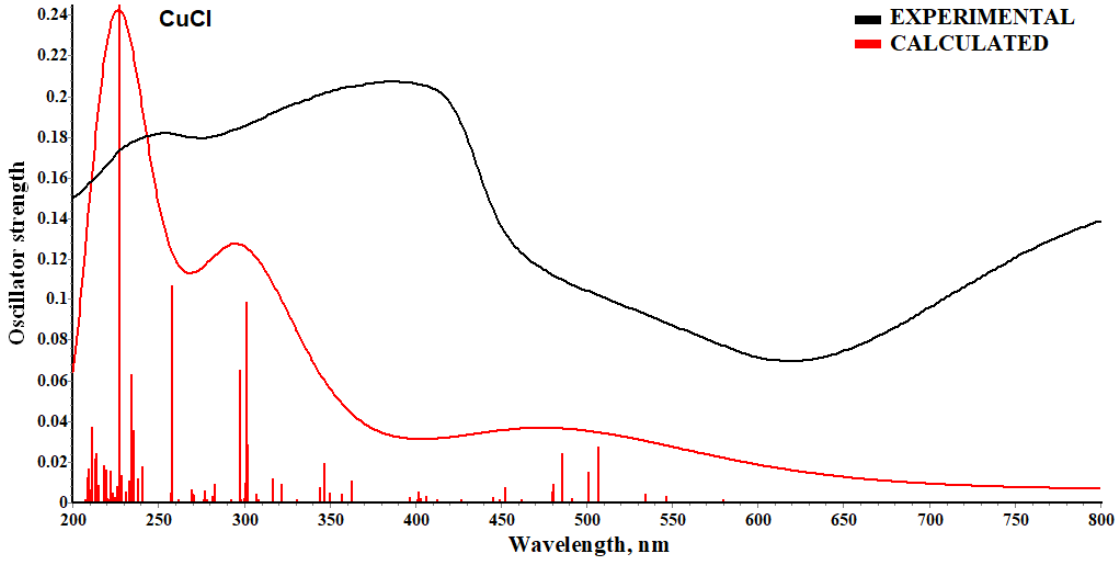


Figure S23. Experimental (black) and calculated (red) UV-Vis spectra of CuCl**.** The most important oscillator strengths are shown as vertical red lines.

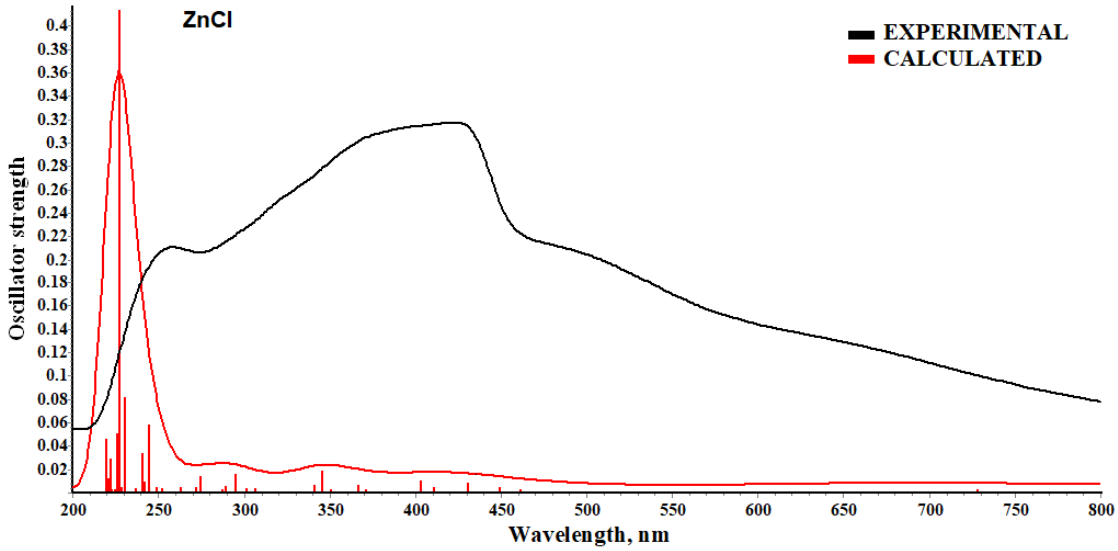


Figure S24. Experimental (black) and calculated (red) UV-Vis spectra of ZnCl**.** The most important oscillator strengths are shown as vertical red lines.

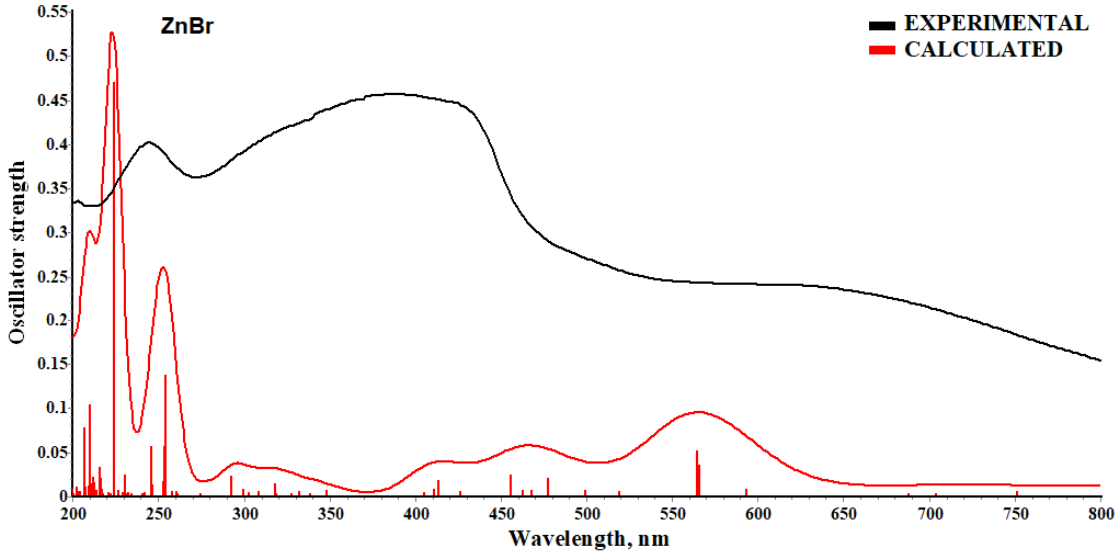


Figure S25. Experimental (black) and calculated (red) UV-Vis spectra of ZnBr**.** The most important oscillator strengths are shown as vertical red lines.

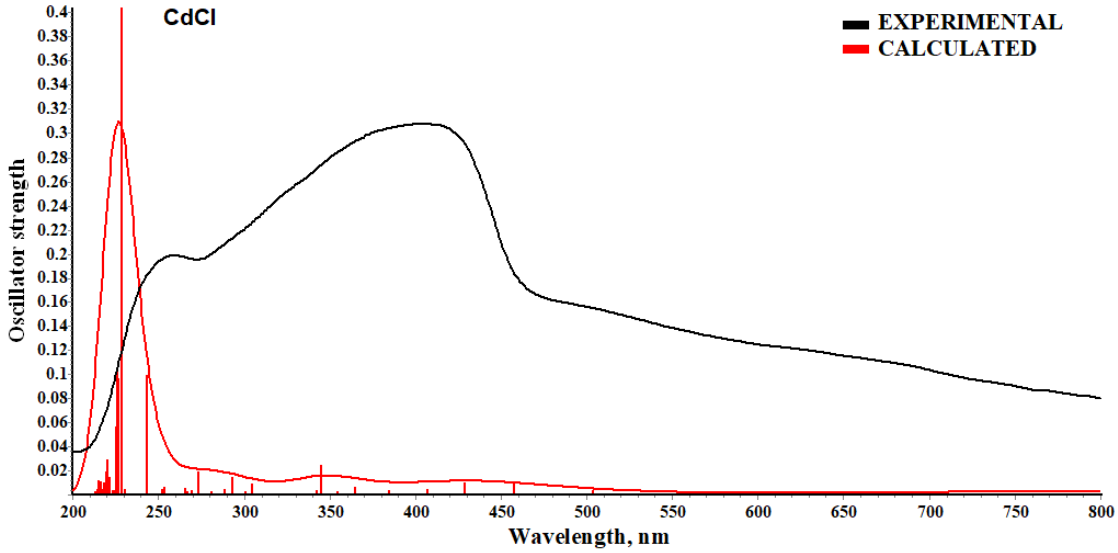


Figure S26. Experimental (black) and calculated (red) UV-Vis spectra of CdCl**.** The most important oscillator strengths are shown as vertical red lines.

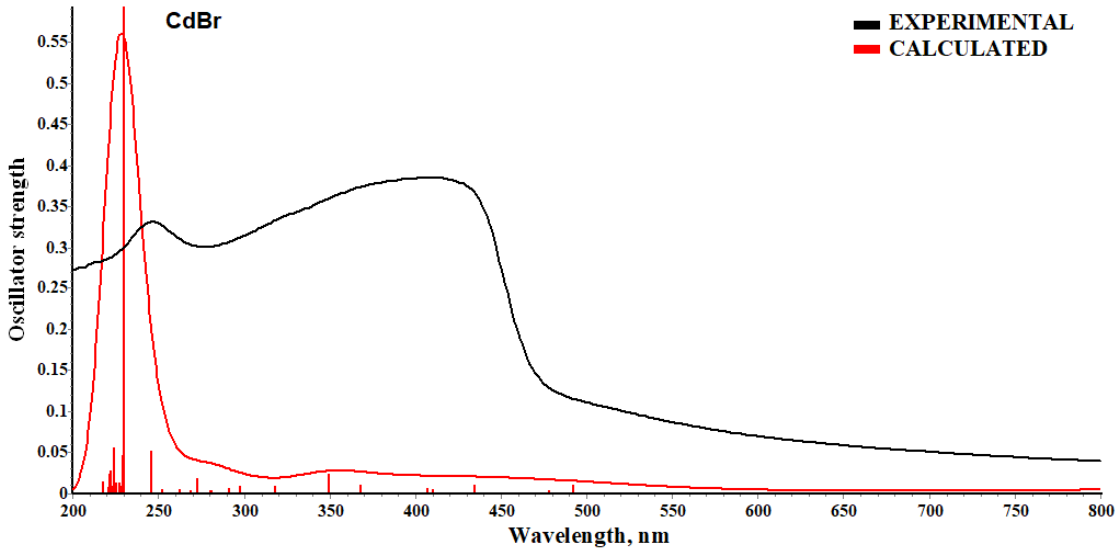


Figure S27. Experimental (black) and calculated (red) UV-Vis spectra of CdBr**.** The most important oscillator strengths are shown as vertical red lines.

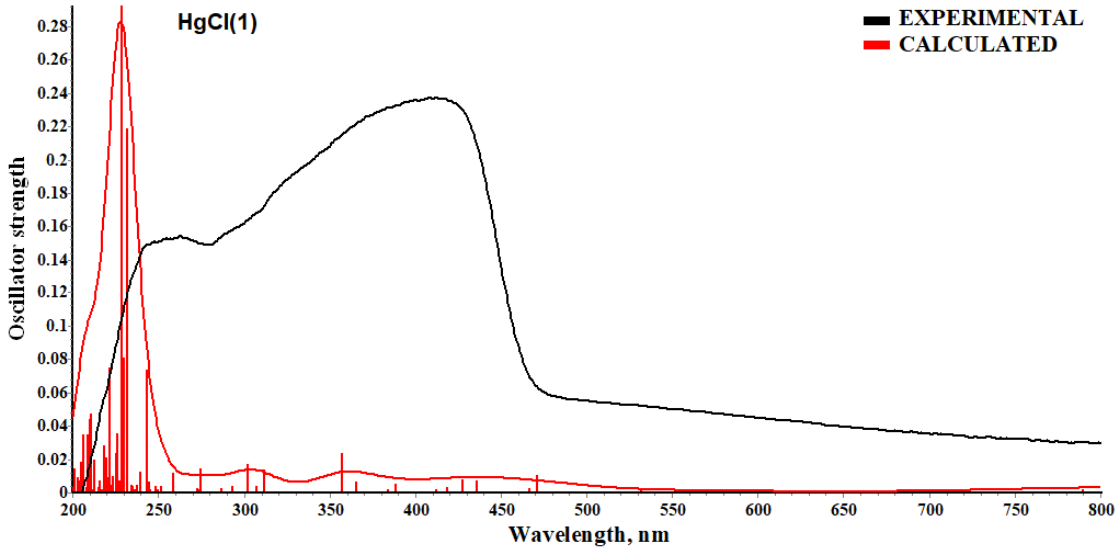


Figure S28. Experimental (black) and calculated (red) UV-Vis spectra of HgCl(1). The most important oscillator strengths are shown as vertical red lines.

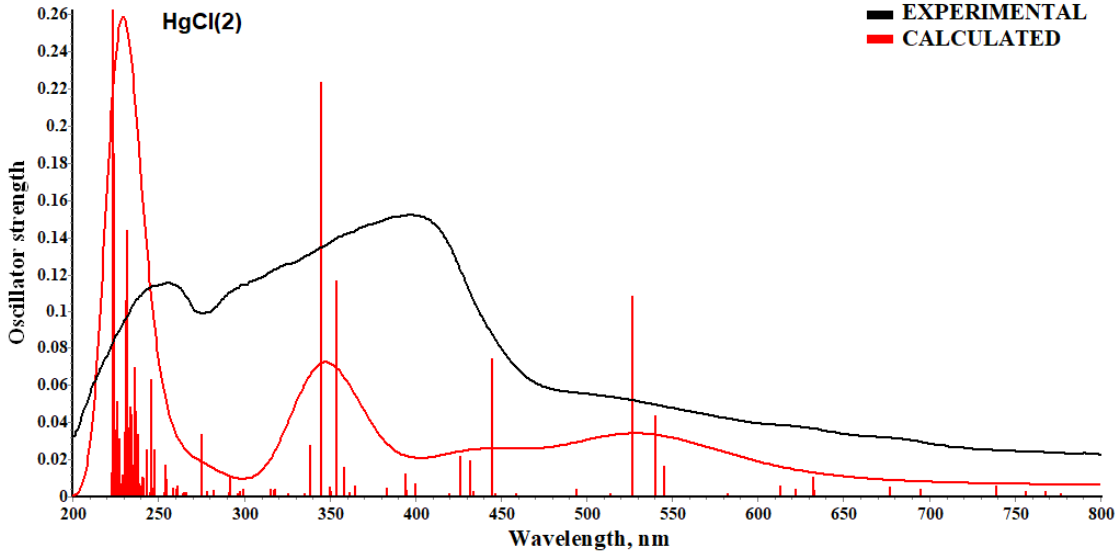


Figure S29. Experimental (black) and calculated (red) UV-Vis spectra of HgCl(2). The most important oscillator strengths are shown as vertical red lines.

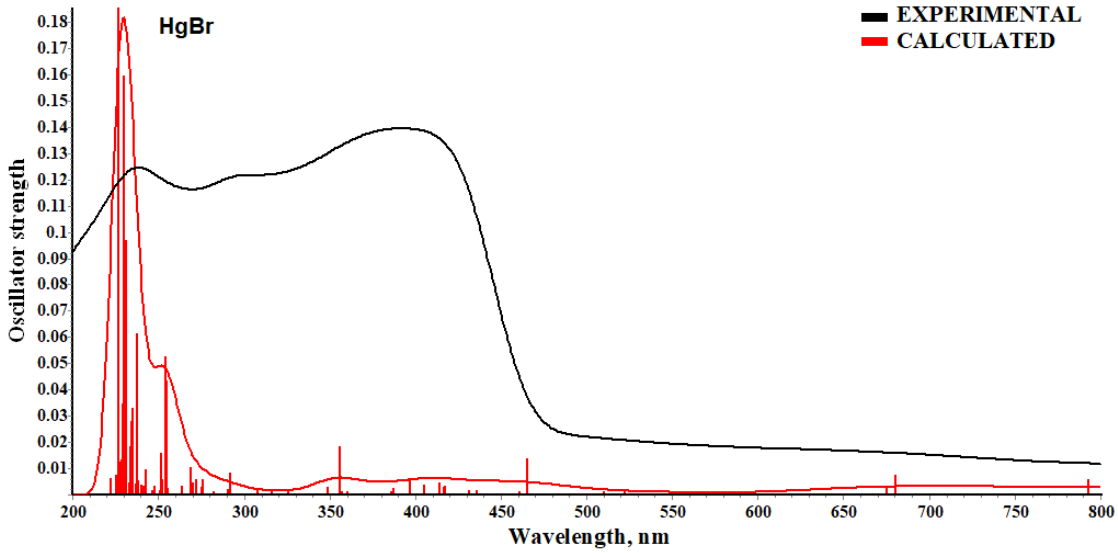


Figure S30. Experimental (black) and calculated (red) UV-Vis spectra of HgBr. The most important oscillator strengths are shown as vertical red lines.

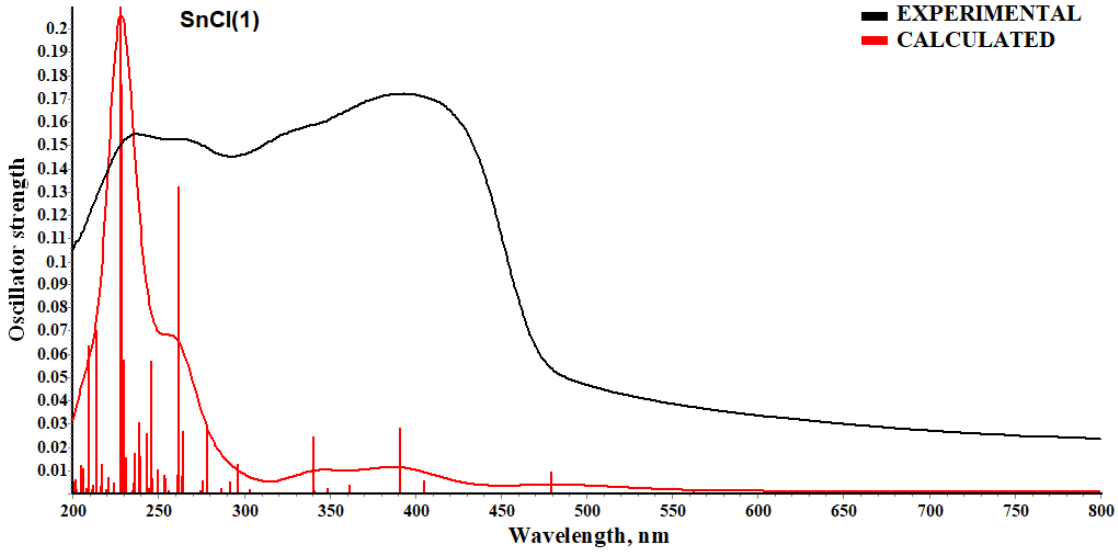


Figure S31. Experimental (black) and calculated (red) UV-Vis spectra of SnCl(1). The most important oscillator strengths are shown as vertical red lines.

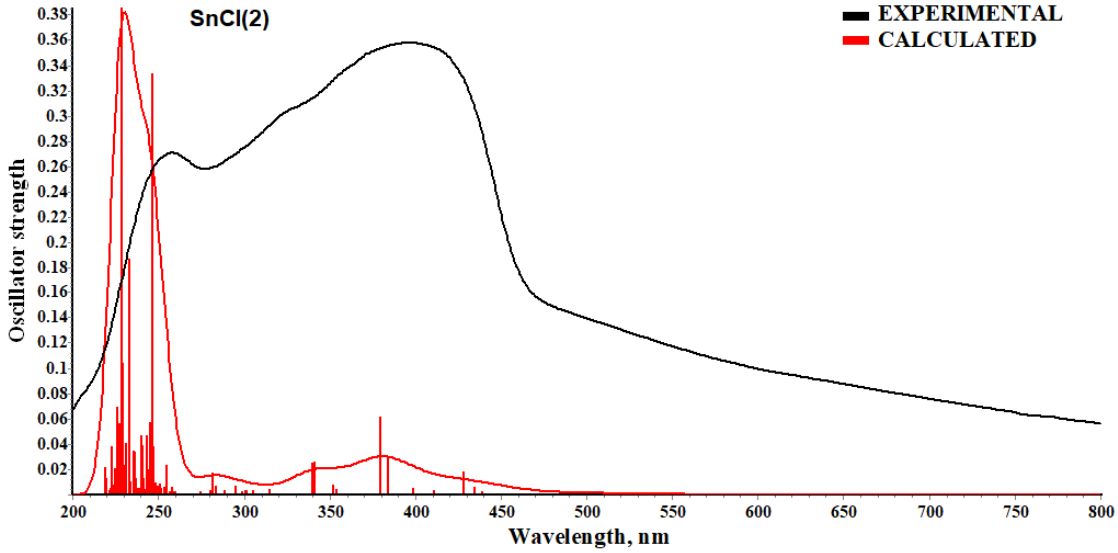


Figure S32. Experimental (black) and calculated (red) UV-Vis spectra of SnCl(2). The most important oscillator strengths are shown as vertical red lines.

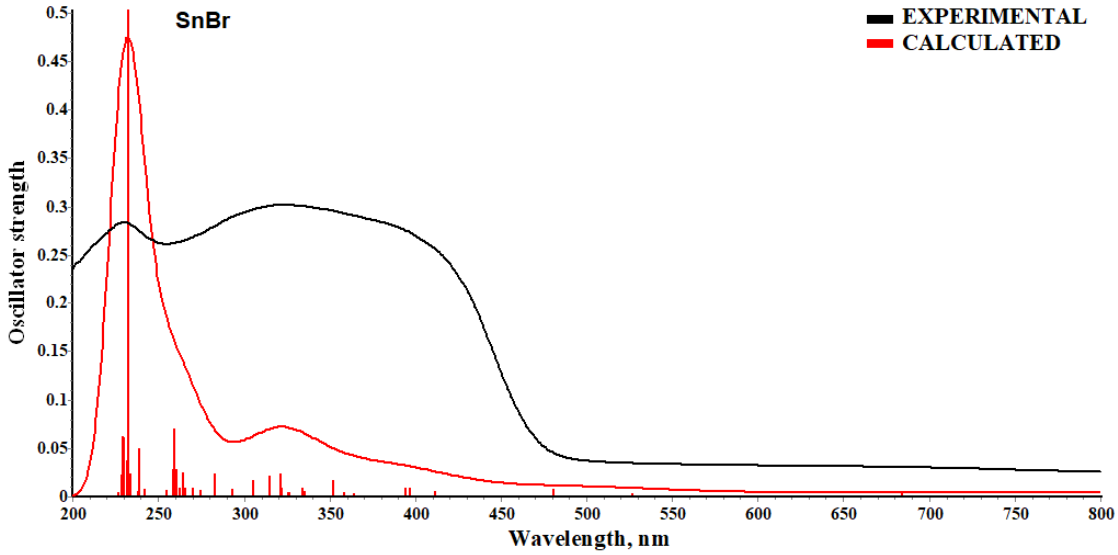


Figure S33. Experimental (black) and calculated (red) UV-Vis spectra of SnBr. The most important oscillator strengths are shown as vertical red lines.

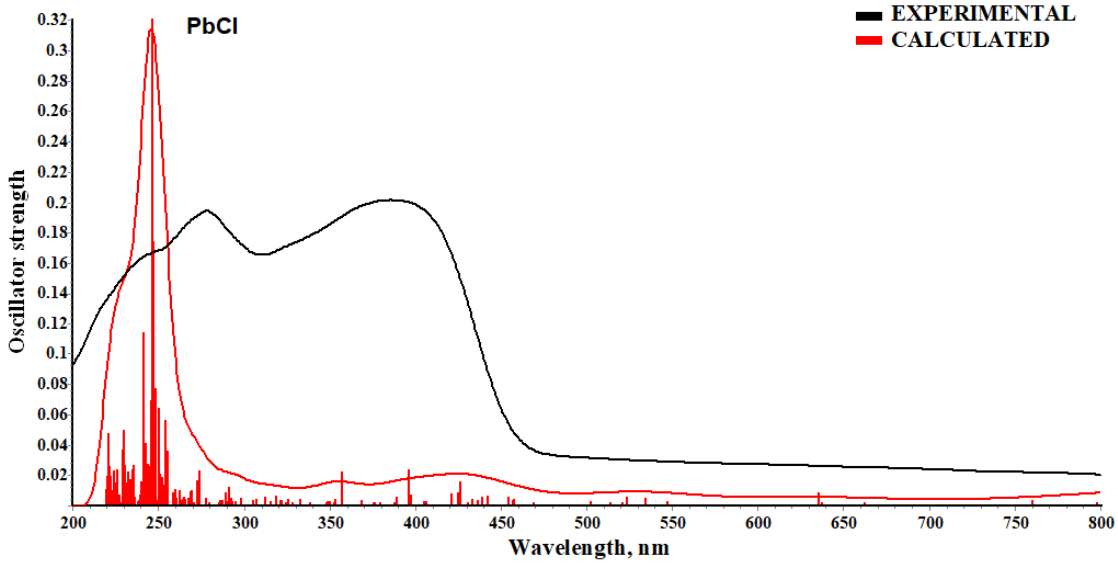


Figure S34. Experimental (black) and calculated (red) UV-Vis spectra of PbCl. The most important oscillator strengths are shown as vertical red lines.

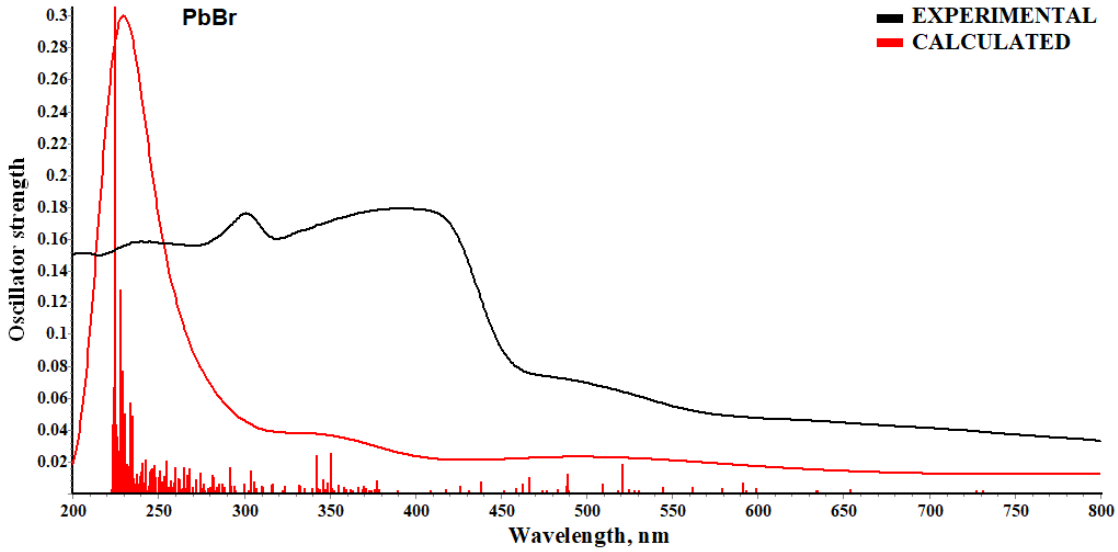


Figure S35. Experimental (black) and calculated (red) UV-Vis spectra of PbBr. The most important oscillator strengths are shown as vertical red lines.

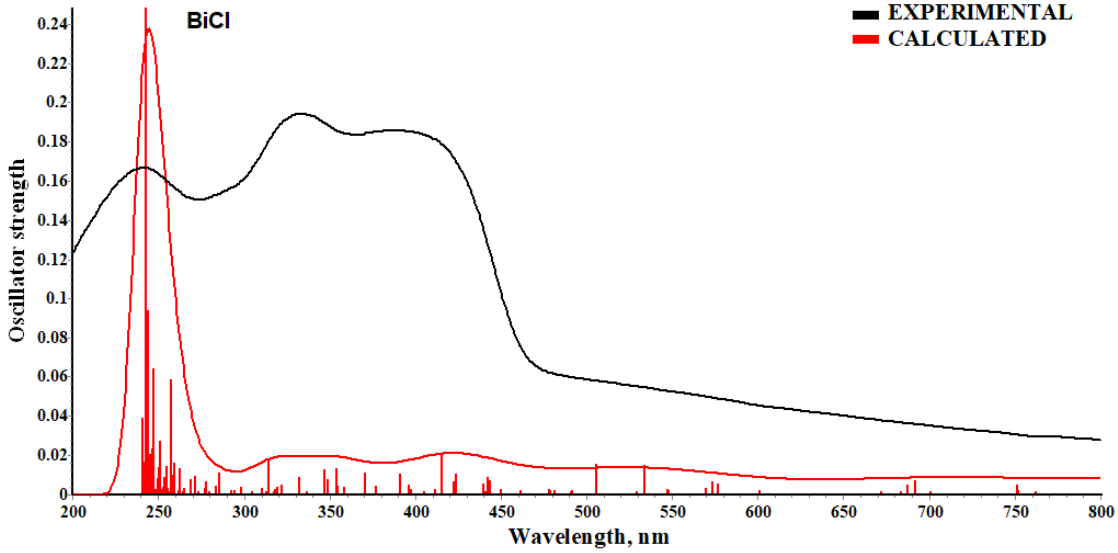


Figure S36. Experimental (black) and calculated (red) UV-Vis spectra of BiCl. The most important oscillator strengths are shown as vertical red lines.

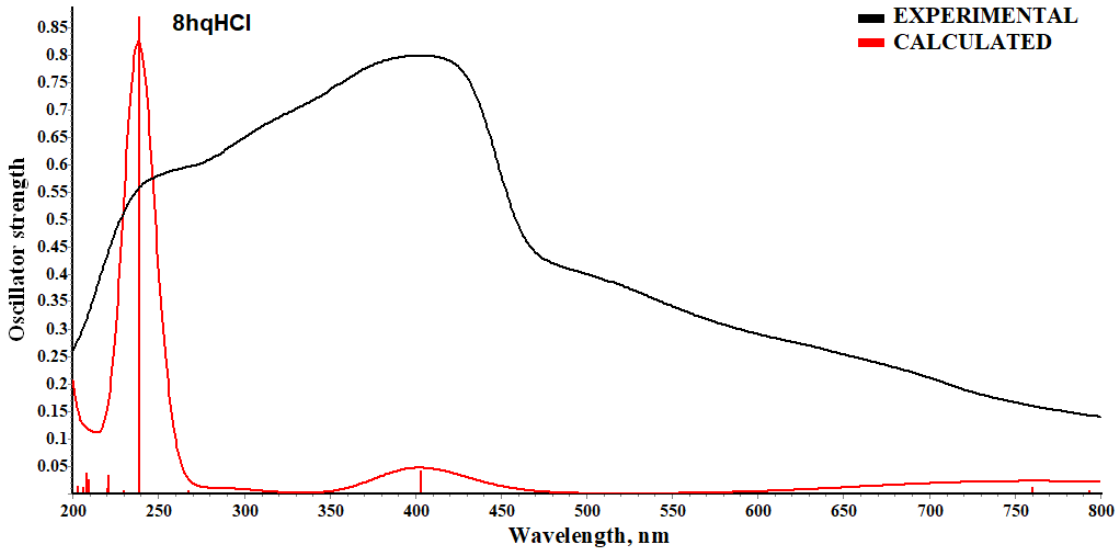


Figure S37. Experimental (black) and calculated (red) UV-Vis spectra of 8hqHCl. The most important oscillator strengths are shown as vertical red lines.

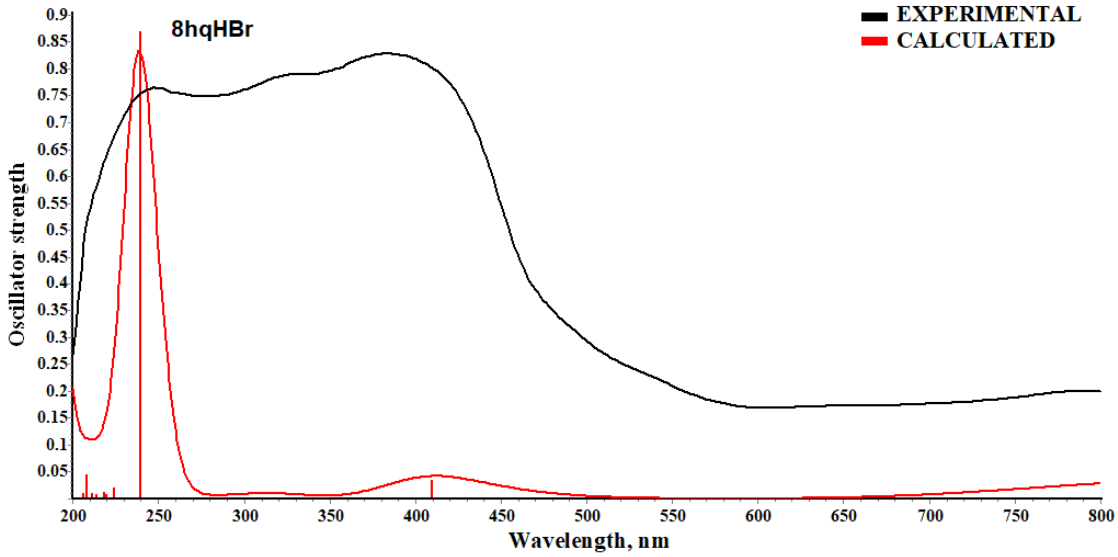


Figure S38. Experimental (black) and calculated (red) UV-Vis spectra of 8hqHBr. The most important oscillator strengths are shown as vertical red lines.

Calculated molecular orbitals of the studied compounds, corresponding to Tables S6-S8. (Figure S39-S56). H letter indicates HOMO, L - LUMO, and +/-(number) represents subsequent orbitals below HOMO and above LUMO, respectively

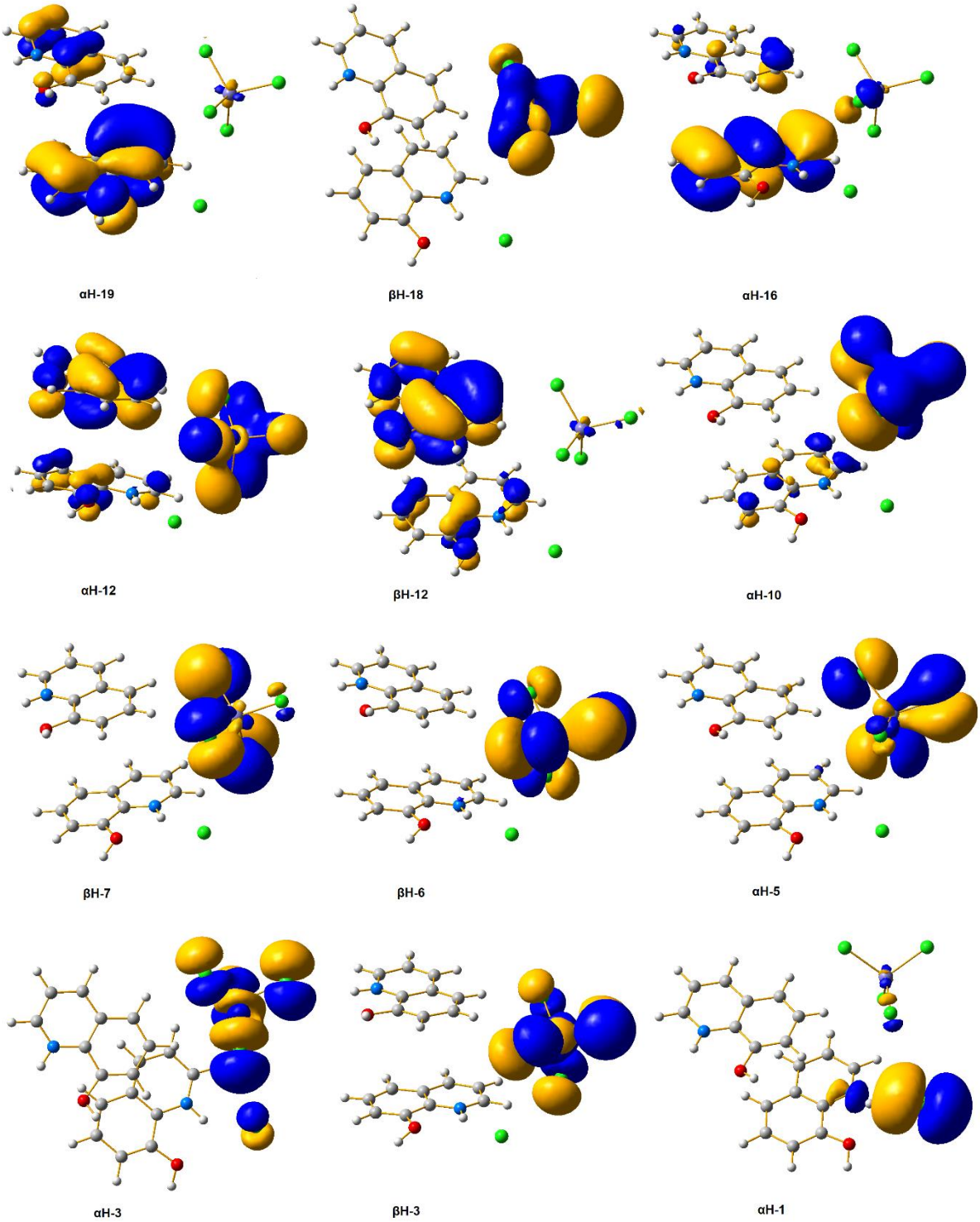


Figure S39. Molecular orbitals of the compound FeCl.

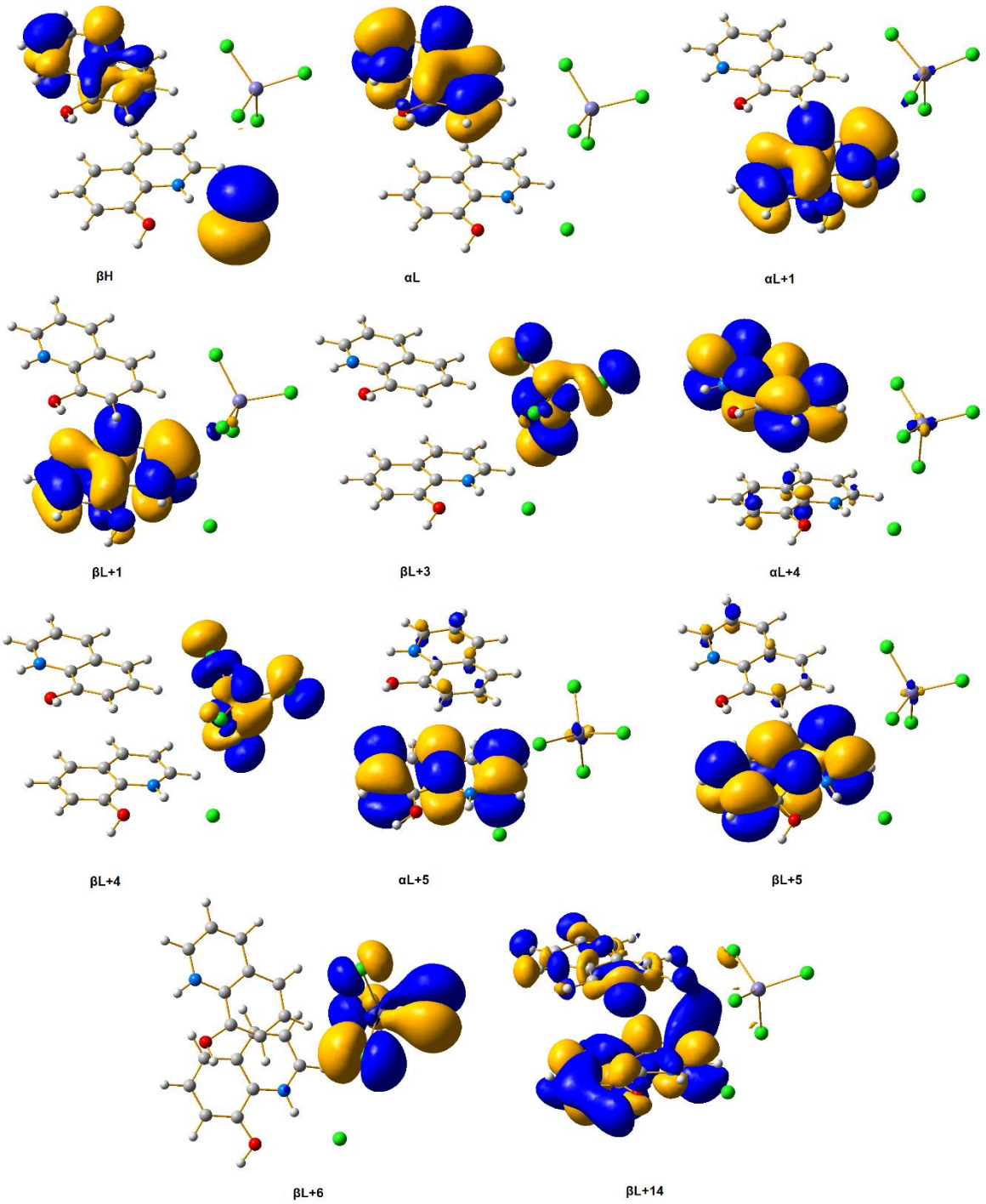


Figure S39. *continued.*

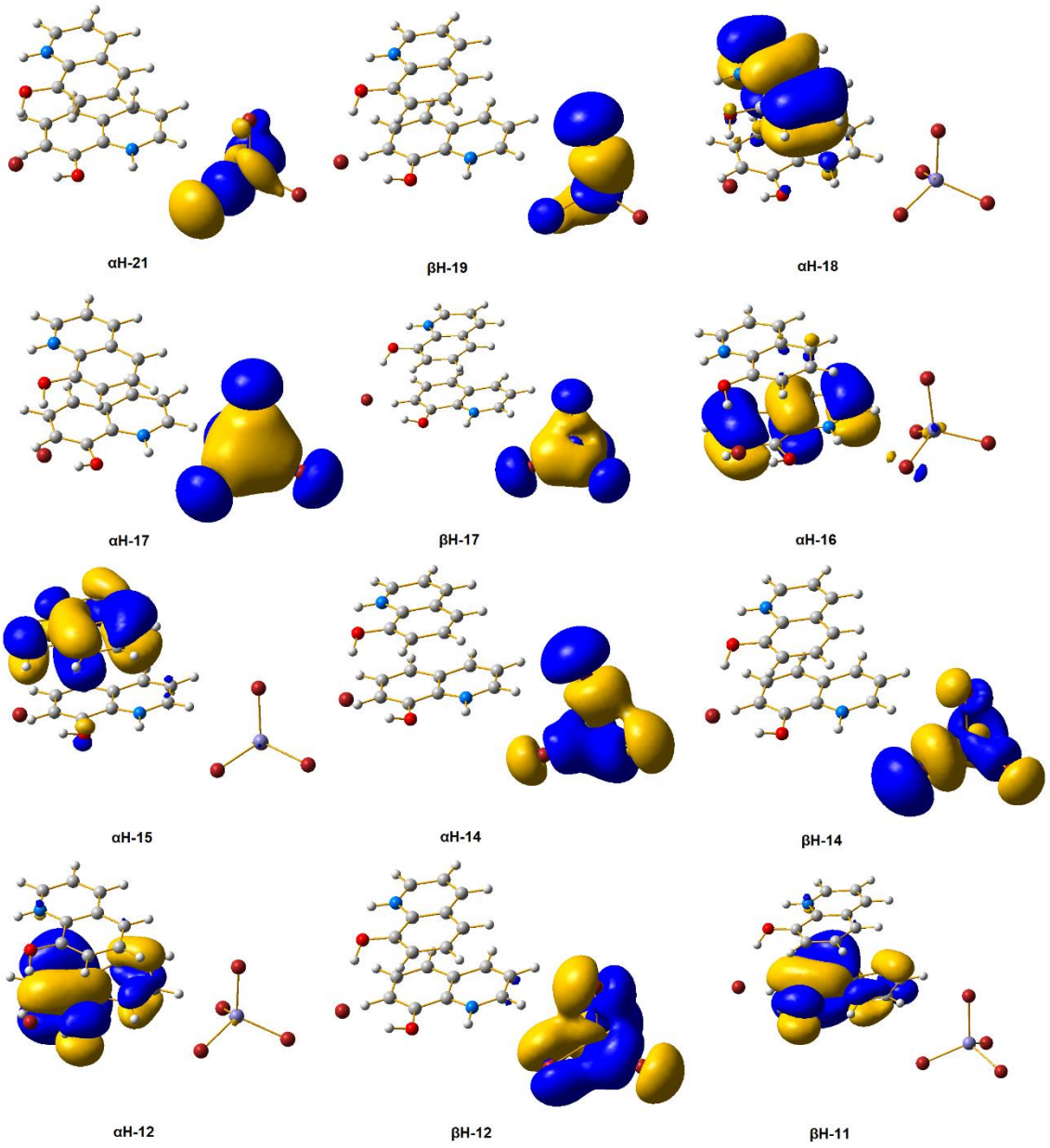


Figure S40. Molecular orbitals of the compound FeBr.

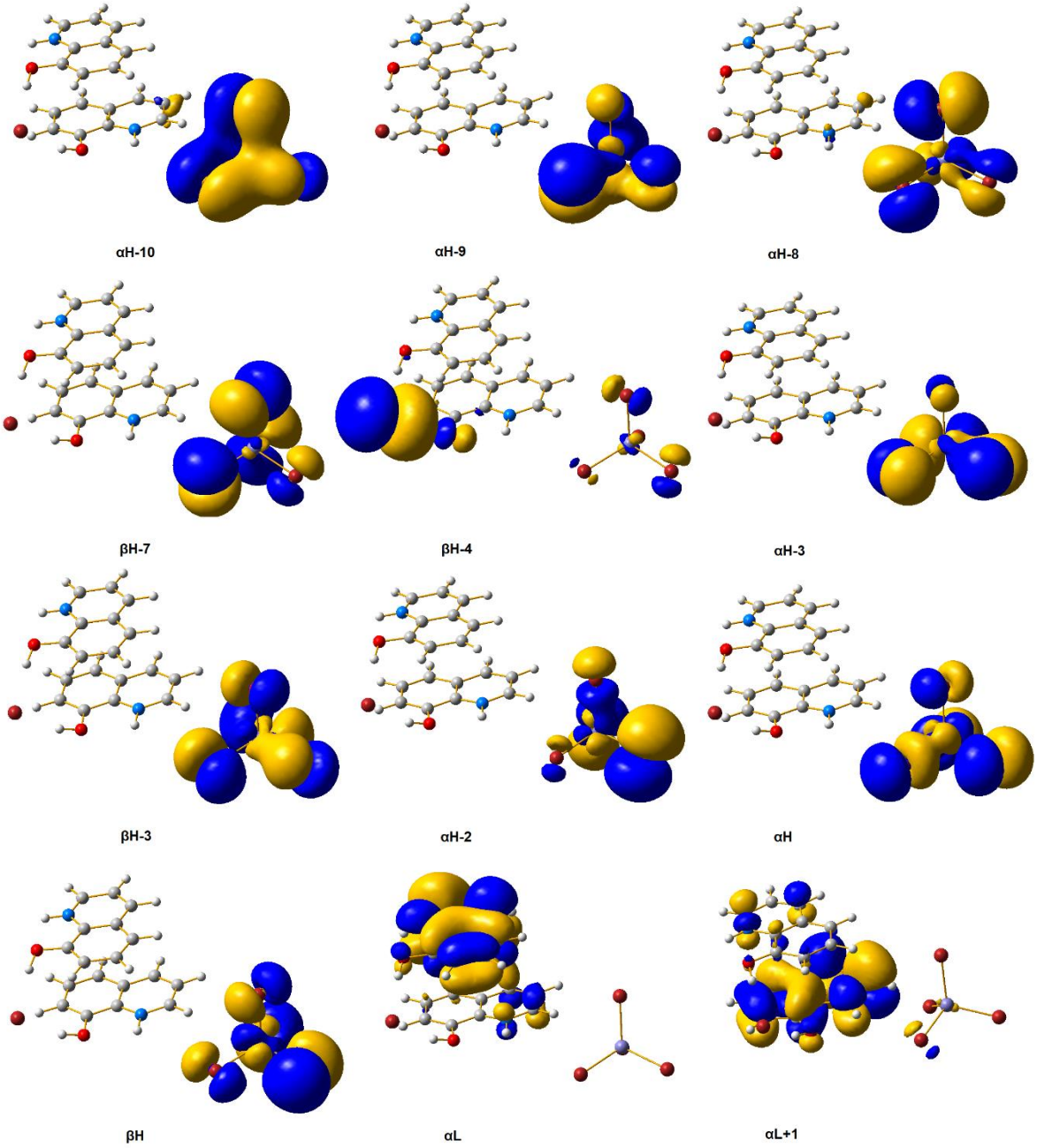


Figure S40. *continued*

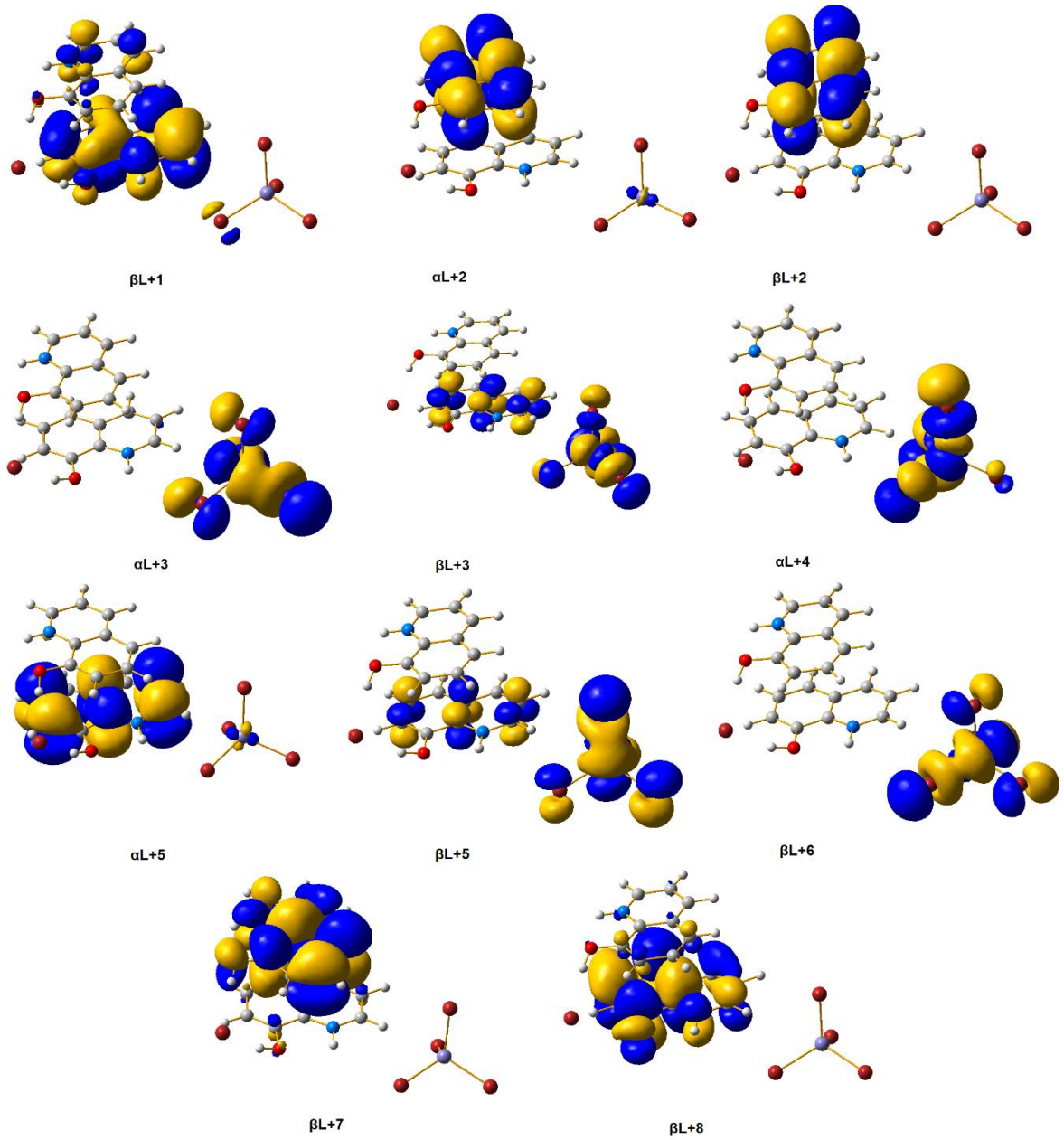


Figure S40. *continued.*

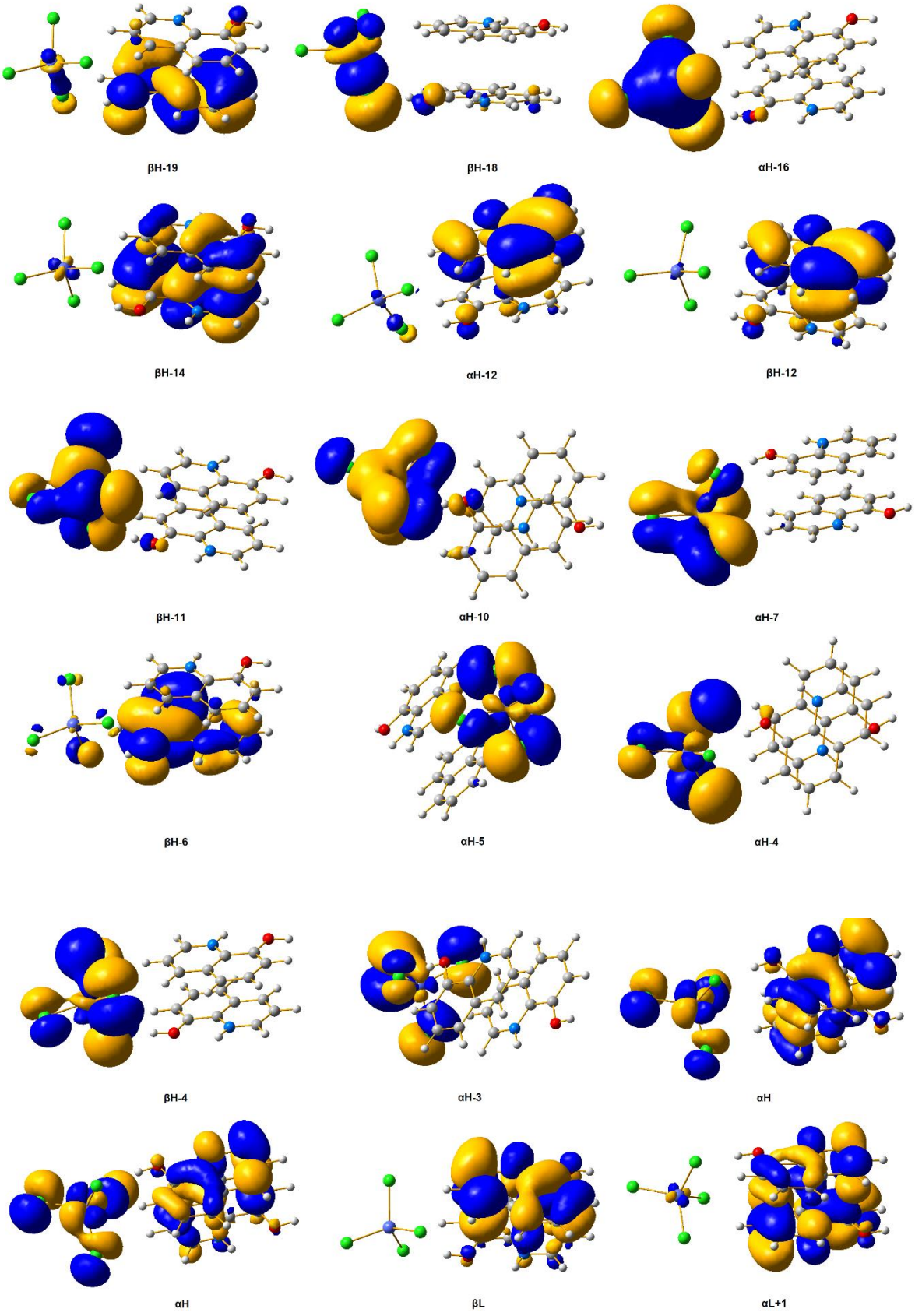


Figure S41. Molecular orbitals of the compound CoCl.

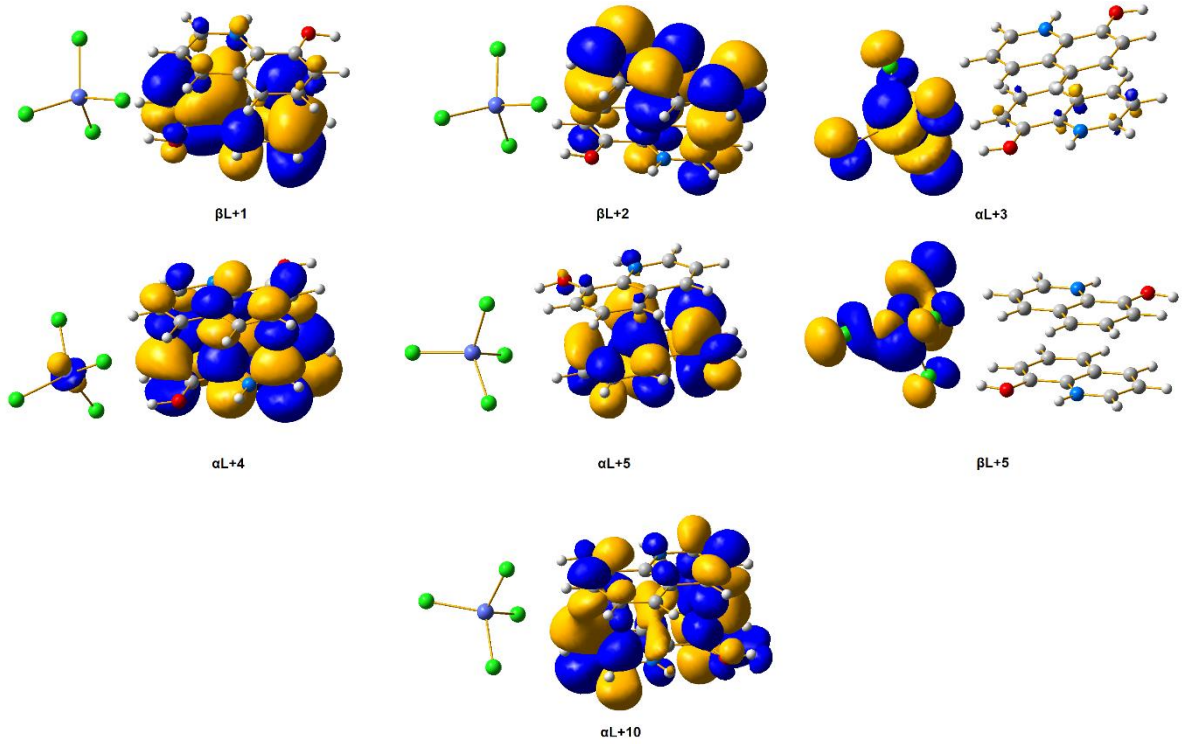


Figure S41. *continued*.

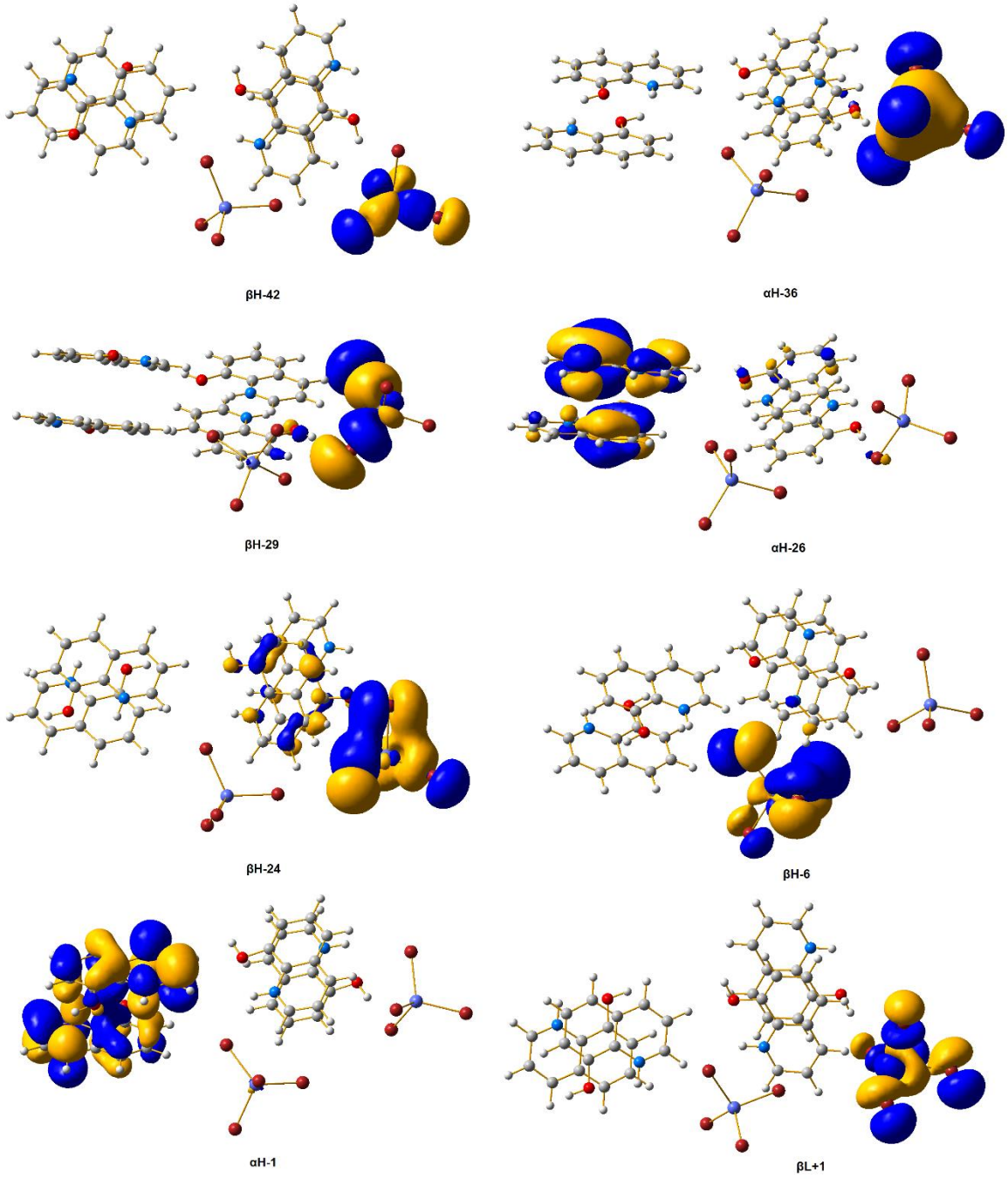


Figure S42. Molecular orbitals of the compound CoBr.

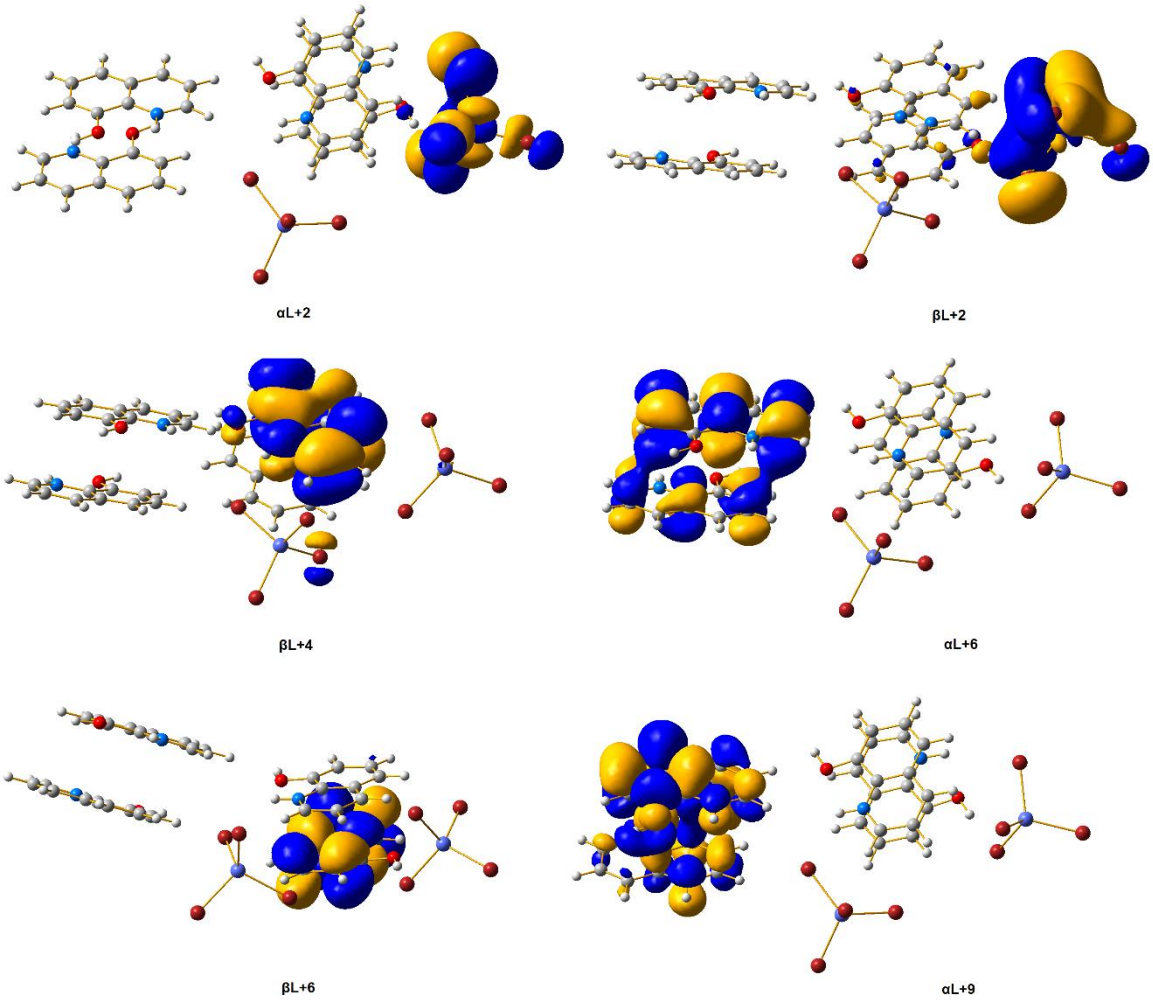


Figure S42. *continued*

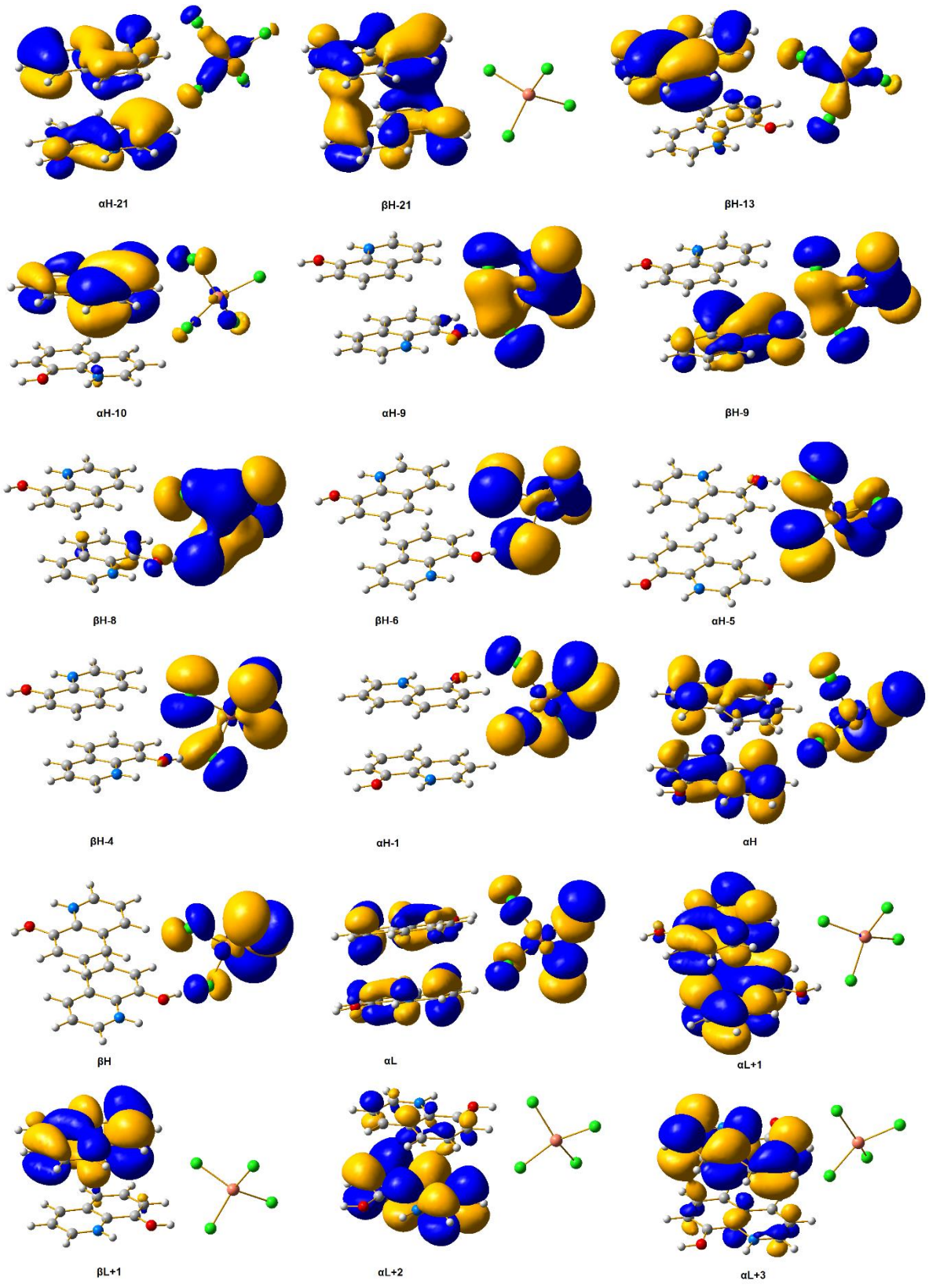


Figure S43. Molecular orbitals of the compound CuCl.

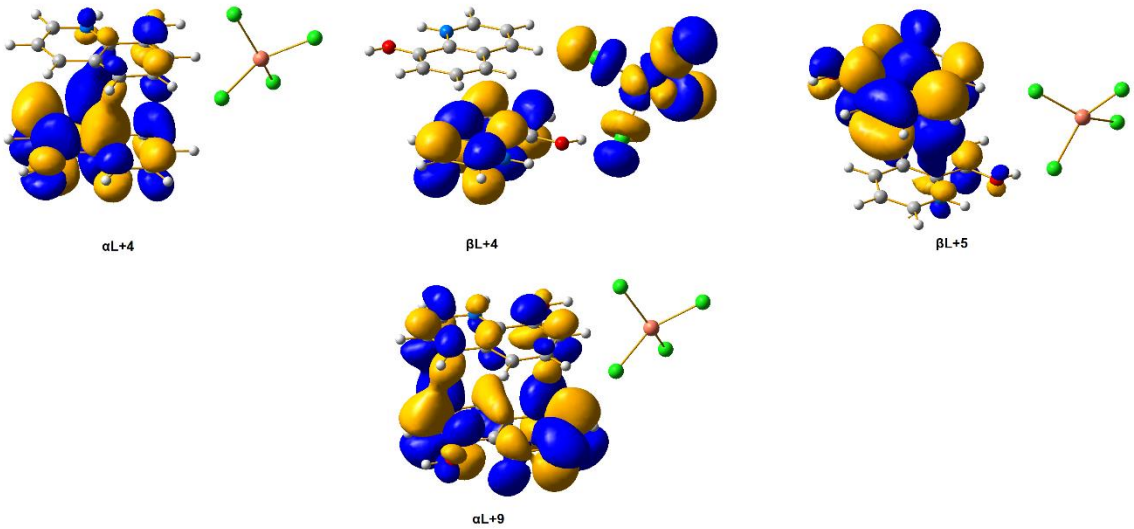


Figure S43. *Continued*

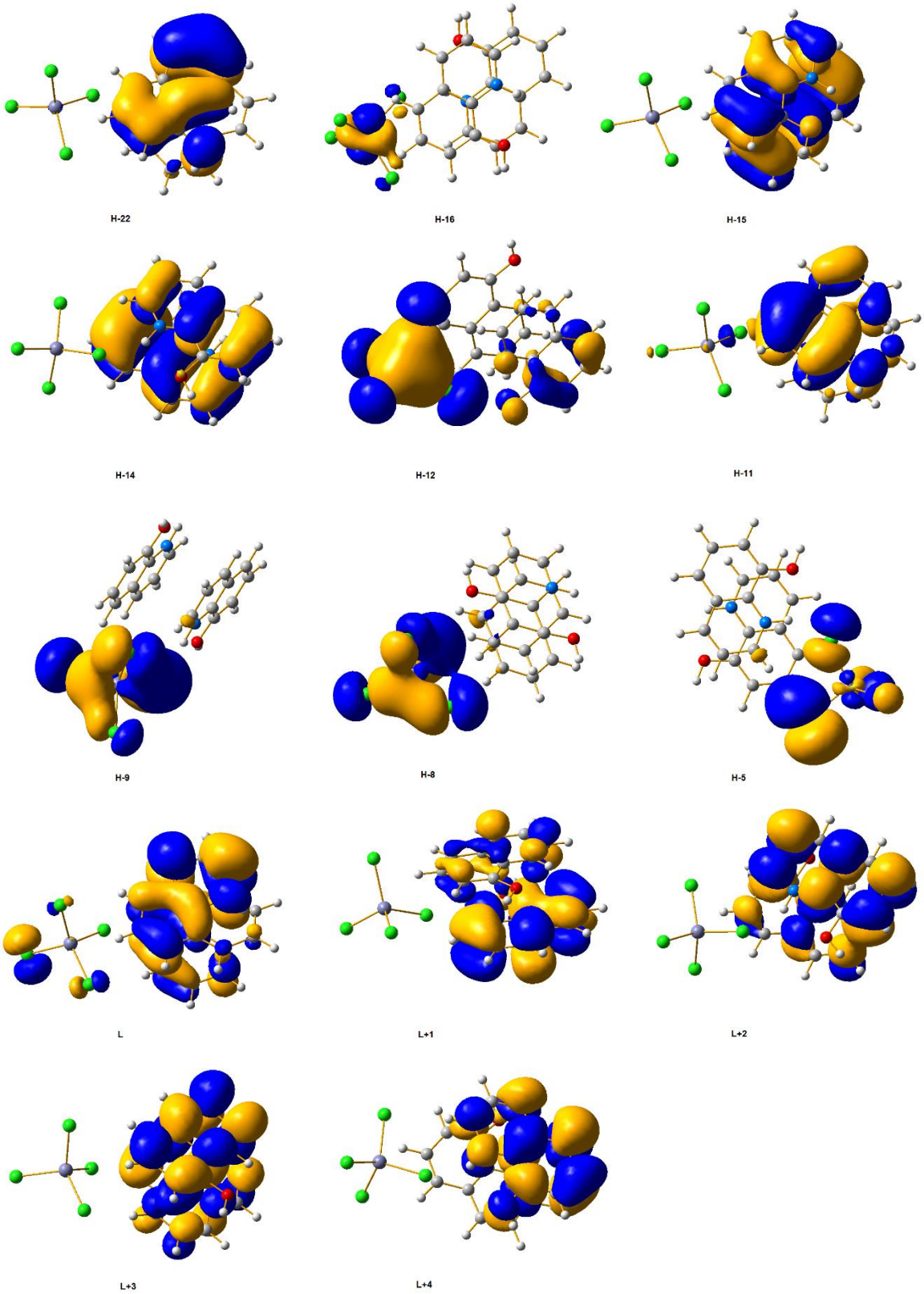


Figure S44. Molecular orbitals of the compound ZnCl.

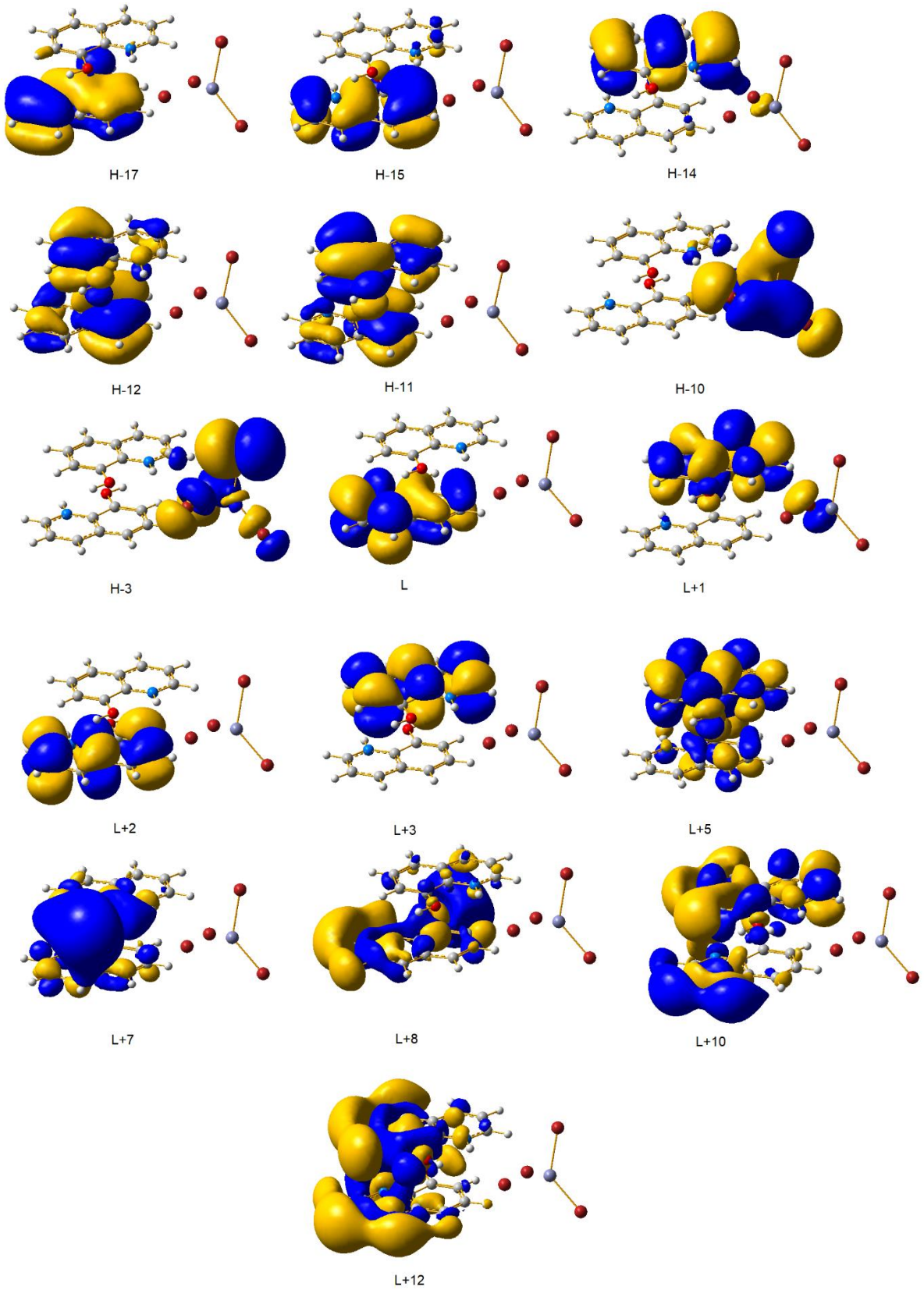


Figure S45. Molecular orbitals of the compound ZnBr.

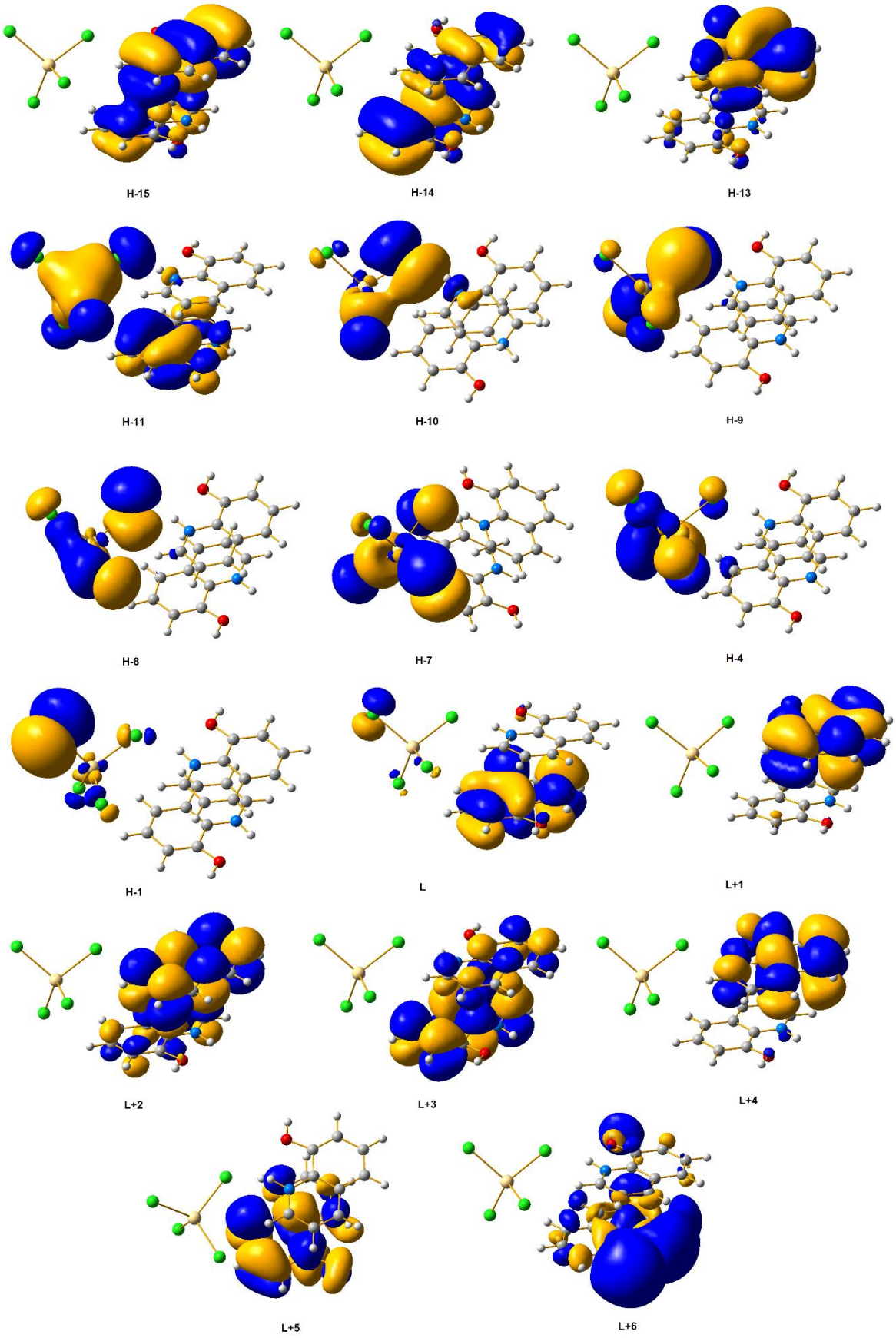


Figure S46. Molecular orbitals of the compound CdCl.

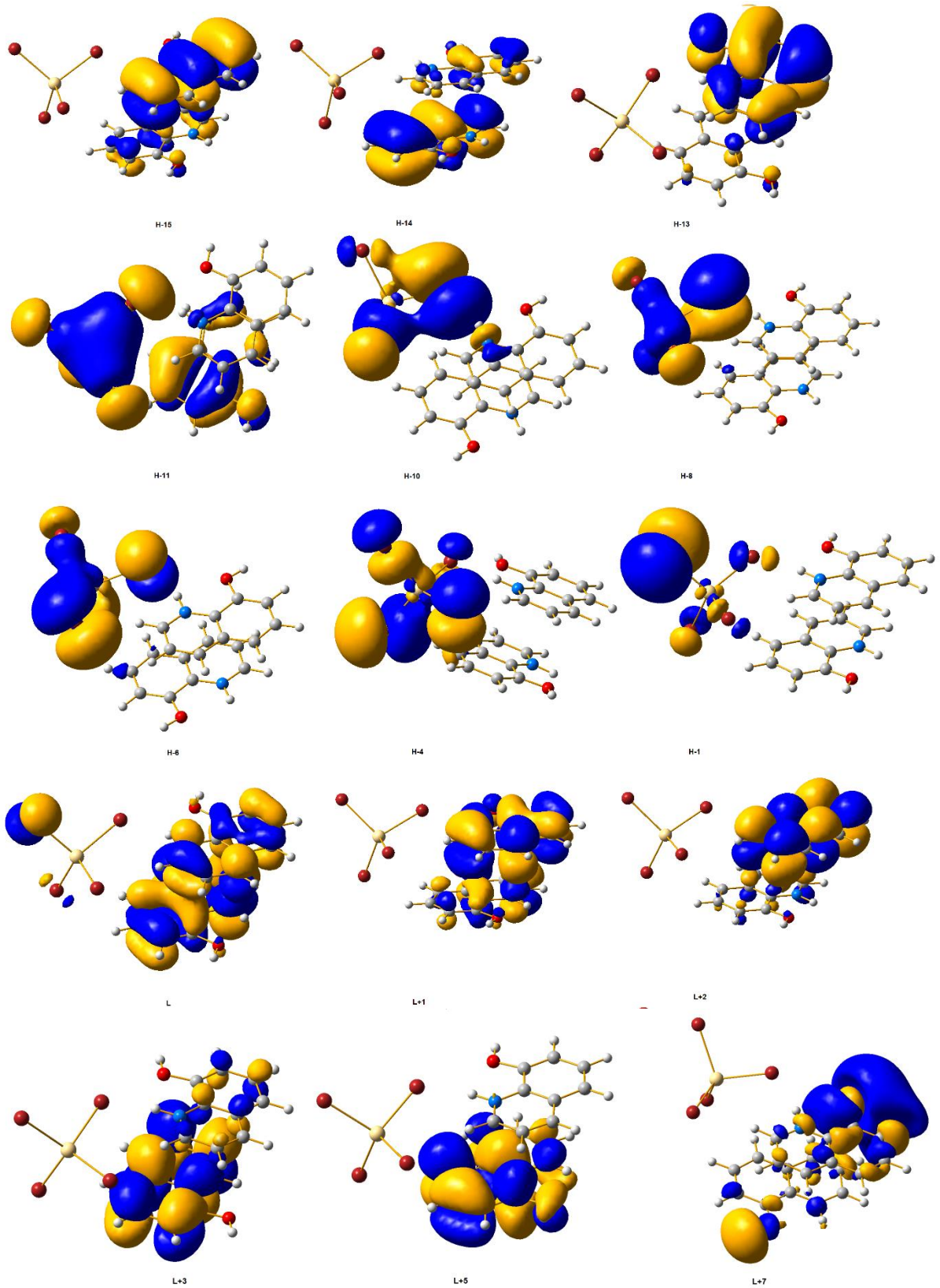


Figure S47. Molecular orbitals of the compound CdBr.

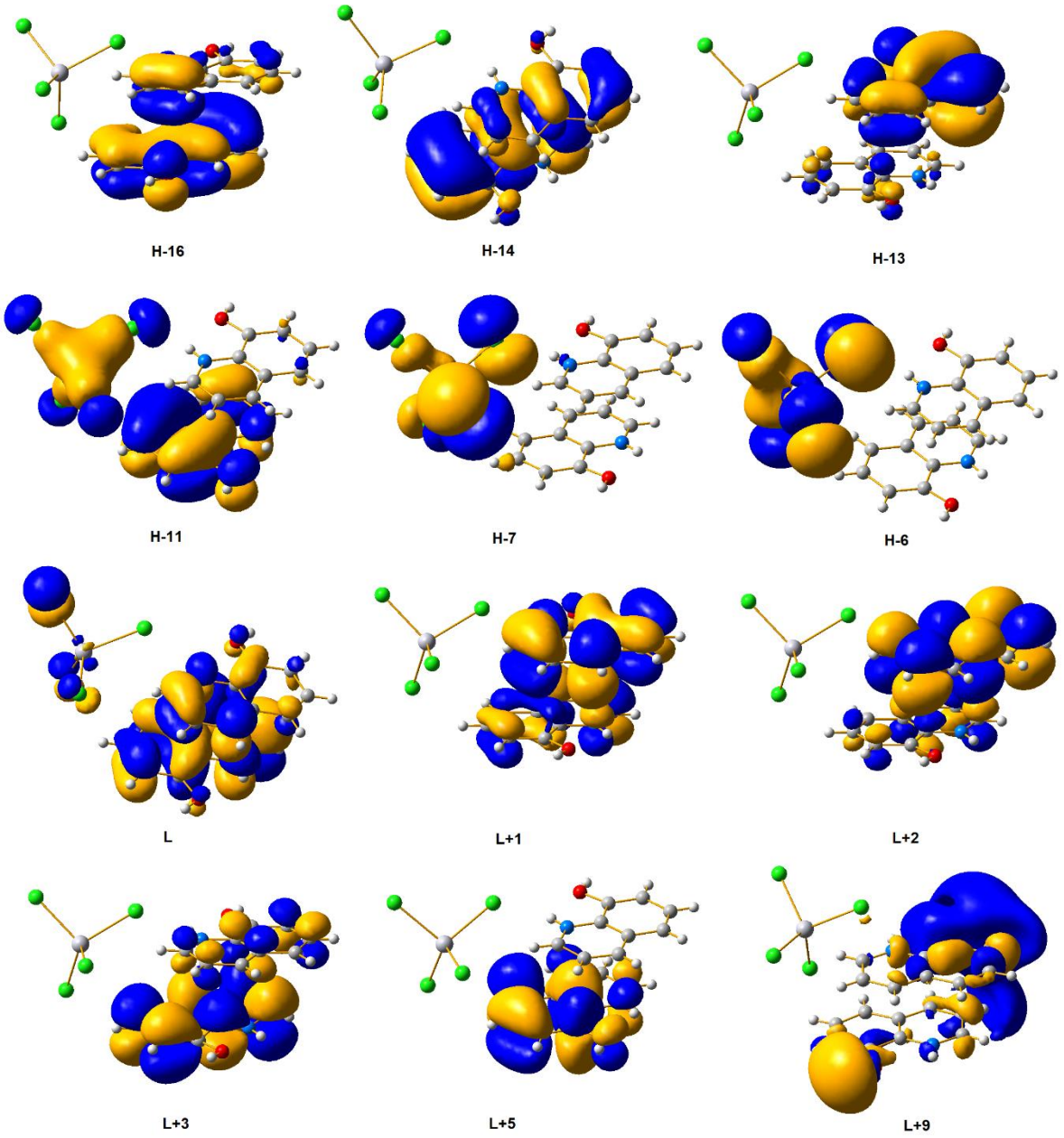


Figure S48. Molecular orbitals of the compound HgCl(1).

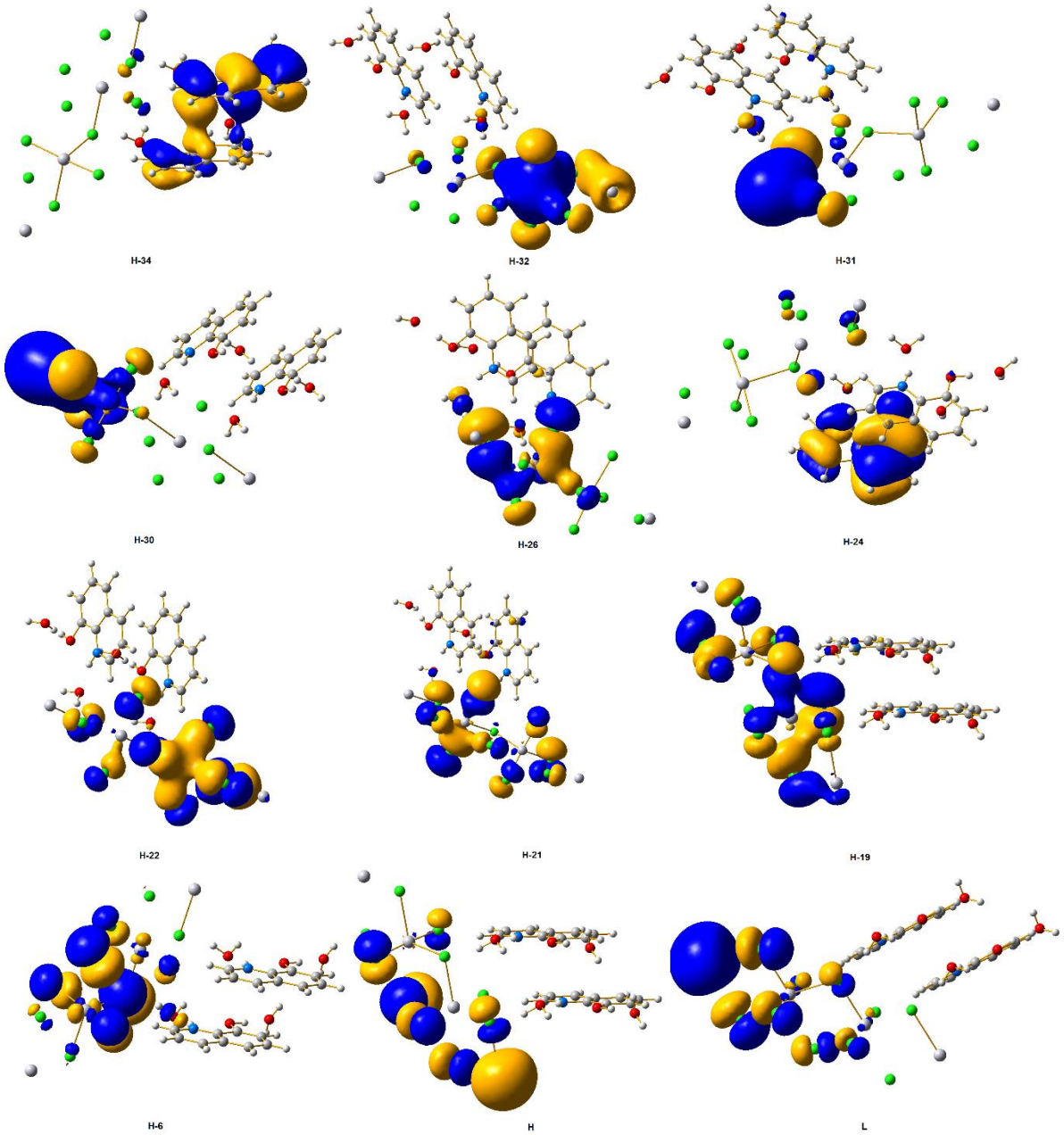


Figure S49. Molecular orbitals of the compound HgCl(2).

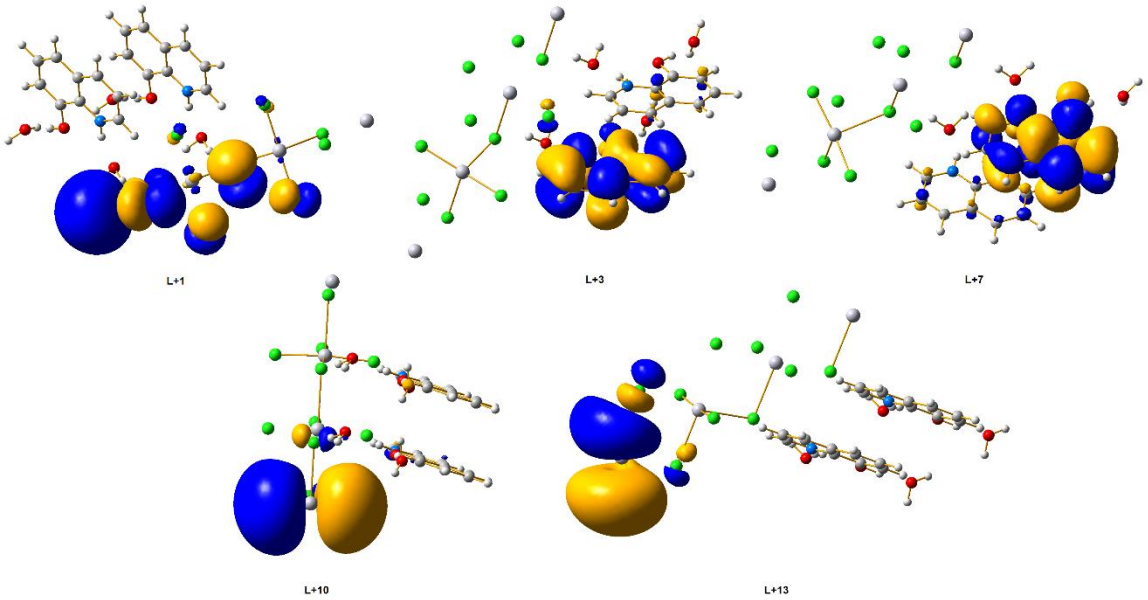


Figure S49. *contiuned*

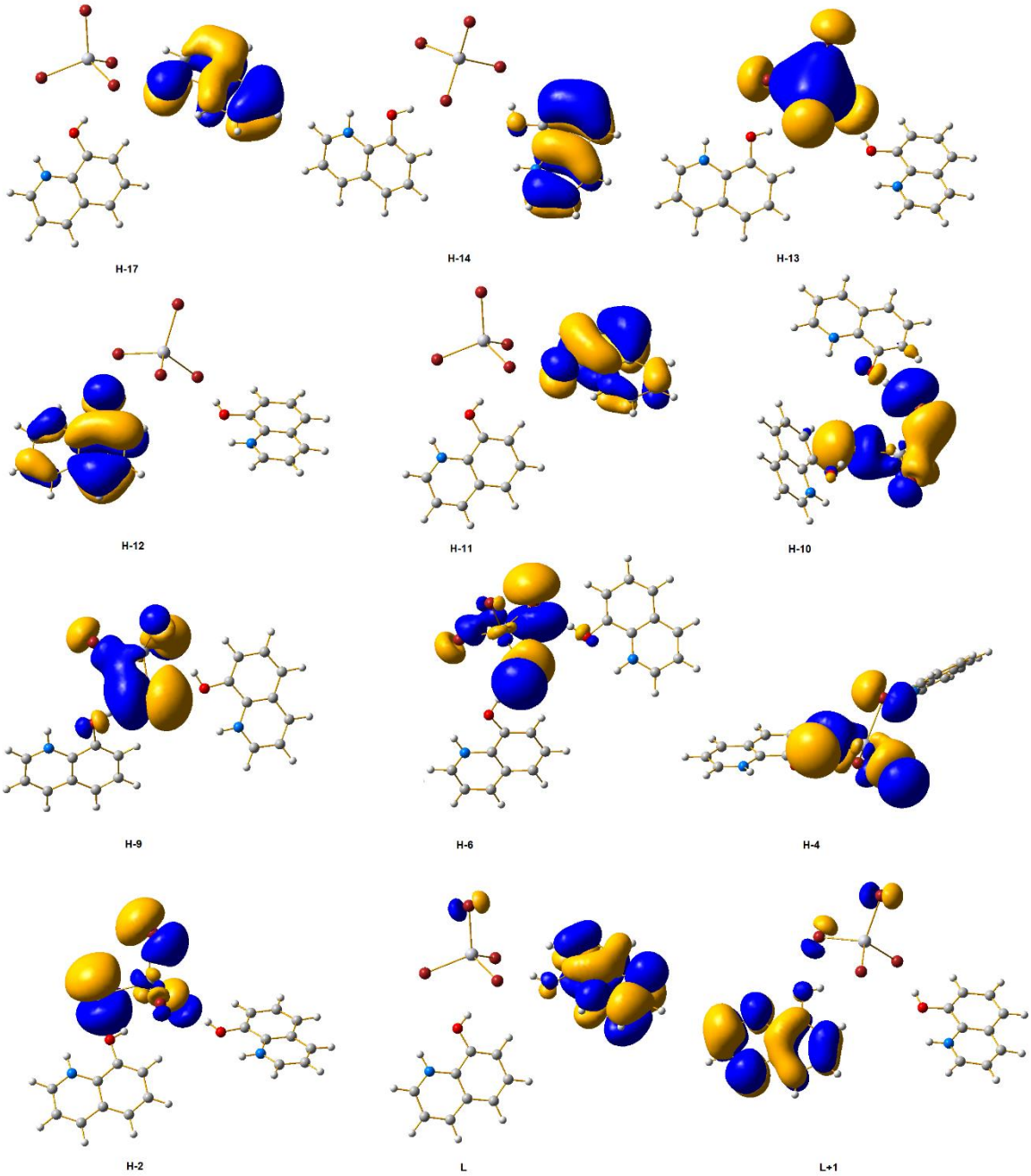


Figure S50. Molecular orbitals of the compound HgBr.

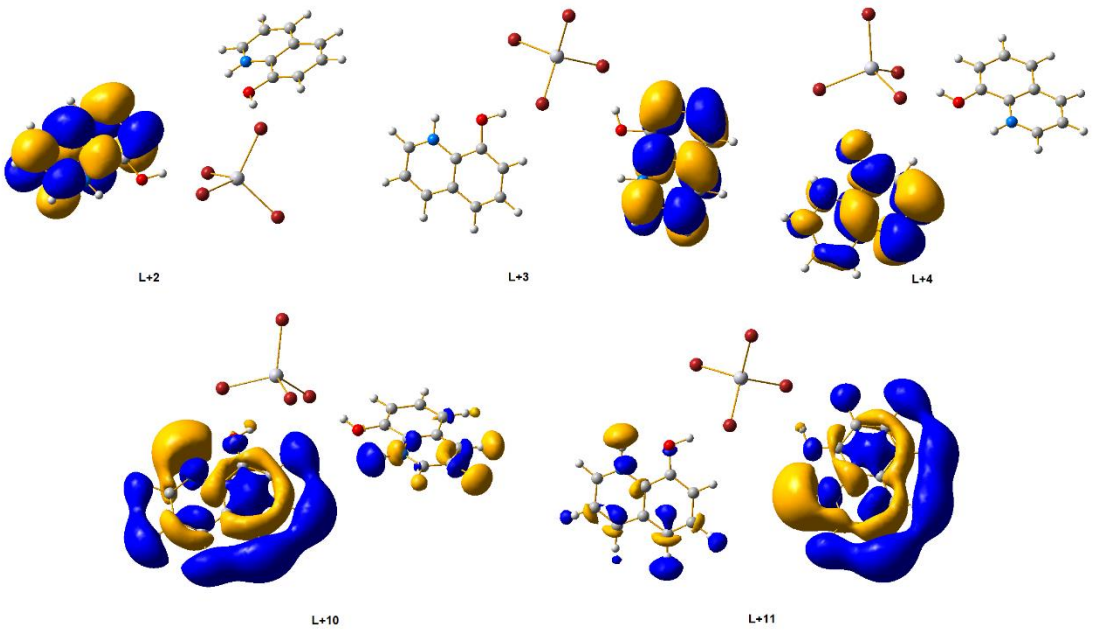


Figure S50. *continued*

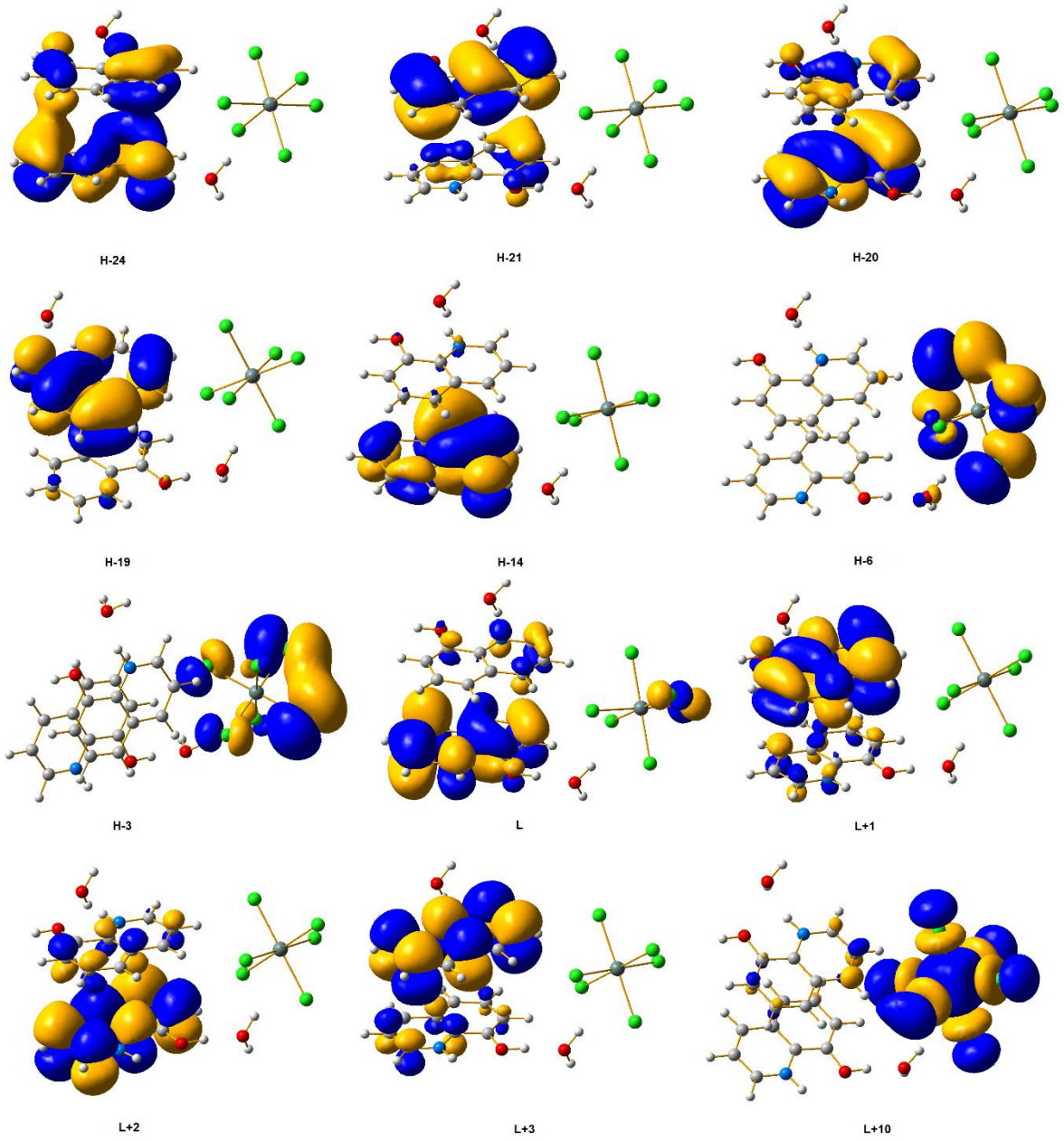


Figure S51. Molecular orbitals of the compound SnCl(1).

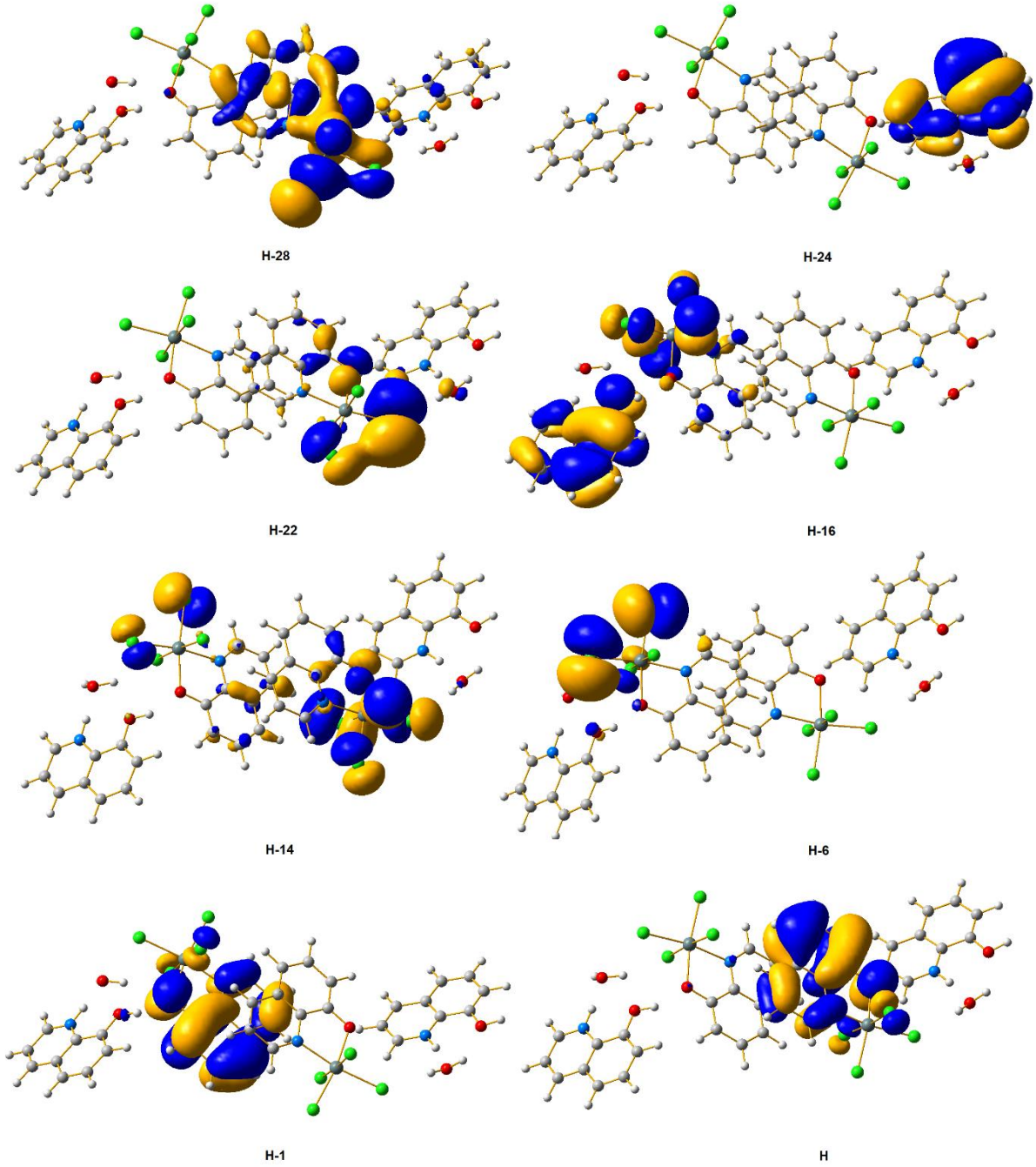


Figure S52. Molecular orbitals of the compound SnCl(2).

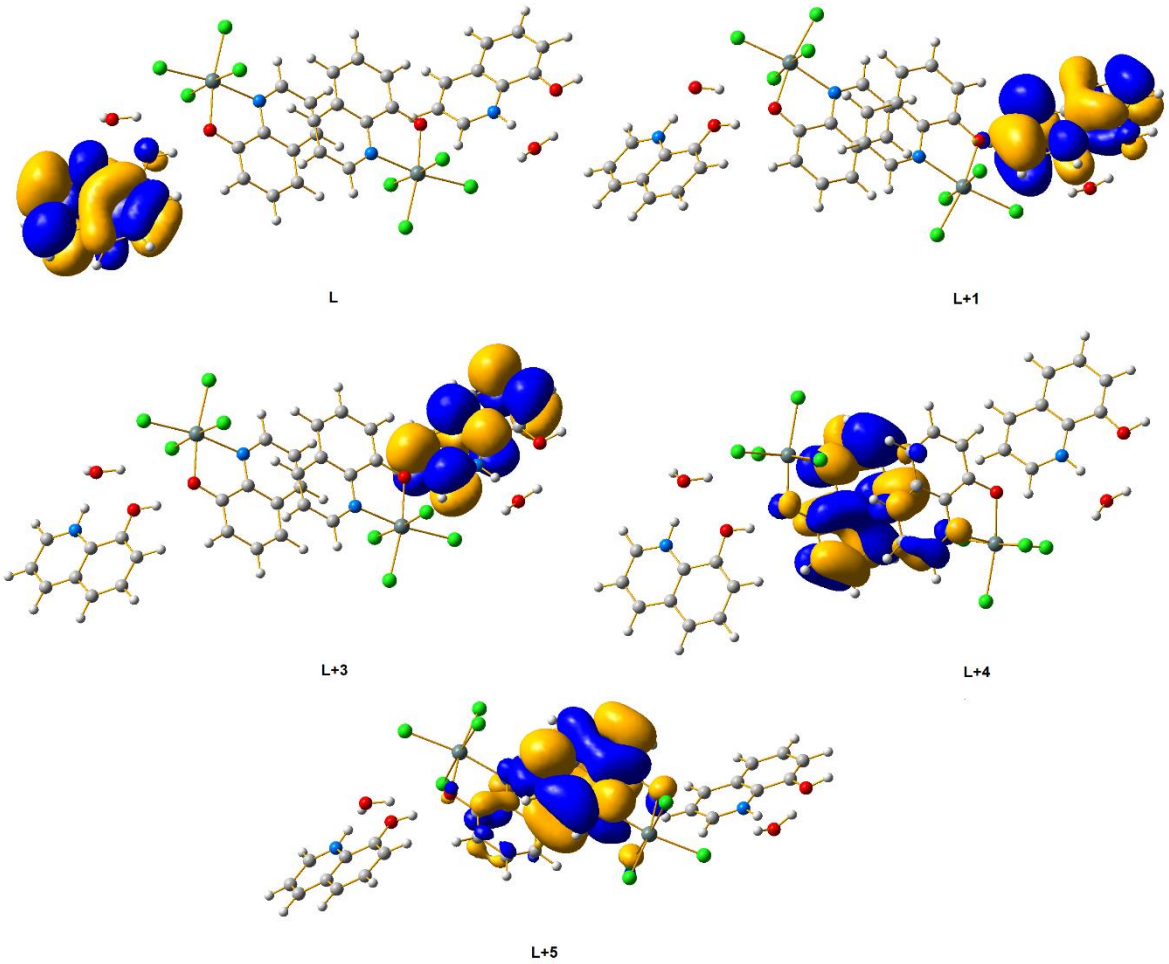


Figure S52. *continued*

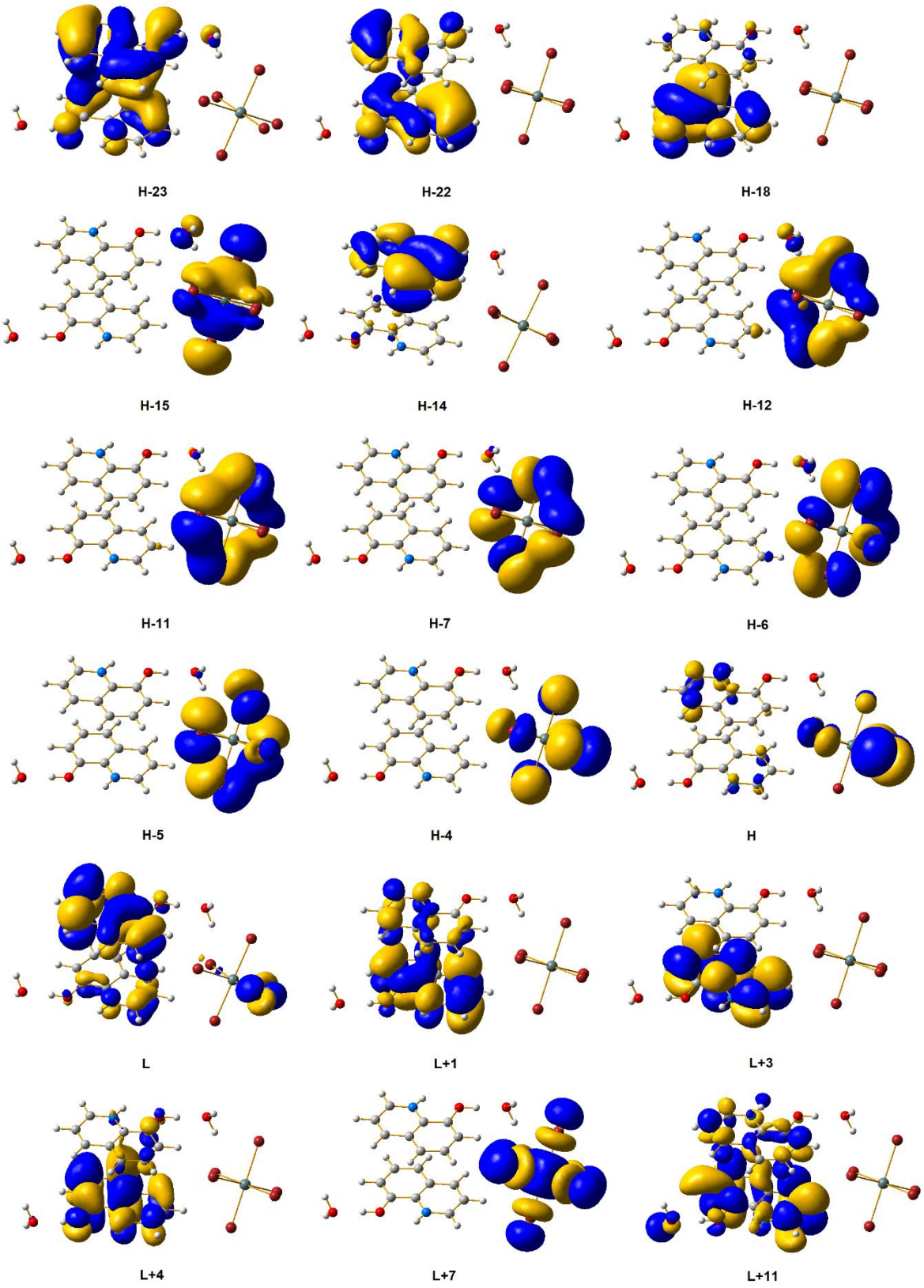


Figure S53. Molecular orbitals of the compound SnBr.

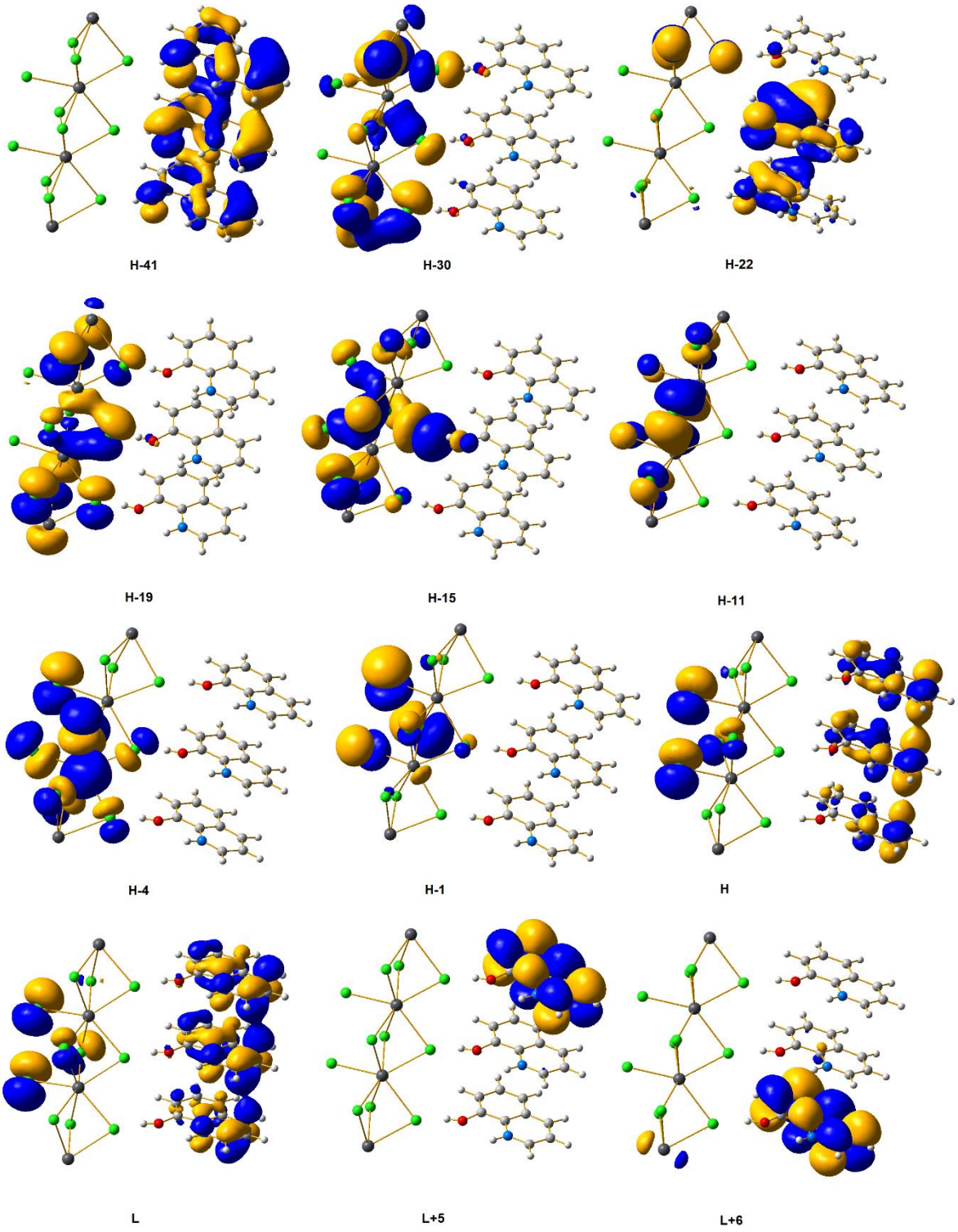


Figure S54. Molecular orbitals of the compound PbCl.

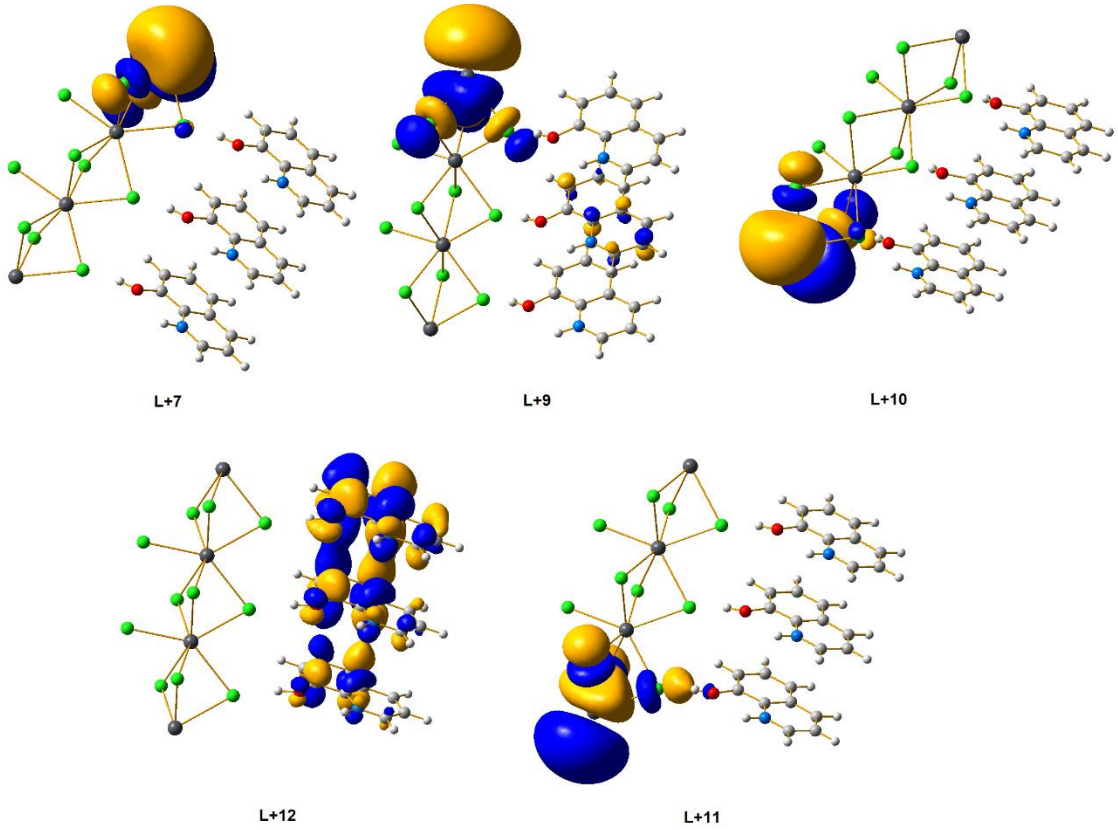


Figure S54. *continued*

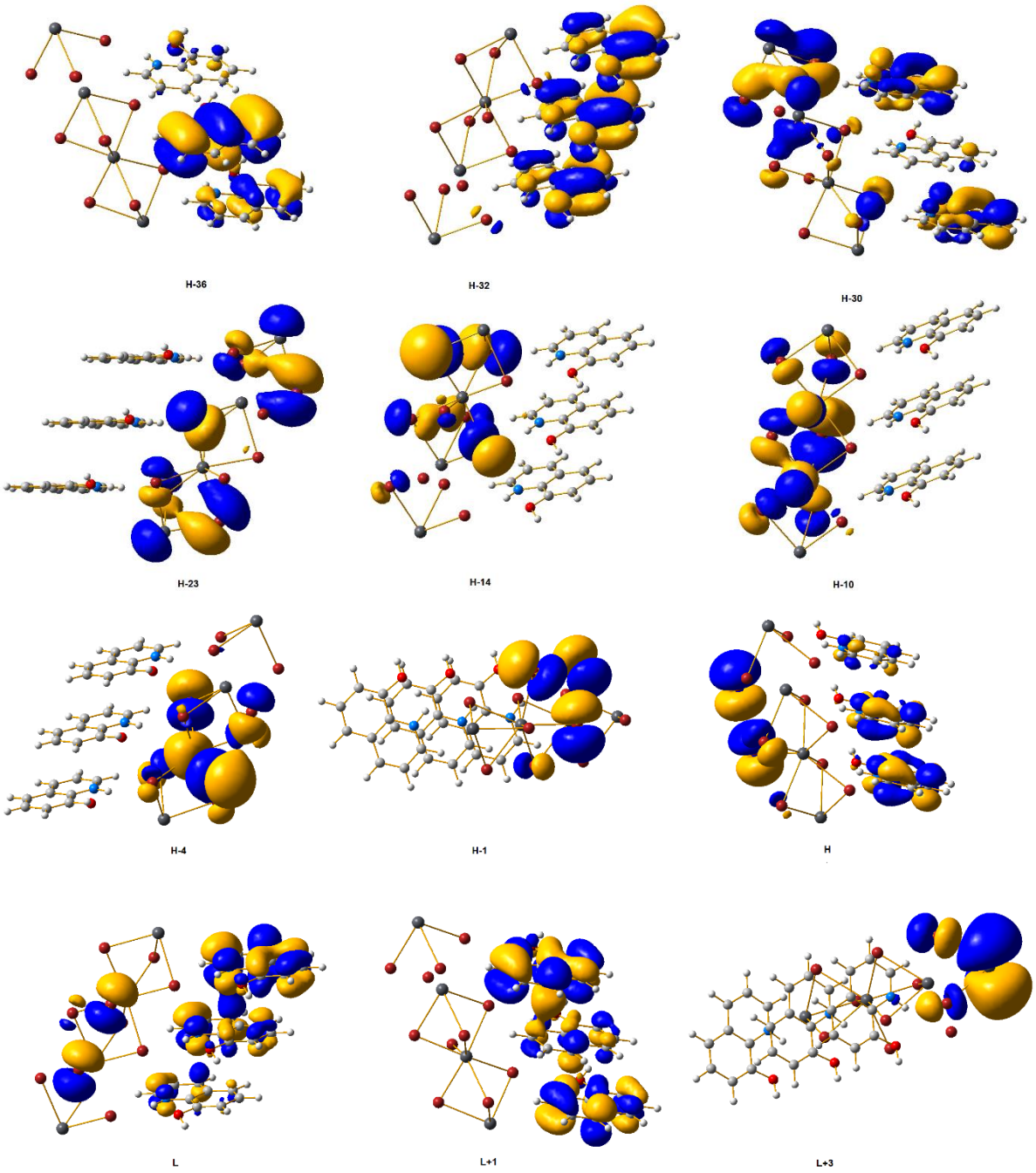


Figure S55. Molecular orbitals of the compound PbBr.

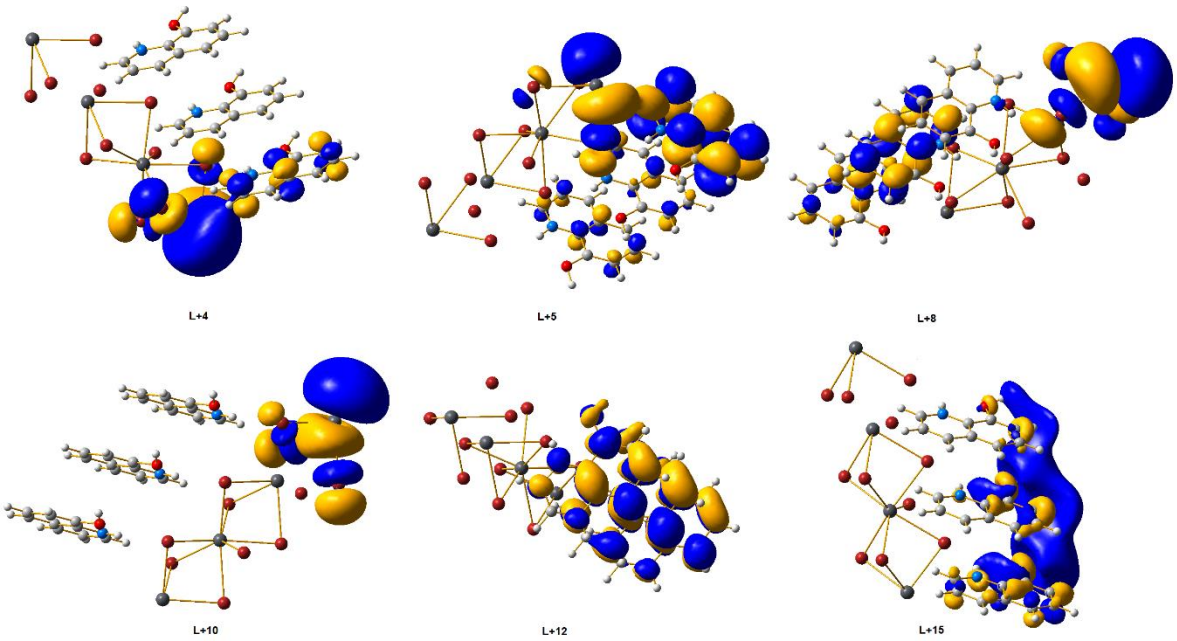


Figure S55. *continued*

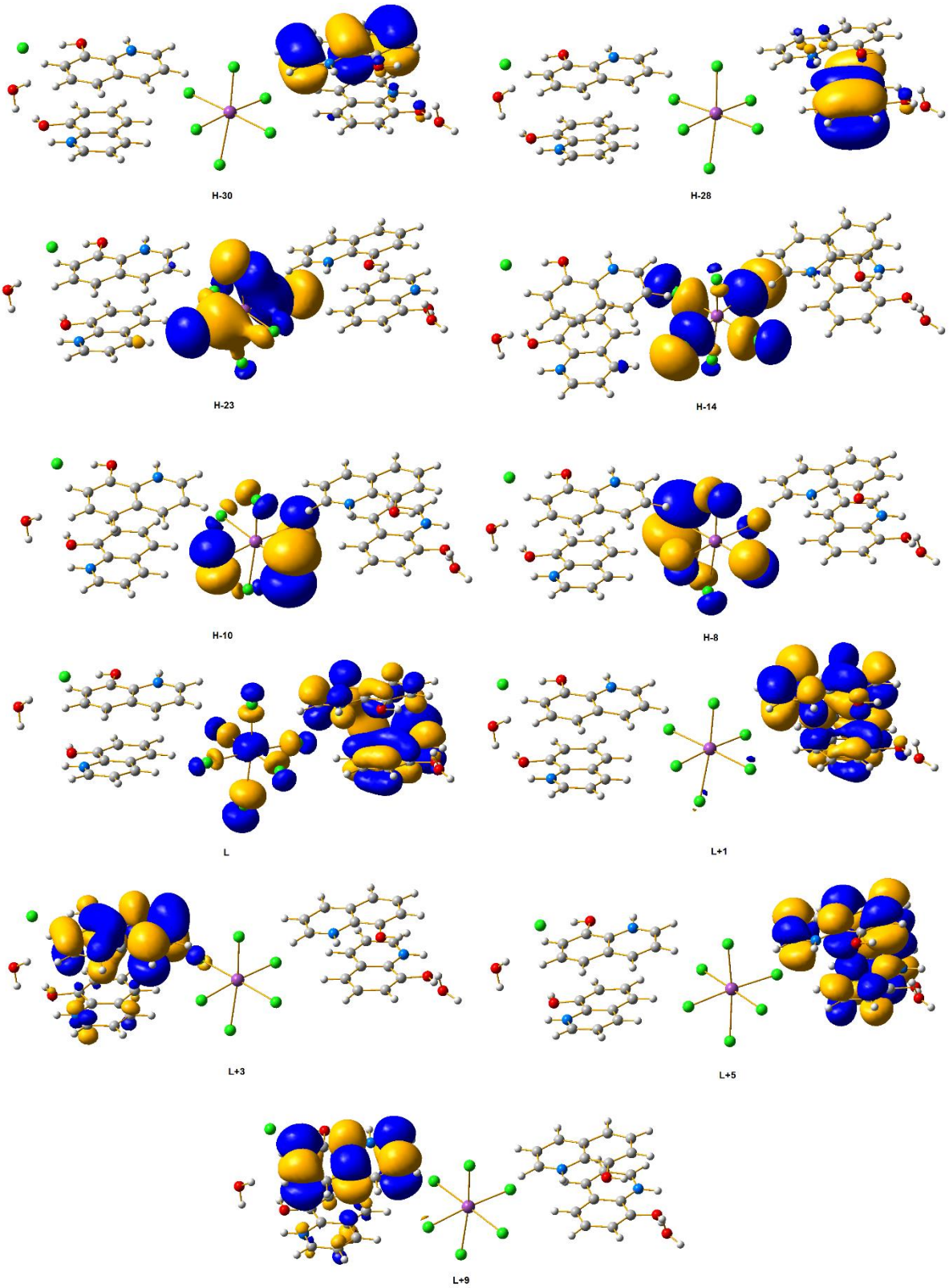


Figure S56. Molecular orbitals of the compound BiCl.

Calculated molecular orbitals involved in the excitation process, corresponding to Table 2 of the main manuscript (Figure S57-S75). H letter indicates HOMO, L - LUMO, and +/-(number) represents subsequent orbitals below HOMO and above LUMO, respectively

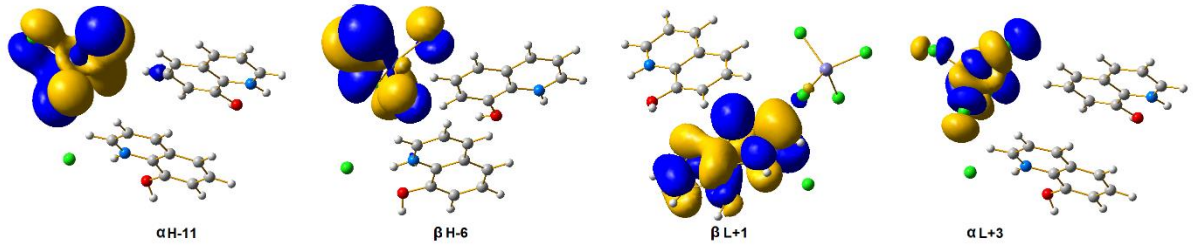


Figure S57. Molecular orbitals of FeCl

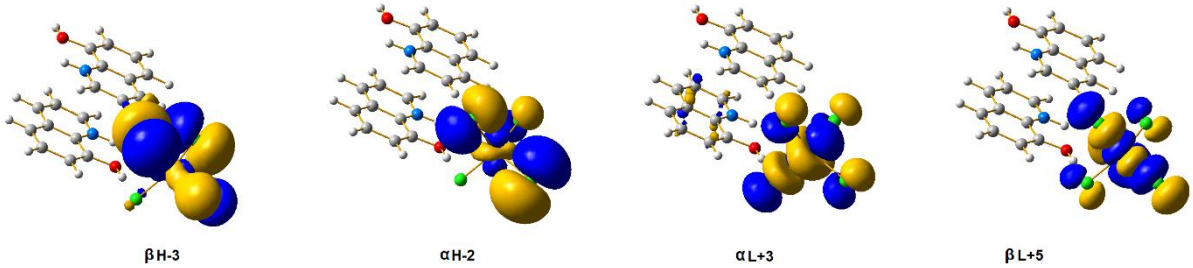


Figure S58. Molecular orbitals of CoCl

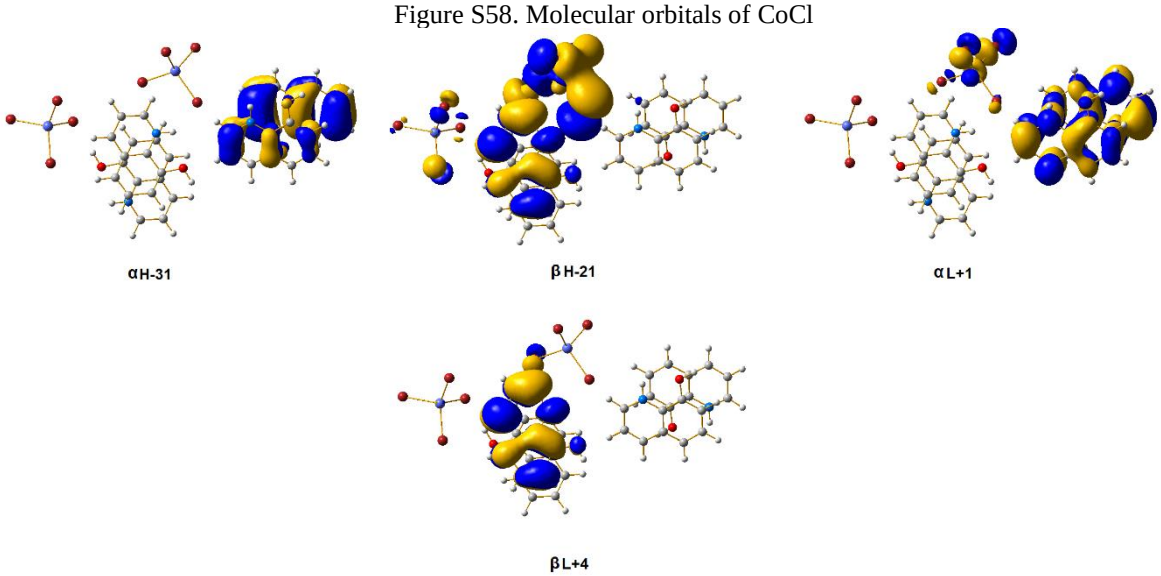


Figure S59. Molecular orbitals of CoBr

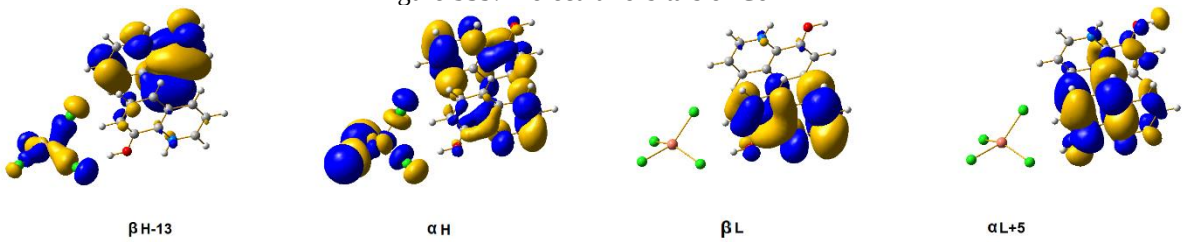


Figure S60. Molecular orbitals of CuCl

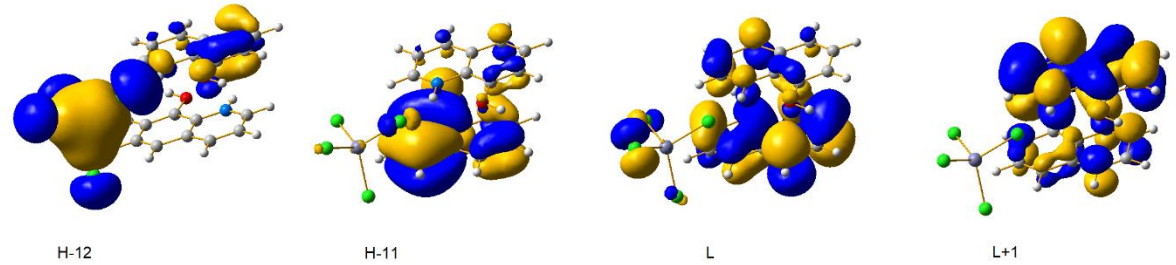


Figure S61. Molecular orbitals of ZnCl

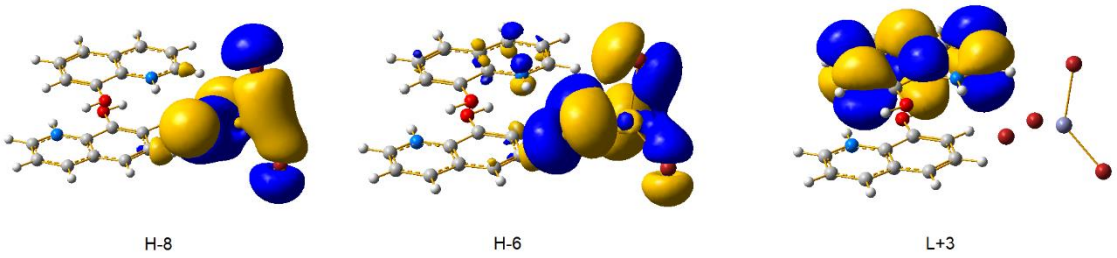


Figure S62. Molecular orbitals of ZnBr

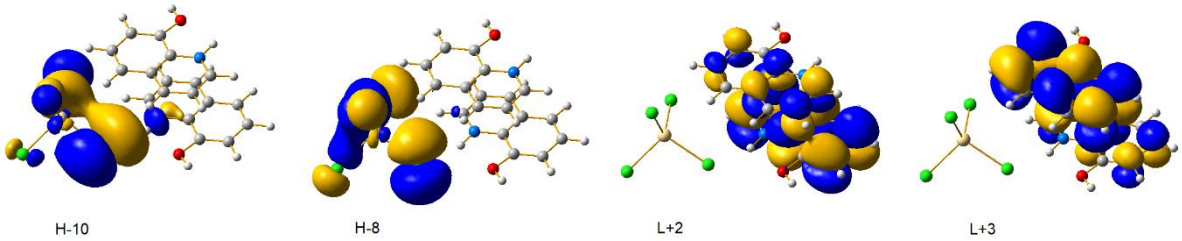


Figure S63. Molecular orbitals of CdCl

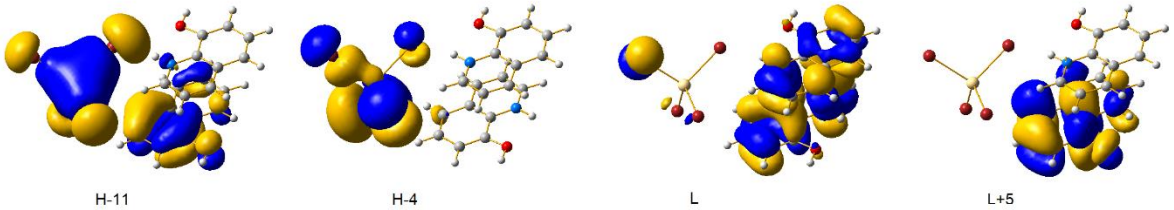


Figure S64. Molecular orbitals of CdBr

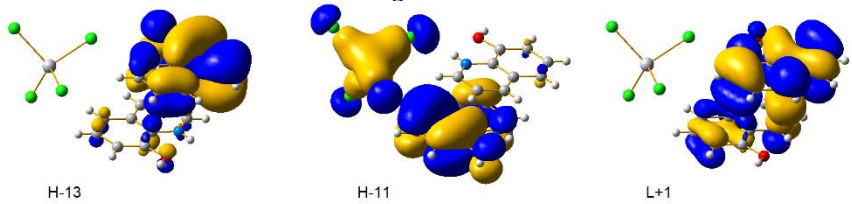


Figure S65. Molecular orbitals of HgCl(1)

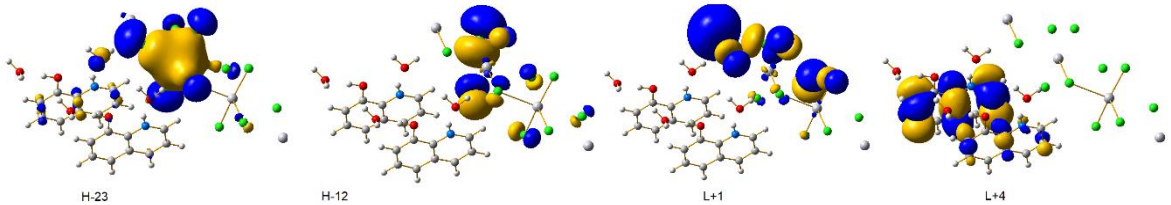


Figure S66. Molecular orbitals of HgCl(2)

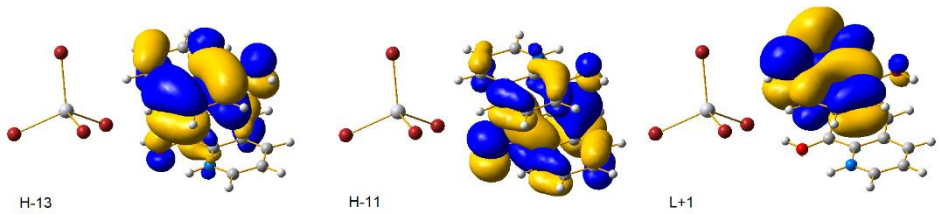


Figure S67. Molecular orbitals of HgBr

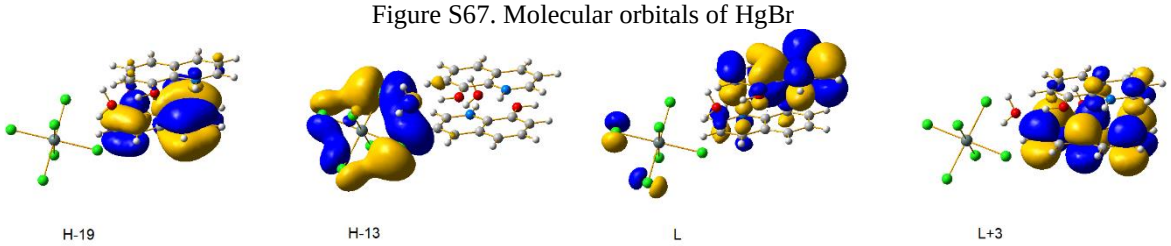


Figure S68. Molecular orbitals of SnCl(1)

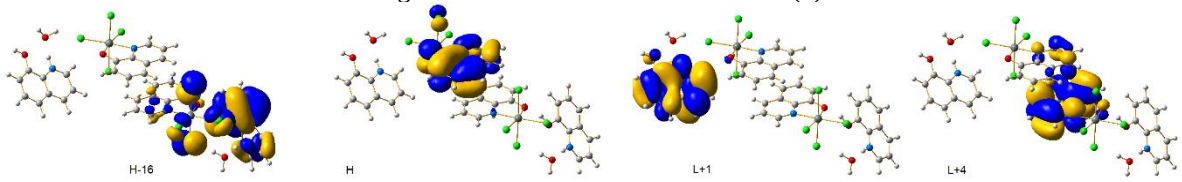


Figure S69. Molecular orbitals of SnCl(2)

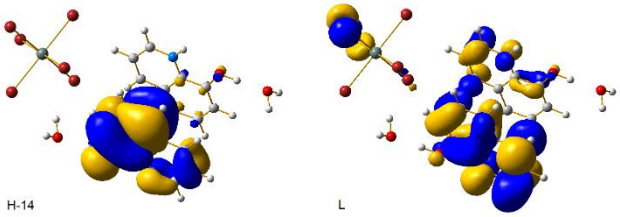


Figure S70. Molecular orbitals of SnBr

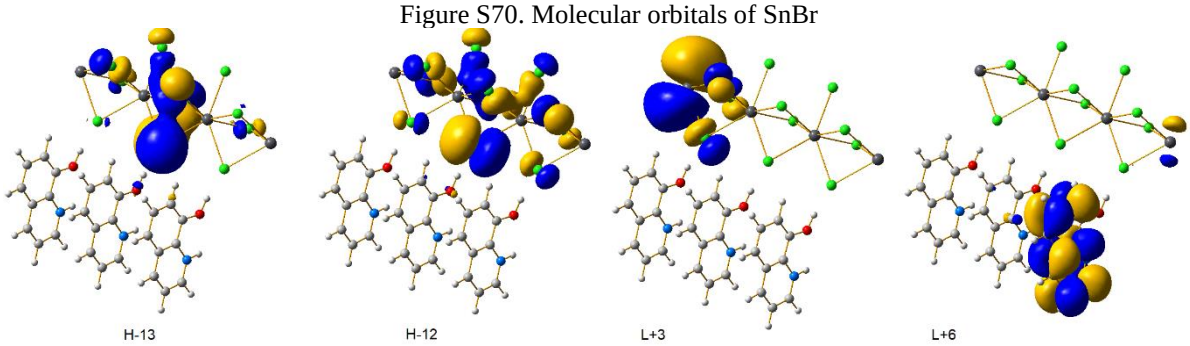


Figure S71. Molecular orbitals of PbCl

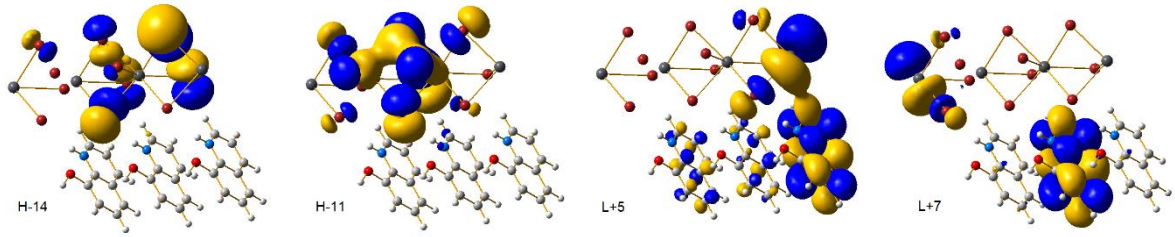
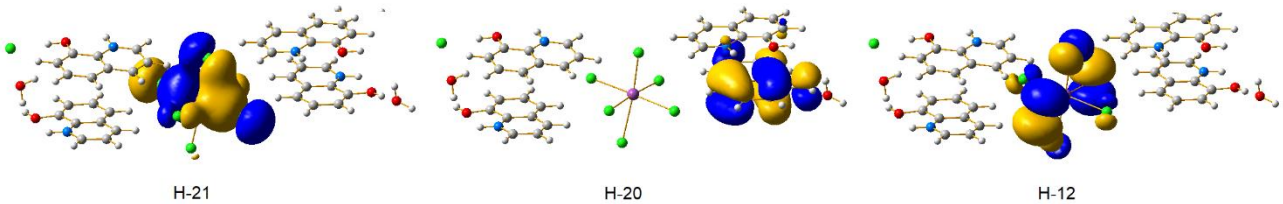


Figure S72. Molecular orbitals of PbBr



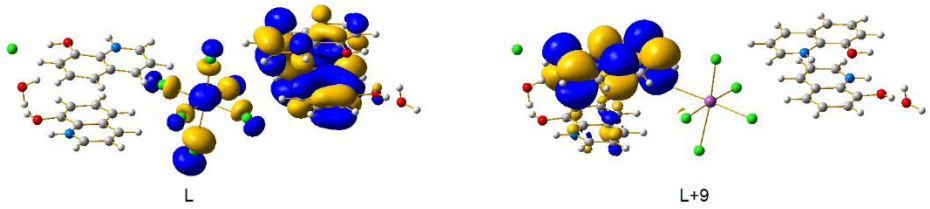


Figure S73. Molecular orbitals of BiCl

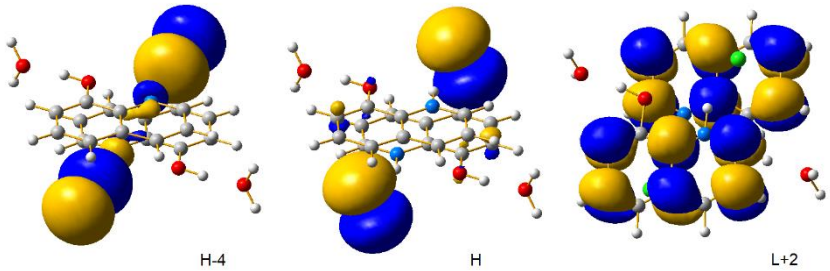


Figure S74. Molecular orbitals of 8hqHCl

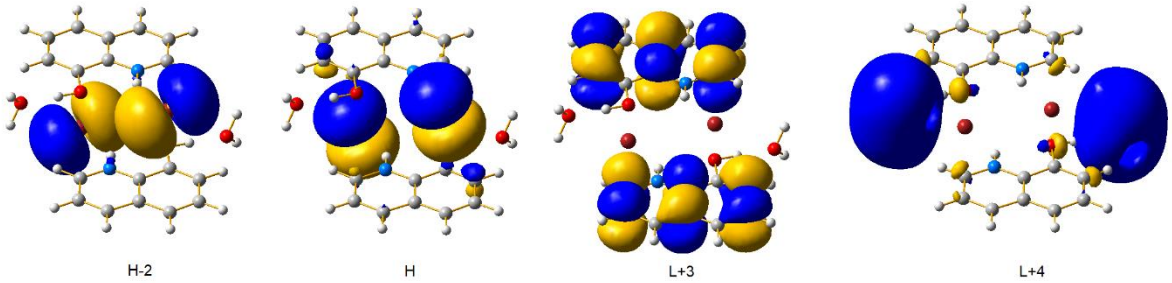


Figure S75. Molecular orbitals of 8hqHBr

3D-EEM fluorescence spectra (Figure S76-S95)

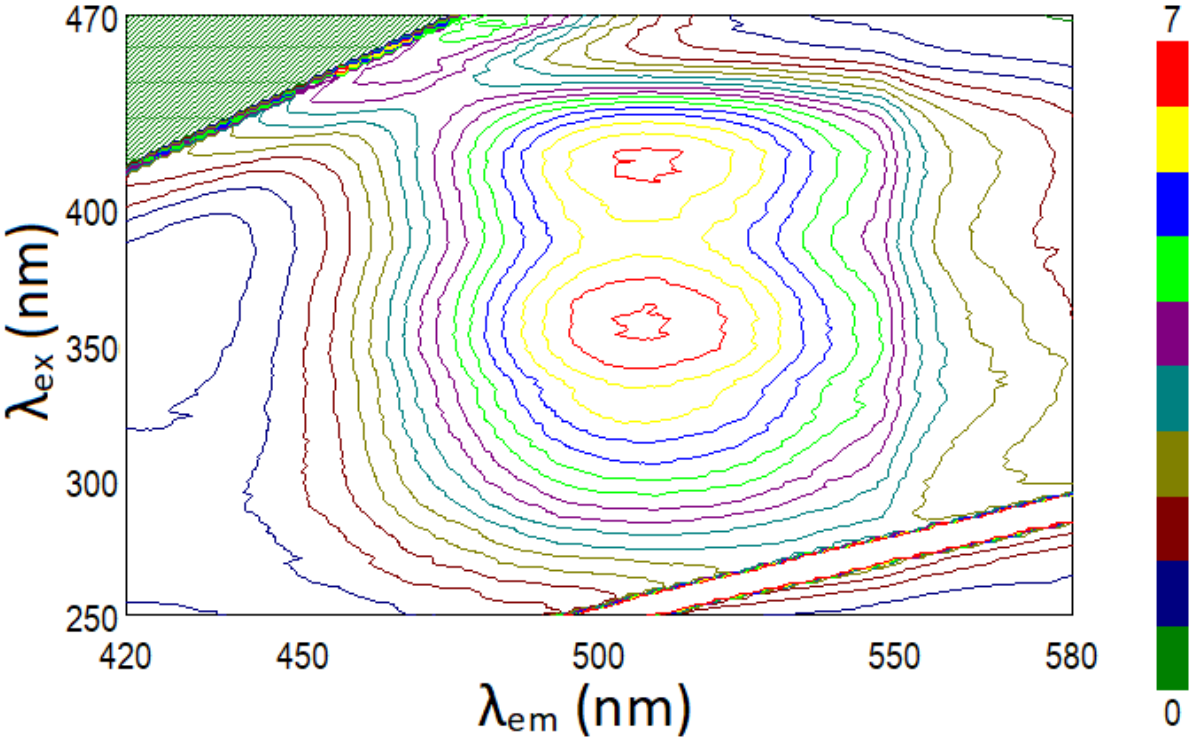


Figure S76. 3D-EEM fluorescence spectrum of FeCl

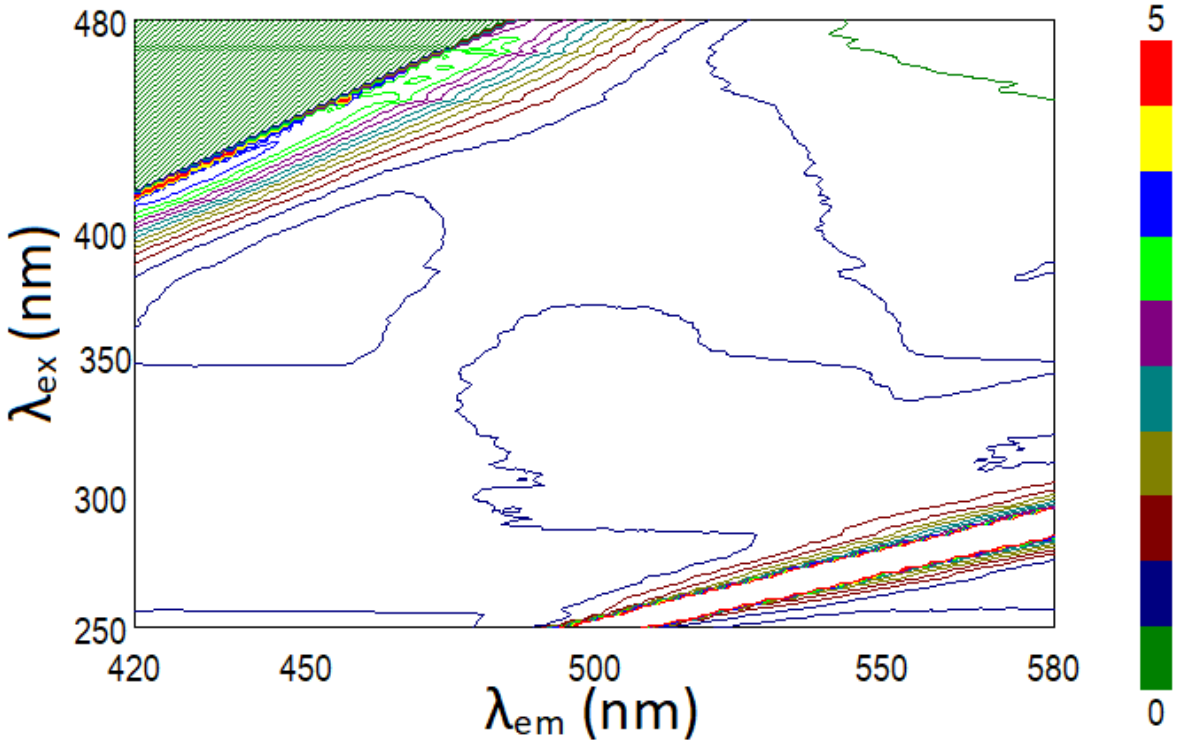


Figure S77. 3D-EEM fluorescence spectrum of FeBr

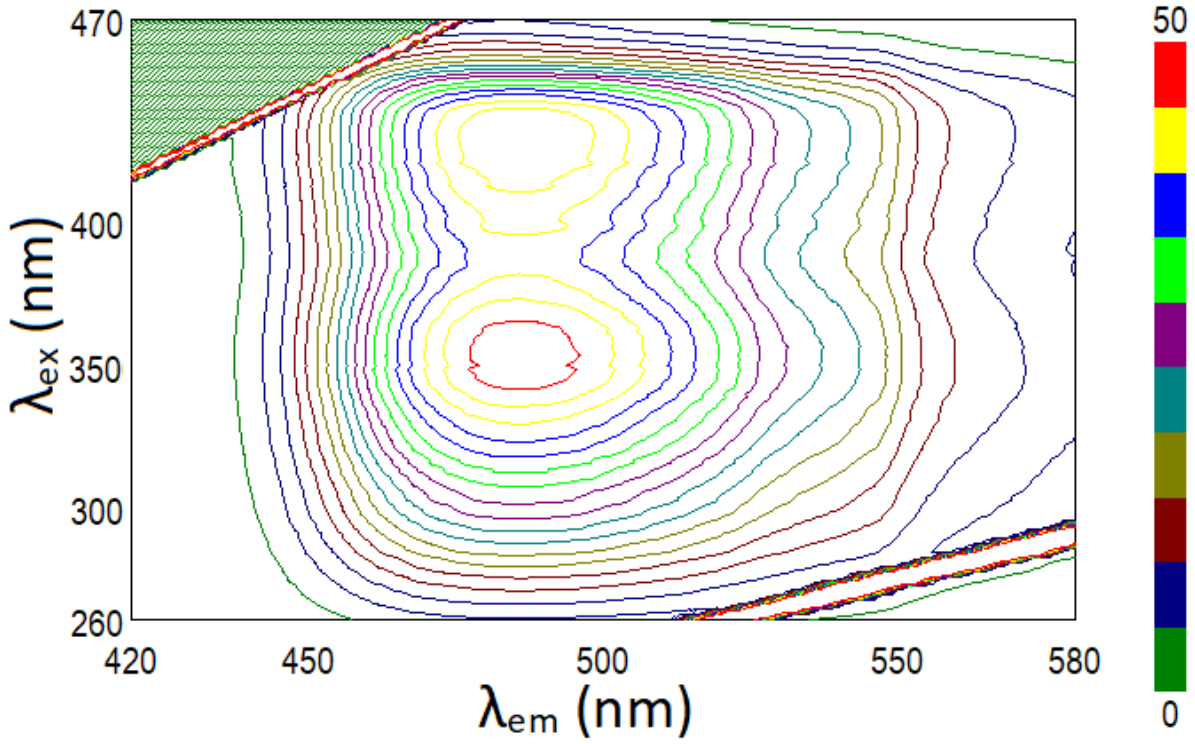


Figure S78. 3D-EEM fluorescence spectrum of CoCl

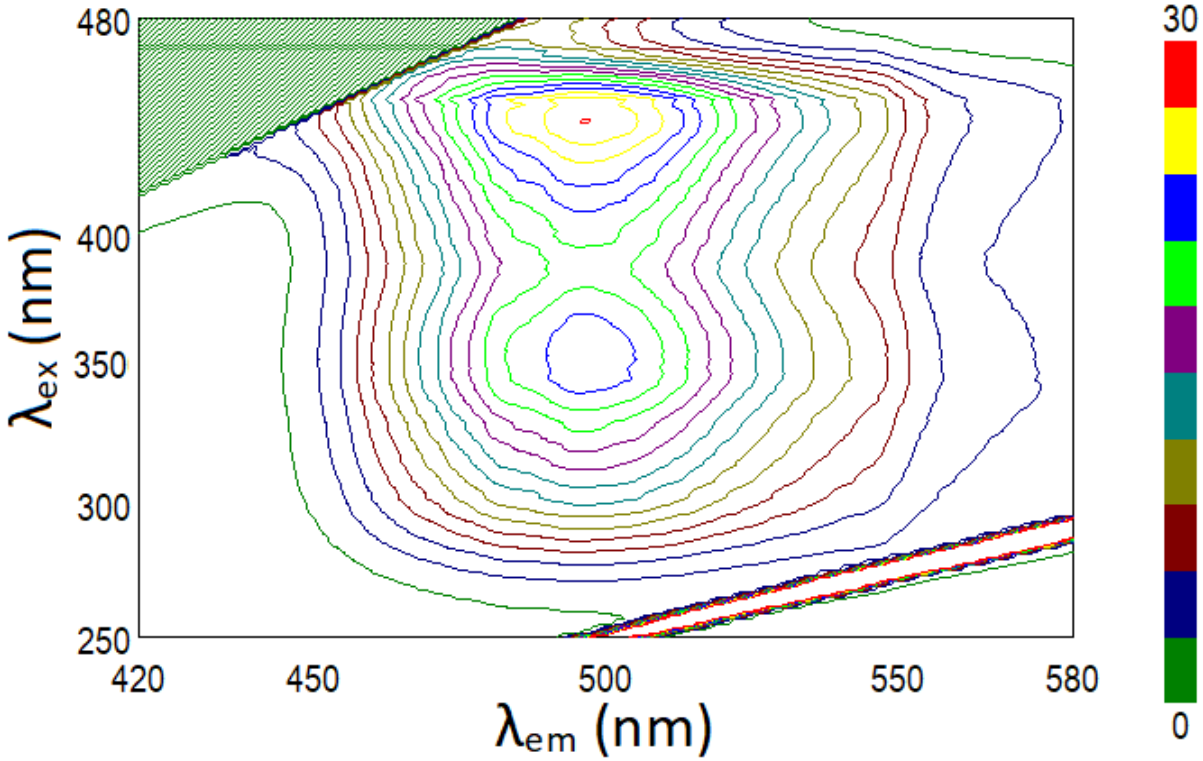


Figure S79. 3D-EEM fluorescence spectrum of CoBr

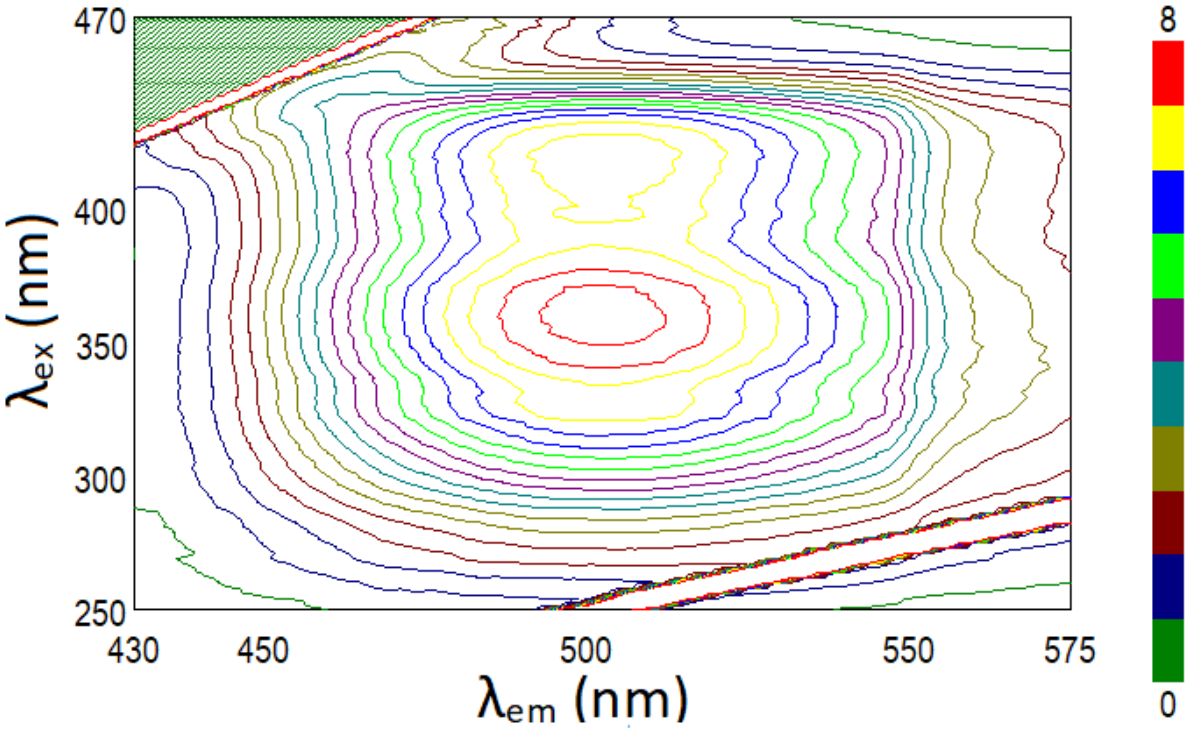


Figure S80. 3D-EEM fluorescence spectrum of CuCl

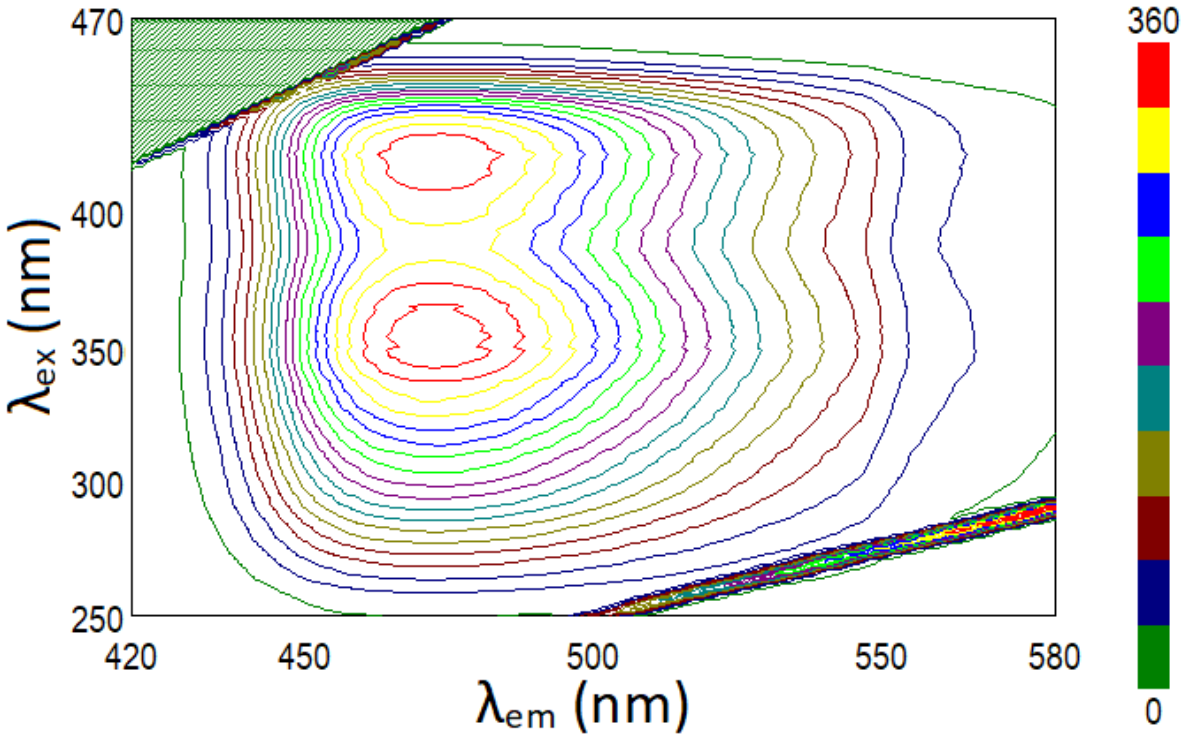


Figure S81. 3D-EEM fluorescence spectrum of ZnCl

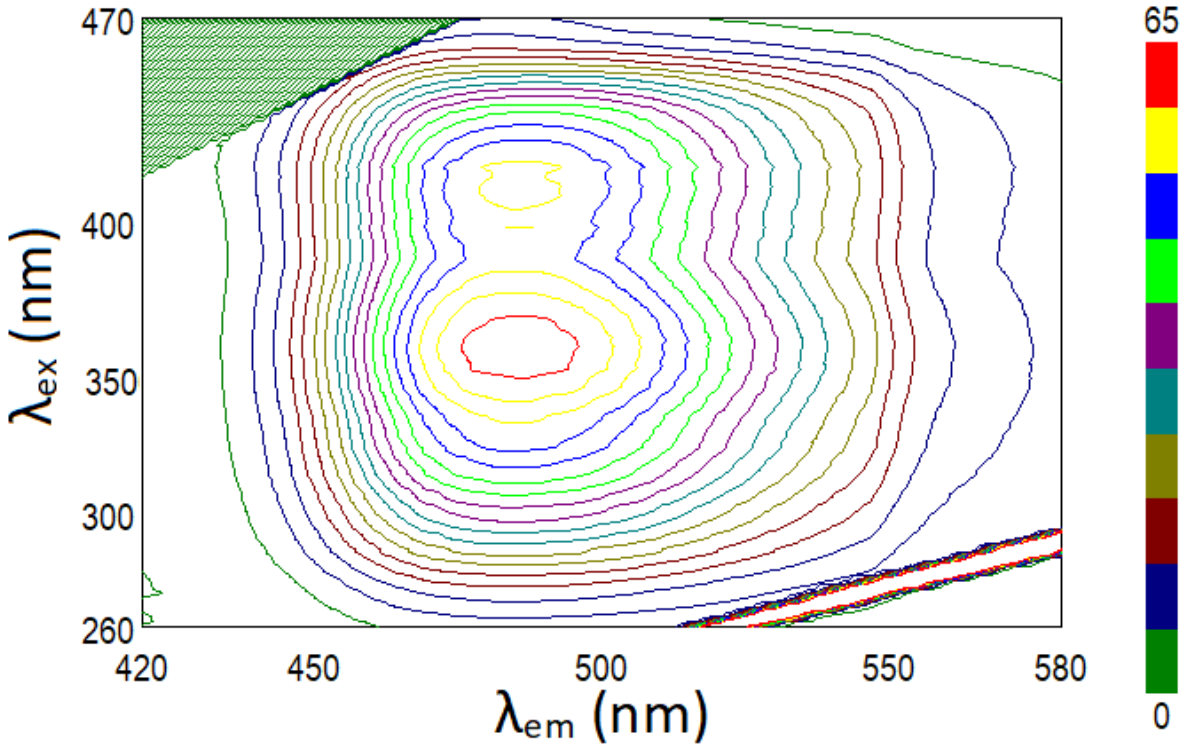


Figure S82. 3D-EEM fluorescence spectrum of ZnBr

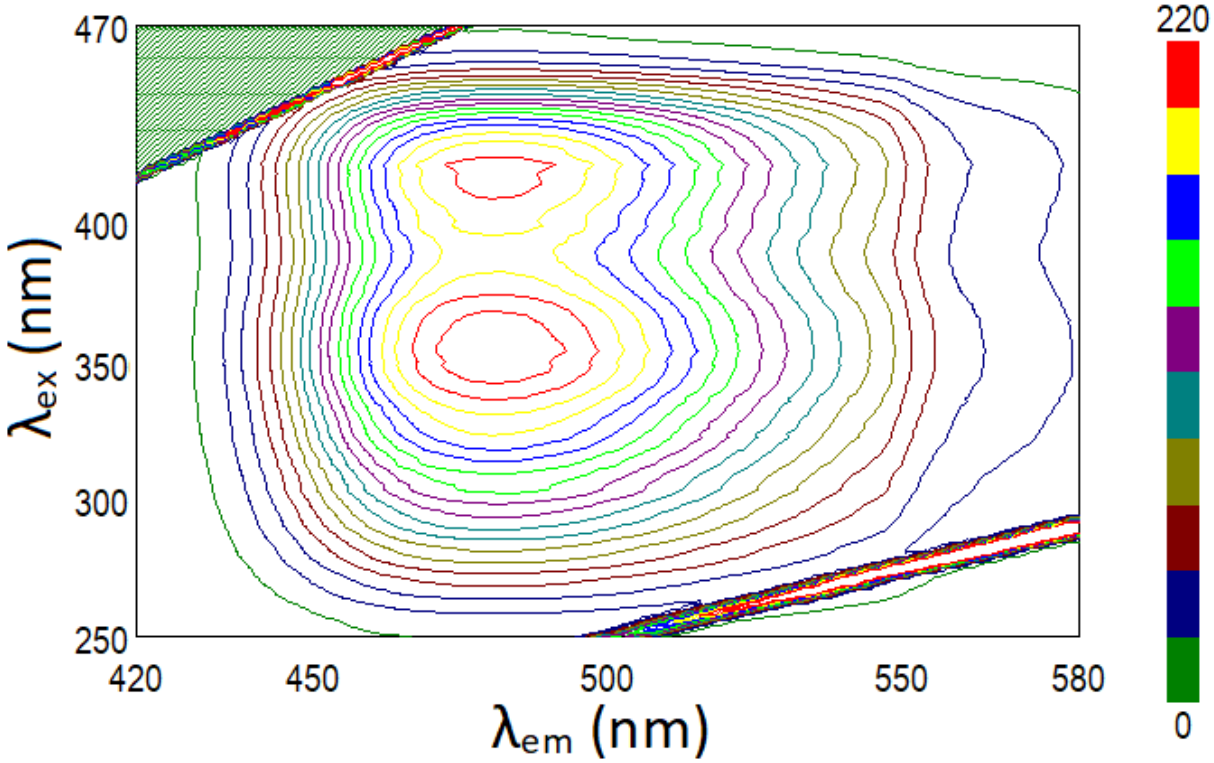


Figure S83. 3D-EEM fluorescence spectrum of CdCl

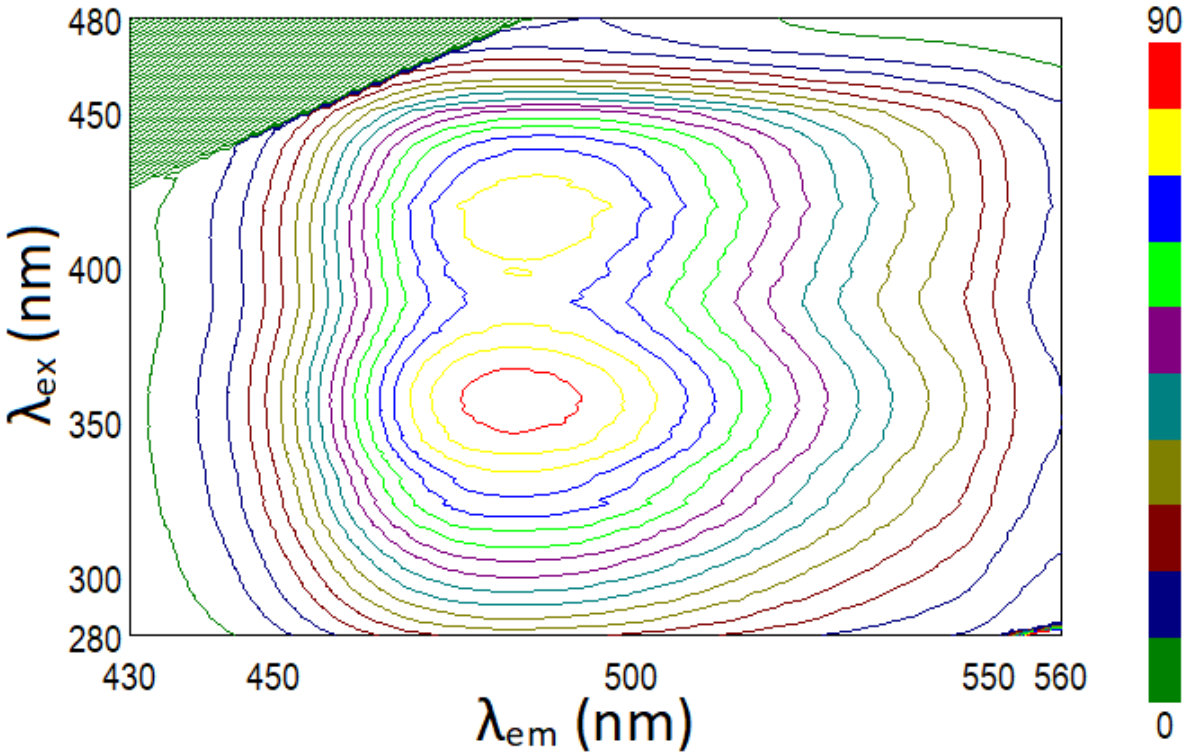


Figure S84. 3D-EEM fluorescence spectrum of CdBr

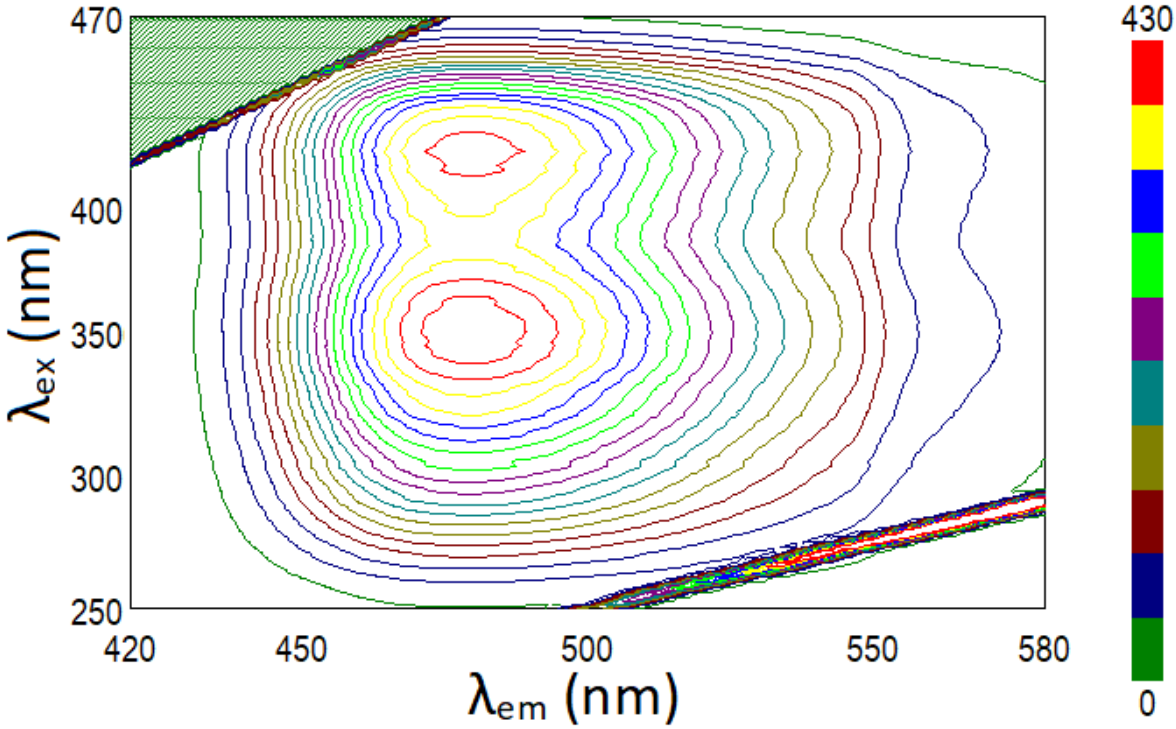


Figure S85. 3D-EEM fluorescence spectrum of HgCl(1)

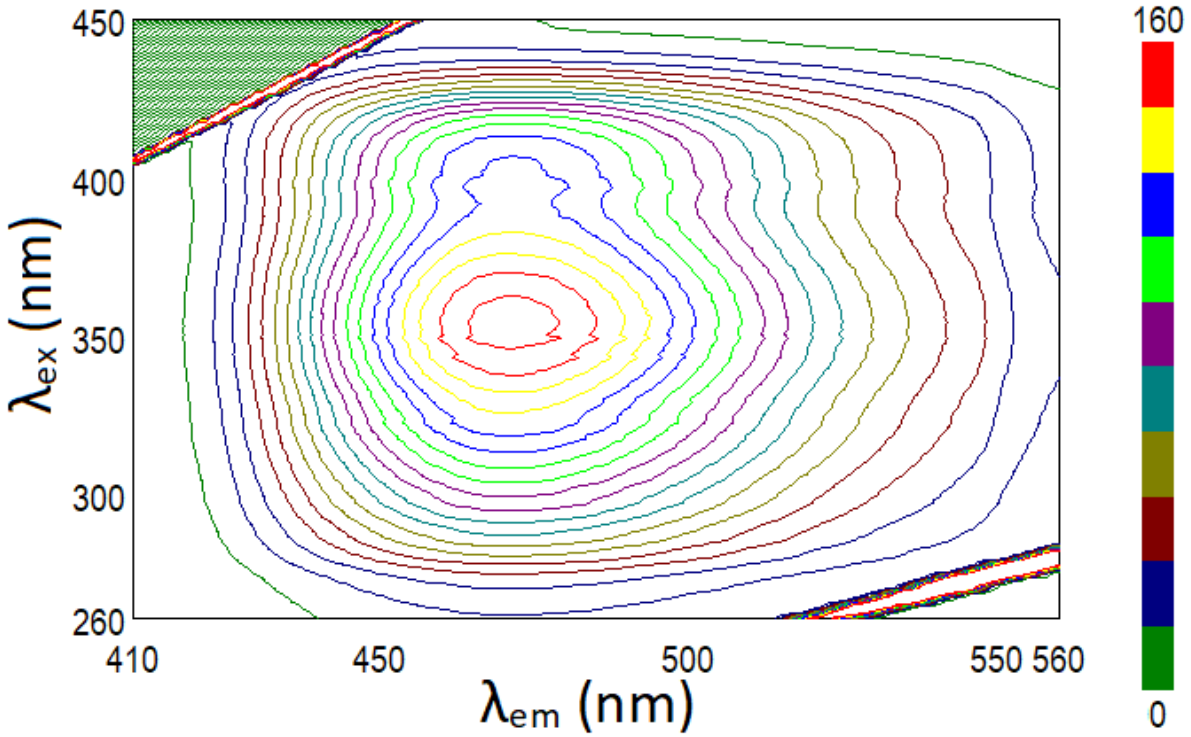


Figure S86. 3D-EEM fluorescence spectrum of HgCl(2)

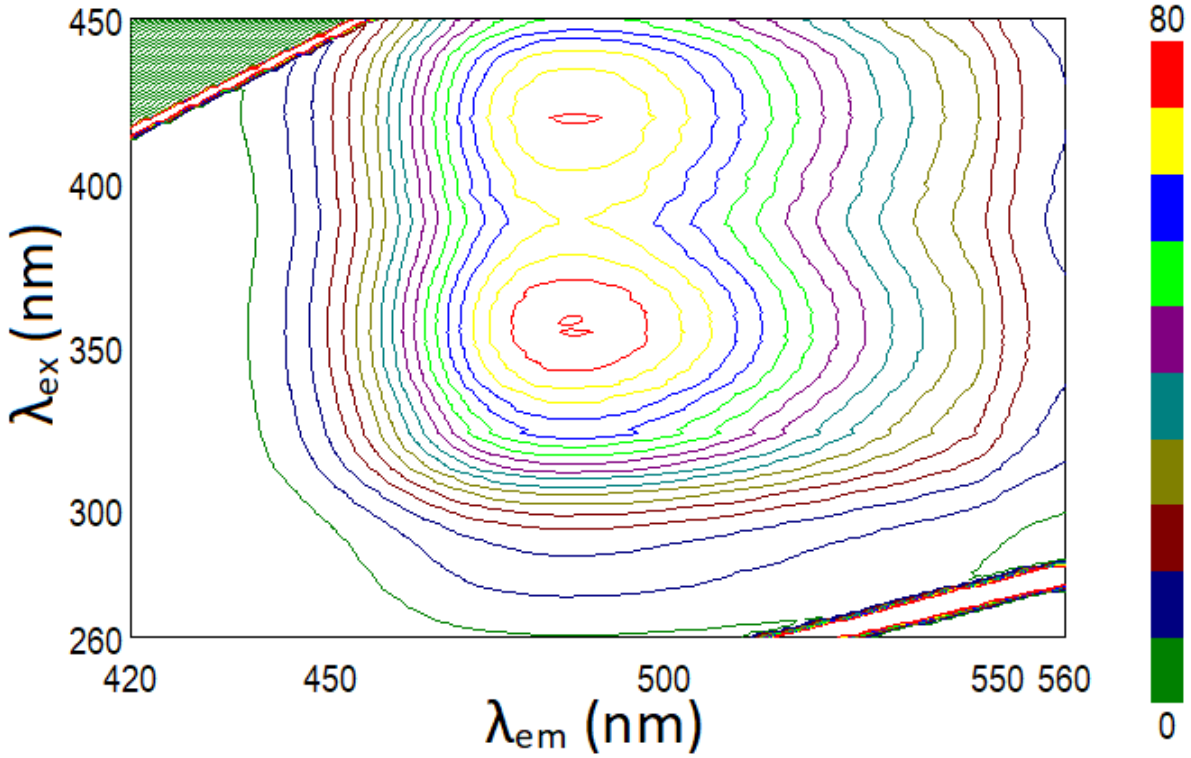


Figure S87. 3D-EEM fluorescence spectrum of HgBr

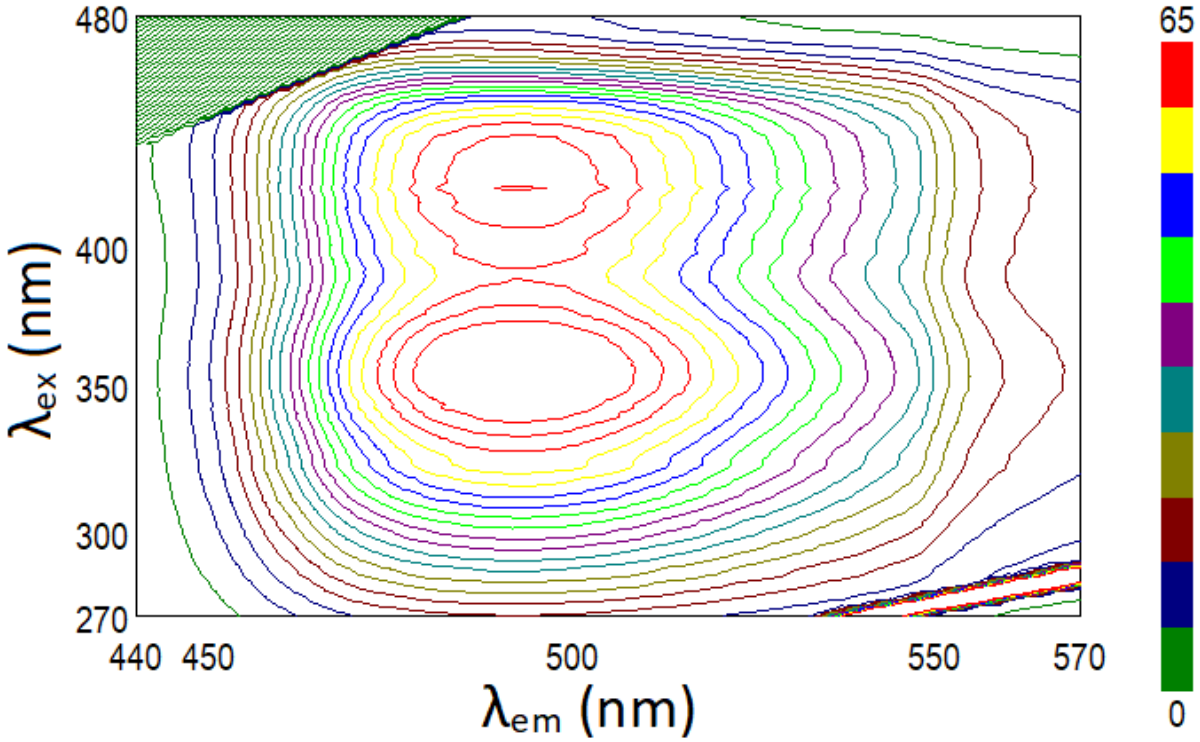


Figure S88. 3D-EEM fluorescence spectrum of SnCl(1)

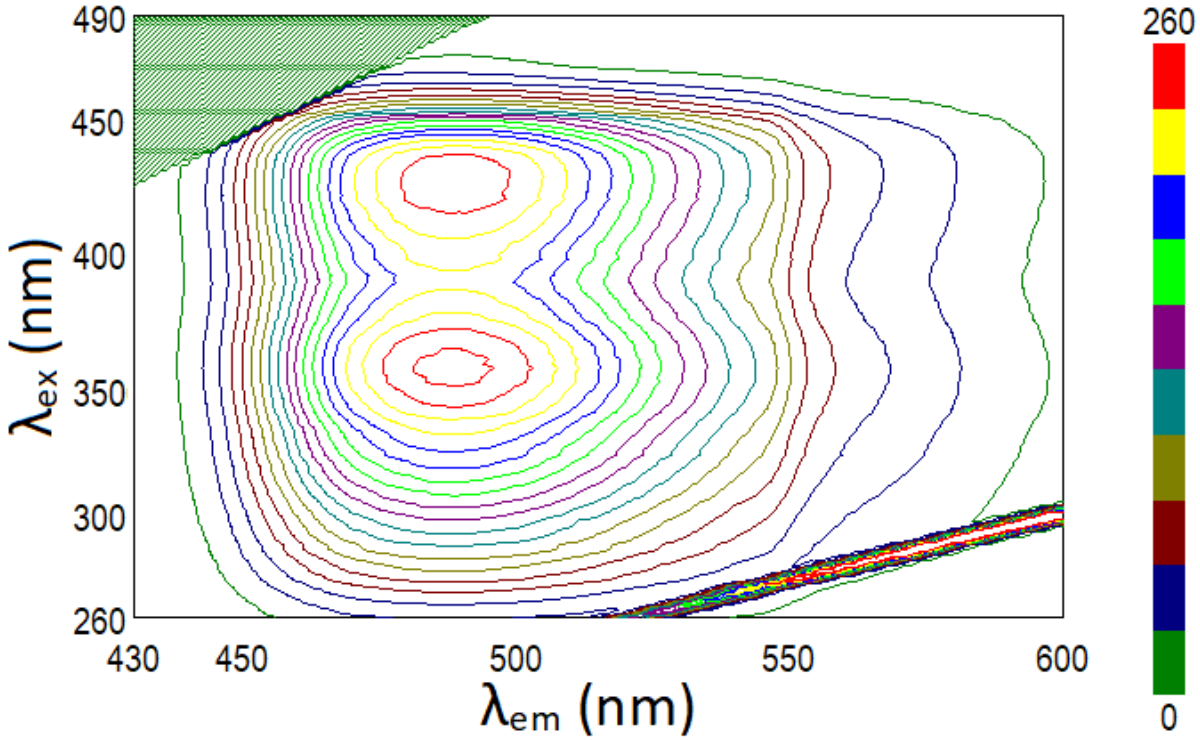


Figure S89. 3D-EEM fluorescence spectrum of SnCl(2)

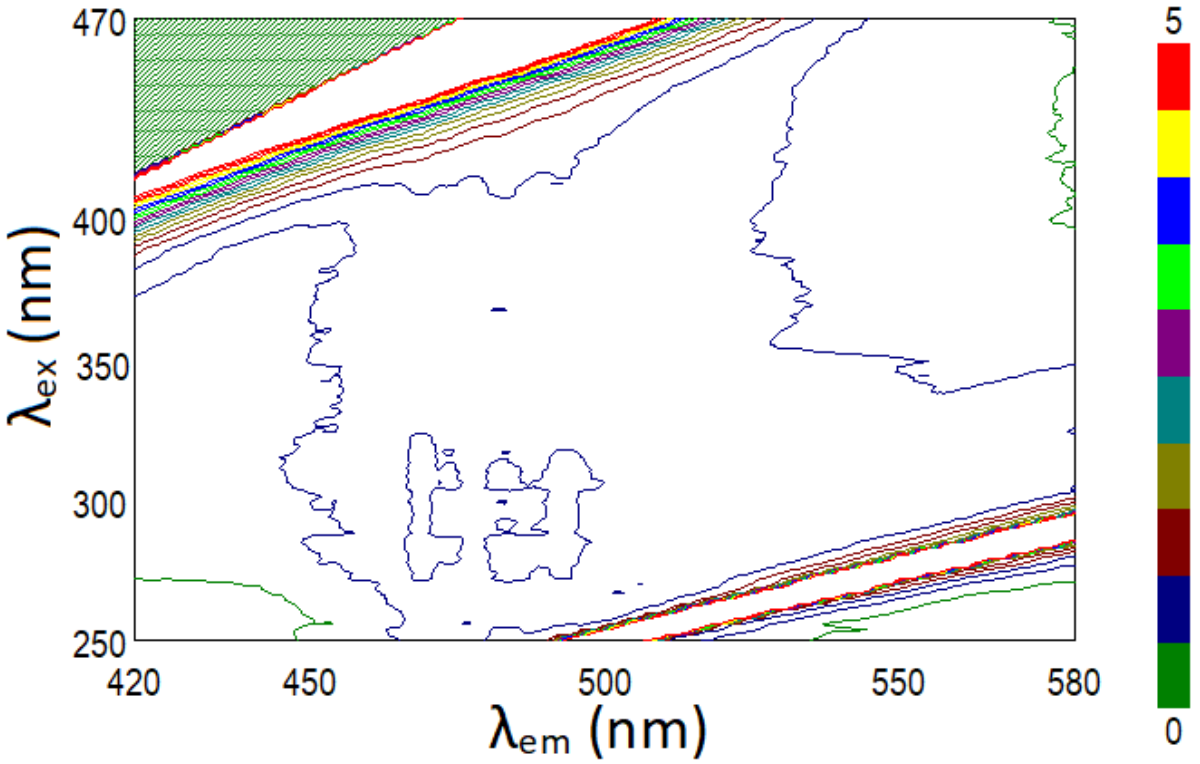


Figure S90. 3D-EEM fluorescence spectrum of SnBr

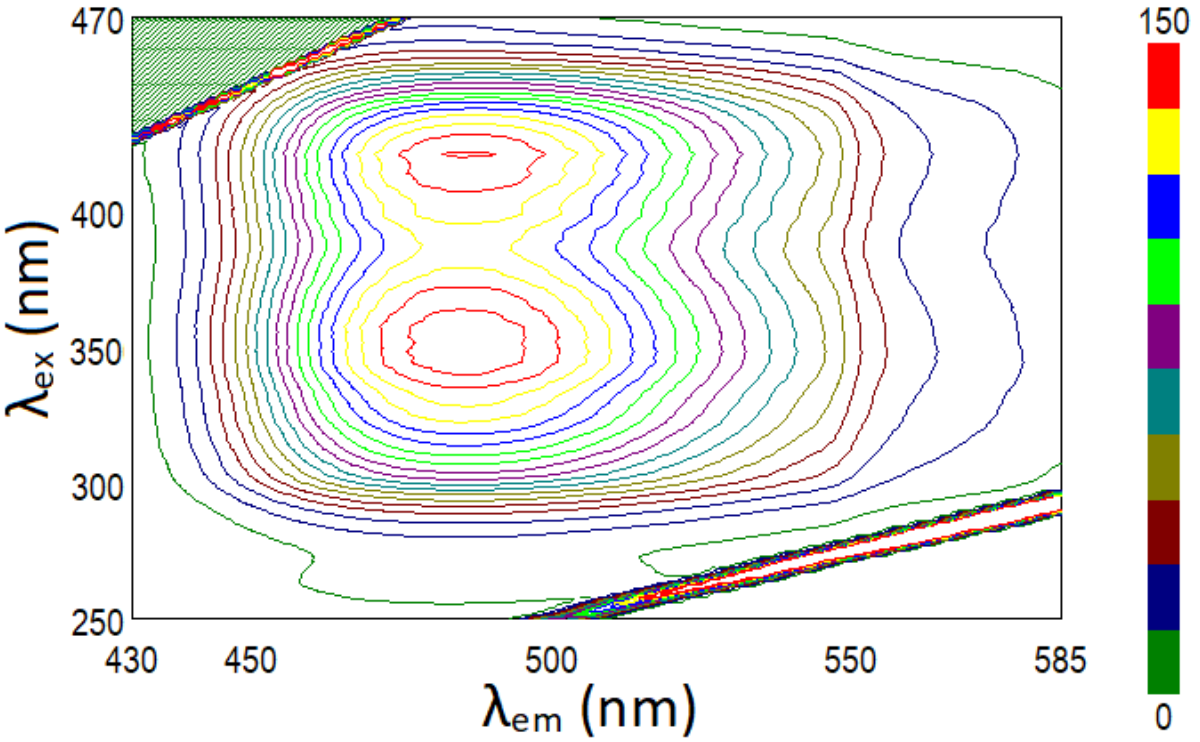


Figure S91. 3D-EEM fluorescence spectrum of PbCl

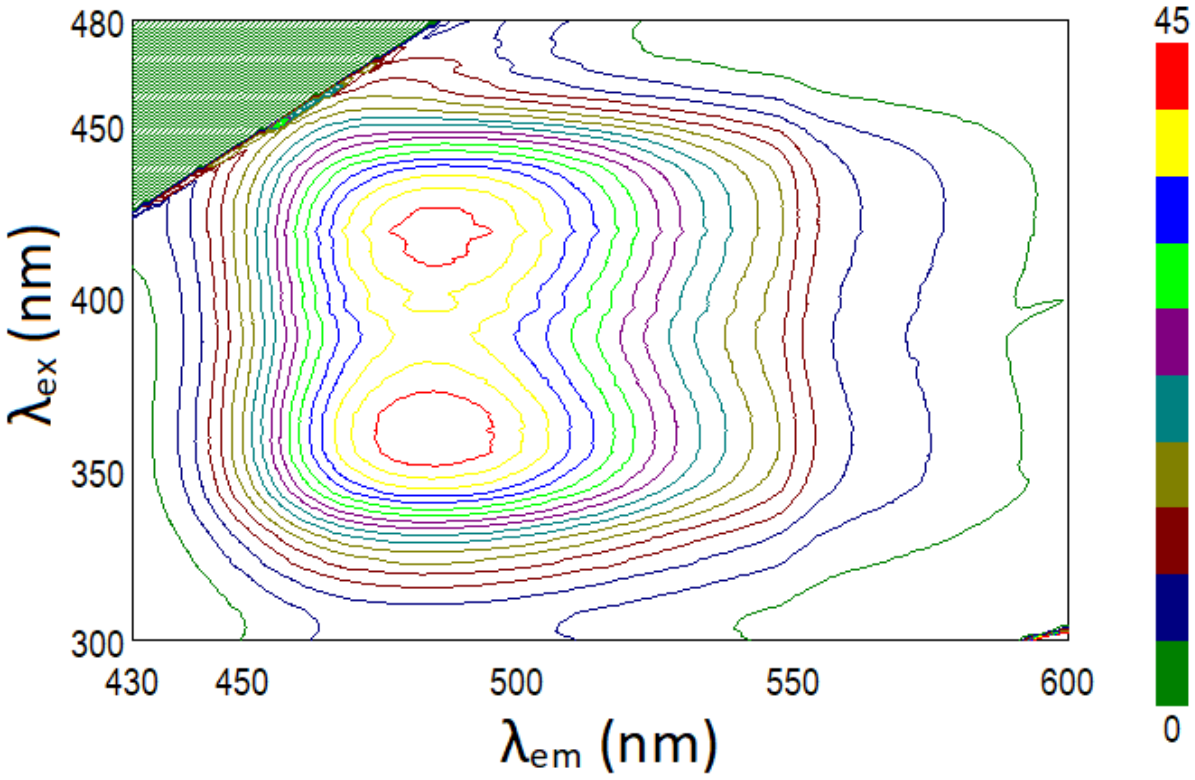


Figure S92. 3D-EEM fluorescence spectrum of PbBr

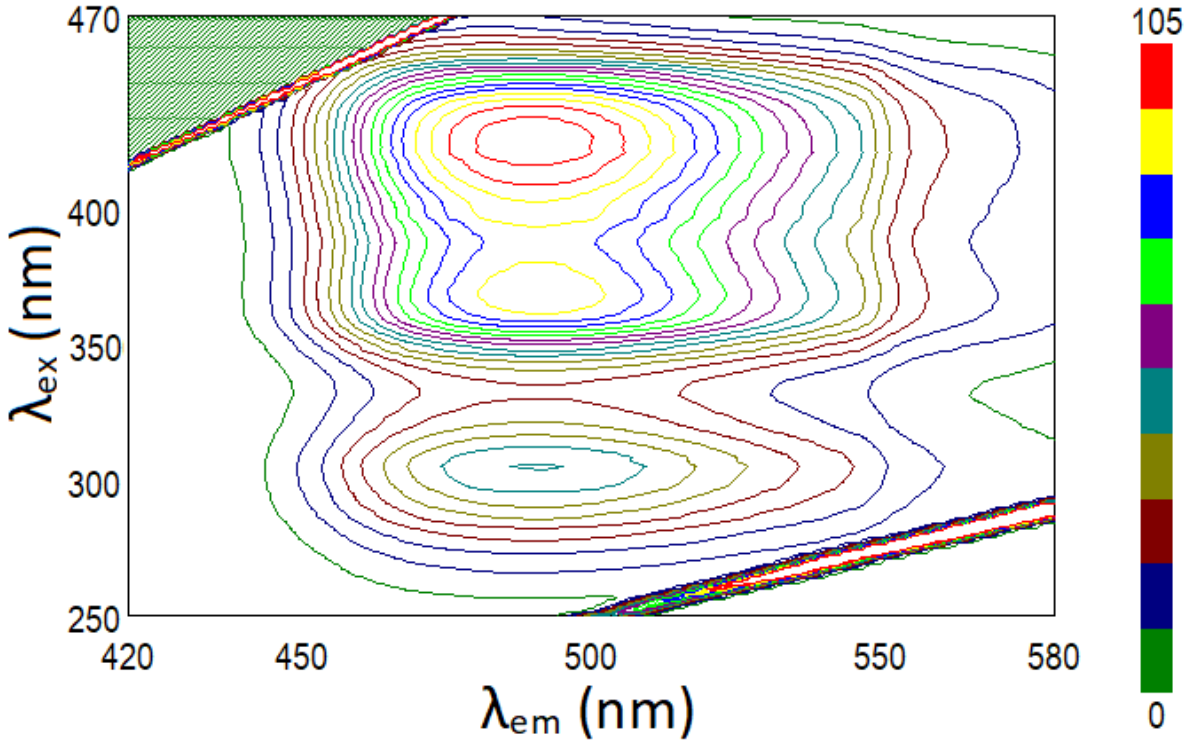


Figure S93. 3D-EEM fluorescence spectrum of BiCl

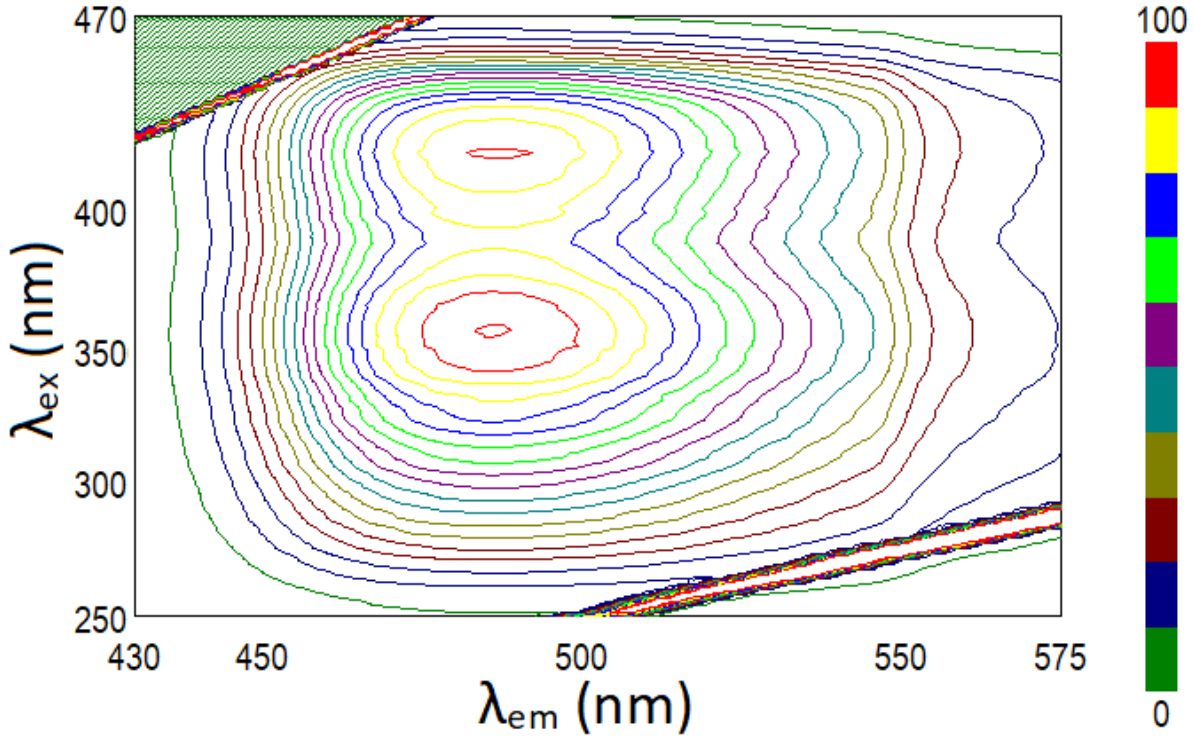


Figure S94. 3D-EEM fluorescence spectrum of 8hqHCl

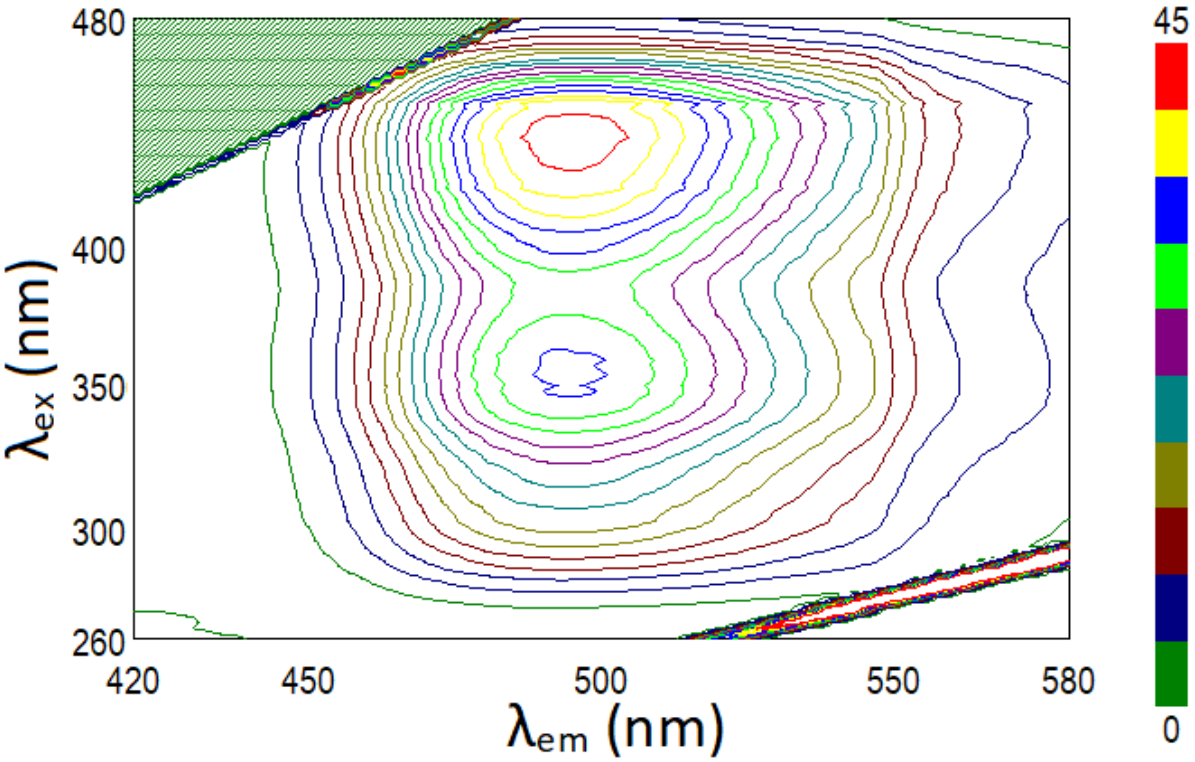
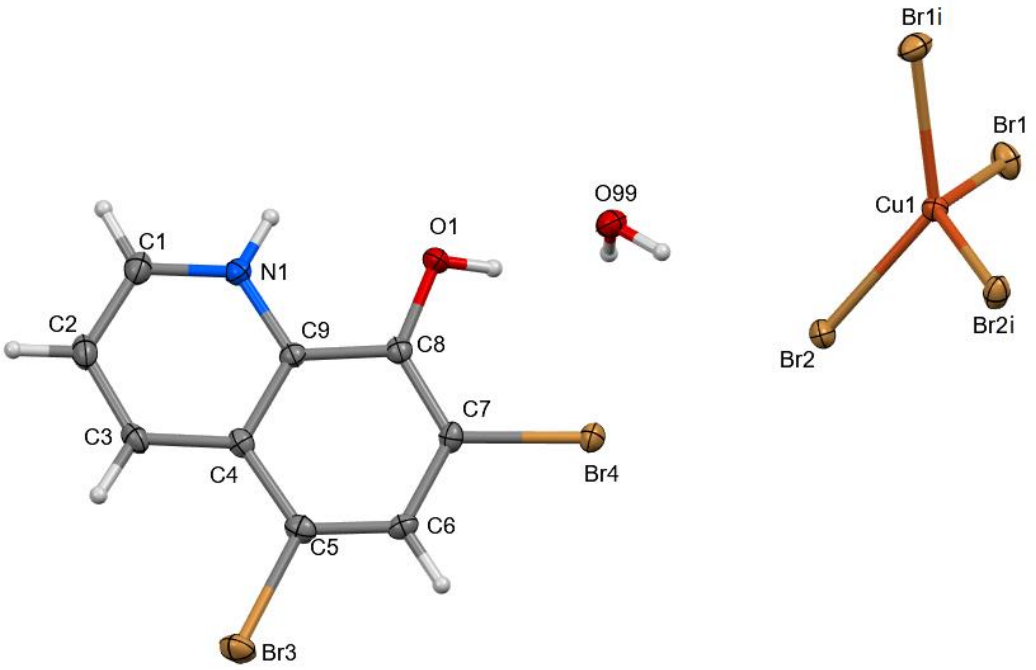


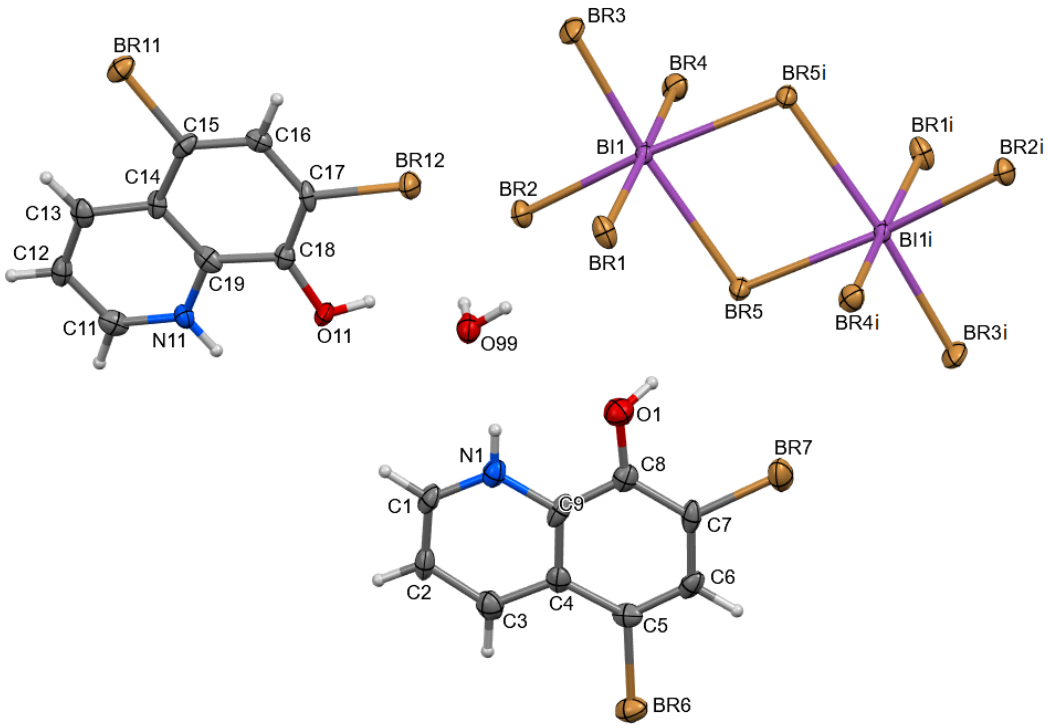
Figure S95. 3D-EEM fluorescence spectrum of 8hqHBr

4. The data concerning the structures of $(8hqBr_2H)_2[CuBr_4]\cdot 2H_2O$ and $(8hqBr_2H)_4[Bi_2Br_{10}]\cdot 2H_2O$

Molecular structure of $(8hqBr_2H)_2[CuBr_4]\cdot 2H_2O$. The equivalent atoms were generated according to symmetry transformations: (i) -x, y, -z+1.5.



Molecular structure of $(8hqBr_2H)_4[Bi_2Br_{10}]\cdot 2H_2O$. The equivalent atoms were generated according to symmetry transformation (i) -x+1, -y+1, -z+2.



Crystal data and structure refinement details

Compound	$(8hqBr_2H)_2[CuBr_4]\cdot 2H_2O$	$(8hqBr_2H)_4[Bi_2Br_{10}]\cdot 2H_2O$
Empirical formula	$C_{18}H_{16}Br_8N_2O_4Cu$	$C_{18}H_{14}BiBr_9N_2O_3$
Formula weight	1027.15	1234.48
Crystal system	Monoclinic	Triclinic
Space group	*C2/c*	*P*-1
Radiation	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
Unit cell dimensions		
a (Å)	7.78250(10)	11.5995(7)
b (Å)	18.1498(3)	11.6721(5)
c (Å)	19.2961(3)	12.3329(6)
α (°)	90.00	68.963(4)
β (°)	99.250(2)	63.154(5)
γ (°)	90.00	76.750(4)
Volume (Å^3)	2690.15(7)	1385.98(14)
Z	4	2
Calculated density (Mg/m^3)	2.536	2.958
Absorption coefficient (mm^{-1})	12.723	19.358
F(000)	1916	1116.0
Min. and max. transmission	0.109 to 327	0.174 and 1.000
θ Range for data collection (°)	5.76 to 63.16	6.134 to 50.052
Index ranges	$-11 \le h \le 10$ $-26 \le k \le 26$ $-23 \le l \le 27$	$-13 \le h \le 13$ $-13 \le k \le 13$ $-14 \le l \le 14$
Reflections collected / unique	44926 / 4192	27907 / 4877
R_{int}	0.0506	0.1006
Completeness (%)	99.9	99.8
Data / restraints / parameters	4192 / 0 / 151	4877 / 0/ 303
Goodness-of-fit on F^2	1.083	0.998
Final *R* indices [$I>2\sigma(I)$]	$R1 = 0.0320$ $wR2 = 0.0692$	$R1 = 0.0382$ $wR2 = 0.0994$
R indices (all data)	$R1 = 0.0403$, $wR2 = 0.0720$	$R1 = 0.0457$ $wR2 = 0.1029$
Largest diff. peak and hole (e·Å^{-3})	1.14 and -0.72	3.06 and -2.09

Structural data of the coordination polyhedra

i—j	d_{ij} [Å]	i—j—k	a_{ijk} [°]	i—j—k	a_{ijk} [°]
$(8hqBr_2H)_2[CuBr_4]\cdot 2H_2O$					
Cu1—Br1	2.3685(5)	Br1—Fe1—Br2	97.387(12)	Br2—Fe1—Br1^{i}	134.770(12)
Cu1—Br2	2.3930(5)	Br1—Fe1—Br1^{i}	99.26(3)	Br2—Fe1—Br2^{i}	99.98(3)
		Br1—Fe1—Br2^{i}	134.766(12)	Br1^{i}—Fe1—Br2^{i}	97.388(12)
$(8hqBr_2H)_4[Bi_2Br_{10}]\cdot 2H_2O$					
Bi1—Br1	2.8830(8)	Br1—Bi1—Br2	89.21(2)	Br2—Bi1—Br5^{i}	174.19(2)
Bi1—Br2	2.7622(8)	Br1—Bi1—Br3	91.82(3)	Br3—Bi1—Br4	91.11(3)
Bi1—Br3	2.7001(8)	Br1—Bi1—Br4	173.98(2)	Br3—Bi1—Br5	172.98(2)
Bi1—Br4	2.8505(8)	Br1—Bi1—Br5	85.80(2)	Br3—Bi1—Br5^{i}	90.84(2)
Bi1—Br5	3.0634(8)	Br1—Bi1—Br5^{i}	93.19(2)	Br4—Bi1—Br5	91.87(2)
Bi1—Br5^{ii}	3.0041(8)	Br2—Bi1—Br3	94.37(3)	Br4—Bi1—Br5^{i}	92.01(2)
		Br2—Bi1—Br4	85.33(3)	Br5—Bi1—Br5^{i}	82.70(2)
		Br2—Bi1—Br5	92.21(2)		

Symmetry transformations used to generate equivalent atoms: (i) -x, y, -z+1.5; (ii) -x+1, -y+1, -z+2.

Stacking interactions in the studied compounds. Each ring is indicated by one atom, which belongs solely to this ring. The α is a dihedral angle between planes I and J, β is an angle between Cg(I)-Cg(J) vector and normal to plane I, d_p is a perpendicular distance of Cg(I) on ring J plane.

R(I)•••R(J)	d(Cg•••Cg) [Å]	α [°]	β [°]	d_p[Å]
$(8hqBr_2H)_2[CuBr_4]\cdot 2H_2O$				
N1•••C8^{i}	3.7008(18)	2.16(15)	24.7	3.3025(12)
C8•••C8^{i}	3.5728(18)	0.03(15)	20.6	3.3437(13)
C8•••C8^{ii}	4.3531(18)	0.03(15)	38.6	3.4001(13)
$(8hqBr_2H)_4[Bi_2Br_{10}]\cdot 2H_2O$				
C8•••C18^{iii}	3.670(5)	3.9(4)	22.7	3.354(4)
C18•••C18^{iv}	3.739(5)	0.0(4)	26.5	3.346(4)

Symmetry transformations used to generate equivalent atoms: (i) -x+1.5, -y+0.5, -z+1; (ii) -x+0.5, -y+0.5, -z+1 (iii) x, y+1, z; (iv) -z+1, -y, -z+1.

Hydrogen bonds in the studied compounds

D-H•••A	d(D—H) [Å]	d(H•••A) [Å]	d(D•••A) [Å]	<(DHA) [°]	$G_d^a(n)$
$(8hqBr_2H)_2[CuBr_4]\cdot 2H_2O$					
N1—H1N•••O99^{i}	0.88	1.94	2.760(4)	155	D(2)
O1—H1O•••O99	0.84	1.92	2.702(3)	154	D(2)
O99—H99O•••Br1^{ii}	0.87	2.93	3.520(2)	127	D(2)
O99—H99O•••Br2^{ii}	0.87	2.66	3.443(2)	150	D(2)
O99—H99P•••Br2	0.87	2.49	3.349(2)	168	D(2)
$(8hqBr_2H)_4[Bi_2Br_{10}]\cdot 2H_2O$					
N1—H1N•••O99	0.88	1.93	2.766(10)	157	D(2)
O1—H1O•••Br5	0.84	2.83	3.647(7)	164	D(2)
N11—H11N•••Br4^{i}	0.88	2.63	3.361(7)	141	D(2)
O11—H11O•••O99	0.84	1.90	2.659(8)	149	D(2)
O99—H99O•••Br1	0.87	2.41	3.273(6)	170	D(2)
O99—H99P•••Br2	0.87	2.53	3.295(7)	148	D(2)

Symmetry transformations used to generate equivalent atoms: (i) -x+1, -y+1, -z+1; (ii) -x+1, y, -z+1.5.