Supporting Information

The effect of halides and coordination mode of 4-amino-2,1,3-benzothiadiazole on the luminescence properties of its Zn complexes

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

Identification code	**1**	**2**	**3**	**4**	**4**(superstr.)
Empirical formula	$C_{12}H_{10}Br_2N_6S_2Zn$	$C_6H_5Br_2N_3SZn$	$C_{12}H_{10}I_2N_6S_2Zn$	$C_6H_5I_2N_3SZn$	$C_6H_5I_2N_3SZn$
Formula weight	527.57	376.38	621.55	470.36	470.36
Temperature/K	296(2)	150(2)	296(2)	150(2)	150(2)
Crystal system	monoclinic	triclinic	triclinic	monoclinic	monoclinic
Space group	*C*2/*c*	*P*–1	*P*–1	*Cc*	*Cc*
a/Å	27.4418(12)	5.9710(5)	7.539(3)	14.5768(5)	14.5782(6)
b/Å	4.7724(2)	7.5328(7)	11.020(5)	10.8025(4)	32.4028(12)
c/Å	12.8595(5)	11.7015(10)	12.373(6)	7.0493(2)	7.0488(3)
α/°	90	79.032(3)	101.973(16)	90	90
β/°	102.417(2)	78.762(3)	101.819(16)	95.8400(10)	95.846(2)
γ/°	90	77.370(3)	109.720(15)	90	90
Volume/Å^3	1644.73(12)	497.70(8)	903.5(7)	1104.26(6)	3312.4(2)
Z	4	2	2	4	12
ρ_{calc}g/cm^3	2.131	2.512	2.285	2.829	2.830
μ/mm^{-1}	6.612	10.658	5.013	7.963	7.964
F(000)	1024.0	356.0	584.0	856.0	2568.0
Crystal size/mm^3	0.42 × 0.03 × 0.03	0.22 × 0.17 × 0.08	0.13 × 0.08 × 0.05	0.2 × 0.1 × 0.1	0.2 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.08 to 52.824	3.592 to 56.062	3.526 to 50.716	4.702 to 52.788	3.076 to 52.76
Index ranges	-34 ≤ h ≤ 28, -5 ≤ k ≤ 5, -16 ≤ l ≤ 15	-7 ≤ h ≤ 7, -9 ≤ k ≤ 9, -15 ≤ l ≤ 15	-9 ≤ h ≤ 8, -12 ≤ k ≤ 13, -14 ≤ l ≤ 14	-18 ≤ h ≤ 17, -13 ≤ k ≤ 13, -8 ≤ l ≤ 8	-14 ≤ h ≤ 18, -30 ≤ k ≤ 40, -8 ≤ l ≤ 8
Reflections collected	4139	4874	8045	4156	8493
Independent reflections	1671 [R_{int} = 0.0261, R_{sigma} = 0.0321]	2394 [R_{int} = 0.0222, R_{sigma} = 0.0305]	3207 [R_{int} = 0.0337, R_{sigma} = 0.0478]	2009 [R_{int} = 0.0738, R_{sigma} = 0.0541]	5020 [R_{int} = 0.0291, R_{sigma} = 0.0488]
Restraints/parameters	0/111	2/124	0/220	4/156	137/342
Goodness-of-fit on F^2	1.038	1.037	1.003	1.080	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0245, wR_2 = 0.0577	R_1 = 0.0214, wR_2 = 0.0494	R_1 = 0.0314, wR_2 = 0.0553	R_1 = 0.0337, wR_2 = 0.0782	R_1 = 0.0566, wR_2 = 0.1464
Final R indexes [all data]	R_1 = 0.0325, wR_2 = 0.0607	R_1 = 0.0260, wR_2 = 0.0508	R_1 = 0.0514, wR_2 = 0.0609	R_1 = 0.0366, wR_2 = 0.0793	R_1 = 0.0646, wR_2 = 0.1527
Largest diff. peak/hole / e Å^{-3}	0.43/-0.41	0.81/-0.40	0.56/-0.58	0.96/-0.47	2.36/-0.97
Flack parameter				0.41(6)	0.37(7)

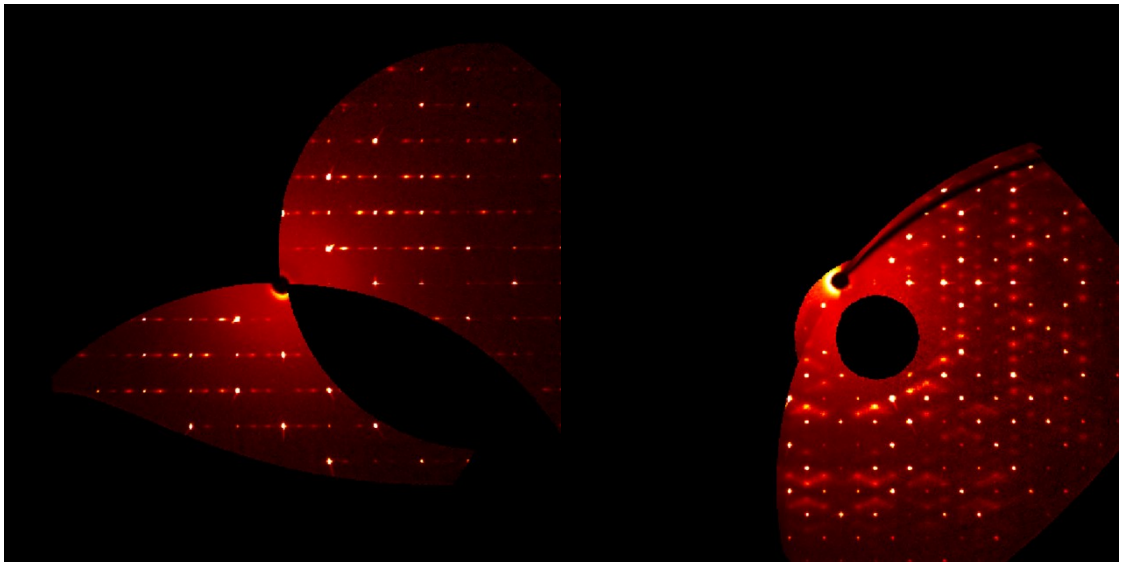
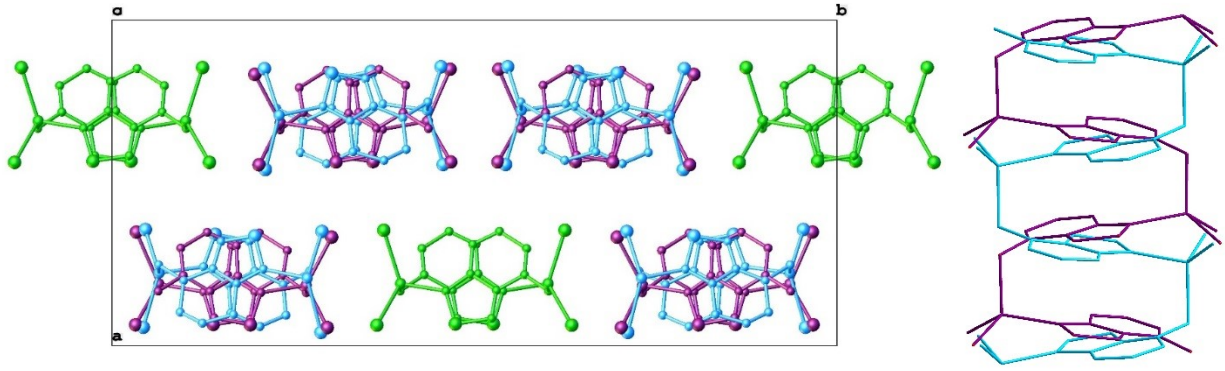


Figure S1. Reciprocal space reconstructions for **4**, the thickness of the layers of 0.10 Å. Left – 0*kl* layer; right – *hk*0 layer.



a) b)

Figure S2. (a) Crystal packing of the superstructure of **4**. Ordered chains are coloured green, disordered ones are coloured blue and violet. (b) Representation of the disordered chain. Hydrogen atoms are omitted.

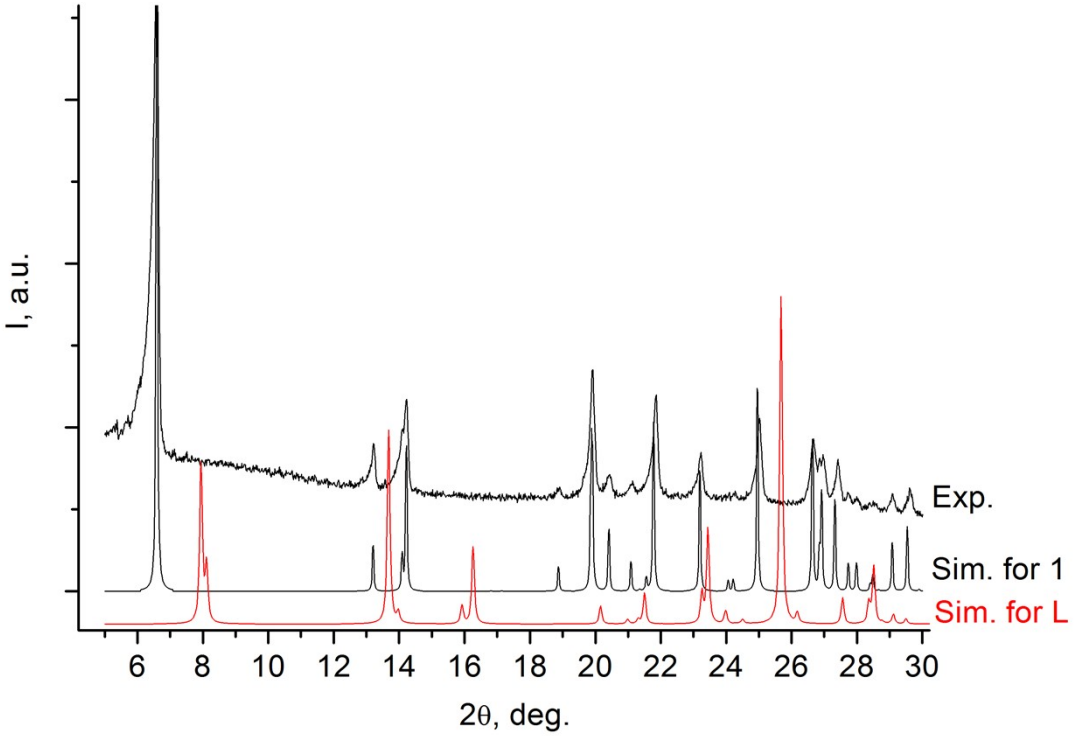


Figure S3. Experimental and simulated powder XRD patterns (Cu Kα radiation) for [ZnL_2Br_2] (**1**). No impurities of solid L is revealed within the accuracy of the method.

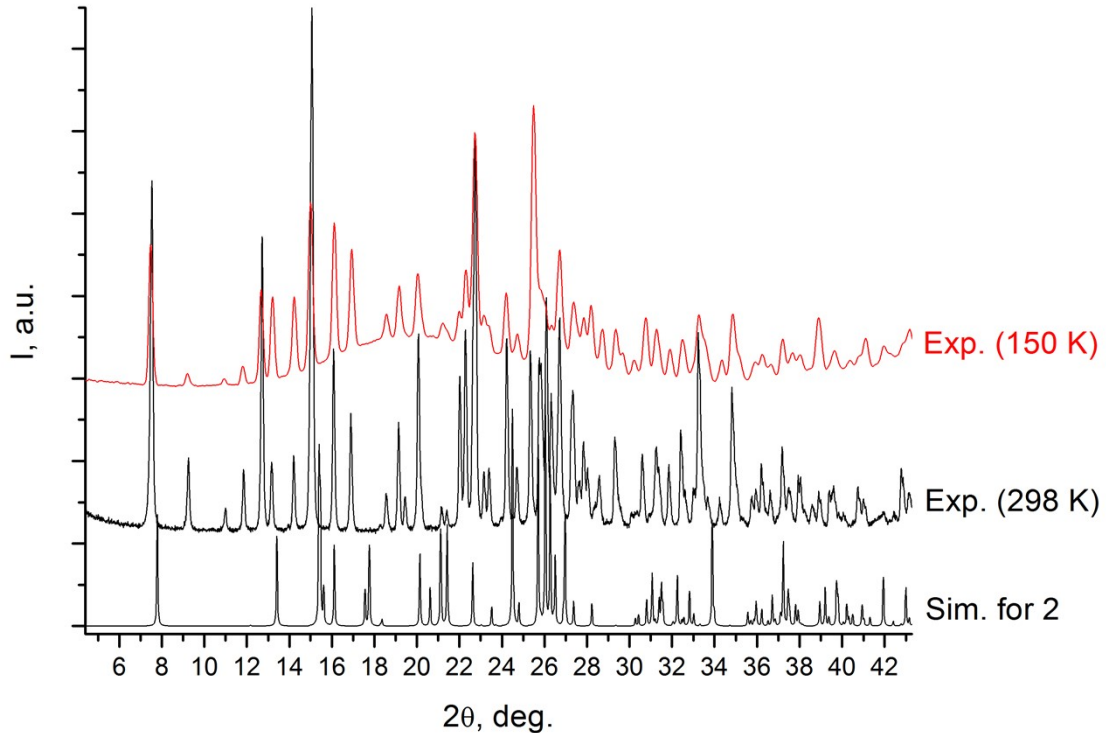


Figure S4. Experimental powder XRD pattern (Cu Kα radiation) for a sample from the reaction between $ZnBr_2$ and L in a molar ratio of 1:1, measured at 298 K (on a Bruker D8 Advance diffractometer) and 150 K (on a Bruker D8 Venture diffractometer). The compound does not correspond to the phase [$ZnLBr_2$] (**2**); the difference in the position of the peaks cannot be ascribed to temperature effects, while no phase transition is observed in the temperature range of 150 – 298K.

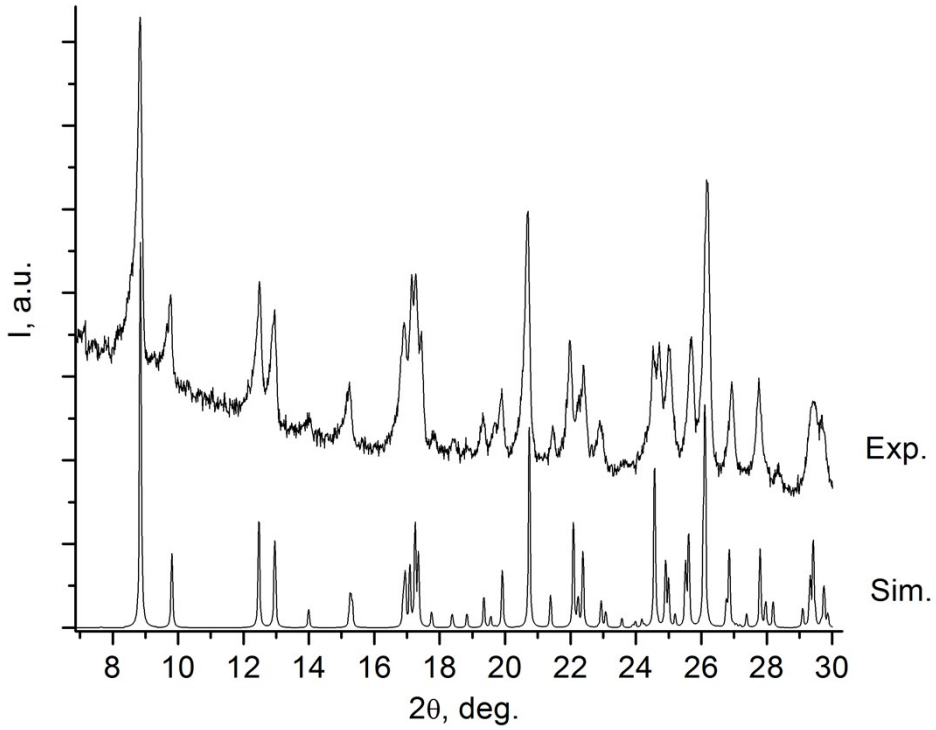


Figure S5. Experimental and simulated powder XRD patterns (Cu Kα radiation) for $[ZnL_2I_2]$ (**3**).

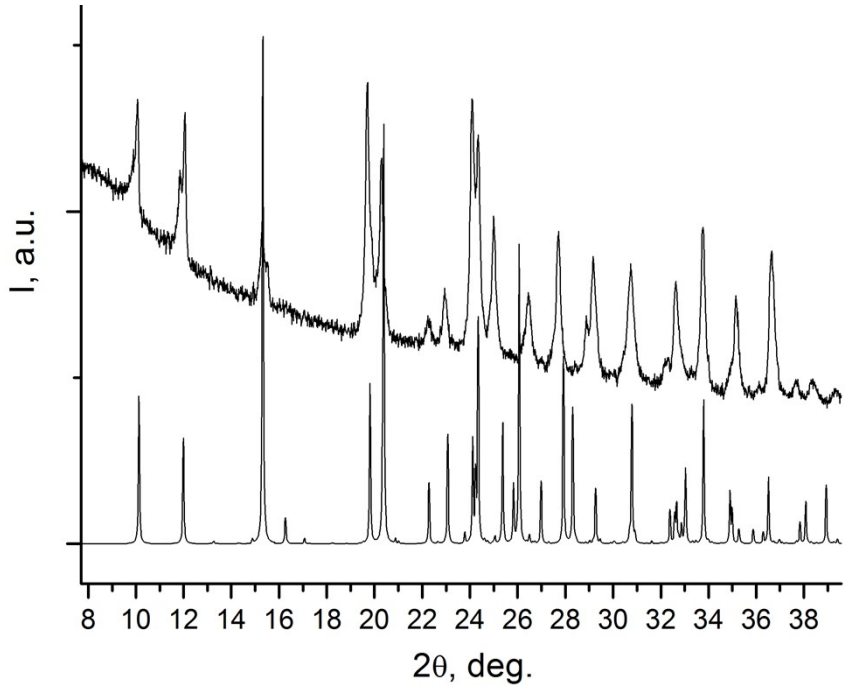


Figure S6. Experimental and simulated powder XRD patterns (Cu Kα radiation) for $[ZnLI_2]_n$ (**4**).

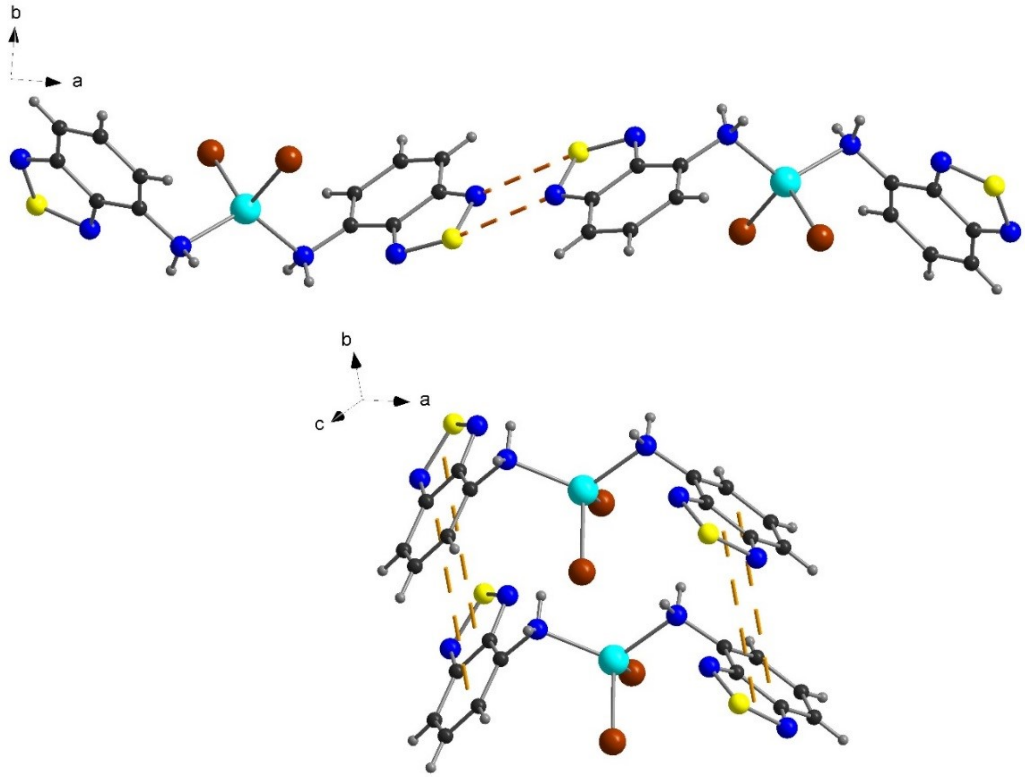


Figure S7. Intermolecular interactions between *btd* moieties in the structure of **1** highlighted by orange dashed lines. Top – S···N contacts (3.16 Å). Bottom – π-π interactions (interplanar separation of 3.37 Å).

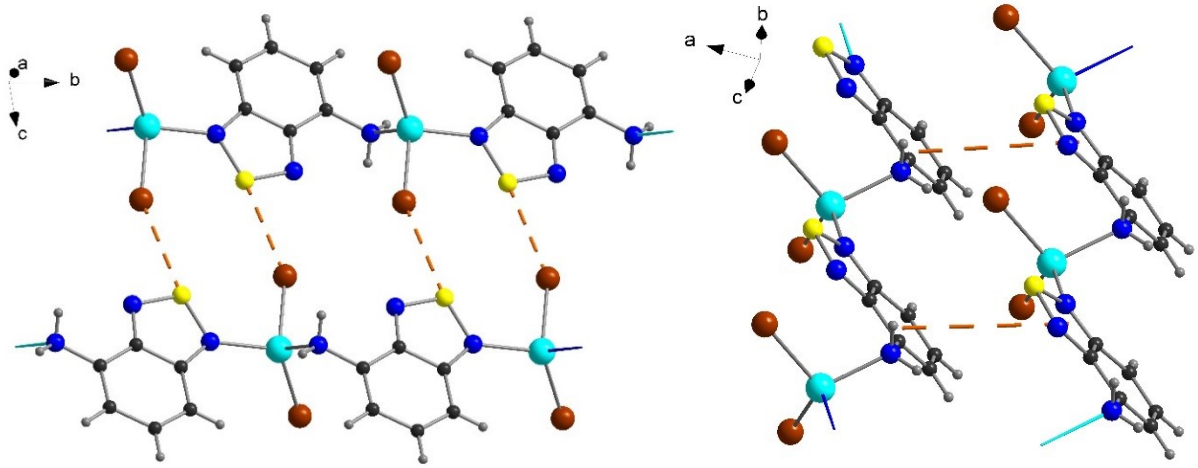


Figure S8. Intermolecular interactions in the structure of **2** highlighted by orange dashed lines. Left – S···Br contacts (3.37 Å). Right – π-π interactions (interplanar separation of 3.50 Å).

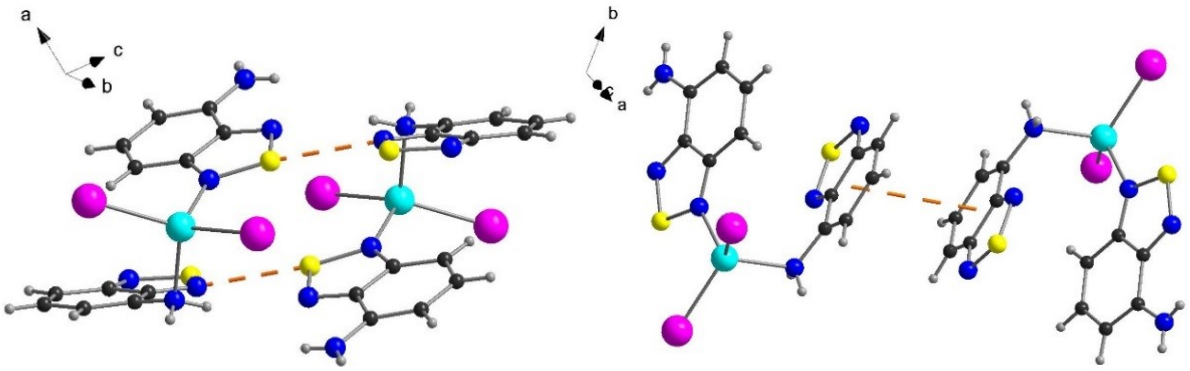


Figure S9. Intermolecular interactions in the structure of **3** highlighted by orange dashed lines. Left – S···N contacts (2.97 Å). Right – π-π interactions (interplanar separation of 3.40 Å).

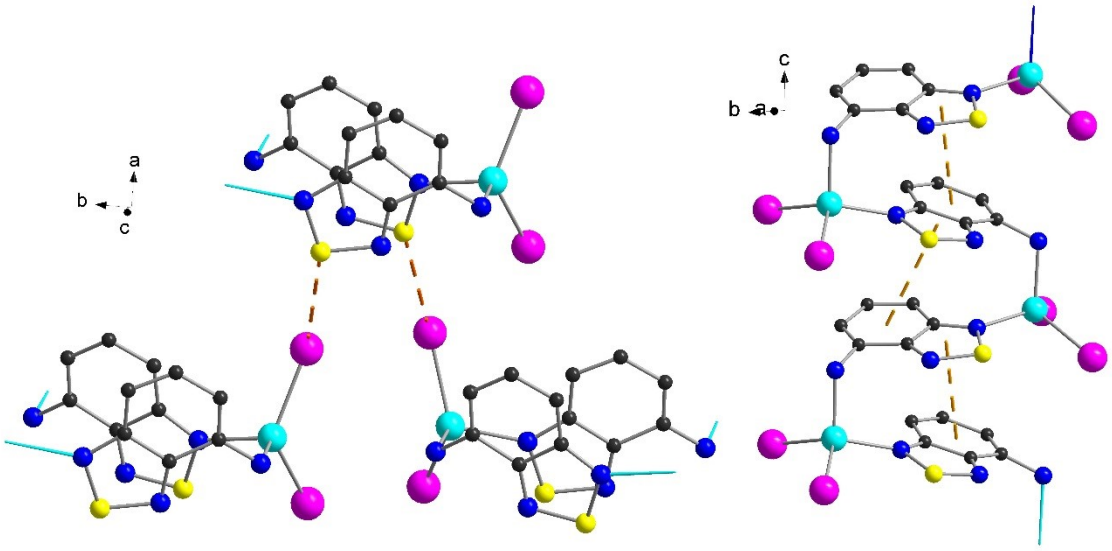


Figure S10. Intermolecular interactions in the structure of **4** highlighted by orange dashed lines. Left – S···I contacts (3.75 Å). Right – π-π interactions (interplanar separation of ca. 3.3 Å).

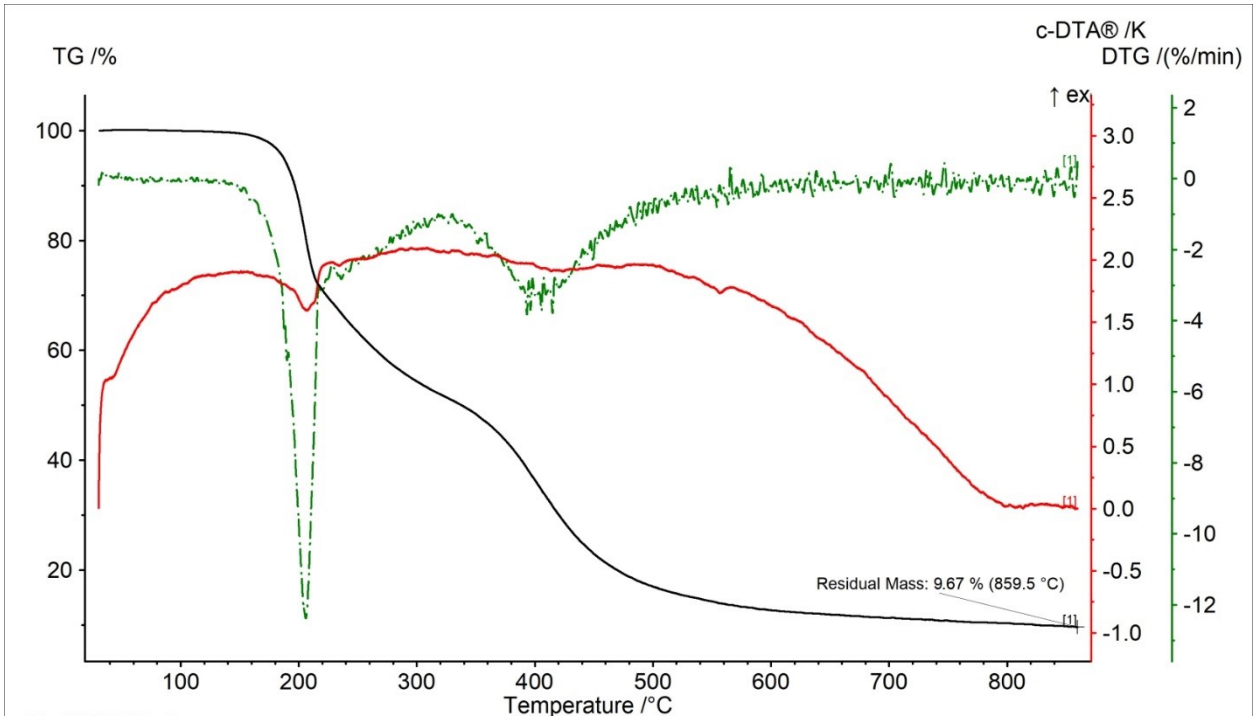


Figure S11. TG (black line), DTG (green line) and DTA (red line) curves depicting thermal decomposition of $[ZnL_2Br_2]$ (**1**). The first step at 170-220°C corresponds to loss of the first L molecule per complex (experimental / calculated mass loss of 30 / 28.7%), the second and the third poorly resolved steps at 220–850°C correspond to loos of the second L and sublimation of $ZnBr_2$.

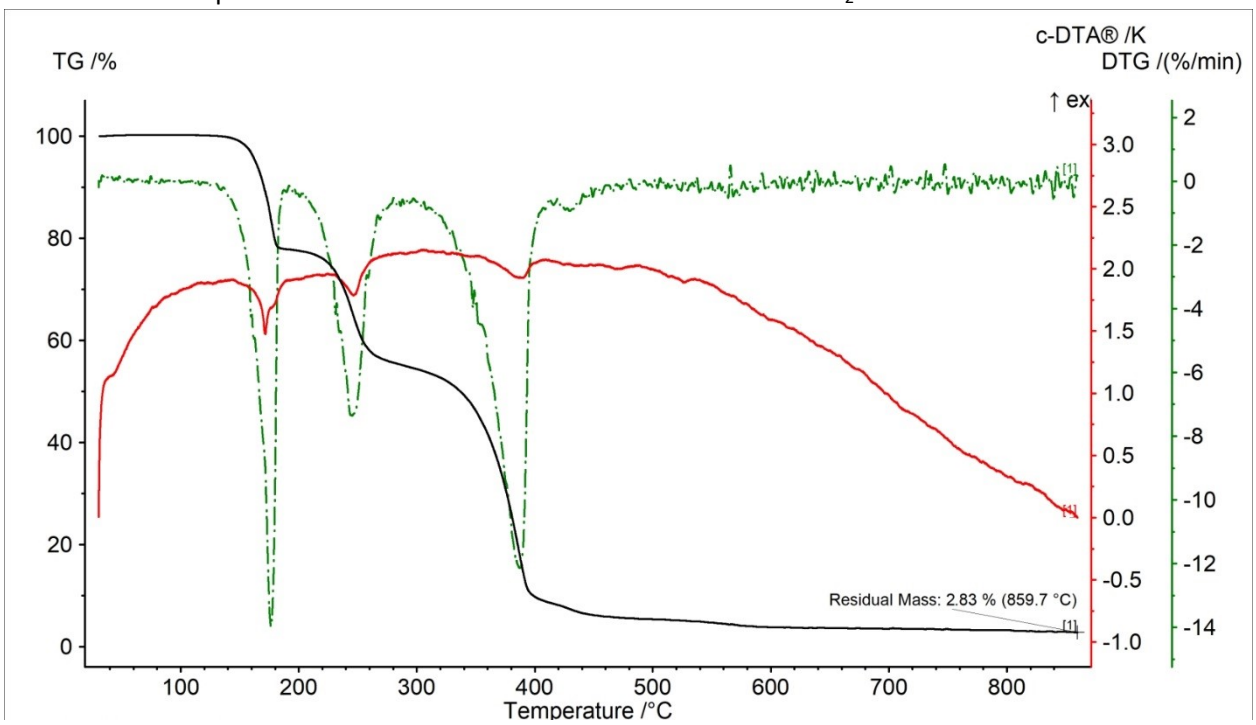


Figure S12. TG (black line), DTG (green line) and DTA (red line) curves depicting thermal decomposition of $[ZnL_2I_2]$ (**3**). The first step at 140-190°C corresponds to loss of the first L molecule per complex (experimental / calculated mass loss of 23 / 24.3%), the second one at 200-285 °C corresponds to loss of the second L (experimental / calculated mass loss of 46 / 48.6%) and the third step at 285–600°C corresponds to sublimation of ZnI_2.

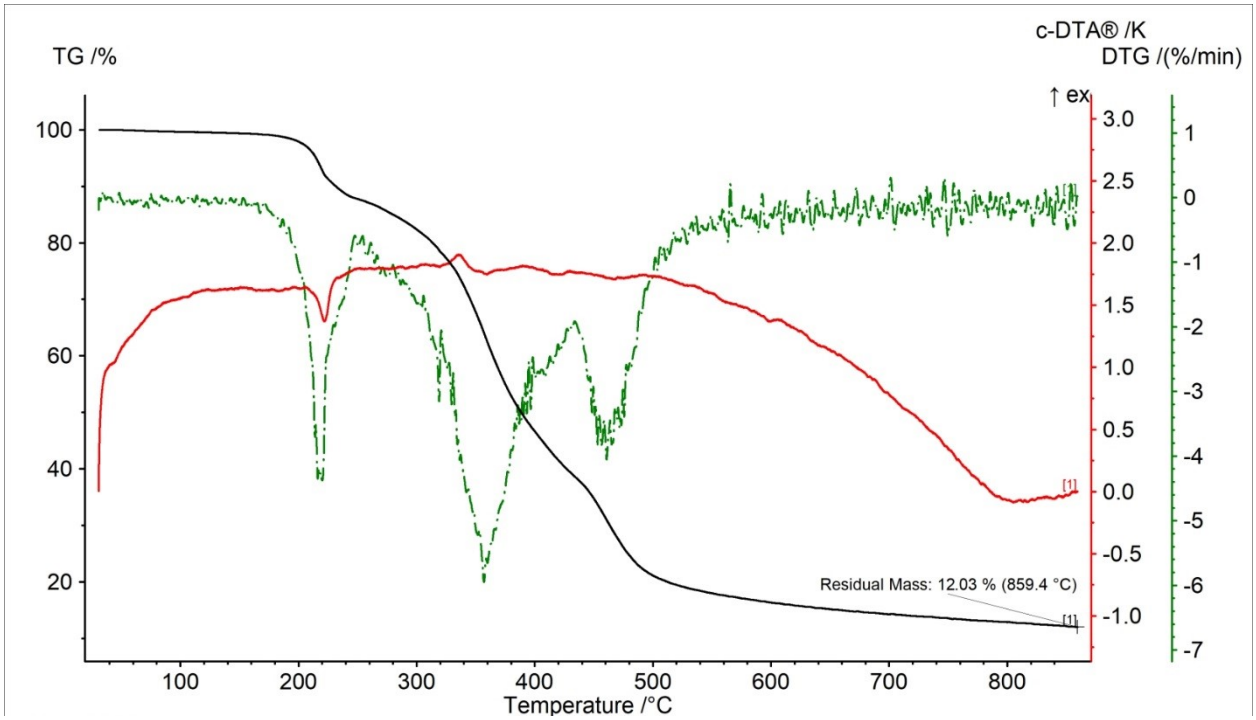


Figure S13. TG (black line), DTG (green line) and DTA (red line) curves depicting thermal decomposition of $[ZnLI_2]_n$ (**4**). The first step at 180-245°C (mass loss of 12%), the second step at 245-435°C (mass loss of 12%) and the third step at 435–850°C (mass loss of 78%) are not assigned.

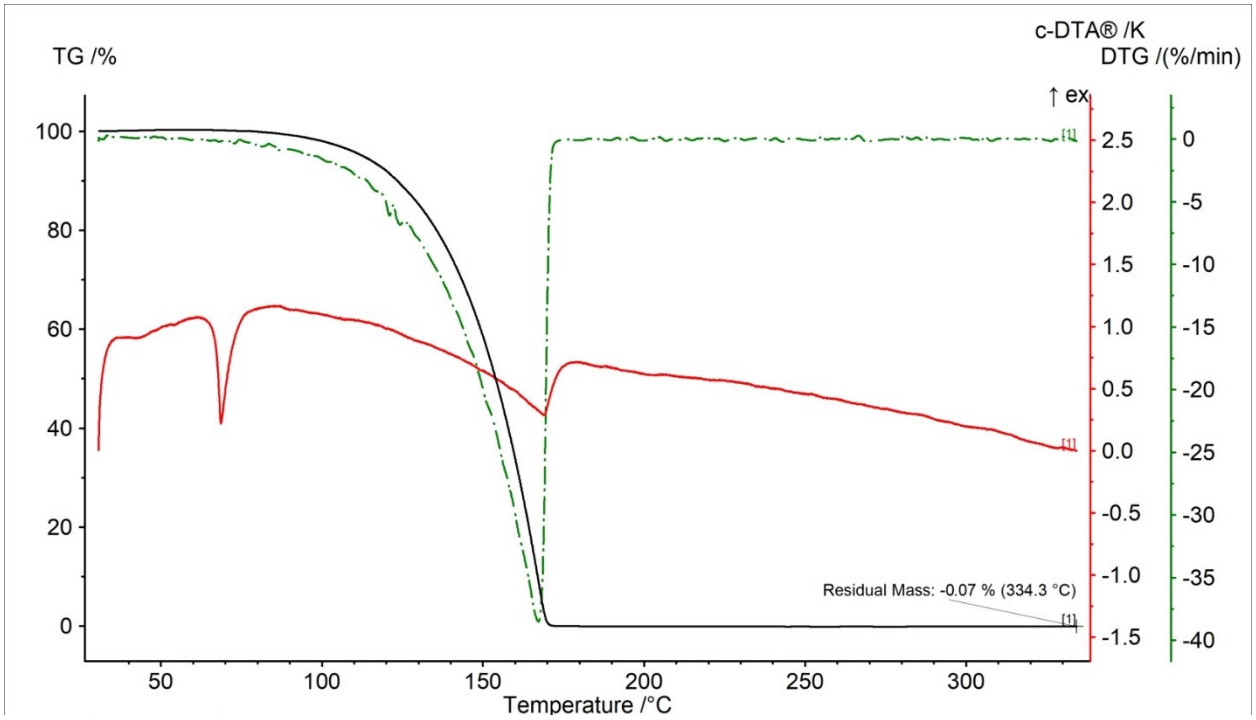


Figure S14. TG (black line), DTG (green line) and DTA (red line) curves depicting thermal decomposition of free L. In the DTA curve, the first endothermic peak at 68 °C corresponds to melting of L, while the second peak at 168 °C corresponds to evaporation of L.

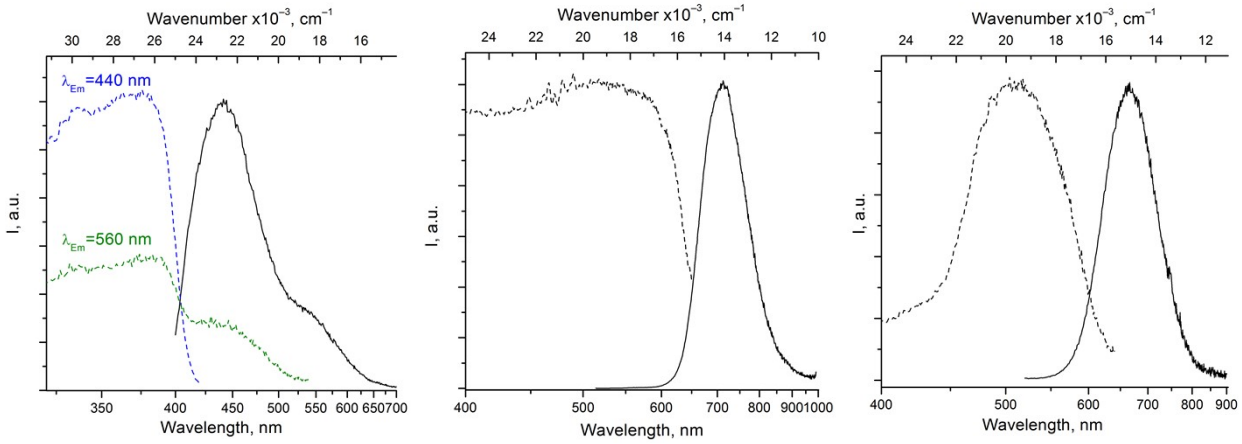


Figure S15. Emission (solid lines) and excitation (dashed lines) spectra for solid compounds **1**, **3** and **4**. For **1**, the excitation spectra are presented for both emission bands at 440 and 560 nm.

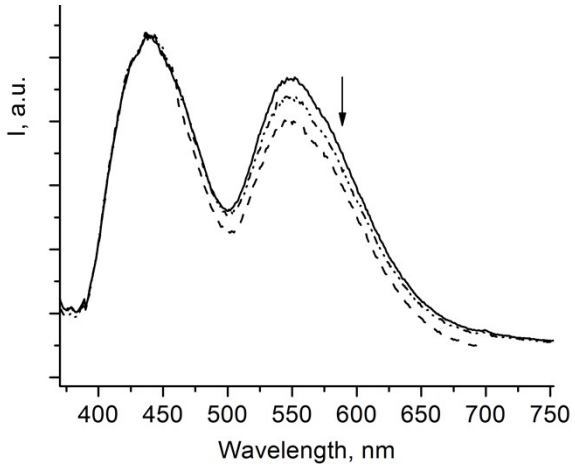


Figure S16. Emission spectra of powder **1** upon aging for 1.5 months. The spectra are normalized on the short wavelength band.

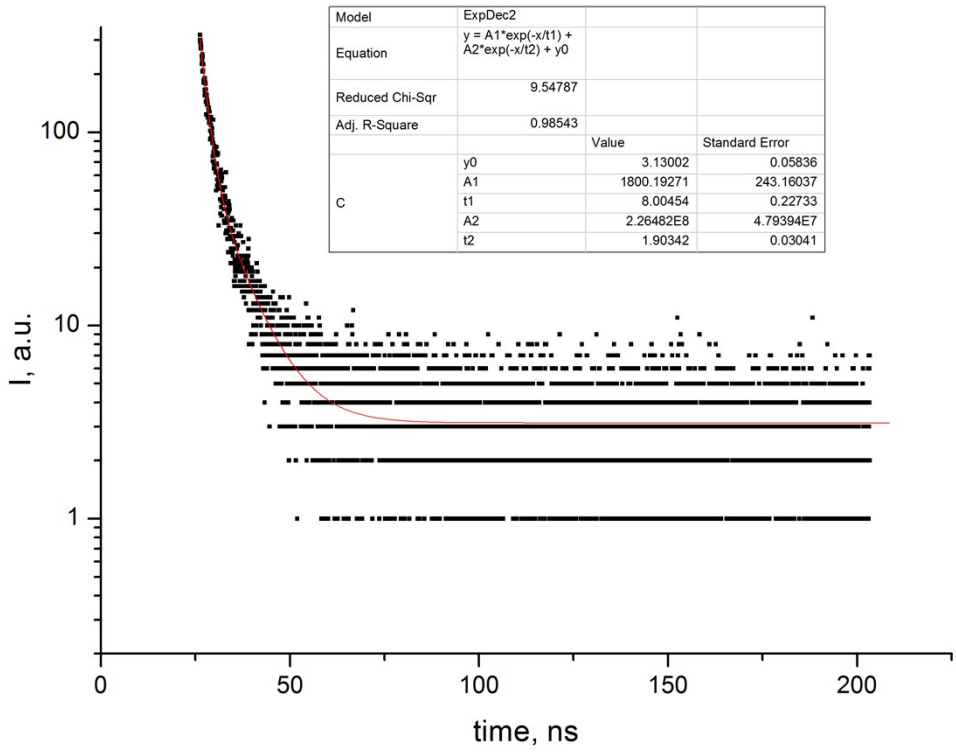
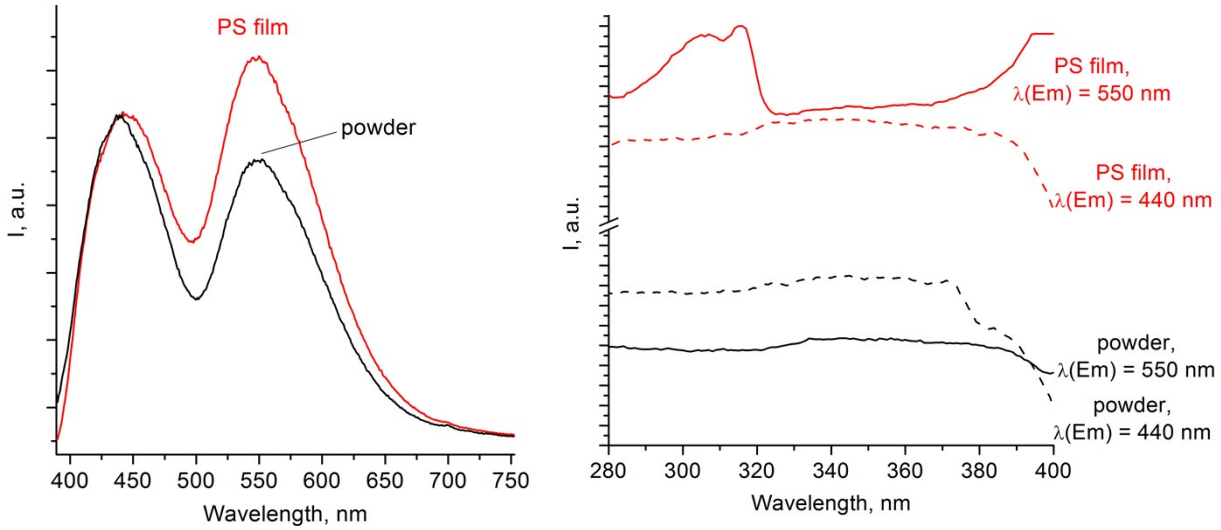


Figure S17. Emission decay curve (black) for **1** and the corresponding fit by two exponential decay (red)



(a) (b)

Figure S18. Normalized emission (excitation at 350 nm; a) and excitation (at two emission wavelengths; b) spectra of powder **1** and film of **1** in polystyrene matrix.

Table S2. Calculated properties of the first singlet excited states $S_0 \rightarrow S_n$ of $[ZnL_2Br_2]$ (**1**) at B3LYP/def2-TZVPP and PBE0/def2-TZVPP level: transition wavelength (λ), oscillator strength (f). H is for HOMO, L is for LUMO abbreviation. The contribution of the individual excitations is listed if larger than 0.1

n	B3LYP				PBE0			
	λ, nm	f	electronic states	contribution	λ, nm	f	electronic states	contribution
1	377.5	0.1088	H-1→L+1	0.2097	363.7	0.1197	H-1→L+1	0.2839
			H→L	0.7696			H→L	0.6958
2	374.1	0.0088	H-1→L	0.3687	360.5	0.0103	H-1→L	0.3816
			H→L+1	0.6036			H→L+1	0.5959
3	361.9	0.0001	H-1→L	0.5639	336.6	0.0000	H-1→L	0.5480
			H→L+1	0.3694			H→L+1	0.3519
4	360.6	0.0000	H-1→L+1	0.6945	335.6	0.0005	H-1→L+1	0.6167
			H→L	0.2013			H→L	0.2482
5	349	0.0027	H-3→L+1	0.1074	325.3	0.0030	H-3→L+1	0.1646
			H-2→L	0.7790			H-2→L	0.6777
6	347.3	0.0003	H-3→L	0.3742	324.3	0.0014	H-3→L	0.4554
			H-2→L+1	0.5203			H-2→L+1	0.3955
7	341.9	0.0032	H-3→L	0.4583	318.8	0.0054	H-4→L	0.2624
			H-2→L+1	0.3911			H-3→L+1	0.5140
							H-2→L	0.1750
8	341.4	0.0043	H-4→L	0.2363	318.7	0.0034	H-4→L+1	0.1072
			H-3→L+1	0.6231			H-3→L	0.3308
			H-2→L	0.1131			H-2→L+1	0.4669
9	325.9	0.0070	H-4→L	0.7195	303.3	0.0103	H-4→L	0.6543
			H-3→L+1	0.2545			H-3→L+1	0.2986
10	324.5	0.0000	H-4→L+1	0.7748	302.3	0.0001	H-5→L	0.1354
			H-3→L	0.1483			H-4→L+1	0.6367
							H-3→L	0.1782
11	320	0.0012	H-5→L	0.8510	299.2	0.0006	H-5→L	0.7275
							H-4→L+1	0.1705
12	317.9	0.0016	H-5→L+1	0.9139	297.5	0.0012	H-5→L+1	0.8723
13	282.4	0.1208	H-6→L	0.8881	275.9	0.2059	H-7→L+1	0.2989
							H-6→L	0.5550
14	280.7	0.1021	H-7→L	0.3210	275.5	0.1107	H-7→L	0.4281
			H-6→L+1	0.5193			H-6→L+1	0.4221
15	280.1	0.0015	H-7→L	0.5821	266.5	0.0000	H-11→L	0.4760
			H-6→L+1	0.3796			H-10→L+1	0.4685
16	278.6	0.0824	H-7→L+1	0.8907	266.5	0.0000	H-11→L+1	0.4602
							H-10→L	0.4838
17	271.8	0.0000	H-11→L	0.4905	263.7	0.0000	H-7→L	0.4630
			H-10→L+1	0.4779			H-6→L+1	0.4768
18	271.8	0.0001	H-11→L+1	0.4677	263.5	0.0034	H-7→L+1	0.5756
			H-10→L	0.5001			H-6→L	0.3397
19	271.2	0.0001	H-8→L	0.9371	255.7	0.0004	H-8→L	0.9154
20	269.6	0.0004	H-8→L+1	0.9404	254.1	0.0000	H-8→L+1	0.9263

Table S3. Calculated properties of the first singlet excited states $S_0 \rightarrow S_n$ of $[ZnL_2Br_2]$ (**1**) at wB97XD/def2-TZVPP and CAM-B3LYP/def2-TZVPP level: transition wavelength (λ), oscillator strength (f). H is for HOMO, L is for LUMO abbreviation. The contribution of the individual excitations is listed if larger than 0.1

n	wB97XD				CAM-B3LYP			
	λ, nm	f	electronic states	contribution	λ, nm	f	electronic states	contribution
1	314.7	0.1859	H-1→L+1	0.4174	334.9	0.1550	H-1→L+1	0.3992
			H→L	0.5372			H→L	0.5636
2	311.8	0.0165	H-1→L	0.4407	332	0.0150	H-1→L	0.4305
			H→L+1	0.5131			H→L+1	0.5313
3	270.2	0.2493	H-7→L+1	0.2113	276.5	0.2167	H-7→L+1	0.1820
			H-6→L	0.2140			H-6→L	0.3198
			H-4→L	0.2091			H-3→L+1	0.2647
			H-2→L+1	0.2144				
4	270	0.1470	H-7→L	0.2144	276.5	0.1157	H-7→L	0.1817
			H-6→L+1	0.2114			H-6→L+1	0.3050
			H-4→L+1	0.2022			H-3→L	0.2899
			H-2→L	0.2215				
5	250.2	0.0003	H-11→L	0.2785	262.6	0.0181	H-11→L+1	0.1170
			H-11→L+1	0.1621			H-10→L	0.1212
			H-10→L	0.1710			H-7→L+1	0.1087
			H-10→L+1	0.2913			H-2→L	0.3492
6	250.2	0.0003	H-11→L	0.1696	262.3	0.0153	H-11→L	0.1329
			H-11→L+1	0.2883			H-10→L+1	0.1379
			H-10→L	0.2817			H-7→L	0.1270
			H-10→L+1	0.1633			H-5→L	0.1005
							H-2→L+1	0.2509
7	224.5	0.0010	H-7→L+1	0.1530	256.7	0.0008	H-11→L+1	0.3273
			H-3→L	0.4089			H-10→L	0.3293
			H-2→L+1	0.1777			H-2→L	0.2203
8	224.4	0.0017	H-7→L	0.1947	256.5	0.0034	H-11→L	0.2956
			H-6→L+1	0.1102			H-10→L+1	0.2972
			H-3→L+1	0.2900			H-3→L	0.1119
			H-2→L	0.2468				
9	220.1	0.0008	H-14→L	0.1416	256.1	0.0001	H-5→L	0.2451
			H-13→L+1	0.1574			H-4→L+1	0.2243
			H-6→L	0.1407			H-3→L	0.1856
			H-5→L+1	0.1243				
			H-4→L	0.1768				
10	219.8	0.0020	H-14→L+1	0.1107	255.7	0.0082	H-5→L+1	0.1517
			H-13→L	0.1245			H-4→L	0.3452
			H-6→L+1	0.1061			H-3→L+1	0.2574
			H-5→L	0.2281				
			H-4→L+1	0.1394				
			H-3→L+1	0.1143				
11	219.4	0.0000	H-14→L+1	0.2843	246.6	0.0040	H-2→L	0.2361
			H-13→L	0.2963			H-1→L+1	0.4045
			H-5→L	0.1997			H→L	0.2637
12	219.1	0.0012	H-14→L	0.2546	246.3	0.0000	H-2→L+1	0.3477
			H-13→L+1	0.2609			H-1→L	0.3260
			H-5→L+1	0.1967			H→L+1	0.2540
			H-3→L	0.1019				
13	206.1	0.0002	H-3→L+1	0.3482	234.3	0.0104	H-4→L	0.4999
			H-1→L	0.2073			H-3→L+1	0.2990
			H→L+1	0.1383				
14	205.8	0.0084	H-5→L+1	0.1234	234	0.0002	H-4→L+1	0.5805
			H-3→L	0.2433			H-3→L	0.2113
			H-1→L+1	0.2876				
			H→L	0.1682				
15	201.3	0.2478	H-12→L	0.1245	232.1	0.0016	H-5→L	0.4352
			H-1→L+3	0.1279			H-2→L+1	0.1346
			H→L+4	0.1244			H→L+1	0.1327
16	200.8	0.1771	H-1→L+4	0.1806	231.4	0.0030	H-5→L+1	0.4933
			H→L+3	0.3278			H-2→L	0.1034
							H→L	0.1162
17	199.9	0.2449	H-1→L+3	0.1926	224	0.0030	H-14→L	0.3963
			H→L+2	0.1565			H-13→L+1	0.3940
			H→L+4	0.1443				

18	199.1	0.0385	H-12→L+1	0.1187	224	0.0008	H-14→L+1	0.3935
			H-4→L+1	0.1548			H-13→L	0.3996
19	196.6	0.0007	H-7→L+1	0.1319	212.7	0.0026	H-8→L	0.8221
			H-6→L	0.1114				
			H-4→L	0.2140				
			H-2→L+1	0.2753				
20	196.5	0.0013	H-6→L+1	0.1159	211.5	0.0038	H-8→L+1	0.7869
			H-4→L+1	0.1945				
			H-2→L	0.2014				

Table S4. Calculated properties of the first singlet excited states $S_0 \rightarrow S_n$ of $[ZnL_2Cl_2]$ at B3LYP/def2-TZVPP level: transition wavelength (λ), oscillator strength (f). H is for HOMO, L is for LUMO abbreviation. The contribution of the individual excitations is listed if larger than 0.1

n	λ, nm	f	electronic states	contribution
1	378.7	0.1035	H-1→L+1	0.1327
			H→L	0.8484
2	374.2	0.0129	H-1→L	0.1848
			H→L+1	0.7917
3	356.2	0.0009	H-1→L	0.7972
			H→L+1	0.1936
4	354.2	0.0029	H-1→L+1	0.8506
			H→L	0.1391
5	308.9	0.0026	H-3→L	0.7981
			H-2→L+1	0.1233
6	307.9	0.0023	H-7→L	0.1006
			H-3→L+1	0.4314
			H-2→L	0.4180
7	303.8	0.0036	H-5→L	0.2113
			H-3→L+1	0.4188
			H-2→L	0.2767
8	303.3	0.0112	H-6→L	0.1769
			H-5→L+1	0.1320
			H-3→L	0.1164
9	294.7	0.0000	H-2→L+1	0.5023
			H-5→L	0.6665
			H-3→L+1	0.1370
10	293.4	0.0102	H-6→L	0.2805
			H-5→L+1	0.3886
			H-2→L+1	0.1950
11	291.3	0.0032	H-6→L	0.4731
			H-5→L+1	0.4199
12	290.3	0.0015	H-6→L+1	0.7943
13	281.7	0.1365	H-4→L	0.8500
14	279.9	0.0957	H-7→L	0.1421
			H-4→L+1	0.6768
15	278.6	0.0076	H-7→L	0.6256
			H-4→L+1	0.2016
16	277.1	0.0571	H-7→L+1	0.7611
			H-2→L+1	0.1076
17	271.4	0.0002	98a→L	0.4796
			99a→L+1	0.4750
18	271.3	0.0006	98a→L+1	0.4537
			99a→L	0.4957
19	247.3	0.0011	H-8→L	0.9597
20	245.9	0.0004	H-8→L+1	0.9396

Table S5. Calculated properties of the first singlet excited states $S_0 \rightarrow S_n$ of $[ZnL_2I_2]$ (**3**) at B3LYP/def2-TZVPP and PBE0/def2-TZVPP level: transition wavelength (λ), oscillator strength (f). H is for HOMO, L is for LUMO abbreviation. The contribution of the individual excitations is listed if larger than 0.1.

n	B3LYP				PBE0			
	λ, nm	f	electronic states	contribution	λ, nm	f	electronic states	contribution
1	511.0	0.0205	H→L	0.8818	488.1	0.0266	H → L	0.9814
2	499.3	0.0022	H-1→L	0.8540	452.2	0.0021	H-1 → L	0.6934
							H → L+1	0.2137
3	481.9	0.0002	H-2→L	0.8345	449.3	0.0193	H-1 → L	0.1890
							H → L+1	0.7710
4	476.0	0.0206	H→L+1	0.8061	437.2	0.0021	H-2 → L	0.7993
			H-1→L+1	0.1061				
5	469.6	0.0054	H-3→L	0.8271	426.4	0.0033	H-3 → L	0.7730
							H-2 → L	0.1087
6	455.1	0.0014	H-4→L	0.9053	414.3	0.0023	H-4 → L	0.8552
7	446.6	0.0007	H-1→L+1	0.8659	403.9	0.0005	H-1 → L+1	0.9414
			H→L+1	0.1090				
8	430.7	0.0015	H-2→L+1	0.9573	393.6	0.0051	H-5 → L	0.6102
							H-2 → L+1	0.3003
9	423.5	0.0057	H-3→L+1	0.9708	388.9	0.0058	H-5 → L	0.3277
							H-2 → L+1	0.6080
10	417.4	0.0059	H-5→L	0.7558	384.8	0.0123	H-3 → L+1	0.8929
			H-4→L+1	0.2271				
11	415.4	0.0127	H-4→L+1	0.2222	381.0	0.0181	H-4 → L+1	0.8573
			H-5→L	0.7570				
12	381.6	0.0279	H-5→L+1	0.9611	361.9	0.0168	H-5 → L+1	0.8988
13	362.5	0.0034	H-6→L	0.9718	335.7	0.0042	H-6 → L	0.9682
14	333.9	0.0029	H-6→L+1	0.9744	308.6	0.0036	H-6 → L+1	0.9581
15	316.2	0.0040	H-7→L	0.9000	303.1	0.0068	H-7 → L	0.9325
16	306.9	0.0083	H-9→L	0.3408	291.9	0.0358	H-8 → L	0.6959
			H-8→L	0.5705			H-8 → L+1	0.1102
17	302.2	0.0138	H-9→L	0.3800	287.9	0.0042	H-9 → L	0.7626
			H-8→L+1	0.3944			H-8 → L+1	0.1510
18	288.2	0.0630	H-8→L+1	0.3890	280.5	0.0675	H-8 → L	0.1583
			H-9→L	0.1908			H-8 → L+1	0.3541
			H-8→L	0.1914			H-7 → L+1	0.1907
19	283.7	0.0536	H-7→L+1	0.4870	277.2	0.0746	H-8 → L+1	0.2828
			H-9→L+1	0.1972			H-7 → L+1	0.5585
			H-8→L+1	0.1500				
20	281.7	0.0386	H-9→L+1	0.6898	268.8	0.0012	H-11 → L+1	0.2568
			H-7→L+1	0.1990			H-10 → L+1	0.2333
							H-9 → L+1	0.2847

Table S6. Calculated properties of the first singlet excited states $S_0 \rightarrow S_n$ of $[ZnL_2I_2]$ (**3**) at wB97XD/def2-TZVPP and CAM-B3LYP/def2-TZVPP level: transition wavelength (λ), oscillator strength (f). H is for HOMO, L is for LUMO abbreviation. The contribution of the individual excitations is listed if larger than 0.1

n	wB97XD				CAM-B3LYP			
	λ, nm	f	electronic states	contribution	λ, nm	f	electronic states	contribution
1	400.3	0.0609	H → L	0.8764	434.9	0.0472	H → L	0.9001
2	326.5	0.0542	H-5 → L	0.1495	361.9	0.0124	H → L+1	0.8766
			H-5 → L+1	0.3289				
			H-4 → L+1	0.1633				
3	309.1	0.0149	H → L+1	0.8698	350.2	0.0425	H-5 → L	0.2502
							H-5 → L+1	0.3555
4	287.3	0.0592	H-8 → L	0.1289	344.8	0.0065	H-3 → L	0.2480
			H-4 → L	0.1113			H-1 → L	0.5547
			H-3 → L	0.2206				
			H-1 → L	0.2615				
5	279.5	0.0471	H-8 → L	0.1406	332.3	0.0021	H-2 → L	0.5761
			H-5 → L	0.1870			H-1 → L	0.1421
			H-1 → L	0.1351				
6	274.9	0.0291	H-2 → L	0.4646	321.5	0.0013	H-3 → L	0.5586
			H-1 → L	0.1060			H-2 → L	0.1344
							H-1 → L	0.2149
7	271.4	0.1239	H-7 → L	0.1179	313.9	0.0265	H-5 → L	0.3095
			H-7 → L+1	0.3890			H-5 → L+1	0.2043
							H-4 → L	0.2872
8	264.3	0.0110	H-3 → L	0.2466	305.3	0.0164	H-5 → L	0.3141
			H-1 → L	0.3767			H-4 → L	0.4327
9	258	0.0088	H-8 → L	0.1489	296.9	0.0125	H-3 → L+1	0.1072
			H-5 → L	0.1531			H-1 → L+1	0.7750
			H-4 → L	0.2935				
			H-2 → L	0.1640				
10	251.7	0.0003	H-11 → L	0.1319	288.2	0.0243	H-3 → L+1	0.6381
			H-11 →L+1	0.5788				
			H-10 →L+1	0.1412				
11	248.1	0.0039	H-5 → L	0.3107	287.1	0.0016	H-4 → L+1	0.2192
			H-4 → L	0.2418			H-2 → L+1	0.6668
			H-3 → L	0.1997				
12	242.4	0.0017	H-14 → L	0.1536	280.6	0.0525	H-8 → L	0.3021
			H-13 → L	0.2542			H-7 → L	0.1190
			H-12 → L	0.1041			H-6 → L	0.1895
13	240.1	0.0075	H-3 → L+1	0.1814	279.4	0.0280	H-8 → L	0.1019
			H-1 → L+1	0.6374			H-5 → L+1	0.1681
							H-4 → L+1	0.3650
							H-2 → L+1	0.1058
14	234.8	0.0057	H-5 → L+1	0.1120	274.9	0.0660	H-7 → L	0.2752
			H-3 → L+1	0.4589			H-7 → L+1	0.2895
			H-1 → L+1	0.1603			H-6 → L	0.1599
15	233.4	0.0021	H-4 → L+1	0.4182	270.6	0.0297	H-8 → L	0.2174
			H-2 → L+1	0.3532			H-7 → L+1	0.1190
							H-6 → L	0.4754
16	230.7	0.0080	H-6 → L	0.5273	260.7	0.0002	H-11 → L	0.1341
			H-2 → L+1	0.1145			H-11 → L+1	0.5264
							H-10 → L+1	0.1390
17	227.7	0.0006	H-5 → L+1	0.1752	256.1	0.0072	H-7 → L	0.4187
			H-4 → L+1	0.2073			H-7 → L+1	0.2639
			H-3 → L+1	0.1139				
			H-2 → L+1	0.1889				
18	226.5	0.0083	H-7 → L	0.5029	250.2	0.0004	H-13 → L	0.2128
			H-7 → L+1	0.1515			H-12 → L	0.1251
							H-9 → L	0.2805
							H-7 → L	0.1208
19	223.3	0.1914	H-8 → L	0.1601	247.8	0.0022	H-8 → L+1	0.2501
			H → L+2	0.3644			H-6 → L+1	0.4740
			H → L+4	0.1275				
20	221.6	0.0937	H-14 →L+1	0.1388	241.9	0.0008	H-8 → L+1	0.4385
			H-8 → L+1	0.2212			H-6 → L+1	0.3836
			H → L+2	0.1313				

Table S7. Calculated properties of the first singlet excited states $S_0 \rightarrow S_n$ of $[Zn_3L_2(NH_3)_2I_6]$ at B3LYP/def2-TZVPP and PBE0/def2-TZVPP level: transition wavelength (λ), oscillator strength (f). H is for HOMO, L is for LUMO abbreviation.

n	B3LYP				PBE0			
	λ, nm	f	electronic states	contribution	λ, nm	f	electronic states	contribution
1	688.9	0.0001	H→L	0.9511	590.9	0.0002	H→L H→L+1	0.8663 0.1108
2	657.4	0.0001	H-1→L	0.9596	565.4	0.0002	H-1→L	0.8656
3	641.7	0.0012	H→L+1	0.8427	560.9	0.0014	H→L H→L+1	0.1257 0.7218
4	632.7	0.0013	H-2→L	0.8815	548.7	0.0023	H-2→L	0.8174
5	614.6	0.0025	H-3→L H-1→L+1	0.7398 0.1772	537.8	0.0034	H-3→L H-3→L+1 H-1→L+1	0.3648 0.1160 0.4296
6	609.7	0.0005	H-3→L H-1→L+1	0.2096 0.7621	532.1	0.0009	H-3→L H-1→L+1	0.5109 0.4387
7	593.6	0.0038	H-2→L+1	0.9140	522.7	0.0044	H-2→L H-2→L+1	0.1193 0.8213
8	574.5	0.0080	H-3→L+1	0.9391	508.6	0.0071	H-3→L+1	0.8581
9	542.1	0.0022	H-4→L	0.9632	482.5	0.0016	H-4→L	0.8547
10	534.9	0.0007	H-6→L	0.9357	479.3	0.0019	H-6→L H-5→L	0.6867 0.2280
11	527.6	0.0015	H-7→L H-5→L	0.3882 0.5753	475.3	0.0020	H-7→L H-5→L	0.4341 0.3653
12	516.7	0.0009	H-7→L H-5→L	0.5107 0.3909	461.7	0.0013	H-8→L H-8→L+1 H-4→L+1	0.1656 0.1045 0.6469
13	511.8	0.0010	H-8→L H-4→L+1	0.3199 0.5889	461.3	0.0007	H-7→L H-6→L H-5→L	0.4139 0.1397 0.3353
14	504.3	0.0069	H-8→L H-4→L+1	0.5916 0.3551	453.5	0.0018	H-11→L	0.8821
15	500.3	0.0003	H-11→L	0.9409	451.7	0.0059	H-8→L H-4→L+1	0.6679 0.2380
16	496.3	0.0076	H-9→L H-5→L+1	0.6765 0.1985	448.5	0.0087	H-9→L H-5→L+1	0.5497 0.1435
17	490.9	0.0023	H-12→L H-10→L H-5→L+1	0.1256 0.4425 0.2931	446.6	0.0053	H-10→L H-5→L+1	0.5257 0.2922
18	488.7	0.0044	H-10→L H-9→L H-5→L+1	0.3249 0.2032 0.3477	441.9	0.0059	H-10→L H-9→L H-5→L+1	0.2295 0.2381 0.4064
19	482.4	0.0009	H-8→L+1	0.7543	438	0.0038	H-9→L H-8→L+1	0.1401 0.5081
20	470	0.0183	H-13→L H-12→L H-7→L+1 H-6→L+1	0.1800 0.3700 0.1074 0.1802	433.7	0.0288	H-8→L+1 H-7→L+1 H-6→L+1	0.2296 0.3417 0.2202

Table S8. Calculated properties of the first singlet excited states $S_0 \rightarrow S_n$ of $[Zn_3L_2(NH_3)_2I_6]$ at wB97XD/def2-TZVPP and CAM-B3LYP/def2-TZVPP level: transition wavelength (λ), oscillator strength (f). H is for HOMO, L is for LUMO abbreviation.

n	wB97XD				CAM-B3LYP			
	λ, nm	f	electronic states	contribution	λ, nm	f	electronic states	contribution
1	360.4	0.0511	H-13→L+1 H-5→L+1	0.1418 0.3423	400	0.0265	H-13→L+1 H-5→L+1 H→L+1	0.1098 0.1514 0.2550
2	345.2	0.0707	H-14→L	0.5947	378.9	0.0158	H-14→L H-2→L+1 H→L+1	0.1147 0.2727 0.2321
3	308.7	0.0259	H-5→L	0.3859	377.5	0.0310	H-14→L H-5→L	0.3217 0.1261
4	300	0.0764	H-2→L+1 H→L+1	0.2820 0.2628	369.6	0.0279	H-14→L H-5→L H→L	0.1190 0.1207 0.1975
5	292.4	0.0033	H-8→L+1 H-4→L+1	0.3671 0.2150	367.4	0.0211	H-3→L+1 H-1→L H-1→L+1	0.3767 0.1324 0.3427
6	291.9	0.0154	H-11→L	0.6232	356.2	0.0007	H-2→L+1 H→L H→L+1	0.3643 0.1127 0.1270
7	287.1	0.0196	H-3→L+1 H-1→L+1	0.3057 0.2697	354.8	0.0047	H-11→L H-7→L H-6→L	0.3071 0.1278 0.2745
8	282.2	0.0032	H-7→L H-6→L	0.1724 0.5320	353.8	0.0083	H-8→L+1 H-4→L+1	0.3309 0.3958
9	281	0.0292	H-9→L+1 H-7→L+1 H-4→L+1	0.1389 0.1271 0.1940	348.5	0.0037	H-11→L H-6→L H-2→L H→L H→L+1	0.1575 0.1027 0.1273 0.2840 0.1026
10	279	0.0924	H-20→L H-11→L H-4→L	0.1353 0.1380 0.1147	345.5	0.0003	H-11→L H-3→L+1 H-1→L	0.1293 0.1534 0.2122
11	274.5	0.0034	H-2→L+1 H→L+1	0.2939 0.2856	344.1	0.0013	H-11→L H-3→L+1 H-1→L+1 H→L	0.1596 0.1753 0.1766 0.1339
12	273.1	0.0291	H-13→L H-10→L	0.1120 0.2427	340.9	0.0126	H-9→L+1 H-7→L+1 H-6→L+1 H-5→L+1 H-4→L+1	0.2155 0.1416 0.1272 0.1006 0.2332
13	271.2	0.0175	H-18→L+1 H-8→L+1 H-4→L+1 H-2→L+1	0.1018 0.1091 0.2157 0.1151	338.6	0.0142	H-8→L H-4→L H-1→L	0.1003 0.2205 0.2246
14	269.7	0.0420	H-18→L+1 H-8→L+1 H-7→L+1	0.1736 0.1728 0.1258	338.1	0.0053	H-4→L H-1→L	0.4251 0.1424
15	268	0.0010	H-12→L H-4→L	0.2203 0.1826	334.1	0.0022	H-10→L H-5→L H-2→L	0.3879 0.1002 0.1651
16	265.4	0.0072	H-3→L+1 H-1→L+1	0.3215 0.3294	332.9	0.0017	H-13→L H-10→L H-2→L	0.1580 0.1099 0.2534
17	262.5	0.0227	H-4→L	0.3303	330.6	0.0052	H-8→L+1 H-4→L+1	0.3817 0.2518
18	258.6	0.0018	H-9→L H-7→L H→L	0.1328 0.2644 0.1459	328.7	0.0015	H-13→L H-12→L H-3→L H-2→L	0.1580 0.1319 0.2330 0.1480
19	257.2	0.0108	H→L	0.3335	326.6	0.0050	H-9→L H-7→L H-6→L H-5→L	0.1366 0.2399 0.1748 0.1869

20	257.1	0.0022	H-14→L+1 H-9→L+1 H-7→L+1	0.1208 0.4393 0.1961	322.5	0.0016	H-13→L H-12→L H-3→L	0.1121 0.2924 0.2608

Table S9. Calculated properties of the first singlet excited states $S_0 \rightarrow S_n$ of $[Zn_4L_3(NH_3)_2I_8]$ at B3LYP/def2-TZVPP and PBE0/def2-TZVPP level: transition wavelength (λ), oscillator strength (f). H is for HOMO, L is for LUMO abbreviation.

n	B3LYP				PBE0			
	λ, nm	f	electronic states	contribution	λ, nm	f	electronic states	contribution
1	856.5	0.0000	H→L	0.9932	699.6	0.0000	H→L	0.9805
2	817.2	0.0001	H-1→L	0.9903	674.6	0.0001	H-1→L	0.9700
3	775.5	0.0008	H-2→L H→L+1	0.8402 0.1296	652.7	0.0025	H-2→L H→L+1	0.1484 0.7042
4	767.6	0.0013	H-2→L H→L+1	0.1490 0.8140	643.4	0.0001	H-2→L H→L+1	0.8168 0.1643
5	742	0.0012	H-3→L H-1→L+1	0.1991 0.7375	633.5	0.0017	H-1→L+1	0.8315
6	735.6	0.0001	H-3→L H-1→L+1	0.7917 0.1973	617.4	0.0001	H-3→L	0.9297
7	709.8	0.0005	H-2→L+1	0.8881	608.5	0.0004	H-2→L+1	0.7465
8	678.5	0.0003	H-4→L	0.9682	582.7	0.0003	H-3→L+1	0.7717
9	676.1	0.0002	H-3→L+1	0.8973	578.4	0.0005	H-4→L	0.9021
10	650.3	0.0001	H-5→L	0.9724	565.5	0.0008	H-2→L+2 H→L+2	0.2715 0.5878
11	640.2	0.0010	H-2→L+2 H→L+2	0.2562 0.6732	556.5	0.0003	H-5→L	0.9042
12	634.1	0.0006	H-4→L+1	0.8991	552.3	0.0007	H-4→L+1	0.8811
13	630.9	0.0015	H-7→L H-6→L	0.1260 0.7912	548.6	0.0069	H-3→L+1 H-3→L+2 H-1→L+2	0.1193 0.1637 0.6122
14	620	0.0010	H-7→L H-6→L	0.8059 0.1231	547.2	0.0036	H-7→L H-6→L	0.2248 0.5995
15	618.2	0.0058	H-3→L+2 H-1→L+2	0.1916 0.7230	536.6	0.0004	H-7→L H-6→L	0.5971 0.2422
16	608.1	0.0005	H-5→L+1	0.9605	531.5	0.0007	H-5→L+1	0.8893
17	589.6	0.0073	H-6→L+1	0.9185	519.3	0.0118	H-6→L+1	0.8698
18	587.1	0.0007	H-2→L+2 H→L+2	0.6757 0.2868	517.9	0.0015	H-2→L+2 H→L+2	0.5556 0.3221
19	579.8	0.0078	H-7→L+1	0.9233	513.9	0.0054	H-7→L+1	0.8568
20	570.5	0.0005	H-8→L	0.8787	511.2	0.0008	H-8→L H-8→L+1	0.7201 0.1520

Table S10. Calculated properties of the first singlet excited states $S_0 \rightarrow S_n$ of $[Zn_4L_3(NH_3)_2I_8]$ at wB97XD/def2-TZVPP and CAM-B3LYP/def2-TZVPP level: transition wavelength (λ), oscillator strength (f). H is for HOMO, L is for LUMO abbreviation.

n	wB97XD				CAM-B3LYP			
	λ, nm	f	electronic states	contribution	λ, nm	f	electronic states	contribution
1	383.5	0.0177	H-13→L+1 H-11→L+1 H-10→L+1	0.1445 0.2928 0.1359	431.9	0.0060	H-2→L+1 H-2→L+2 H→L+1 H→L+2	0.1229 0.3236 0.1413 0.2491
2	375.9	0.0653	H-8→L+1 H-8→L+2 H-1→L+2	0.1650 0.2645 0.1145	427.1	0.0148	H-8→L+1 H-1→L+1 H-1→L+2	0.1191 0.2553 0.2289
3	351	0.0062	H-2→L+1 H-2→L+2 H→L+2	0.1011 0.4356 0.2584	415.2	0.0304	H-13→L+1 H-11→L+1 H-10→L+1 H-7→L+1	0.2037 0.1847 0.1115 0.1328
4	348.6	0.0362	H-21→L H-20→L	0.2234 0.3685	404.6	0.0011	H-8→L+1 H-3→L+1 H-3→L+2 H-1→L+2	0.2449 0.1023 0.2354 0.1246
5	334.3	0.0124	H-8→L+1 H-3→L+2 H-1→L+2	0.1781 0.2910 0.2934	385.6	0.0055	H-11→L H-4→L+1	0.1367 0.1007
6	330.5	0.0418	H-8→L+1 H-8→L+2 H-1→L+1	0.1441 0.2652 0.1535	384.5	0.0063	H-11→L H-4→L+1	0.1039 0.3701
7	320.1	0.0238	H-13→L H-11→L H-10→L	0.1402 0.2276 0.1893	384	0.0291	H-8→L+2 H-4→L+1 H-1→L+1	0.2599 0.2084 0.1236
8	313.8	0.0149	H-6→L+1 H-6→L+2 H-4→L+1 H-4→L+2	0.1022 0.1935 0.2107 0.2144	380.9	0.0002	H-2→L+2 H→L H→L+1	0.1001 0.4597 0.3325
9	312.1	0.0342	H-14→L	0.6509	375.1	0.0006	H-1→L H→L H→L+1	0.1637 0.3641 0.3487
10	302.9	0.0163	H-6→L+1 H-4→L+1	0.1024 0.3725	373.6	0.0151	H-21→L H-14→L H-10→L	0.1849 0.2005 0.2412
11	298.9	0.0226	H-6→L+1 H-5→L+1 H-5→L+2	0.1015 0.1802 0.1682	372.2	0.0073	H-6→L+1 H-5→L+1	0.2836 0.2384
12	297.4	0.0368	H-15→L H-11→L H-10→L	0.2531 0.1096 0.1911	370	0.0005	H-1→L H→L	0.6292 0.1357
13	294.3	0.0379	H-17→L+1 H-5→L+1	0.1015 0.1404	369.3	0.0036	H-6→L+1 H-5→L+1 H-2→L+1 H-5→L+1	0.2119 0.2808 0.1294 0.1606
14	292.8	0.0260	H→L+1	0.1247	367.7	0.0007	H-2→L H-2→L+1 H→L+2	0.1067 0.3925 0.1376
15	292.3	0.0276	H-14→L H-11→L H-10→L	0.1006 0.1541 0.1720	365.2	0.0338	H-21→L H-14→L	0.2087 0.4521
16	290.2	0.0315	H→L+1	0.1717	358.3	0.0038	H-1→L+1	0.2774
17	288.7	0.0025	H-6→L+1 H-4→L+2	0.2955 0.2169	357.5	0.0015	H-15→L H-10→L	0.1049 0.1859
18	287.7	0.0013	H-7→L+1 H-5→L+1 H-4→L+2	0.1630 0.1081 0.1347	356.5	0.0036	H-2→L	0.4432
19	285.6	0.0386	H-13→L	0.2687	356	0.0025	H-10→L H-7→L+1 H-2→L	0.1101 0.1405 0.2069
20	282.7	0.0176	complex	complex	355.1	0.0005	H-4→L+2 H-3→L H-3→L+1	0.1185 0.1425 0.3630

Table S11. Calculated properties of the first singlet excited states $S_0 \rightarrow S_n$ of $[ZnLI_2]_n$ (**4**) with B3LYP functional: transition wavelength (λ), oscillator strength (f). H is for HOCO, L is for LUCO crystalline orbitals abbreviation.

n	λ, nm	f	electronic states	Excitation amplitude
1	457.0	0.0169	H→L	0.9924
			H-2→L+1	0.1001
2	452.2	0.0000	H-1→L	0.9939
			H→L+2	-0.0512
3	449.5	0.0000	H→L+1	0.8893
			H-2→L	0.4521
4	445.2	0.0000	H-2→L	-0.8826
			H→L+1	0.4512
			H-5→L+2	0.0872
5	444.2	0.0079	H-1→L+1	-0.9880
			H-3→L	-0.1016
			H-2→L+2	0.0555
6	438.2	0.0689	H-2→L+1	0.9774
			H-5→L	-0.1579
			H→L	-0.0953
			H-4→L+1	-0.0737
7	431.8	0.0606	H-3→L	-0.9694
			H-9→L+1	-0.1497
			H-1→L+1	0.1074
			H→L+3	0.0863
			H-7→L+1	0.0539
			H-10→L+2	0.0506
8	426.4	0.0000	H-4→L	-0.8243
			H-5→L+1	-0.5073
			H-1→L+3	0.1544
			H-6→L+1	-0.1106
			H-12→L	0.859
			H-7→L+3	0.0724
			H-2→L	-0.0658
			H→L+1	0.0559
9	426.1	0.0004	H-5→L	0.8158
			H-4→L+1	0.4964
			H-2→L+1	0.1645
			H-6→L	0.1376
			H-12→L+1	-0.1168
			H-1→L+2	-0.0956
			H-7→L+2	-0.0793
10	424.9	0.0000	H-3→L+1	0.8279
			H→L+2	-0.5025
			H-9→L	0.1692
			H-2→L+3	0.0669
			H-4→L+3	-0.0606
			H-1→L	-0.0582
			H-10→L+3	-0.0550
			H-5→L+2	-0.0526
			H-7→L	-0.0501

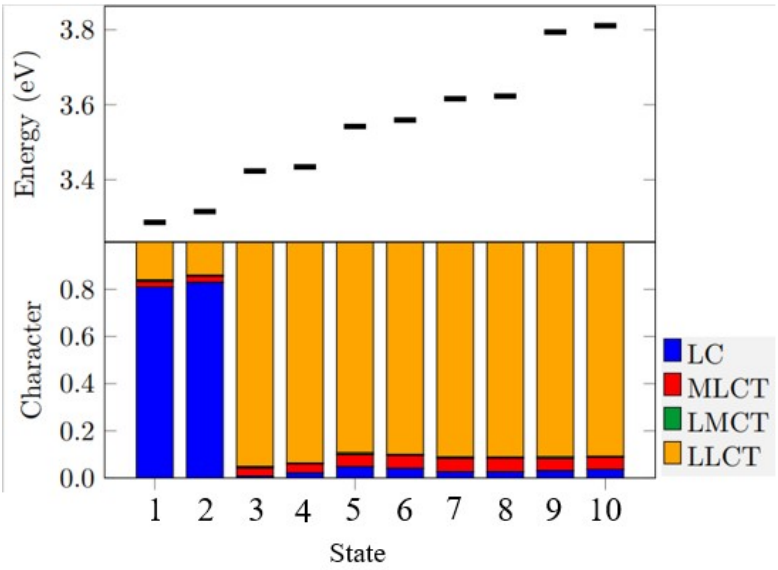


Figure S19. Decomposition of 10 vertical excitation states for $[ZnL_2Br_2]$ (**1**) in terms of contribution from excitation types. LC – ligand-centered, MLCT – metal-to-ligand charge transfer, LMCT – ligand-to-metal charge transfer, LLCT – ligand-to-ligand charge transfer

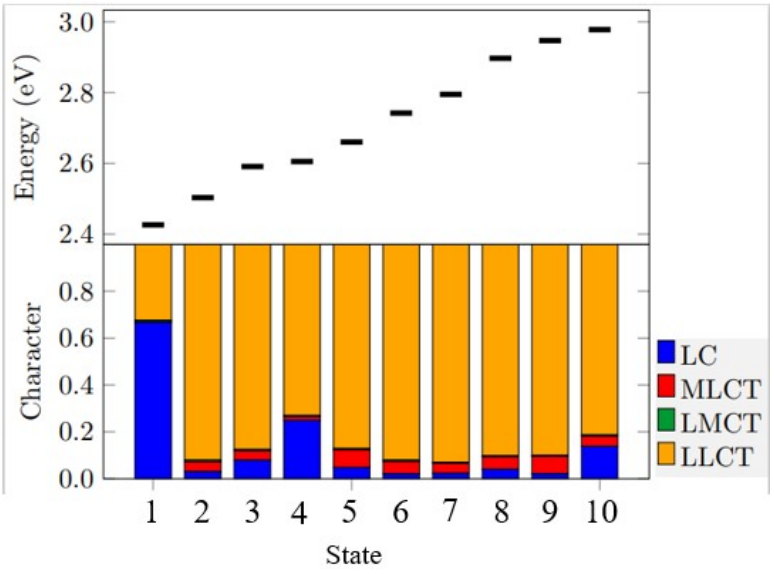
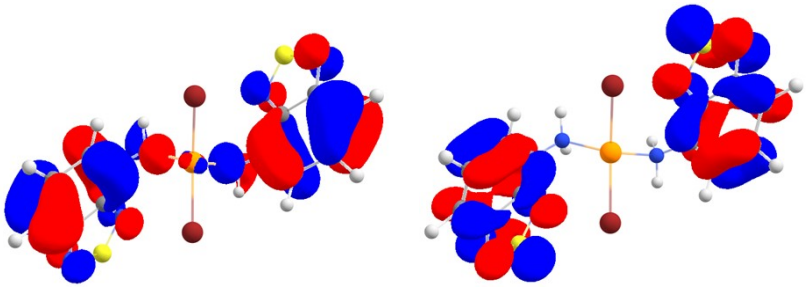
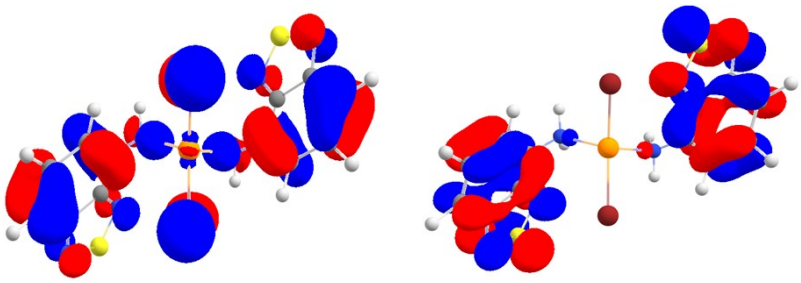


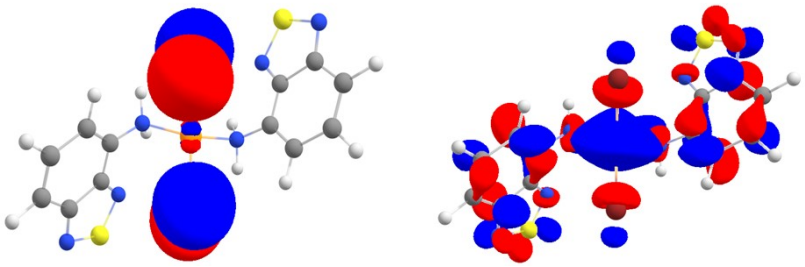
Figure S20. Decomposition of 10 vertical excitation states for $[ZnL_2I_2]$ (**3**) in terms of contribution from excitation types. LC – ligand-centered, MLCT – metal-to-ligand charge transfer, LMCT – ligand-to-metal charge transfer, LLCT – ligand-to-ligand charge transfer



H L

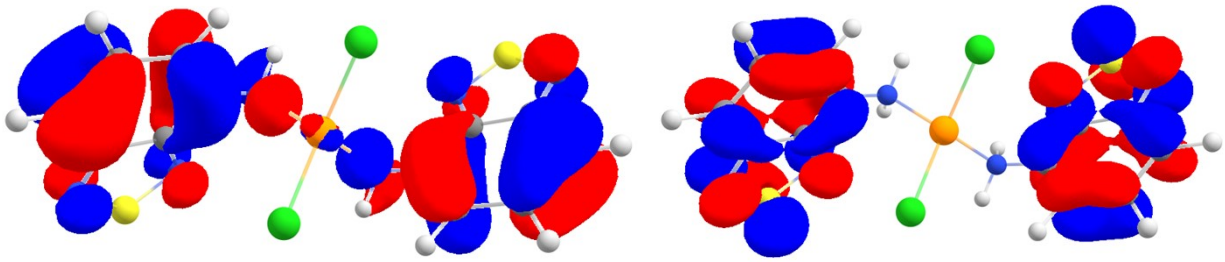


H-1 L+1



H-2 L+2

Figure S21. Frontier orbitals of [ZnL_2Br_2] (**1**) (B3LYP/def2-TZVPP, isovalue = 0.03 a.u.). H is for HOMO, L is for LUMO abbreviation



H L

Figure S22. Frontier orbitals of [ZnL_2Cl_2] (B3LYP/def2-TZVPP, isovalue = 0.03 a.u.). H is for HOMO, L is for LUMO abbreviation

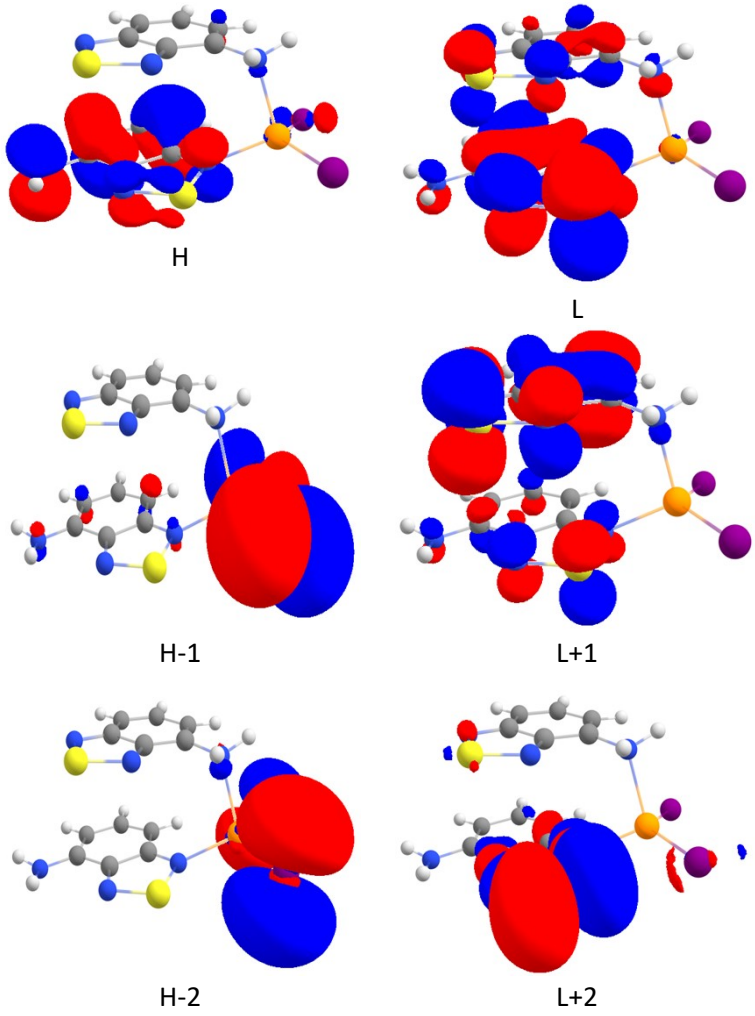


Figure S23. Frontier orbitals of [ZnL_2I_2] (**3**) (B3LYP/def2-TZVPP, isovalue = 0.03 a.u.). H is for HOMO, L is for LUMO abbreviation

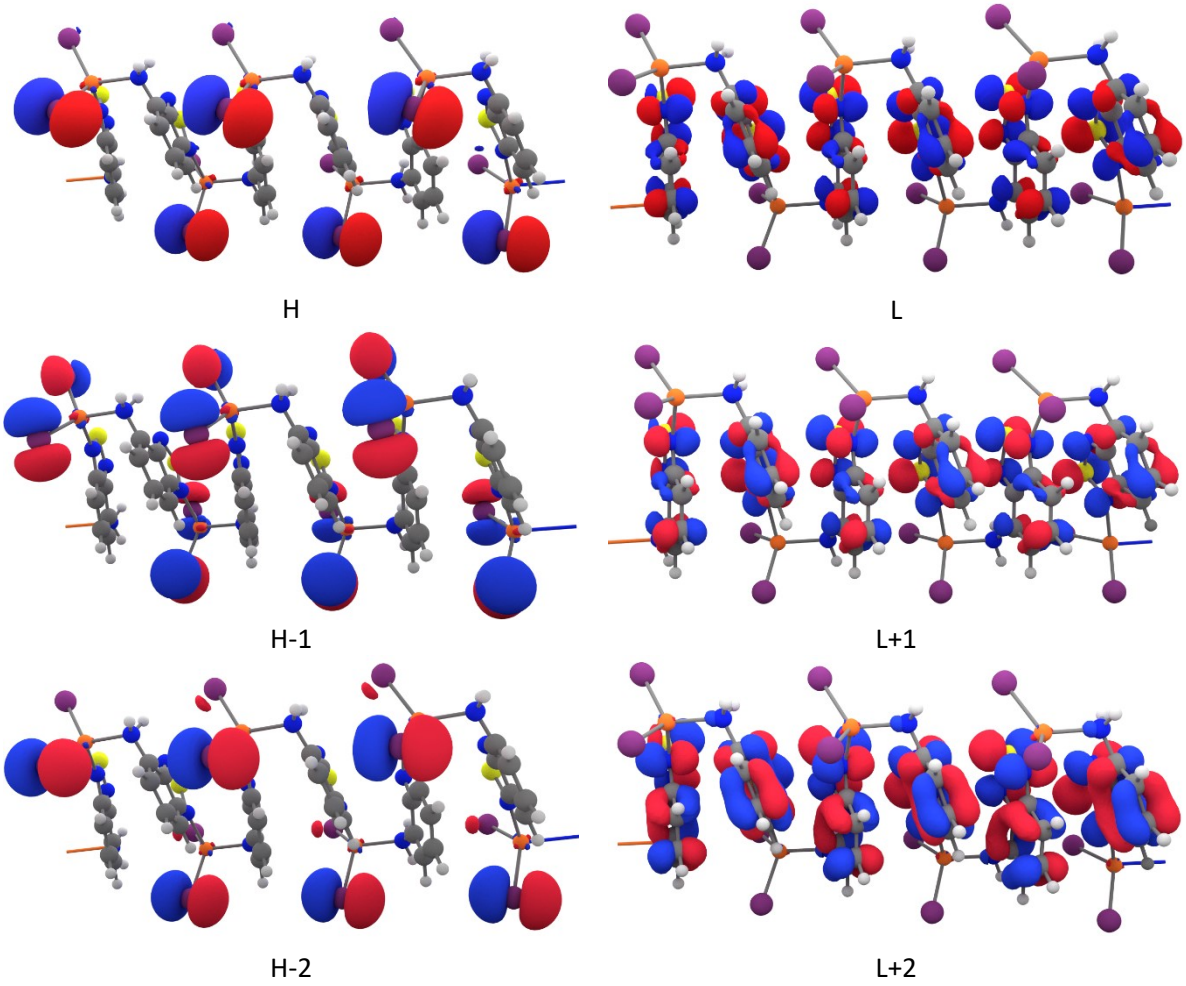


Figure S24. Frontier orbitals of $[ZnLI_2]_n$ (**4**). isovalue = 0.03. H is for HOCO, L is for LUCO abbreviation

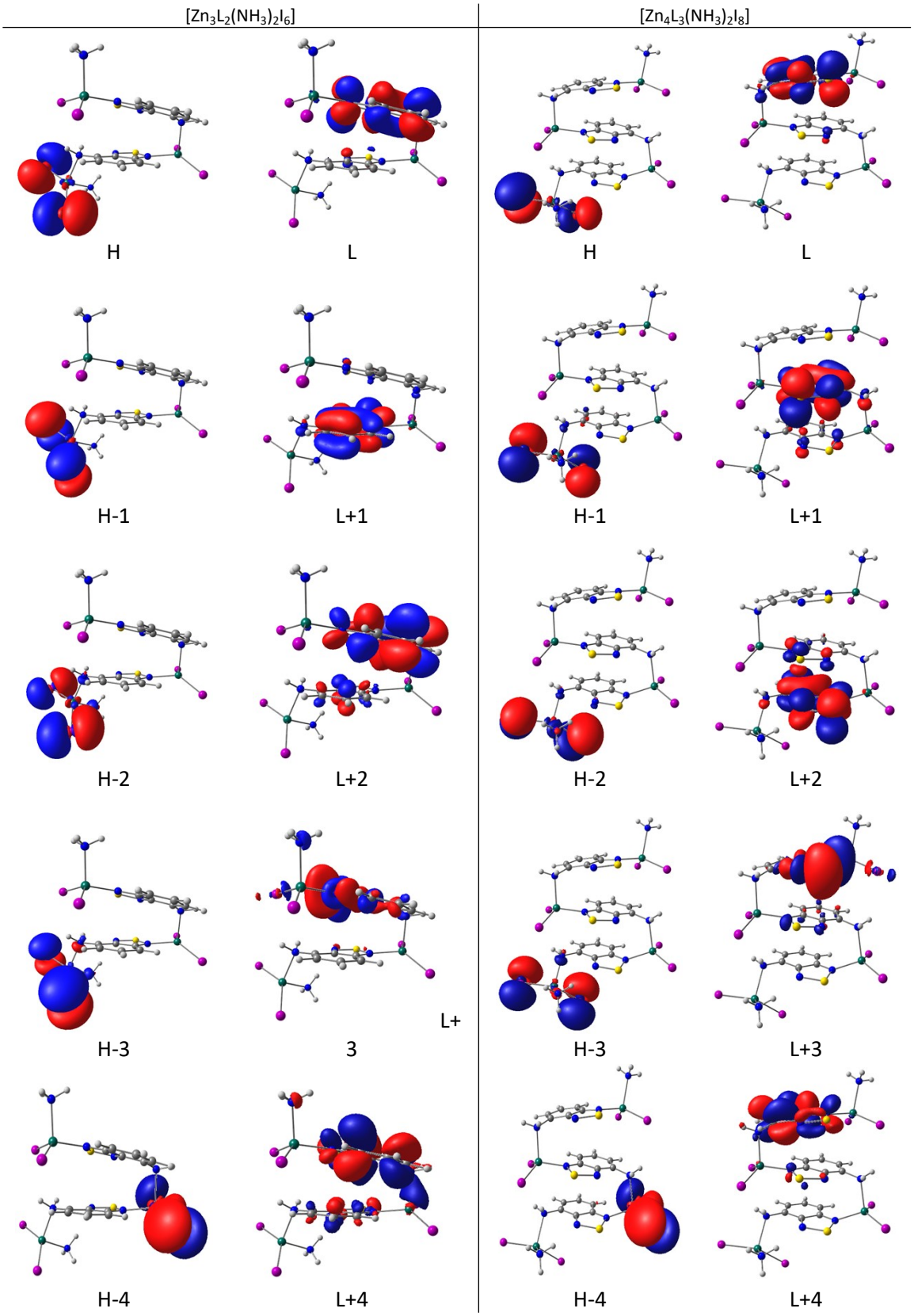


Figure S25. Frontier molecular orbitals of $[Zn_3L_2(NH_3)_2I_6]$ and $[Zn_4L_3(NH_3)_2I_8]$ calculated at B3LYP/def2TZVPP level (isovalue = 0.03 a.u.). H is for HOMO, L is for LUMO abbreviation

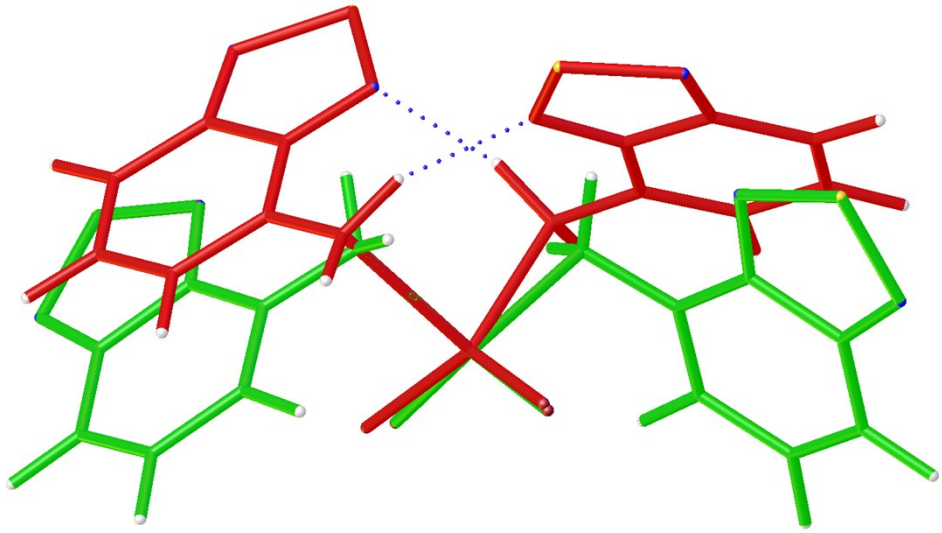


Figure S26. Overlay of optimized geometry of complex **1** in the ground state (green) and S_1 state (red).

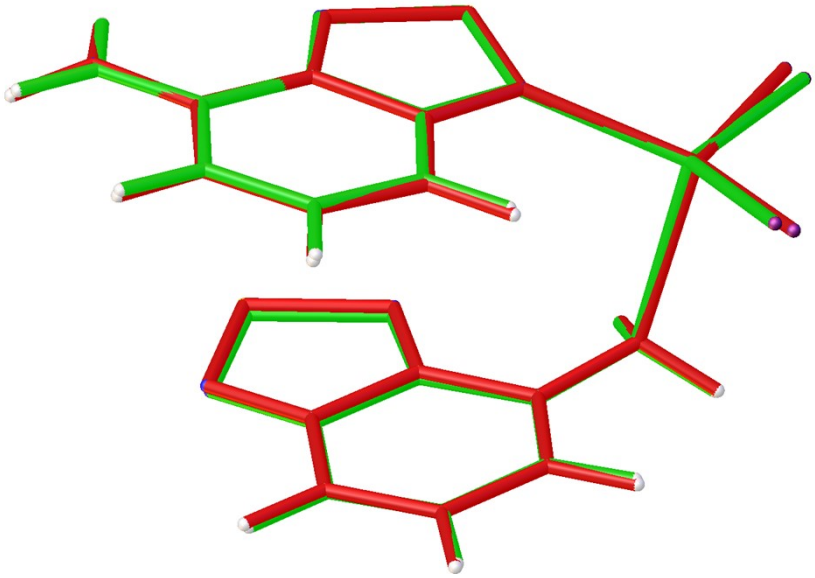


Figure S27. Overlay of optimized geometry of complex **3** in the ground state (green) and S_1 state (red).

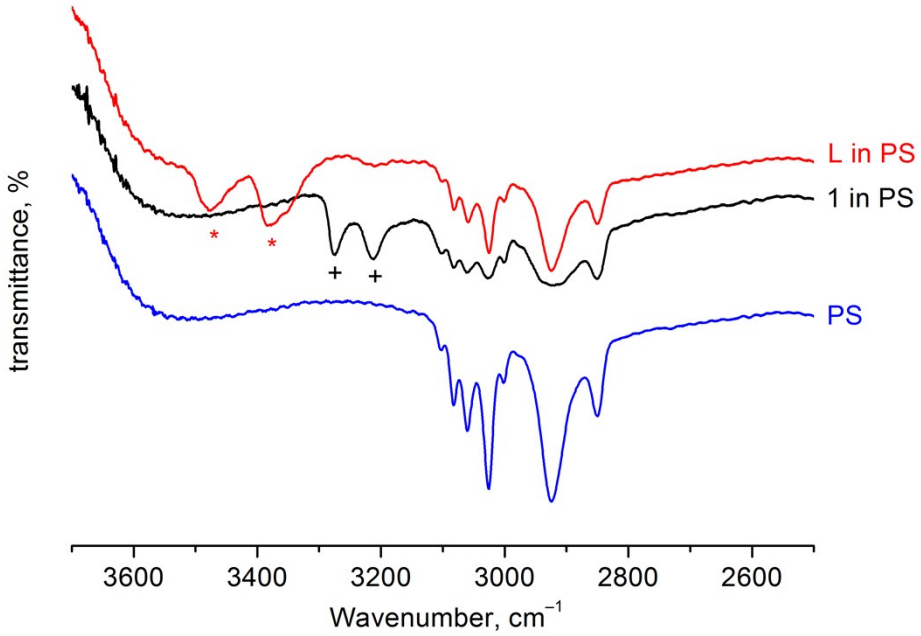


Figure S28. Infrared spectra of polystyrene (PS) (blue), L in PS film (red) and **1** in PS film (black). Bands assigned to NH-vibrations of L are marked with "*", while those assigned to **1** are marked with "+".