Electronic Supplementary Information

Efficient emission of Zn(II) and Cd(II) complexes with nopinane-annelated 4,5-diazaluorene and 4,5-diazaluoren-9-one ligands: how slight structural modification alters fluorescence mechanism

Tatyana E. Kokina,*[a] Nikita A. Shekhovtsov,*[a] Eugene S. Vasilyev,[b] Ludmila A. Glinskaya,[a] Aleksandr V. Mikheylis,[c] Victor F. Plyusnin,*[c] Alexey V. Tkachev*[b] and Mark B. Bushuev *[a]

[a] Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, 3, Acad. Lavrentiev Ave., Novosibirsk 630090, Russia. E-mail addresses: kokina@niic.nsc.ru (Tatiana E. Kokina), shekhovtsov@niic.nsc.ru (Nikita A. Shekhovtsov), bushuev@niic.nsc.ru (Mark B. Bushuev).
[b] N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of Russian Academy of Sciences, 9, Acad. Lavrentiev Ave., Novosibirsk 630090, Russia. E-mail address: atkachev@nioch.nsc.ru (Alexey V. Tkachev)
[c] Voevodsky Institute of Chemical Kinetic and Combustion, Siberian Branch of Russian Academy of Sciences, 3, Institutskaya st., Novosibirsk 630090, Russia. E-mail address: plyusnin@kinetics.nsc.ru (Victor F. Plyusnin)

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Experimental part

Crystallographic data

Table S1. Crystallographic characteristics, experimental data and structure refinement for **[ZnL^{O}Cl$_2$]·MeCN** and **[CdL^{O}Cl$_2$]$_n$·nH$_2$O**.

Complex	**[ZnL^{O}Cl$_2$]·MeCN**	**[CdL^{O}Cl$_2$]$_n$·nH$_2$O**
Empirical formula	C$_{27}$H$_{28}$Cl$_2$N$_3$OZn	C$_{25}$H$_{26}$CdCl$_2$N$_2$O·H$_2$O
Formula weight	546.79	571.79
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1$
a, Å	10.2980(5)	6.9333 (3)
b, Å	14.6532(7)	28.6315 (14)
c, Å	17.2961(9)	12.6065 (7)
β,°		99.520 (2)
V, Å^3	2610.0(2)	2468.1 (2)
Z; d_{calc}, g/cm^3	4, 1.392	4, 1.539
μ (mm^{-1})	1.170	1.126
Crystal size, mm	0.2 x 0.15 x 0.1	0.16 x 0.05 x 0.03
Theta range for data collection (°)	3.642 – 62.19	3.572 – 60.06
Reflections collected	39080	40701
Independent reflections	7626	12477
(R_{int})	0.0578	0.0485
Number of reflections with $I > 2 s(I)$	5839	10189
Number of refined parameters	312	591
GOOF on F^2	0.997	1.021
Final R indices ($I > 2\sigma_I$) R_1	0.0419	0.0342
wR_2	0.0857	0.0732
R indices (all data) R_1	0.0697	0.0514
wR_2	0.0941	0.0776
Largest diff. peak and hole (e/Å^3)	0.88/ −0.49	0.85/ −0.92
Flack parameter	0.013(5)	-0.013(11)

Table S2. Selected bond lengths (Å) and angles (°) for **[ZnL^OCl₂]·MeCN**.
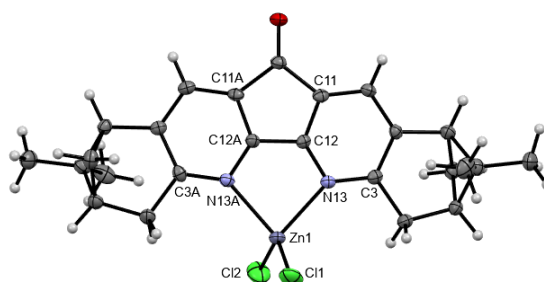
Bond	d (Å)
Zn(1)−Cl(1)	2.180(1)
Zn(1)−Cl(2)	2.190(1)
Zn(1)−N(13)	2.138(3)
Zn(1)−N(13A)	2.157(3)
N(13)−C(12)	1.335(5)
N(13)−C(3)	1.357(5)
N(13A)−C(12A)	1.330(5)
N(13)−C(3A)	1.344(5)
C(11)−C(12)	1.389(5)
C(12)−C(12a)	1.441(5)
Angle	ω (deg.)
Cl(1)−Zn(1)−Cl(2)	123.0(1)
N(13)−Zn(1)−N (13A)	84.2(1)
N(13)−Zn(1)−Cl(1)	111.6(1)
N(13) −Zn(1)−Cl(2)	111.6(1)
N(13A)−Zn(1)−Cl(1)	1114.(1)
N(13A)−Zn(1)−Cl(2)	105.5(1)

Table S3. Selected bond lengths (Å) and angles (º) for **[CdL^{O}Cl$_2$]$_n$·nH$_2$O**.
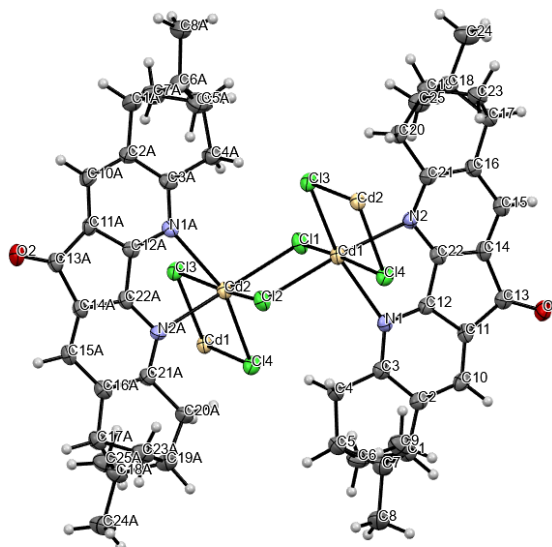
Bond	d (Å)	Bond	d (Å)
Cd(1)–Cl(1)	2.602(1)	Cd(2)–Cl(1)	2.588(1)
Cd(1)–Cl(2)	2.570(1)	Cd(2)–Cl(2)	2.593(1)
Cd(1)–Cl(3)	2.564(1)	Cd(2)–Cl(3)[2]	2.684(1)
Cd(1)–Cl(4)[1]	2.675(1)	Cd(2)–Cl(4)	2.571(1)
Cd(1)–N(1)	2.441(4)	Cd(2)–N(1A)	2.426(4)
Cd(1)–N(2)	2.439(4)	Cd(2)–N(2A)	2.482(4)
Angle	ω (deg.)	Angle	ω (deg.)
Cl(1)Cd(1)Cl(4)[1]	172.1(1)	Cl(1)Cd(2)Cl(4)	93.9(1)
Cl(2)Cd(1)Cl(4)[1]	96.4(1)	Cl(2)Cd(2)Cl(4)	103.2(1)
Cl(3)Cd(1)Cl(4)[1]	85.7(1)	Cl(3)[2]Cd(2)Cl(4)	85.4(1)
Cl(1)Cd(1)Cl(2)	86.0(1)	Cl(1)Cd(2)Cl(2)	85.9(1)
Cl(1)Cd(1)Cl(3)	101.8(1)	Cl(1)Cd(2)Cl(3)[2]	97.5(1)
Cl(2)Cd(1)Cl(3)	91.2(1)	Cl(2)Cd(2)Cl(3)[2]	170.7(1)
N(1)Cd(1)Cl(1)	93.8(1)	N(1A)Cd(2)Cl(1)	102.3(1)
N(1)Cd(1)Cl(2)	97.7(1)	N(1A)Cd(2)Cl(2)	94.7(1)
N(1)Cd(1)Cl(4)[1]	78.4(1)	N(1A)Cd(2)Cl(4)	156.7(1)
N(1)Cd(1)Cl(3)	162.6(1)	N(1A)Cd(2)Cl(3)[2]	76.1(1)
N(2)Cd(1)Cl(1)	88.1(1)	N(2A)Cd(2)Cl(1)	166.5(1)
N(2)Cd(1)Cl(2)	170.9(1)	N(2A)Cd(2)Cl(2)	81.2(1)
N(2)Cd(1)Cl(4)[1]	88.6(1)	N(2A)Cd(2)Cl(4)	93.1(1)
N(2)Cd(1)Cl(3)	96.9(1)	N(2A)Cd(2)Cl(3)[2]	94.7(1)
N(1)Cd(1)N(2)	75.8(1)	N(1A)Cd(2)N(2A)	74.8(1)

[1] -1+X,+Y,+Z, [2] 1+X,+Y,+Z
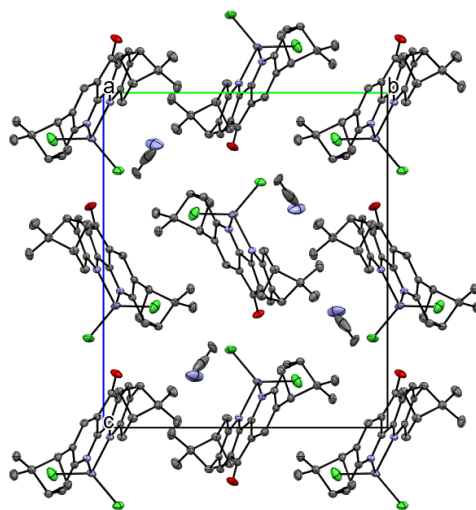
Figure S1. Packing diagram of **[ZnL^{O}Cl$_2$]·MeCN**, view along the *a* axis.
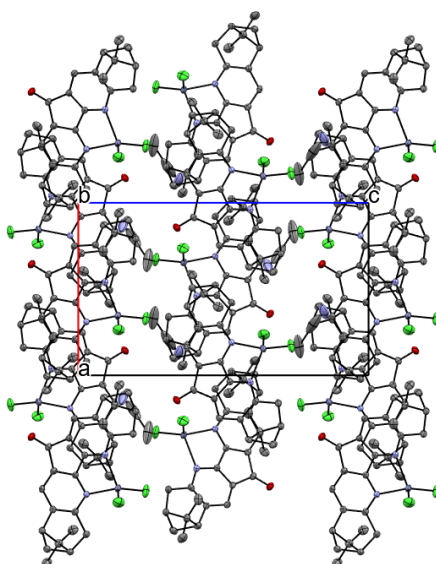
Figure S2. Packing diagram of **[ZnL^{O}Cl$_2$]·MeCN**, view along the *b* axis.
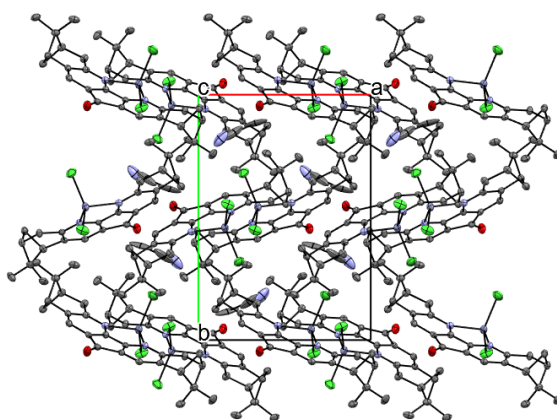
Figure S3. Packing diagram of **[ZnL^{O}Cl$_2$]·MeCN**, view along the *c* axis.
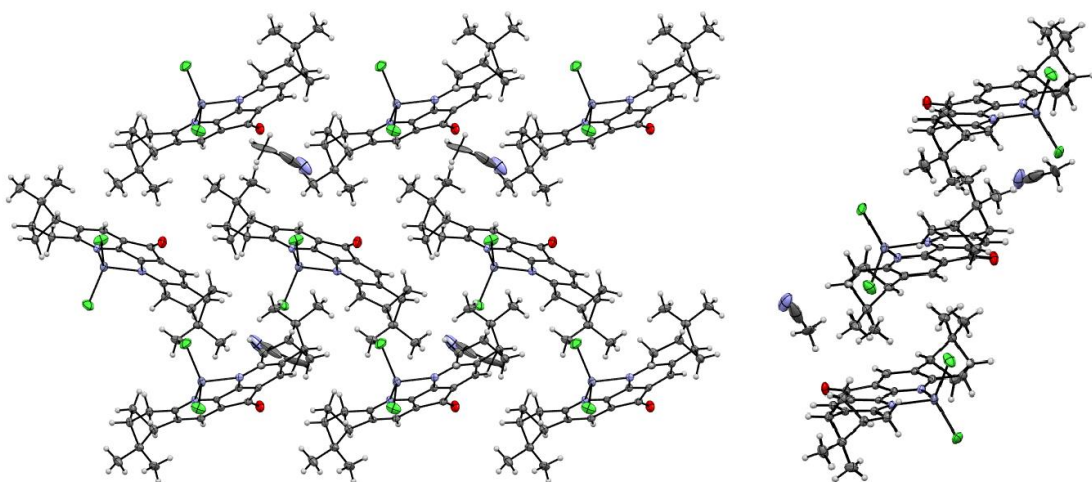
Figure S4. A 2D supramolecular layer in the structure of **[ZnL^{O}Cl$_2$]·MeCN** (frontal view and side view).
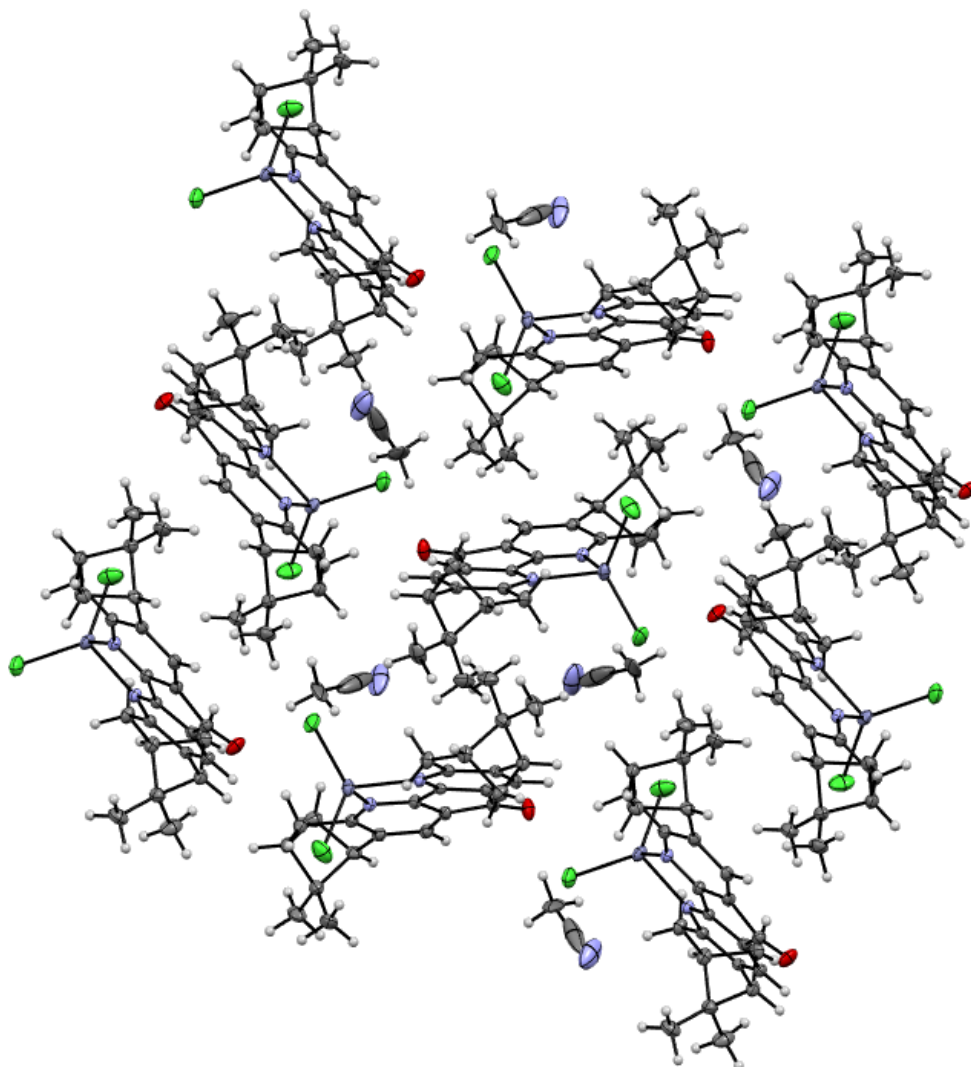
Figure S5. Packing of 2D supramolecular layers in the structure of **[ZnL^{O}Cl$_2$]·MeCN** (side view).
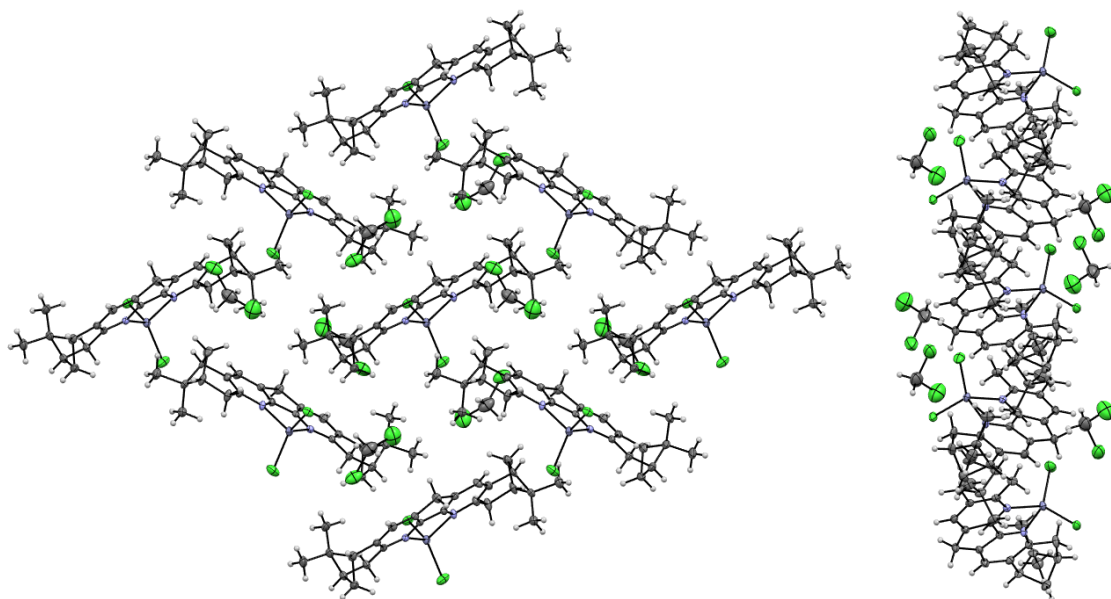
Figure S6. A 2D supramolecular layer in the structure of **[ZnLCl₂]·CH₂Cl₂** (frontal view and side view).
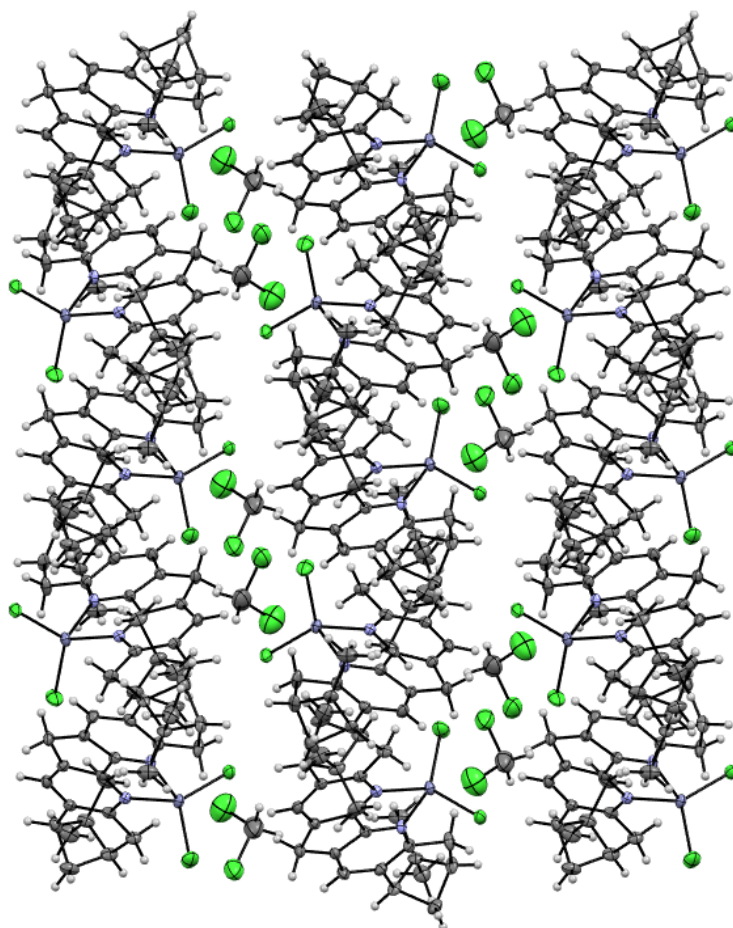
Figure S7. Packing of 2D supramolecular layers in the structure of **[ZnLCl₂]·CH₂Cl₂** (side view).
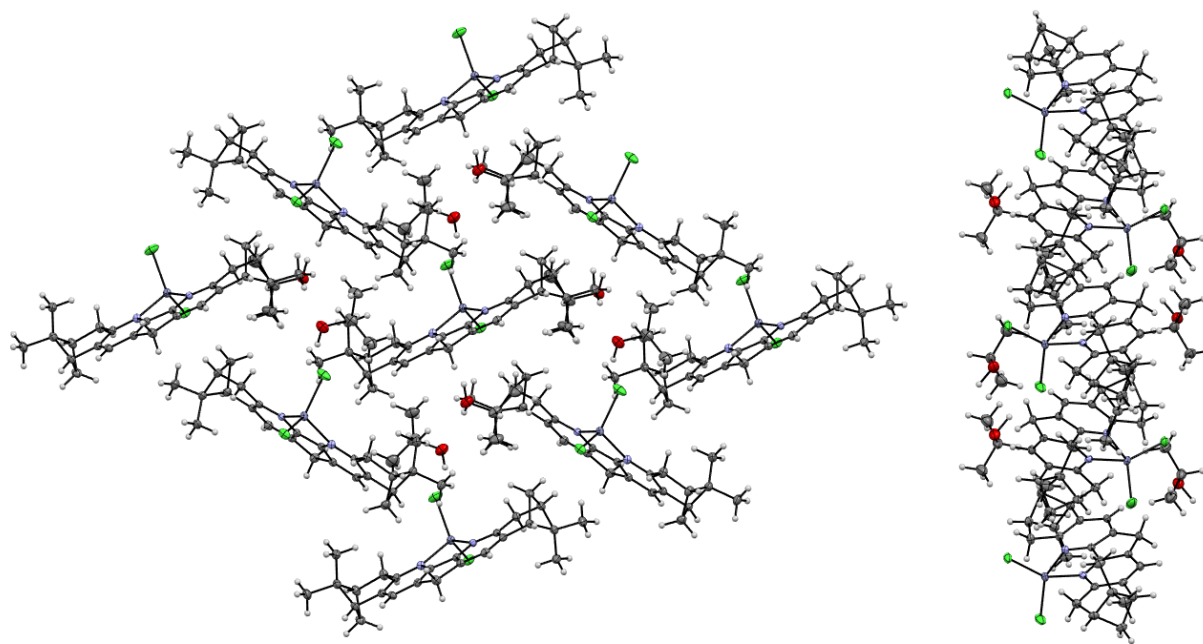
Figure S8. A 2D supramolecular layer in the structure of **[ZnLCl₂]·*i*PrOH** (frontal view and side view)
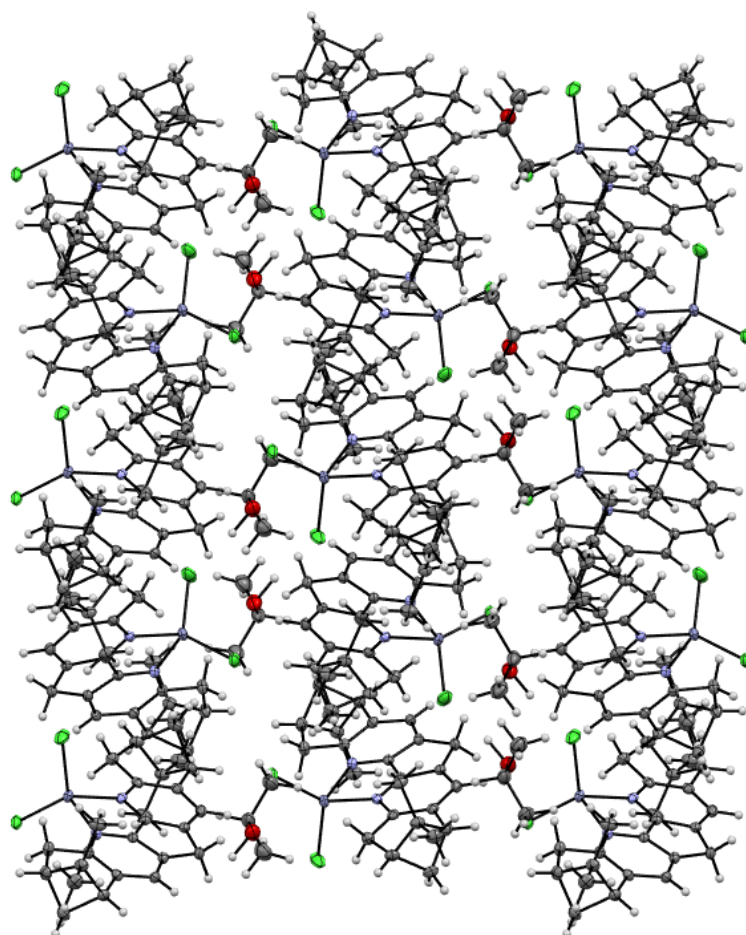
Figure S9. Packing of 2D supramolecular layers in the structure of **[ZnLCl₂]·*i*PrOH** (side view).
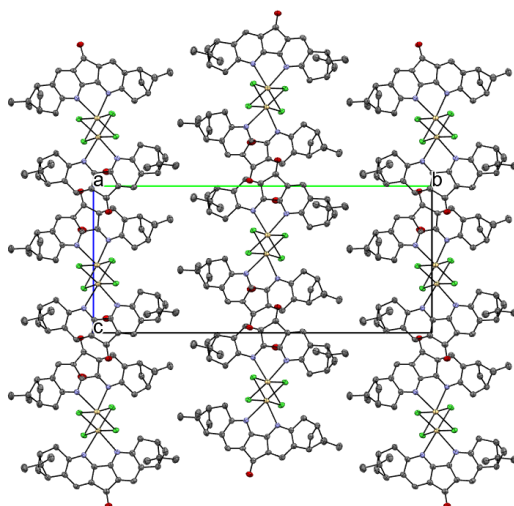
Figure S10. Packing diagram of **[CdL^{O}Cl$_2$]$_n$·nH$_2$O**, view along the *a* axis.
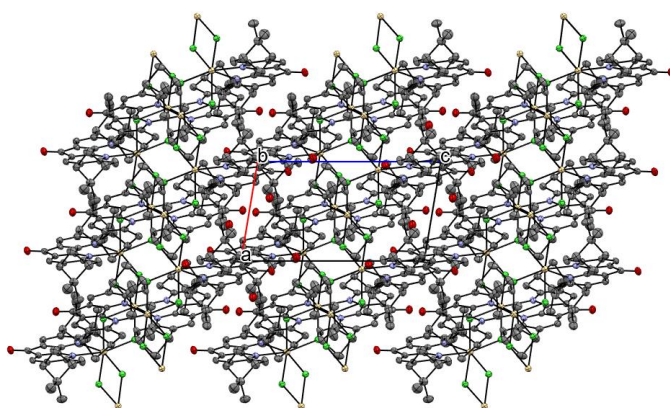
Figure S11. Packing diagram of **[CdL^{O}Cl$_2$]$_n$·nH$_2$O**, view along the *b* axis.
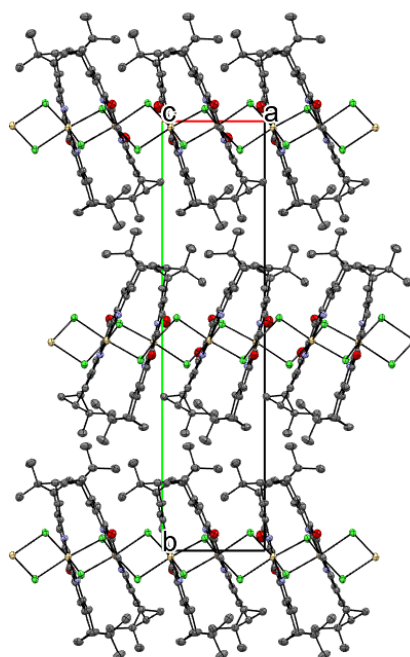
Figure S12. Packing diagram of **[CdL^{O}Cl$_2$]$_n$·nH$_2$O**, view along the *c* axis.
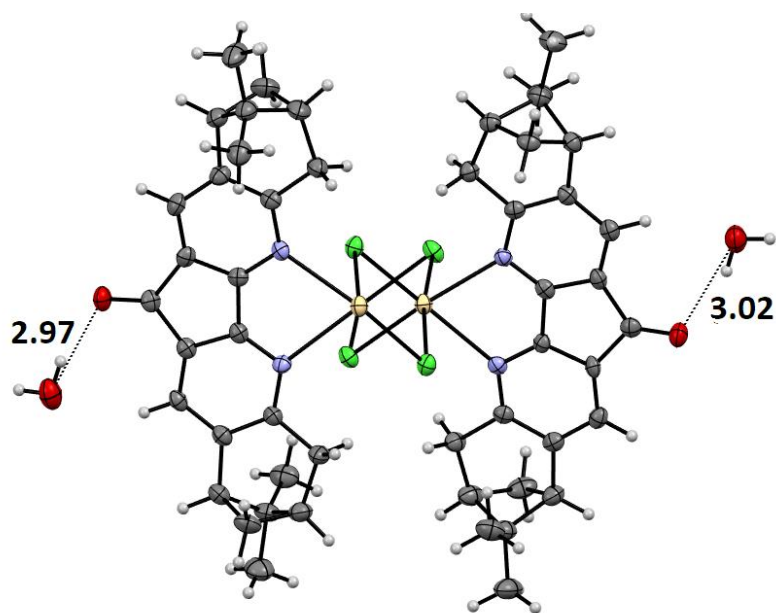
Figure S13. Hydrogen bonds between the H_2O molecules and 1D polymeric chain in the structure of $[CdL^OCl_2]_n \cdot nH_2O$.
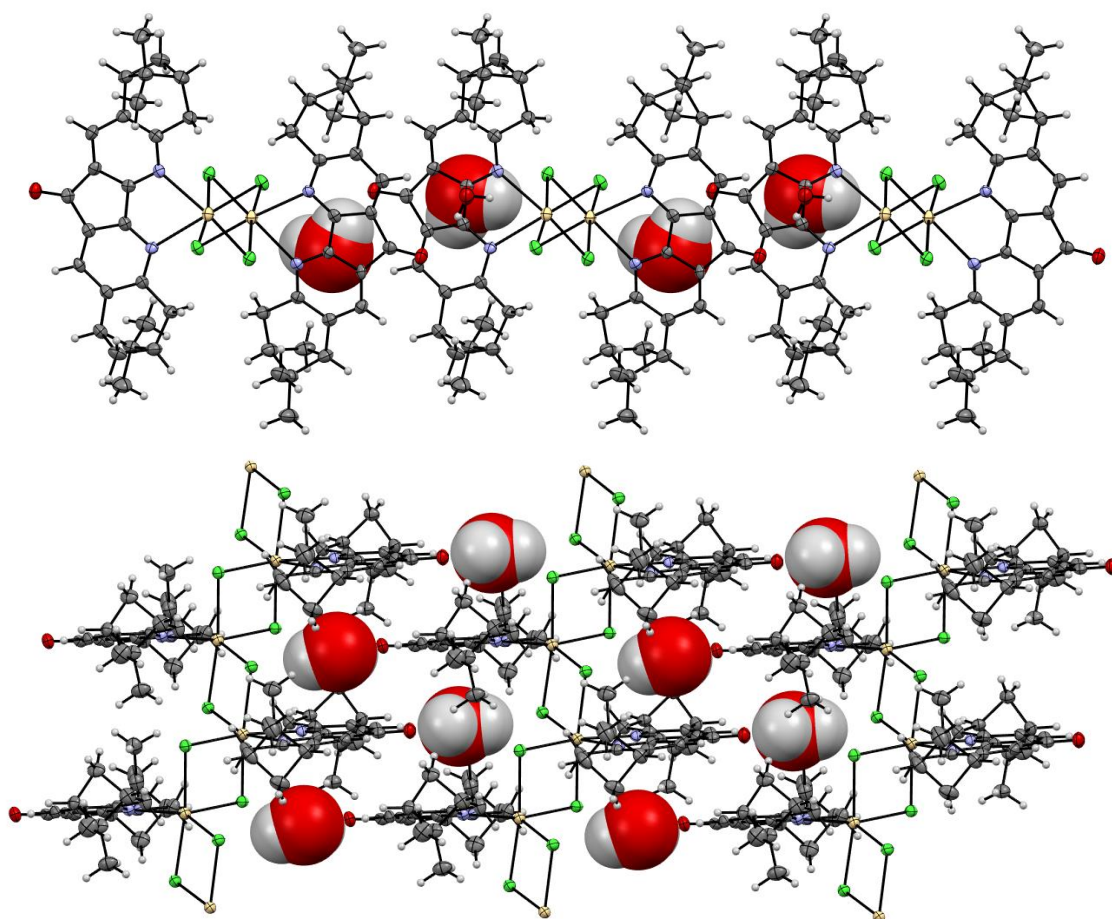
Figure S14. The H_2O molecules between the 1D polymeric chain in the structure of $[CdL^OCl_2]_n \cdot nH_2O$.
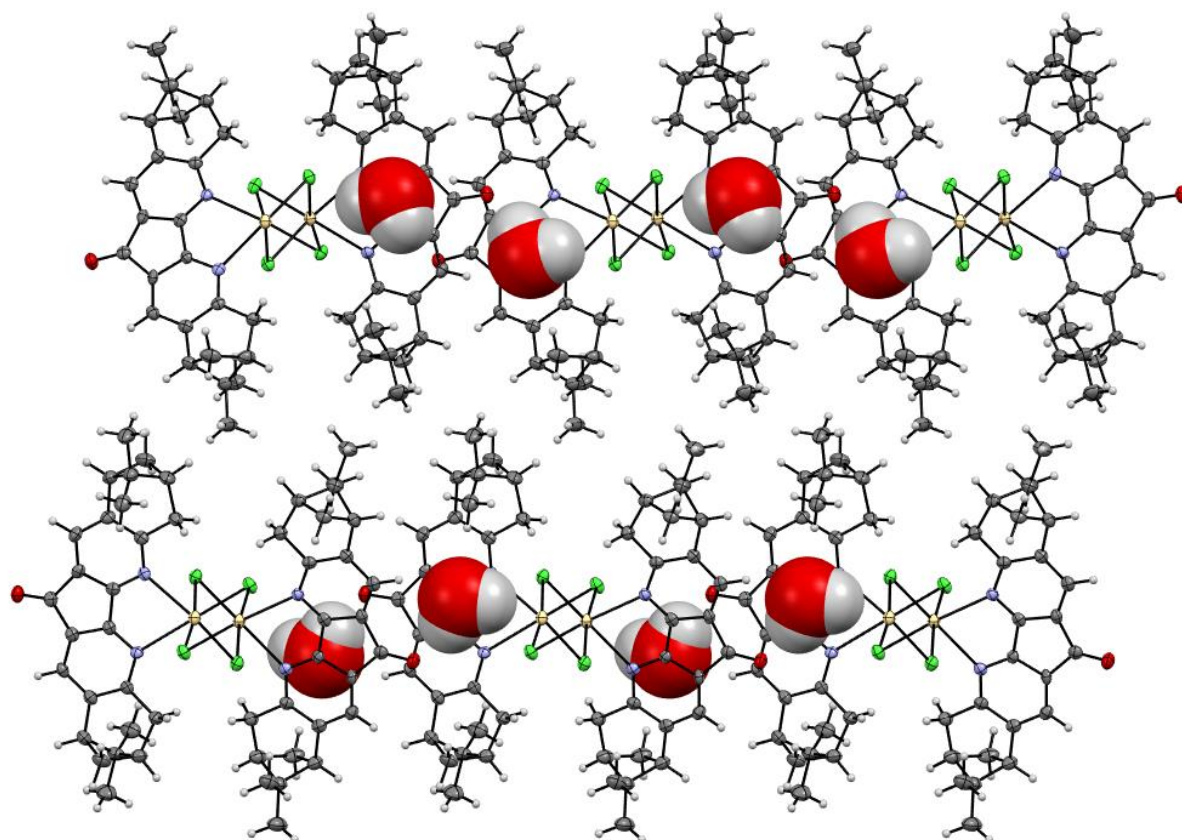
Figure S15. The packing of supramolecular layers in the structure of **[CdL^{O}Cl$_2$]$_n$·nH$_2$O** (two layers are shown).
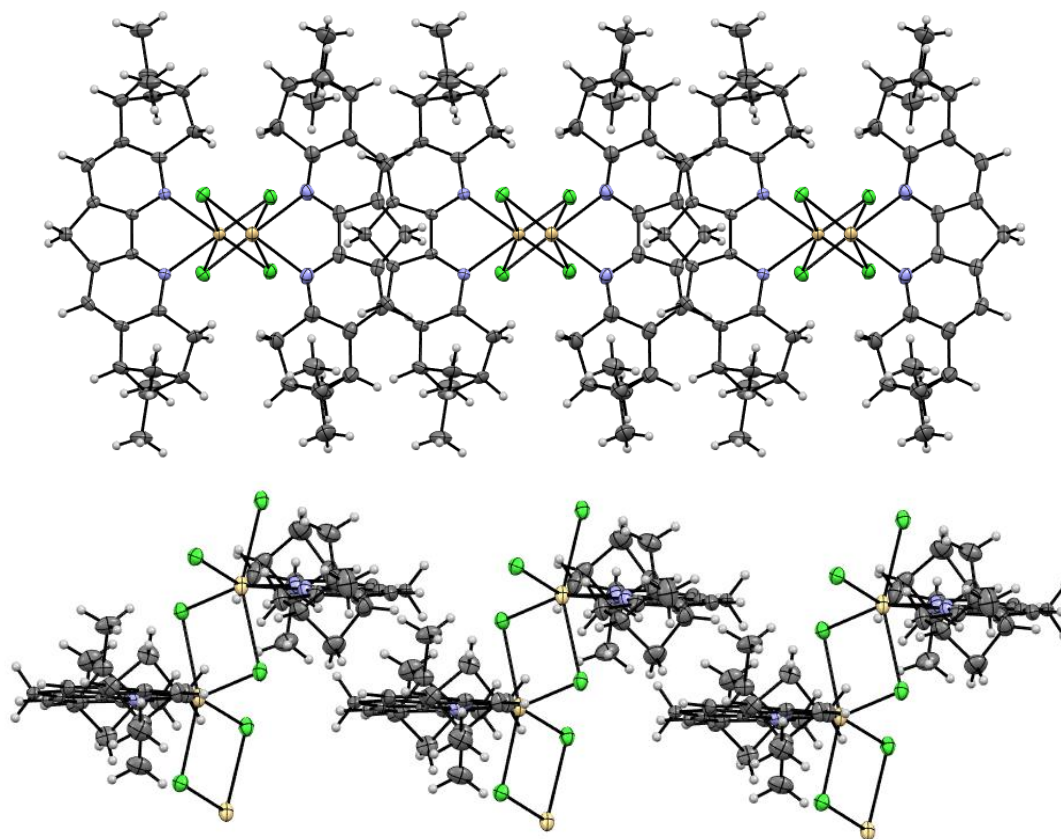
Figure S16. The packing of 1D supramolecular chains in the structure of **[CdLCl$_2$]$_n$**.
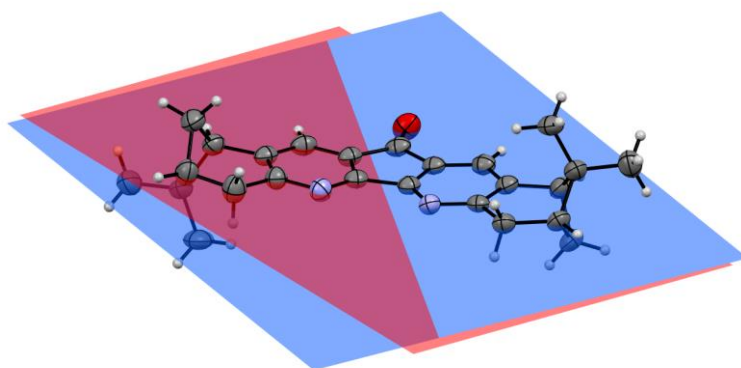
Figure S17. The angle between the planes of two pyridine moieties (6.02°) in the structure of L^O.
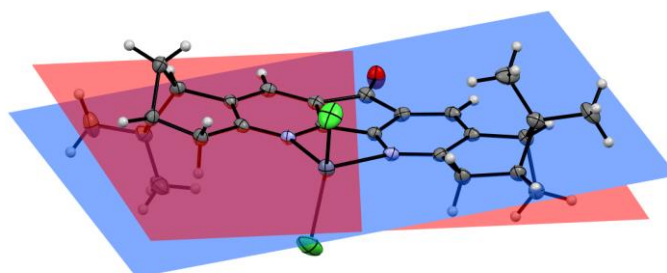
Figure S18. The angle between the planes of two pyridine moieties (8.77°) in the structure of $[ZnL^OCl_2]·MeCN$.
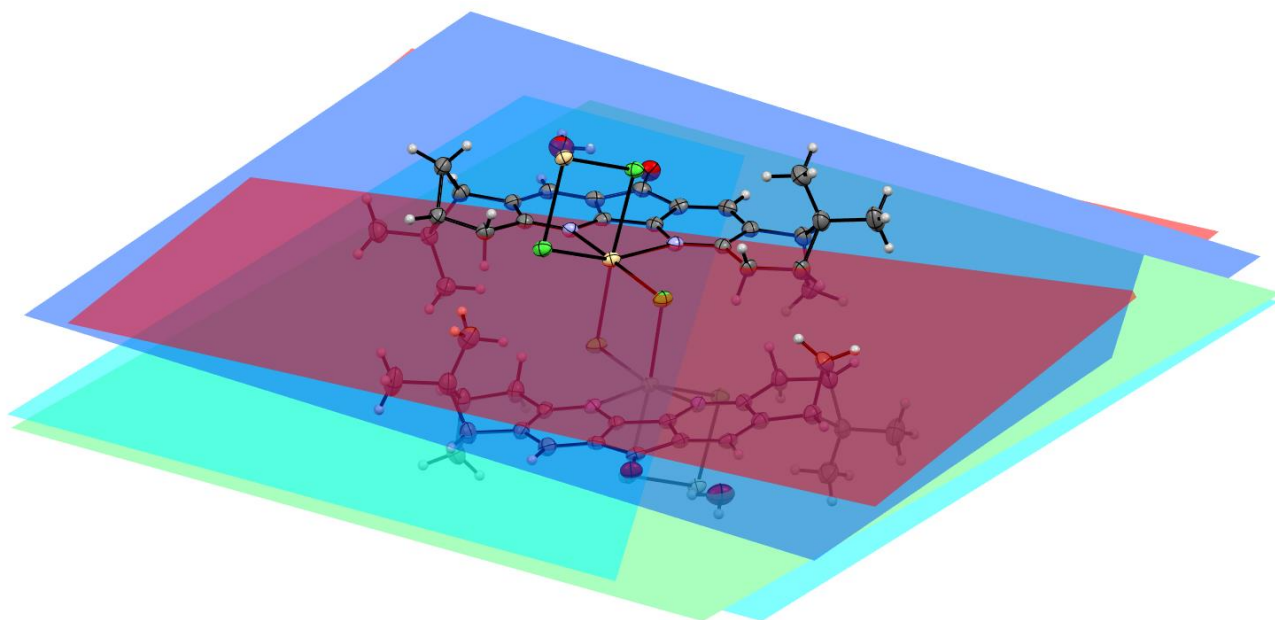
Figure S19. The angles between the planes of the pyridine moieties (3.62 and 4.17°) in the structure of $[CdL^OCl_2]_n·nH_2O$.

Thermogravimetric analysis
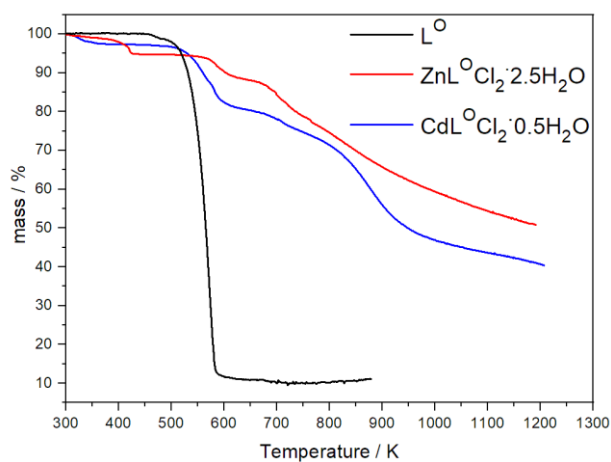
Figure S20. TGA data for **L^O**, **ZnL^OCl₂·2.5H₂O** and **CdL^OCl₂·0.5H₂O**.

IR spectroscopy
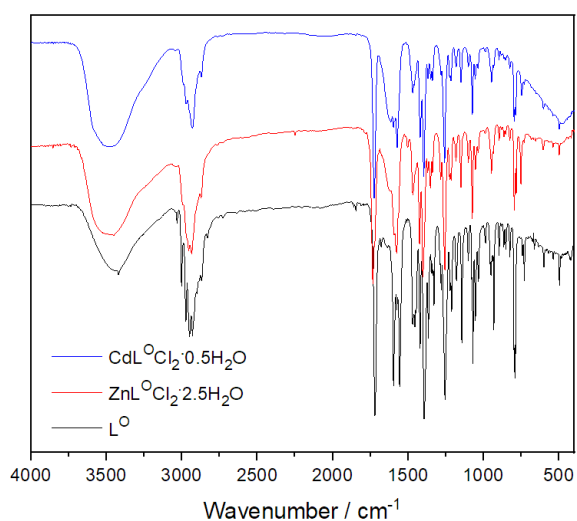
Figure S21. IR spectra of **L^O**, **ZnL^OCl₂·2.5H₂O** and **CdL^OCl₂·0.5H₂O** in KBr in the 4000 − 400 cm^{-1} range.
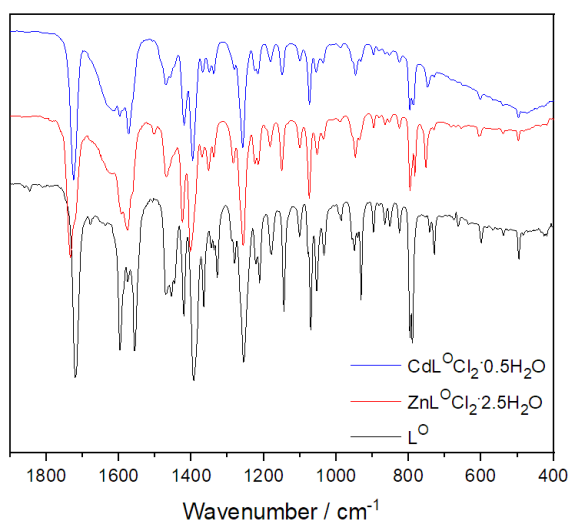
Figure S22. IR spectra of **L^O**, **ZnL^OCl₂·2.5H₂O** and **CdL^OCl₂·0.5H₂O** in KBr in the 1900 − 400 cm^{-1} range.

Table S4. Main vibrational frequencies (cm^{-1}) in the IR spectra of **L^O**, **ZnL^{O}Cl$_2$·2.5H$_2$O** and **CdL^{O}Cl$_2$·0.5H$_2$O**.

Compound	aromatic ν(C–H)	aliphatic ν(C–H)	ν(C=O)	ν(C=N)	ν(C=O)
L^O	3031, 3002	2971, 2948, 2927, 2900, 2868, 2828	1720	1597, 1576, 1559	1470, 1455, 1446,1421
ZnL^{O}Cl$_2$·2.5H$_2$O	3037, 2996	2969, 2954, 2934, 2872	1733	1617, 1594, 1577	1469, 1458, 1447, 1424
CdL^{O}Cl$_2$·0.5H$_2$O	3042, 2992	2973, 2950, 2928, 2868	1725	1617, 1597, 1572	1470, 1457, 1446, 1420

Theoretical part

Table S5. Optimized geometry of the **ground state** of **L** in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/6-31+g(d) level of theory.

C	1.533888000000	5.235059000000	-0.355896000000
H	1.679093000000	4.163737000000	-0.512152000000
H	2.073617000000	5.509892000000	0.559560000000
H	2.014763000000	5.764007000000	-1.188806000000
C	0.061896000000	5.641610000000	-0.248356000000
C	-0.887984000000	4.836650000000	0.727168000000
H	-0.974038000000	5.184774000000	1.762888000000
C	-0.597873000000	3.358095000000	0.638484000000
C	-0.442313000000	2.510338000000	1.736995000000
H	-0.510704000000	2.904347000000	2.749811000000
C	-0.204926000000	1.162936000000	1.492004000000
C	0.000000000000	0.000000000000	2.440342000000
H	0.866734000000	0.152472000000	3.098786000000
C	0.000000000000	7.155402000000	0.009440000000
H	-1.019893000000	7.538991000000	0.103849000000
H	0.482022000000	7.700212000000	-0.812195000000
H	0.536067000000	7.410132000000	0.932364000000
C	-2.045953000000	5.140292000000	-0.273706000000
H	-2.821112000000	4.373323000000	-0.373418000000
H	-2.523150000000	6.106222000000	-0.096692000000
C	-0.945567000000	5.190094000000	-1.370318000000
H	-1.087782000000	5.870836000000	-2.217854000000
C	-0.656546000000	3.755145000000	-1.845901000000
H	-1.472645000000	3.397087000000	-2.487532000000
H	0.251737000000	3.713418000000	-2.461303000000
C	-0.502816000000	2.809693000000	-0.663488000000
N	-0.271350000000	1.517065000000	-0.913217000000
C	-0.129279000000	0.725748000000	0.155939000000
C	-1.533888000000	-5.235059000000	-0.355896000000
H	-1.679093000000	-4.163737000000	-0.512152000000
H	-2.073617000000	-5.509892000000	0.559560000000
H	-2.014763000000	-5.764007000000	-1.188806000000
C	-0.061896000000	-5.641610000000	-0.248356000000
C	0.887984000000	-4.836650000000	0.727168000000
H	0.974038000000	-5.184774000000	1.762888000000
C	0.597873000000	-3.358095000000	0.638484000000
C	0.442313000000	-2.510338000000	1.736995000000
H	0.510704000000	-2.904347000000	2.749811000000
C	0.204926000000	-1.162936000000	1.492004000000
H	-0.866734000000	-0.152472000000	3.098786000000
C	0.000000000000	-7.155402000000	0.009440000000
H	1.019893000000	-7.538991000000	0.103849000000
H	-0.482022000000	-7.700212000000	-0.812195000000
H	-0.536067000000	-7.410132000000	0.932364000000
C	2.045953000000	-5.140292000000	-0.273706000000
H	2.821112000000	-4.373323000000	-0.373418000000
H	2.523150000000	-6.106222000000	-0.096692000000
C	0.945567000000	-5.190094000000	-1.370318000000

H	1.087782000000	-5.870836000000	-2.217854000000
C	0.656546000000	-3.755145000000	-1.845901000000
H	1.472645000000	-3.397087000000	-2.487532000000
H	-0.251737000000	-3.713418000000	-2.461303000000
C	0.502816000000	-2.809693000000	-0.663488000000
N	0.271350000000	-1.517065000000	-0.913217000000
C	0.129279000000	-0.725748000000	0.155939000000

Table S6. Optimized geometry of the **first singlet excited state** of **L** in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/6-31+g(d) level of theory.

C	1.531796000000	5.213966000000	-0.336031000000
H	1.670467000000	4.142282000000	-0.496738000000
H	2.059492000000	5.478167000000	0.589430000000
H	2.028077000000	5.746554000000	-1.157671000000
C	0.061465000000	5.628454000000	-0.247190000000
C	-0.905785000000	4.810575000000	0.722910000000
H	-1.002144000000	5.164009000000	1.755701000000
C	-0.617042000000	3.345862000000	0.639369000000
C	-0.450577000000	2.494449000000	1.763701000000
H	-0.524552000000	2.889878000000	2.774099000000
C	-0.204623000000	1.163874000000	1.508230000000
C	0.000000000000	0.000000000000	2.458338000000
H	0.866412000000	0.151547000000	3.117369000000
C	0.000000000000	7.138630000000	0.024736000000
H	-1.019488000000	7.525439000000	0.108750000000
H	0.494364000000	7.688501000000	-0.786779000000
H	0.526190000000	7.383887000000	0.955737000000
C	-2.050018000000	5.133534000000	-0.297672000000
H	-2.829110000000	4.373143000000	-0.412370000000
H	-2.520893000000	6.101775000000	-0.112108000000
C	-0.936112000000	5.182281000000	-1.377138000000
H	-1.065424000000	5.862312000000	-2.227543000000
C	-0.649962000000	3.746112000000	-1.846151000000
H	-1.463593000000	3.388351000000	-2.493005000000
H	0.259591000000	3.691609000000	-2.459911000000
C	-0.505845000000	2.789515000000	-0.675417000000
N	-0.260323000000	1.509459000000	-0.953542000000
C	-0.120770000000	0.700677000000	0.144792000000
C	-1.531796000000	-5.213966000000	-0.336031000000
H	-1.670467000000	-4.142282000000	-0.496738000000
H	-2.059492000000	-5.478167000000	0.589430000000
H	-2.028077000000	-5.746554000000	-1.157671000000
C	-0.061465000000	-5.628454000000	-0.247190000000
C	0.905785000000	-4.810575000000	0.722910000000
H	1.002144000000	-5.164009000000	1.755701000000
C	0.617042000000	-3.345862000000	0.639369000000
C	0.450577000000	-2.494449000000	1.763701000000
H	0.524552000000	-2.889878000000	2.774099000000
C	0.204623000000	-1.163874000000	1.508230000000
H	-0.866412000000	-0.151547000000	3.117369000000
C	0.000000000000	-7.138630000000	0.024736000000
H	1.019488000000	-7.525439000000	0.108750000000

H	-0.494364000000	-7.688501000000	-0.786779000000
H	-0.526190000000	-7.383887000000	0.955737000000
C	2.050018000000	-5.133534000000	-0.297672000000
H	2.829110000000	-4.373143000000	-0.412370000000
H	2.520893000000	-6.101775000000	-0.112108000000
C	0.936112000000	-5.182281000000	-1.377138000000
H	1.065424000000	-5.862312000000	-2.227543000000
C	0.649962000000	-3.746112000000	-1.846151000000
H	1.463593000000	-3.388351000000	-2.493005000000
H	-0.259591000000	-3.691609000000	-2.459911000000
C	0.505845000000	-2.789515000000	-0.675417000000
N	0.260323000000	-1.509459000000	-0.953542000000
C	0.120770000000	-0.700677000000	0.144792000000

Table S7. Optimized geometry of the **ground state** of **L^O** in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/6-31+g(d) level of theory.

N	1.543141000000	-1.047981000000	-0.152652000000
C	0.741953000000	0.010781000000	-0.074156000000
O	-0.000017000000	3.478020000000	-0.000096000000
N	-1.543182000000	-1.047962000000	0.152951000000
C	1.180553000000	1.346848000000	-0.118264000000
C	-3.400293000000	0.525185000000	0.344744000000
C	-0.741966000000	0.010798000000	0.074369000000
C	-2.534260000000	1.618463000000	0.254545000000
H	-2.901685000000	2.641444000000	0.291857000000
C	3.400258000000	0.525114000000	-0.344791000000
C	2.534246000000	1.618422000000	-0.254597000000
H	2.901701000000	2.641388000000	-0.292024000000
C	2.854499000000	-0.779772000000	-0.286079000000
C	-4.895734000000	0.621885000000	0.524996000000
H	-5.241206000000	1.659402000000	0.589958000000
C	5.264487000000	-1.473999000000	-0.546128000000
H	5.956508000000	-2.319417000000	-0.634134000000
C	0.000003000000	2.259396000000	0.000026000000
C	-2.854525000000	-0.779731000000	0.286301000000
C	4.895694000000	0.621801000000	-0.525165000000
H	5.241137000000	1.659319000000	-0.590294000000
C	-5.633677000000	-0.344953000000	-0.486322000000
C	-1.180554000000	1.346854000000	0.118330000000
C	3.814260000000	-1.955003000000	-0.361407000000
H	3.517570000000	-2.602957000000	-1.197009000000
H	3.703682000000	-2.564757000000	0.545007000000
C	-5.288865000000	-0.382574000000	1.652366000000
H	-4.582351000000	-0.490540000000	2.481998000000
H	-6.285951000000	-0.201147000000	2.057488000000
C	-5.264563000000	-1.473910000000	0.546188000000
H	-5.956574000000	-2.319334000000	0.634227000000
C	5.633728000000	-0.344893000000	0.486201000000
C	-5.120165000000	-0.449812000000	-1.924649000000
H	-4.042197000000	-0.614406000000	-1.993192000000
H	-5.346941000000	0.469813000000	-2.478889000000
H	-5.618412000000	-1.276707000000	-2.446677000000

C	5.120409000000	-0.449473000000	1.924620000000
H	4.042504000000	-0.614375000000	1.993355000000
H	5.346967000000	0.470410000000	2.478525000000
H	5.618968000000	-1.276034000000	2.446877000000
C	7.146108000000	-0.075896000000	0.535155000000
H	7.605092000000	0.013502000000	-0.453537000000
H	7.658330000000	-0.889536000000	1.063794000000
H	7.352822000000	0.853041000000	1.081021000000
C	-3.814311000000	-1.954941000000	0.361637000000
H	-3.703641000000	-2.564799000000	-0.544698000000
H	-3.517709000000	-2.602794000000	1.197346000000
C	5.288736000000	-0.382789000000	-1.652436000000
H	4.582168000000	-0.490826000000	-2.482013000000
H	6.285814000000	-0.201438000000	-2.057625000000
C	-7.146045000000	-0.075925000000	-0.535510000000
H	-7.605145000000	0.013691000000	0.453104000000
H	-7.658231000000	-0.889660000000	-1.064042000000
H	-7.352652000000	0.852903000000	-1.081599000000

Table S8. Optimized geometry of the **first singlet excited state** of L^O in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/6-31+g(d) level of theory.

N	1.536293000000	-1.095523000000	-0.152702000000
C	0.703695000000	-0.028499000000	-0.071119000000
O	0.000005000000	3.524349000000	0.000040000000
N	-1.536291000000	-1.095527000000	0.152595000000
C	1.142619000000	1.362815000000	-0.115673000000
C	-3.362044000000	0.532634000000	0.348340000000
C	-0.703696000000	-0.028501000000	0.071000000000
C	-2.506881000000	1.619941000000	0.256220000000
H	-2.874915000000	2.641996000000	0.296142000000
C	3.362053000000	0.532642000000	-0.348341000000
C	2.506887000000	1.619947000000	-0.256225000000
H	2.874922000000	2.642003000000	-0.296113000000
C	2.817285000000	-0.821384000000	-0.286623000000
C	-4.843055000000	0.629284000000	0.529340000000
H	-5.188702000000	1.665609000000	0.598382000000
C	5.243736000000	-1.469141000000	-0.543538000000
H	5.950400000000	-2.302290000000	-0.629554000000
C	-0.000003000000	2.269796000000	-0.000049000000
C	-2.817278000000	-0.821391000000	0.286568000000
C	4.843071000000	0.629298000000	-0.529283000000
H	5.188720000000	1.665625000000	-0.598283000000
C	-5.591063000000	-0.335839000000	-0.488241000000
C	-1.142618000000	1.362811000000	0.115612000000
C	3.803596000000	-1.974318000000	-0.362560000000
H	3.523212000000	-2.624393000000	-1.202498000000
H	3.701888000000	-2.591371000000	0.539842000000
C	-5.246510000000	-0.384125000000	1.652794000000
H	-4.541821000000	-0.507979000000	2.481639000000
H	-6.237650000000	-0.175978000000	2.059690000000
C	-5.243720000000	-1.469155000000	0.543551000000
H	-5.950381000000	-2.302306000000	0.629571000000

C	5.591042000000	-0.335853000000	0.488297000000
C	-5.067348000000	-0.439014000000	-1.923112000000
H	-3.993367000000	-0.632717000000	-1.983969000000
H	-5.262816000000	0.492532000000	-2.468555000000
H	-5.583270000000	-1.246197000000	-2.458341000000
C	5.067278000000	-0.439063000000	1.923148000000
H	3.993296000000	-0.632777000000	1.983964000000
H	5.262719000000	0.492474000000	2.468616000000
H	5.583188000000	-1.246251000000	2.458380000000
C	7.096506000000	-0.037171000000	0.542005000000
H	7.557895000000	0.054610000000	-0.445396000000
H	7.619362000000	-0.840216000000	1.076481000000
H	7.284099000000	0.897221000000	1.084818000000
C	-3.803588000000	-1.974327000000	0.362504000000
H	-3.701913000000	-2.591354000000	-0.539920000000
H	-3.523173000000	-2.624428000000	1.202413000000
C	5.246571000000	-0.384080000000	-1.652750000000
H	4.541915000000	-0.507911000000	-2.481627000000
H	6.237727000000	-0.175922000000	-2.059600000000
C	-7.096529000000	-0.037155000000	-0.541889000000
H	-7.557886000000	0.054593000000	0.445528000000
H	-7.619401000000	-0.840181000000	-1.076377000000
H	-7.284137000000	0.897256000000	-1.084665000000

Table S9. Optimized geometry of the **ground state** of **[ZnLCl₂]** in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/LANL2DZ/6-31+g(d) level of theory.

Zn	-0.000076000000	-1.766385000000	-0.000146000000
Cl	-0.250426000000	-2.688284000000	-2.050337000000
Cl	0.250148000000	-2.692427000000	2.048079000000
N	-1.455688000000	-0.053557000000	0.161257000000
C	-3.365605000000	1.403054000000	0.367378000000
N	1.455732000000	-0.053569000000	-0.160273000000
C	2.778354000000	0.113231000000	-0.303326000000
C	4.862792000000	1.429265000000	-0.553550000000
H	5.254213000000	2.449947000000	-0.622295000000
C	-1.185531000000	2.372191000000	0.128784000000
C	3.673909000000	-1.105449000000	-0.381644000000
H	3.345395000000	-1.735998000000	-1.218862000000
H	3.538139000000	-1.707774000000	0.526342000000
C	-0.718423000000	1.058431000000	0.079451000000
C	3.365614000000	1.403022000000	-0.366847000000
C	0.718470000000	1.058426000000	-0.078570000000
C	2.559829000000	2.545902000000	-0.276372000000
H	3.014095000000	3.533216000000	-0.324952000000
C	-2.778329000000	0.113258000000	0.304096000000
C	0.000012000000	3.324066000000	0.000280000000
H	-0.094597000000	3.979828000000	-0.875305000000
H	0.094611000000	3.979940000000	0.875780000000
C	5.141796000000	-0.682882000000	-0.571887000000
H	5.795071000000	-1.557142000000	-0.661154000000
C	-5.141838000000	-0.682865000000	0.572218000000
H	-5.795102000000	-1.557143000000	0.661397000000

C	1.185560000000	2.372187000000	-0.128142000000
C	-2.559815000000	2.545922000000	0.276857000000
H	-3.014085000000	3.533243000000	0.325248000000
C	5.559919000000	0.431027000000	0.458186000000
C	-5.205634000000	0.404580000000	1.680485000000
H	-4.492722000000	0.323486000000	2.507598000000
H	-6.207435000000	0.544878000000	2.089250000000
C	5.205350000000	0.404494000000	-1.680244000000
H	6.207070000000	0.544743000000	-2.089227000000
H	4.492255000000	0.323378000000	-2.507191000000
C	-3.673887000000	-1.105420000000	0.382366000000
H	-3.345592000000	-1.735863000000	1.219757000000
H	-3.537858000000	-1.707861000000	-0.525500000000
C	5.048100000000	0.350532000000	1.899071000000
H	5.515399000000	-0.494321000000	2.419847000000
H	3.965295000000	0.225408000000	1.978388000000
H	5.314732000000	1.261589000000	2.449827000000
C	-4.862803000000	1.429283000000	0.553815000000
H	-5.254293000000	2.449949000000	0.622389000000
C	-5.047538000000	0.350413000000	-1.898773000000
H	-3.964749000000	0.225022000000	-1.977820000000
H	-5.313806000000	1.261568000000	-2.449550000000
H	-5.514903000000	-0.494296000000	-2.419719000000
C	-5.559718000000	0.430961000000	-0.458027000000
C	-7.082257000000	0.637641000000	-0.501209000000
H	-7.328803000000	1.557447000000	-1.045975000000
H	-7.542166000000	0.706342000000	0.488746000000
H	-7.560174000000	-0.196451000000	-1.029427000000
C	7.082485000000	0.637604000000	0.501015000000
H	7.329239000000	1.557225000000	1.045993000000
H	7.542115000000	0.706596000000	-0.489047000000
H	7.560493000000	-0.196685000000	1.028842000000

Table S10. Optimized geometry of the **first singlet excited state** of **[ZnLCl₂]** in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/LANL2DZ/6-31+g(d) level of theory.

Zn	-0.000005000000	-1.750898000000	0.000002000000
Cl	-0.279438000000	-2.777380000000	-2.017232000000
Cl	0.279417000000	-2.777441000000	2.017204000000
N	-1.433498000000	-0.074232000000	0.166678000000
C	-3.349858000000	1.412442000000	0.382847000000
N	1.433488000000	-0.074233000000	-0.166654000000
C	2.759759000000	0.117798000000	-0.315443000000
C	4.834025000000	1.438757000000	-0.565582000000
H	5.230938000000	2.456726000000	-0.635774000000
C	-1.186968000000	2.403852000000	0.133342000000
C	3.660387000000	-1.091259000000	-0.386458000000
H	3.336210000000	-1.724848000000	-1.225464000000
H	3.510781000000	-1.698901000000	0.517256000000
C	-0.697065000000	1.071481000000	0.081022000000
C	3.349850000000	1.412437000000	-0.382831000000
C	0.697056000000	1.071480000000	-0.080996000000
C	2.546277000000	2.589120000000	-0.284478000000

H	3.007342000000	3.571161000000	-0.335679000000
C	-2.759770000000	0.117800000000	0.315459000000
C	-0.000003000000	3.354263000000	0.000012000000
H	-0.097795000000	4.010077000000	-0.875018000000
H	0.097790000000	4.010077000000	0.875042000000
C	5.130068000000	-0.676868000000	-0.567318000000
H	5.781459000000	-1.553568000000	-0.647413000000
C	-5.130078000000	-0.676863000000	0.567320000000
H	-5.781476000000	-1.553558000000	0.647407000000
C	1.186961000000	2.403850000000	-0.133317000000
C	-2.546284000000	2.589124000000	0.284498000000
H	-3.007348000000	3.571165000000	0.335697000000
C	5.542022000000	0.438088000000	0.461245000000
C	-5.198624000000	0.400390000000	1.681357000000
H	-4.494867000000	0.309712000000	2.514609000000
H	-6.203752000000	0.554147000000	2.078427000000
C	5.198620000000	0.400388000000	-1.681352000000
H	6.203752000000	0.554145000000	-2.078415000000
H	4.494866000000	0.309713000000	-2.514608000000
C	-3.660399000000	-1.091258000000	0.386471000000
H	-3.336230000000	-1.724847000000	1.225481000000
H	-3.510789000000	-1.698901000000	-0.517241000000
C	5.020414000000	0.368936000000	1.898207000000
H	5.495072000000	-0.463879000000	2.431786000000
H	3.938292000000	0.232661000000	1.966988000000
H	5.271408000000	1.289514000000	2.440235000000
C	-4.834032000000	1.438761000000	0.565588000000
H	-5.230951000000	2.456729000000	0.635776000000
C	-5.020333000000	0.368935000000	-1.898195000000
H	-3.938206000000	0.232661000000	-1.966926000000
H	-5.271304000000	1.289510000000	-2.440239000000
H	-5.494966000000	-0.463884000000	-2.431791000000
C	-5.542000000000	0.438092000000	-0.461257000000
C	-7.060326000000	0.661700000000	-0.507635000000
H	-7.296600000000	1.585797000000	-1.049364000000
H	-7.525178000000	0.727066000000	0.480096000000
H	-7.542258000000	-0.165999000000	-1.043417000000
C	7.060349000000	0.661695000000	0.507558000000
H	7.296647000000	1.585796000000	1.049269000000
H	7.525155000000	0.727051000000	-0.480196000000
H	7.542303000000	-0.166001000000	1.043325000000

Table S11. Optimized geometry of the **ground state** of **[ZnL^{O}Cl$_2$]** in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/LANL2DZ/6-31+g(d) level of theory.

Zn	0.000052000000	-1.895996000000	0.000201000000
Cl	-0.254841000000	-2.787935000000	-2.055622000000
Cl	0.254748000000	-2.789366000000	2.055299000000
N	-1.460583000000	-0.167356000000	0.161642000000
N	1.460537000000	-0.167296000000	-0.161248000000
C	-4.871431000000	1.330790000000	0.553621000000
H	-5.259701000000	2.352207000000	0.621874000000
C	4.871282000000	1.331035000000	-0.553692000000

H	5.259471000000	2.352493000000	-0.621794000000
C	-3.374420000000	1.301845000000	0.367965000000
C	3.374328000000	1.301987000000	-0.367513000000
C	-2.789398000000	0.011535000000	0.304766000000
C	2.789337000000	0.011650000000	-0.304535000000
C	-3.685426000000	-1.204137000000	0.383206000000
H	-3.355192000000	-1.834099000000	1.220612000000
H	-3.546062000000	-1.806995000000	-0.524221000000
C	3.685373000000	-1.203985000000	-0.383600000000
H	3.354764000000	-1.833837000000	-1.220927000000
H	3.546473000000	-1.806980000000	0.523822000000
C	-5.153346000000	-0.781371000000	0.572014000000
H	-5.806103000000	-1.655818000000	0.660889000000
C	5.153192000000	-0.781116000000	-0.572893000000
H	5.805955000000	-1.655506000000	-0.662298000000
C	-5.568912000000	0.332763000000	-0.458725000000
C	5.569149000000	0.332704000000	0.458060000000
C	-5.216066000000	0.306252000000	1.679951000000
H	-4.504514000000	0.224561000000	2.508225000000
H	-6.217785000000	0.448827000000	2.087419000000
C	5.215464000000	0.306852000000	-1.680507000000
H	4.503577000000	0.225461000000	-2.508517000000
H	6.217031000000	0.449526000000	-2.088309000000
C	-7.090999000000	0.542383000000	-0.502415000000
H	-7.551457000000	0.611538000000	0.487170000000
H	-7.569715000000	-0.290700000000	-1.031299000000
H	-7.335103000000	1.462770000000	-1.046923000000
C	7.091269000000	0.542214000000	0.501237000000
H	7.570275000000	-0.291794000000	1.028411000000
H	7.335699000000	1.461653000000	1.047180000000
H	7.551127000000	0.613092000000	-0.488497000000
C	-5.056317000000	0.251529000000	-1.899284000000
H	-5.320110000000	1.163390000000	-2.449656000000
H	-5.525558000000	-0.591987000000	-2.420297000000
H	-3.973746000000	0.123554000000	-1.979792000000
C	5.057105000000	0.250850000000	1.898779000000
H	5.526345000000	-0.593083000000	2.419141000000
H	3.974528000000	0.123117000000	1.979636000000
H	5.321341000000	1.162325000000	2.449559000000
C	-2.563729000000	2.443193000000	0.276908000000
H	-2.994979000000	3.439936000000	0.322134000000
C	2.563629000000	2.443308000000	-0.275988000000
H	2.994866000000	3.440065000000	-0.321029000000
C	-1.194618000000	2.248568000000	0.129694000000
C	1.194550000000	2.248622000000	-0.128601000000
C	-0.725743000000	0.937409000000	0.080176000000
C	0.725700000000	0.937436000000	-0.079383000000
C	-0.000049000000	3.170321000000	0.000633000000
O	-0.000076000000	4.383378000000	0.000619000000

Table S12. Optimized geometry of the **first singlet excited state** of **[ZnL^{O}Cl$_2$]** in Cartesian (XYZ) coordinates as calculated in Gaussian at the B3LYP/LANL2DZ/6-31+g(d) level of theory.

Zn	-0.000005000000	-1.931224000000	-0.000063000000
Cl	-0.265916000000	-2.834038000000	-2.050521000000
Cl	0.265829000000	-2.834541000000	2.050158000000
N	-1.459436000000	-0.209884000000	0.166491000000
N	1.459459000000	-0.209921000000	-0.166593000000
C	-4.818907000000	1.358391000000	0.556829000000
H	-5.205836000000	2.379335000000	0.624485000000
C	4.818992000000	1.358267000000	-0.556752000000
H	5.205935000000	2.379197000000	-0.624547000000
C	-3.338320000000	1.322927000000	0.372846000000
C	3.338373000000	1.322844000000	-0.373013000000
C	-2.759015000000	-0.018105000000	0.310432000000
C	2.759055000000	-0.018174000000	-0.310422000000
C	-3.684858000000	-1.208801000000	0.394069000000
H	-3.373008000000	-1.837986000000	1.240024000000
H	-3.550972000000	-1.826007000000	-0.504793000000
C	3.684909000000	-1.208889000000	-0.393676000000
H	3.373192000000	-1.838236000000	-1.239559000000
H	3.550881000000	-1.825921000000	0.505284000000
C	-5.142846000000	-0.757731000000	0.574125000000
H	-5.813045000000	-1.618729000000	0.662714000000
C	5.142926000000	-0.757858000000	-0.573589000000
H	5.813137000000	-1.618876000000	-0.661904000000
C	-5.531273000000	0.358312000000	-0.461356000000
C	5.531191000000	0.358384000000	0.461739000000
C	-5.182516000000	0.327684000000	1.681178000000
H	-4.475144000000	0.229857000000	2.511043000000
H	-6.179772000000	0.504582000000	2.086437000000
C	5.182774000000	0.327342000000	-1.680845000000
H	4.475532000000	0.229355000000	-2.510803000000
H	6.180093000000	0.504164000000	-2.085980000000
C	-7.045790000000	0.605856000000	-0.512283000000
H	-7.509918000000	0.683803000000	0.474941000000
H	-7.538820000000	-0.217320000000	-1.043950000000
H	-7.265865000000	1.530768000000	-1.058644000000
C	7.045701000000	0.605929000000	0.512862000000
H	7.538644000000	-0.217140000000	1.044775000000
H	7.265693000000	1.530952000000	1.059071000000
H	7.509989000000	0.683675000000	-0.474303000000
C	-5.005895000000	0.273136000000	-1.896902000000
H	-5.231093000000	1.198678000000	-2.440763000000
H	-5.498502000000	-0.548730000000	-2.430569000000
H	-3.927113000000	0.108889000000	-1.966760000000
C	5.005583000000	0.273493000000	1.897217000000
H	5.498093000000	-0.548274000000	2.431125000000
H	3.926787000000	0.109275000000	1.966932000000
H	5.230705000000	1.199140000000	2.440933000000
C	-2.530170000000	2.454231000000	0.277027000000
H	-2.958174000000	3.451924000000	0.321903000000
C	2.530208000000	2.454169000000	-0.277575000000
H	2.958211000000	3.451852000000	-0.322671000000
C	-1.153963000000	2.268566000000	0.127055000000
C	1.153970000000	2.268537000000	-0.127837000000
C	-0.692932000000	0.902160000000	0.078438000000

|			
C	0.692934000000	0.902143000000	-0.078967000000
C	-0.000021000000	3.180438000000	-0.000716000000
O	0.000144000000	4.430432000000	0.000633000000

Table S13. Excited state properties of **L** at the relaxed ground state geometry (**S₀**) as calculated in Gaussian at the B3LYP/6-31+g(d) level of theory. Transitions with contribution >10% are shown.
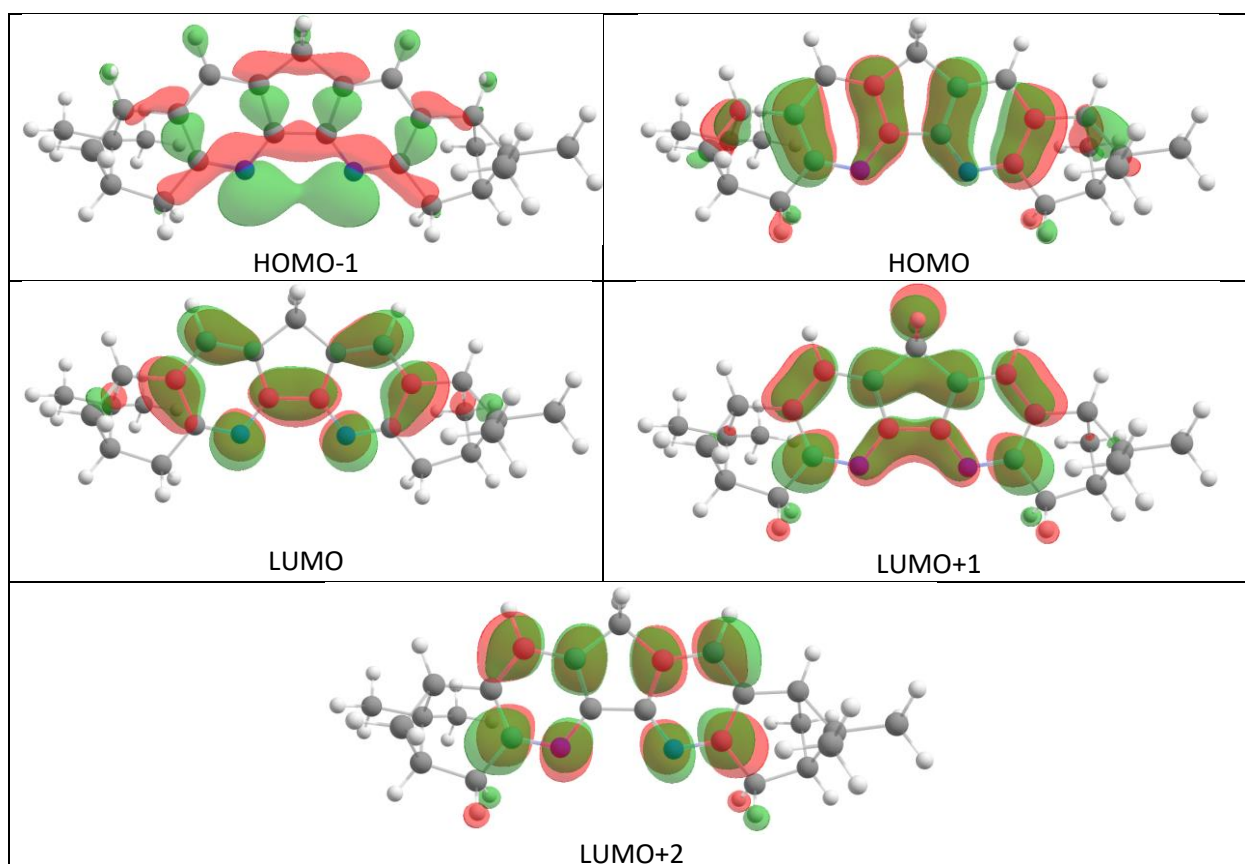
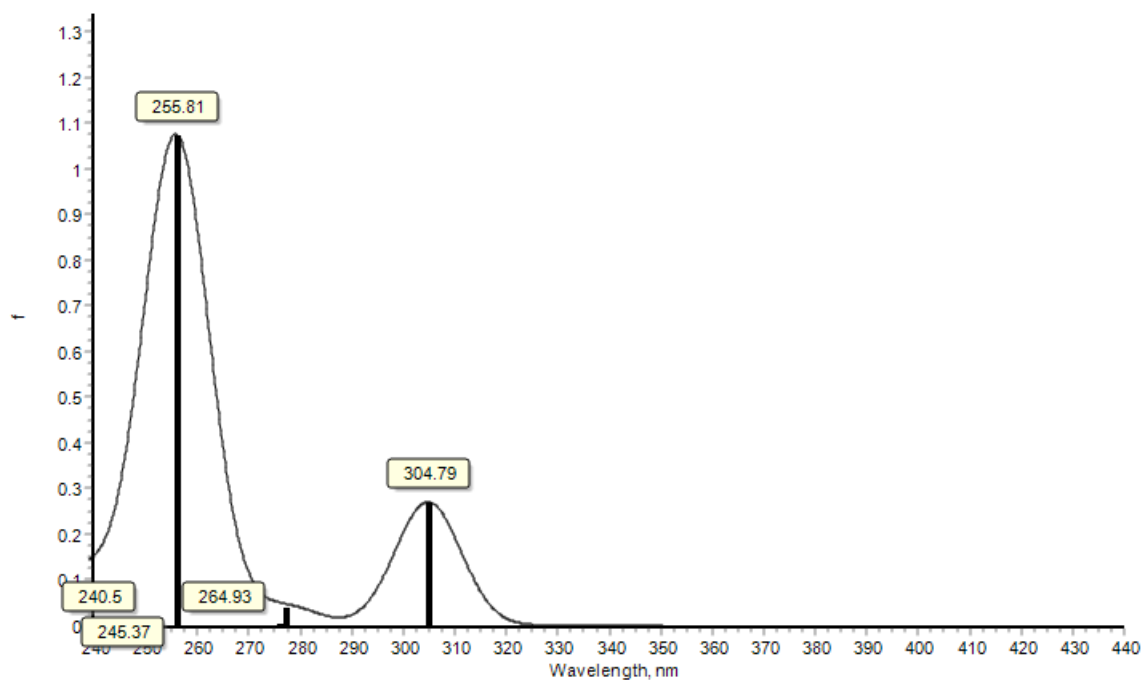| State	Energy (eV)	Energy (nm)	Contributions (%)	Oscillator strength	Character
S1	4.1800	297	HOMO -> LUMO (91.5)	0.7010	$\pi - \pi^*$
S2	4.3715	284	HOMO-1 -> LUMO (97.2)	0.0032	$\sigma - \pi^*, n - \pi^*$
S3	4.4654	278	HOMO-2 -> LUMO (94.5)	0.0000	$\sigma - \pi^*, n - \pi^*$
S4	4.5770	271	HOMO -> LUMO+1 (91.0)	0.1071	$\pi - \pi^*$
S5	4.8167	257	HOMO-3 -> LUMO (21.8) HOMO -> LUMO+3 (67.0)	0.0113	$\pi - \pi^*$
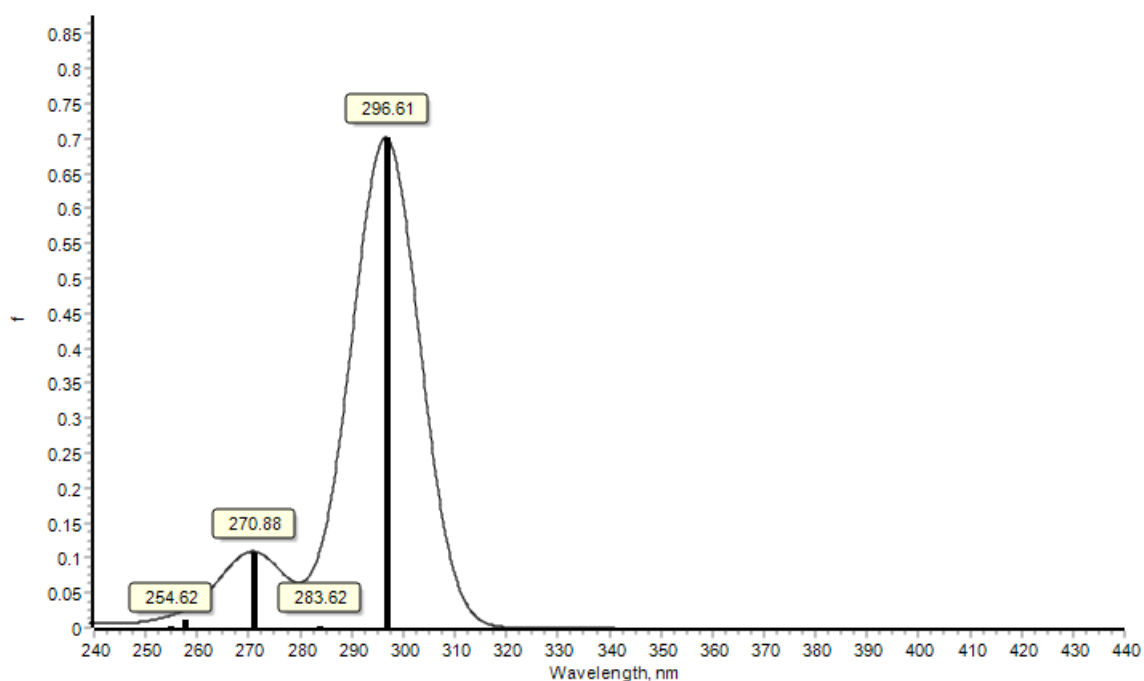
Figure S23. Calculated absorption spectrum of **L**.

Table S14. Isosurface contour plots of the molecular orbitals of **L** at the relaxed ground state geometry (**S₀**) as calculated in Gaussian at the B3LYP/6-31+g(d) level of theory.
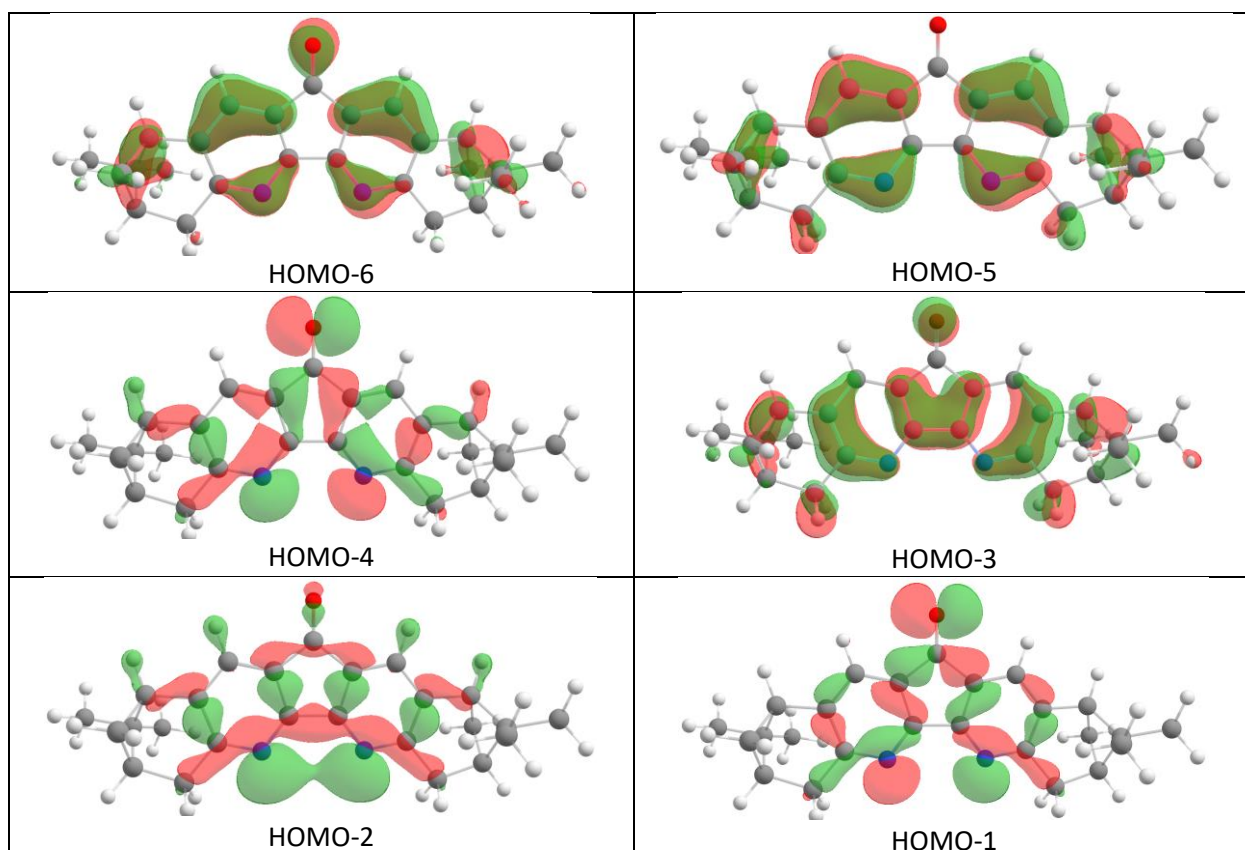

HOMO-3	HOMO-2

	HOMO-1	HOMO
	LUMO	LUMO+1
	LUMO+2	
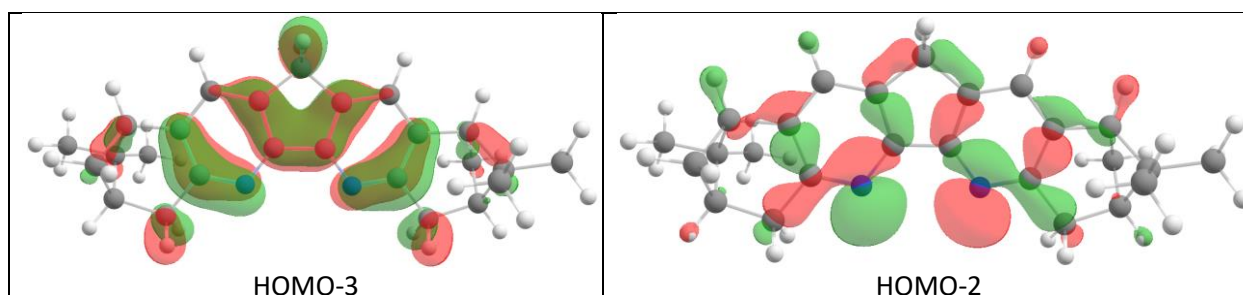
Table S15. Excited state properties of **L⁰** at the relaxed ground state geometry (**S₀**) as calculated in Gaussian at the B3LYP/6-31+g(d) level of theory. Transitions with contribution >10% are shown.
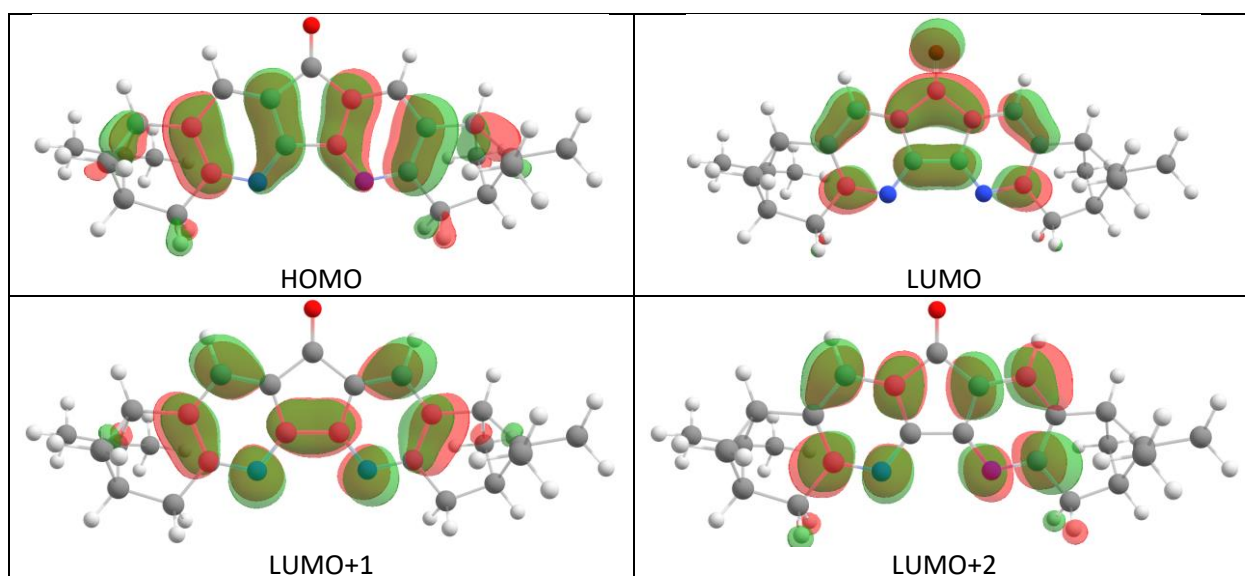
State	Energy (eV)	Energy (nm)	Contributions (%)	Oscillator strength	Character
S1	2.9420	421	HOMO -> LUMO (99.1)	0.0001	$\pi - \pi^*$, ILCT
S2	2.9776	416	HOMO-1 -> LUMO (93.5)	0.0000	$\sigma - \pi^*$, $n - \pi^*$
S3	3.6193	343	HOMO-2 -> LUMO (97.9)	0.0000	$\sigma - \pi^*$, $n - \pi^*$
S4	4.0013	310	HOMO-4 -> LUMO (86.1)	0.0000	$\sigma - \pi^*$, $n - \pi^*$
S5	4.0678	305	HOMO-5 -> LUMO (20.6) HOMO -> LUMO+1 (76.8)	0.2702	$\pi - \pi^*$, ILCT
S6	4.2474	292	HOMO-1 -> LUMO+1 (90.1)	0.0000	$\sigma - \pi^*$, $n - \pi^*$
S7	4.4757	277	HOMO-3 -> LUMO (84.3)	0.0396	$\pi - \pi^*$, ILCT
S8	4.4983	276	HOMO-2 -> LUMO+1 (92.0)	0.0039	$\sigma - \pi^*$, $n - \pi^*$
S9	4.6798	265	HOMO-6 -> LUMO (46.1) HOMO -> LUMO+2 (42.3)	0.0015	$\pi - \pi^*$, ILCT
S10	4.8468	256	HOMO-5 -> LUMO (77.4) HOMO -> LUMO+1 (20.5)	1.0717	$\pi - \pi^*$, ILCT

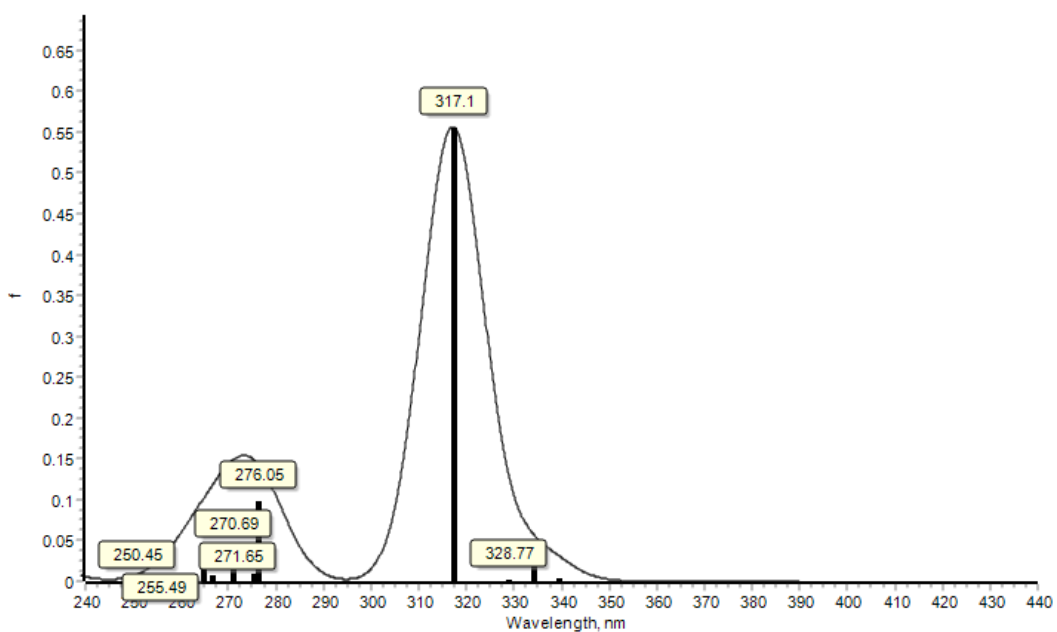**Figure S24**. Calculated absorption spectrum of **L^O**.

Table S16. Isosurface contour plots of the molecular orbitals of **L^O** at the relaxed ground state geometry (**S$_0$**) as calculated in Gaussian at the B3LYP/6-31+g(d) level of theory.
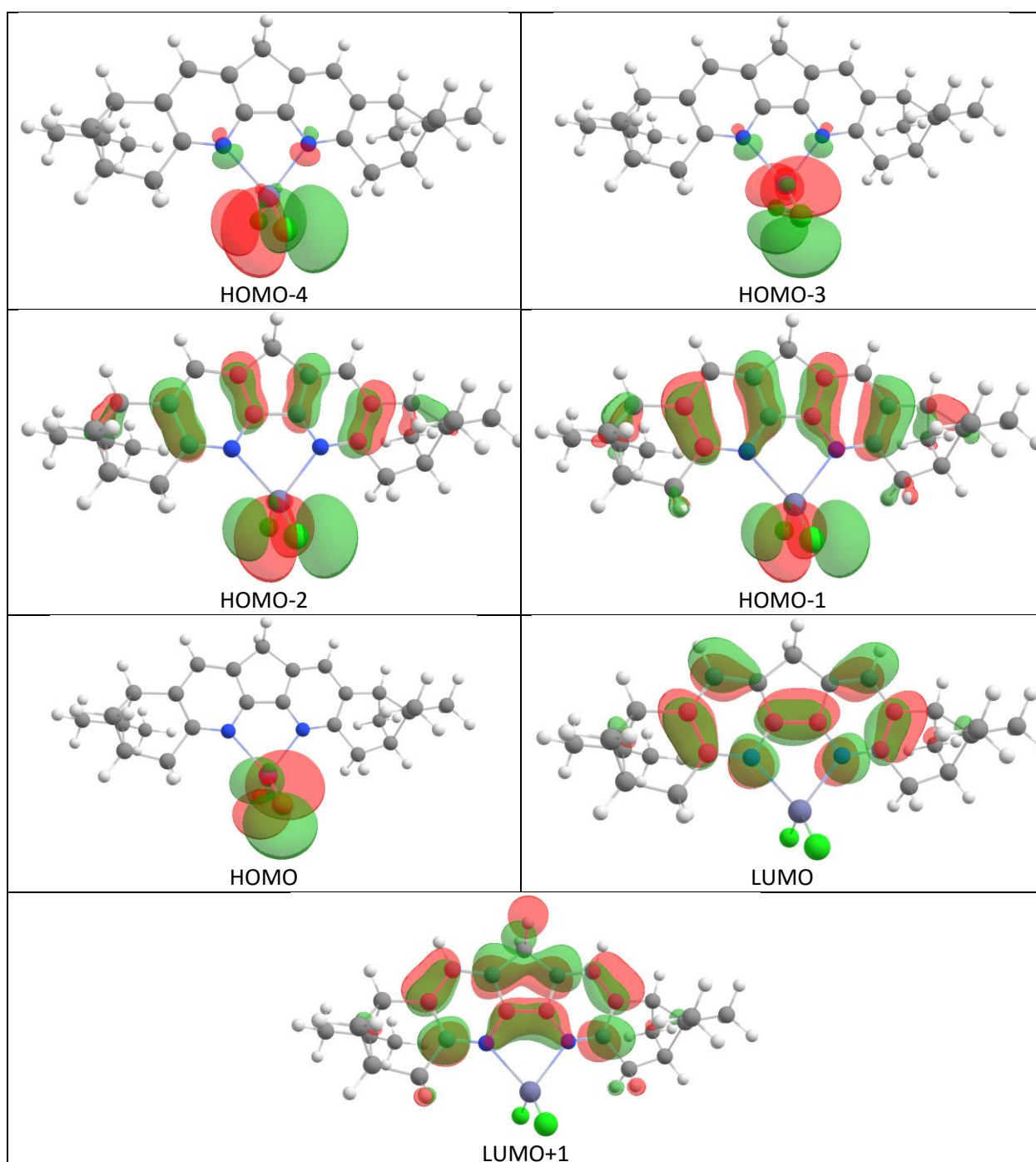

HOMO-6	HOMO-5
HOMO-4	HOMO-3
HOMO-2	HOMO-1

HOMO

LUMO

LUMO+1

LUMO+2

Table S17. Excited state properties of **[ZnLCl₂]** at the relaxed ground state geometry (**S₀**) as calculated in Gaussian at the B3LYP/LANL2DZ/6-31+g(d) level of theory. Transitions with contribution >10% are shown.

State	Energy (eV)	Energy (nm)	Contributions (%)	Oscillator strength	Character
S1	3.6555	339	HOMO -> LUMO (99.9)	0.0030	XLCT
S2	3.7116	334	HOMO-2 -> LUMO (29.9) HOMO-1 -> LUMO (69.7)	0.0378	XLCT, $\pi - \pi^*$
S3	3.7712	329	HOMO-3 -> LUMO (99.4)	0.0026	XLCT
S4	3.8398	323	HOMO-4 -> LUMO (99.4)	0.0000	XLCT
S5	3.9099	317	HOMO-2 -> LUMO (67.9) HOMO-1 -> LUMO (27.6)	0.5545	XLCT, $\pi - \pi^*$
S6	4.4501	279	HOMO -> LUMO+1 (94.9)	0.0002	XLCT
S7	4.4914	276	HOMO-1 -> LUMO+1 (94.5)	0.0982	XLCT, $\pi - \pi^*$

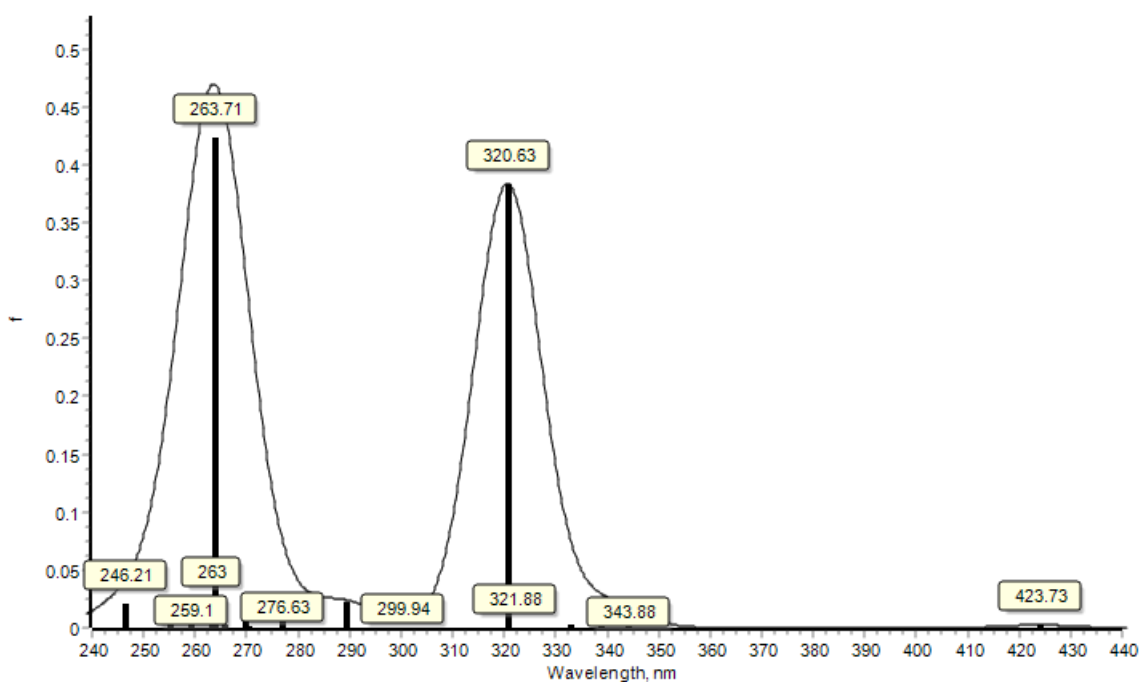
Figure S25. Calculated absorption spectrum of **[ZnLCl₂]**.

Table S18. Isosurface contour plots of the molecular orbitals of **[ZnLCl₂]** at the relaxed ground state geometry (**S₀**) as calculated in Gaussian at the B3LYP/LANL2DZ/6-31+g(d) level of theory.

HOMO-4	HOMO-3
HOMO-2	HOMO-1
HOMO	LUMO
LUMO+1	

Table S19. Excited state properties of **[ZnL^{O}Cl₂]** at the relaxed ground state geometry (**S₀**) as calculated in Gaussian at the B3LYP/LANL2DZ/6-31+g(d) level of theory. Transitions with contribution >10% are shown.

State	Energy (eV)	Energy (nm)	Contributions (%)	Oscillator strength	Character
S1	2.9260	424	HOMO-3 -> LUMO (51.5) HOMO-1 -> LUMO (47.7)	0.0025	XLCT, $\pi - \pi^*$, ILCT
S2	2.9829	416	HOMO -> LUMO (99.8)	0.0000	XLCT
S3	3.0525	406	HOMO-6 -> LUMO (47.6)	0.0000	$\pi - \pi^*$, ILCT

|			HOMO-4 -> LUMO (49.5)		
S4	3.0763	403	HOMO-3 -> LUMO (47.6)	0.0000	XLCT, $\pi - \pi^*$, ILCT
			HOMO-1 -> LUMO (52.0)		
S5	3.1013	400	HOMO-2 -> LUMO (99.4)	0.0000	XLCT
S6	3.2734	379	HOMO-6 -> LUMO (46.8)	0.0000	$\pi - \pi^*$, ILCT
			HOMO-4 -> LUMO (50.2)		
S7	3.6055	344	HOMO -> LUMO+1 (99.7)	0.0032	XLCT
S8	3.6603	339	HOMO-1 -> LUMO+1 (96.4)	0.0191	XLCT
S12	3.8669	321	HOMO-3 -> LUMO+1 (87.7)	0.3829	XLCT, $\pi - \pi^*$
S23	4.7015	264	HOMO-11 -> LUMO (84.7)	0.4227	$\pi - \pi^*$, ILCT

Figure S26. Calculated absorption spectrum of **[ZnL^{O}Cl$_2$]**.

Table S20. Isosurface contour plots of the molecular orbitals of **[ZnL^{O}Cl$_2$]** at the relaxed ground state geometry (**S$_0$**) as calculated in Gaussian at the B3LYP/LANL2DZ/6-31+g(d) level of theory.

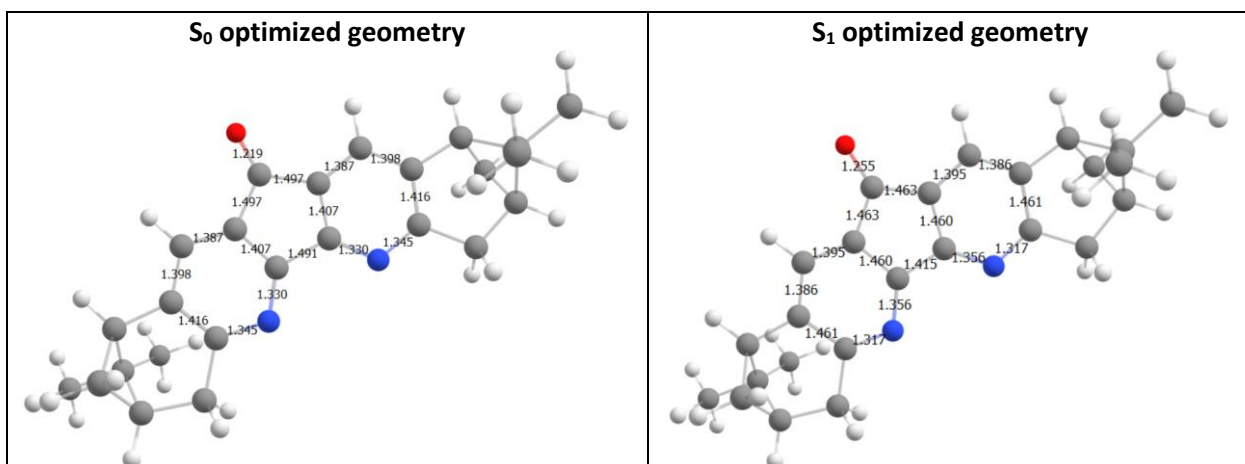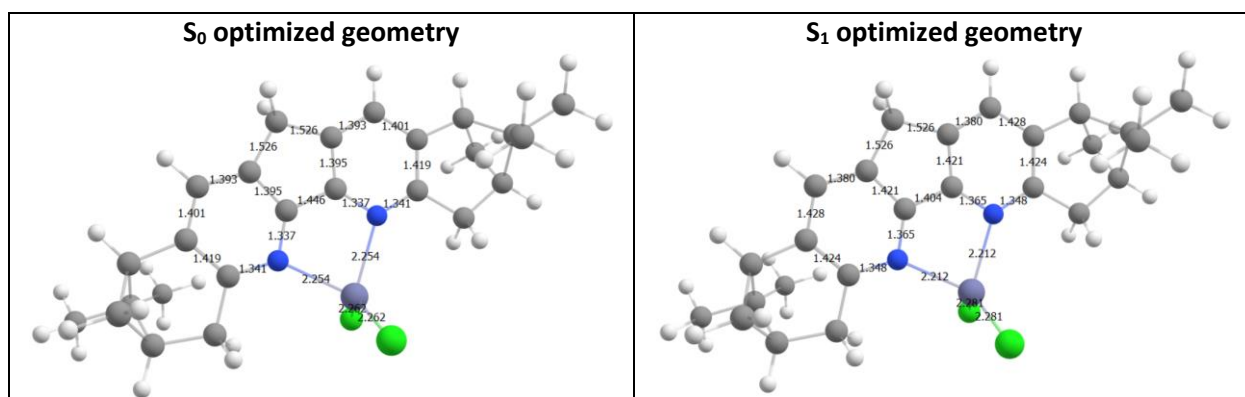| HOMO-1 | HOMO |
| LUMO | LUMO+1 |
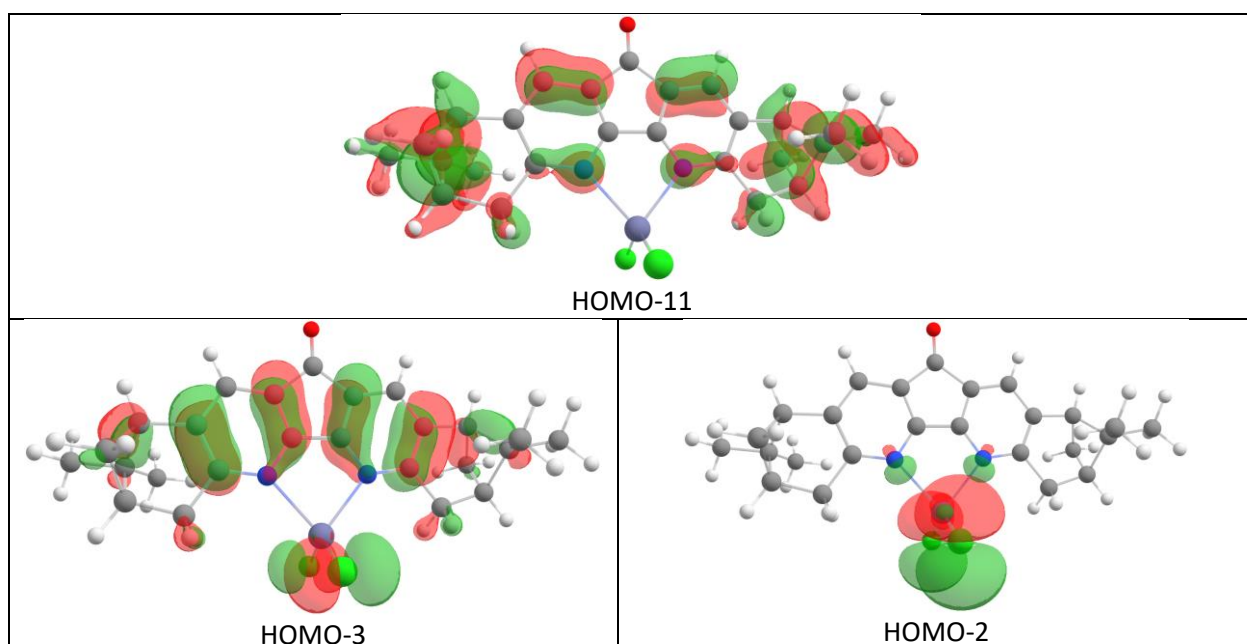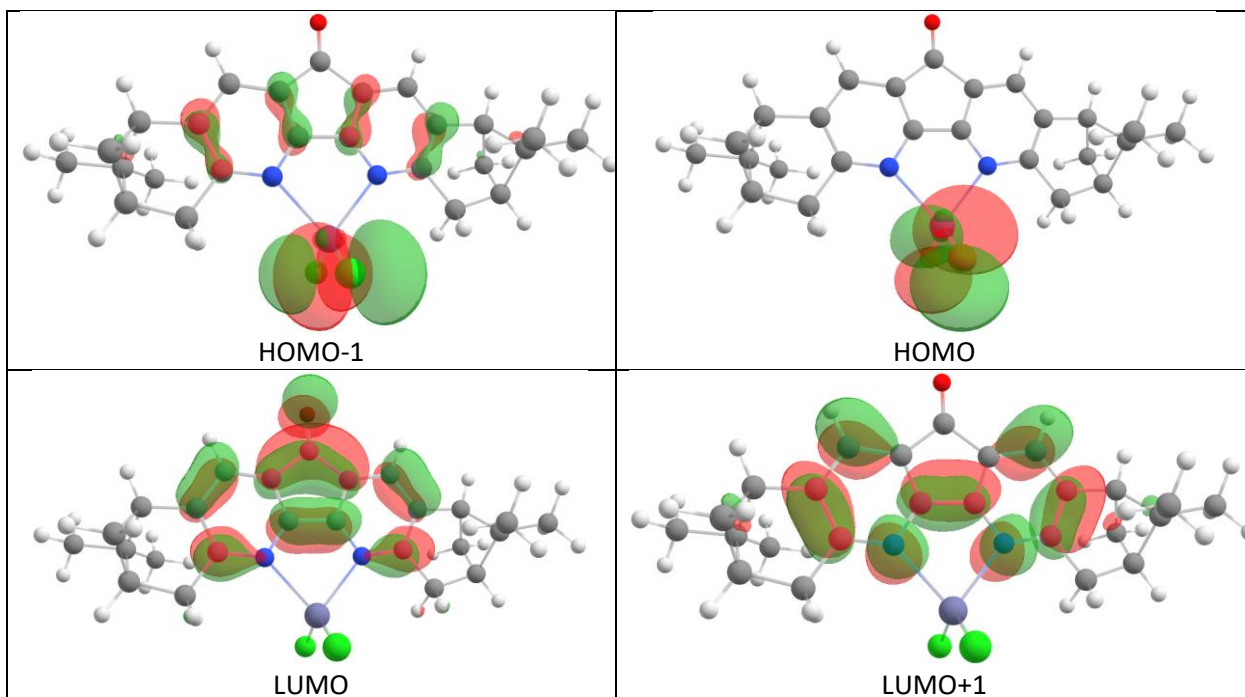
Table S21. Comparison of the most relevant bond lengths for **L**.

| S$_0$ optimized geometry | S$_1$ optimized geometry |
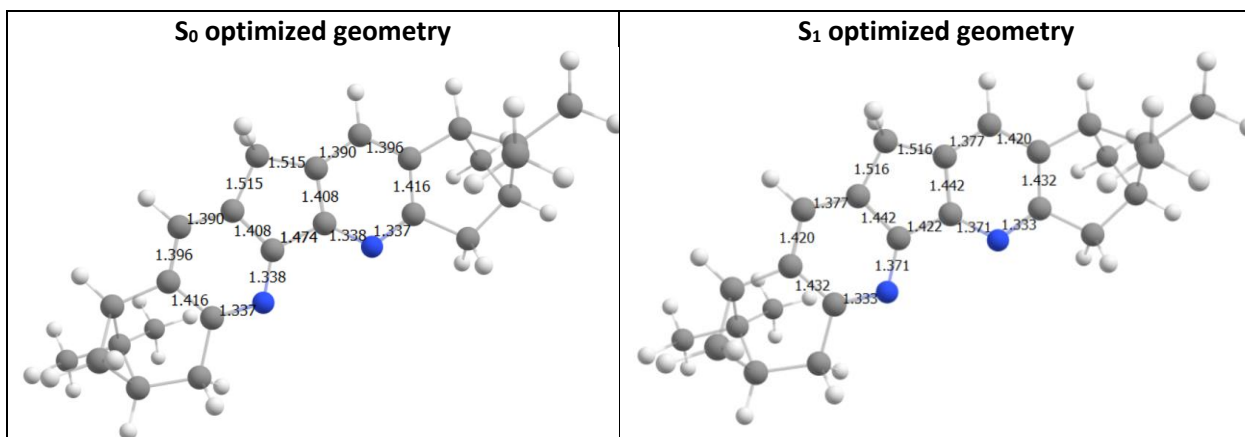
Table S22. Comparison of the most relevant bond lengths for **L^O**.

| S$_0$ optimized geometry | S$_1$ optimized geometry |

Table S23. Comparison of the most relevant bond lengths for **[ZnLCl$_2$]**.

S$_0$ optimized geometry	S$_1$ optimized geometry

Table S24. Comparison of the most relevant bond lengths for **[ZnL^{O}Cl$_2$]**.

S$_0$ optimized geometry	S$_1$ optimized geometry