Electronic Supplementary Information

N-Hydroxy – N-oxide photoinduced tautomerization and excitation wavelength dependent luminescence of ESIPT-capable zinc(II) complexes with a rationally designed 1-hydroxy-2,4-di(pyridin-2-yl)-1*H*-imidazole ESIPT-ligand

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Table S1. Crystal data and structure refinement for **1** – **3**.

Complex	**1**	**2**	**3**
Empirical formula	$C_{14}H_{12}Cl_2N_4OZn$	$C_{14}H_{12}Br_2N_4OZn$	$C_{14}H_{12}I_2N_4OZn$
Formula weight	388.55	477.47	571.45
Crystal system	Monoclinic		
Space group, Z	$P2_1/c$, 4		
a(Å)	11.4076(3)	11.6350(3)	12.0424(9)
b(Å)	7.9255(2)	7.9633(3)	8.1386(6)
c(Å)	16.5642(3)	16.9065(5)	17.4214(15)
β(°)	91.408(1)	91.484(1)	91.506(2)
V(Å^3)	1497.13(6)	1565.91(9)	1706.9(2)
d_{Calc}(g/cm^3)	1.724	2.025	2.224
μ (mm^{-1})	2.003	6.677	5.062
F(000)	784	928	1072
Crystal size (mm)	0.250 x 0.120 x 0.080	0.250 x 0.120 x 0.080	0.250 x 0.150 x 0.050
Theta range for data collection (°)	2.460 - 26.019	2.410 - 26.021	2.339 - 26.022
Index ranges	$-14 \le h \le 13$ $-9 \le k \le 9$ $-16 \le l \le 20$	$-14 \le h \le 14$ $-9 \le k \le 9$ $-20 \le l \le 20$	$-11 \le h \le 14$ $-10 \le k \le 9$ $-21 \le l \le 21$
Reflections collected	10188	11925	11233
Independent reflections (R_{int})	2951 (R_{int} = 0.0363)	3079 9 (R_{int} = 0.0357)	3346 (R_{int} = 0.0498)
Completeness to theta = 25.500°	99.9 %	99.8 %	99.8 %
Data / restraints / parameters	2951 / 0 / 210	3079 / 0 / 210	3346 / 0 / 210
Goodness-of-fit on F^2	1.032	1.072	1.163
Final *R* indices ($I>2\sigma_I$)	R_1 = 0.0280, wR_2 = 0.0712	R_1 = 0.0321, wR_2 = 0.0710	R_1 = 0.0493, wR_2 = 0.1234
R indices (all data)	R_1 = 0.0308, wR_2 = 0.0723	R_1 = 0.0390, wR_2= 0.0729	R_1 = 0.0541, wR_2 = 0.1257
Largest diff. peak and hole (e/Å^3)	0.542 and -0.333	0.870 and -0.450	2.288 and -1.513

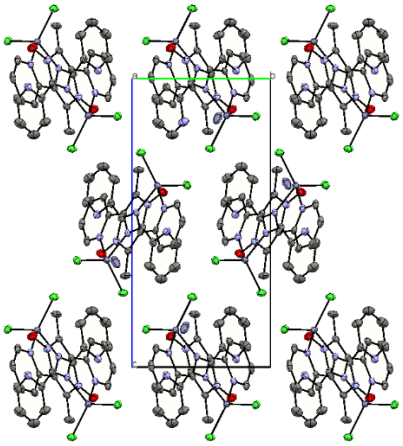


Figure S1. Packing of **1** (view along the *a* axis).

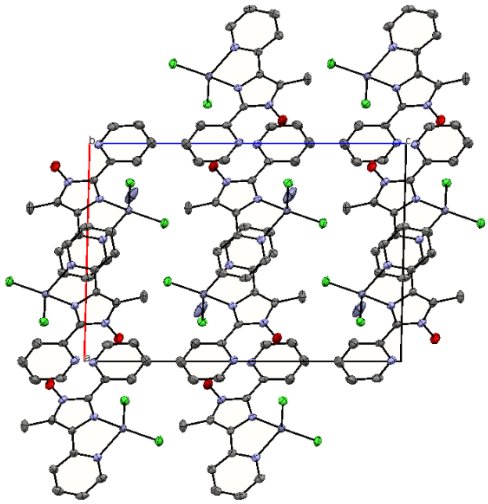


Figure S2. Packing of **1** (view along the *b* axis).

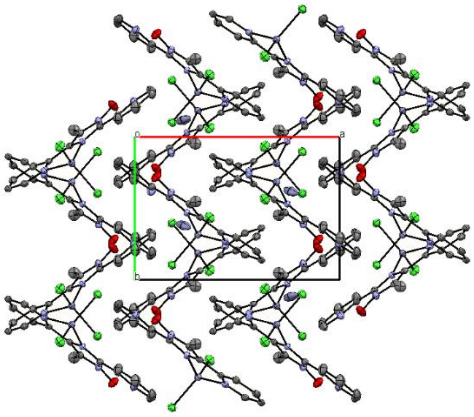


Figure S3. Packing of **1** (view along the *c* axis).

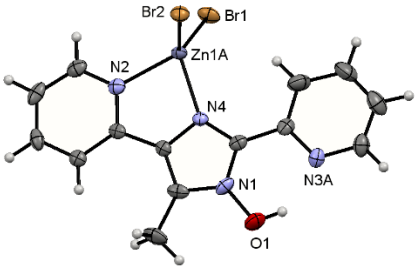


Figure S4. Molecular structure of the major component of [Zn(HL)Br_2] in the structure of **2**.

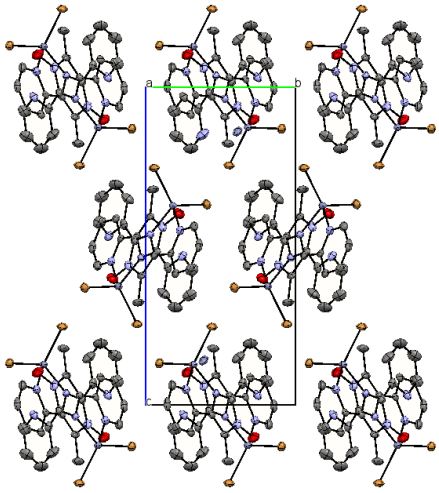


Figure S5. Packing of **2** (view along the *a* axis).

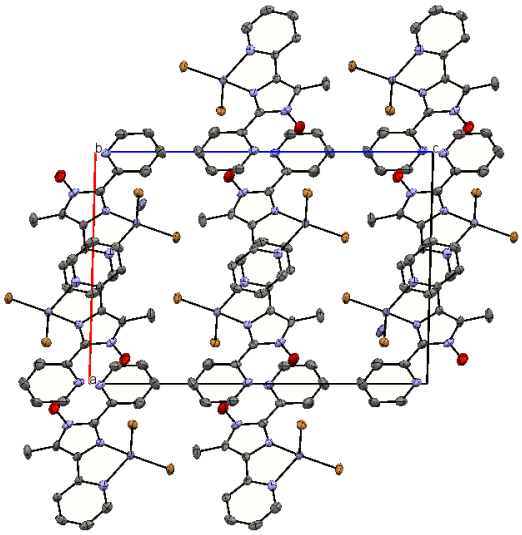


Figure S6. Packing of **2** (view along the *b* axis).

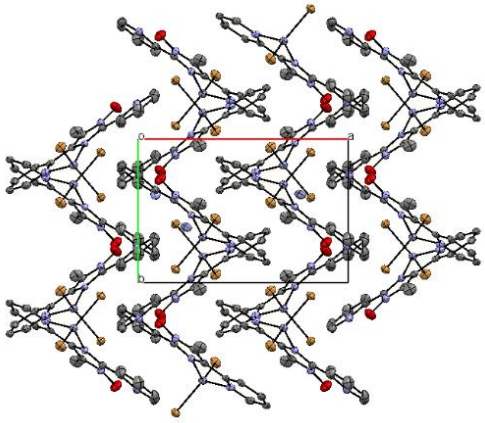


Figure S7. Packing of **2** (view along the *c* axis).

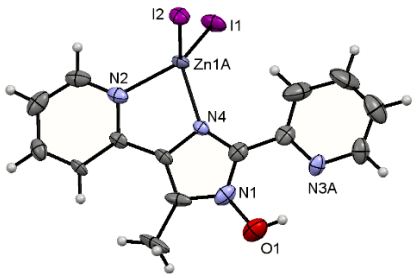


Figure S8. Molecular structure of the major component of $[Zn(HL)I_2]$ in the structure of **3**.

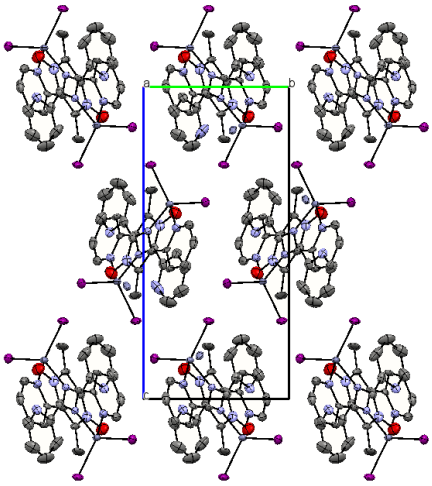


Figure S9. Packing of **3** (view along the *a* axis).

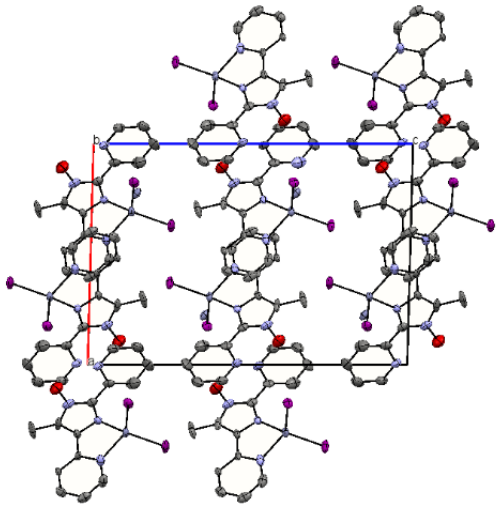


Figure S10. Packing of **3** (view along the *b* axis).

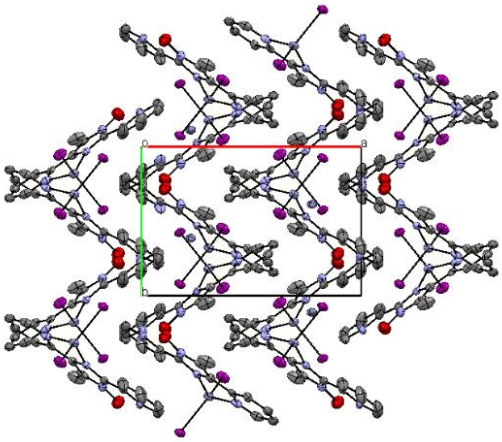


Figure S11. Packing of **3** (view along the *c* axis).

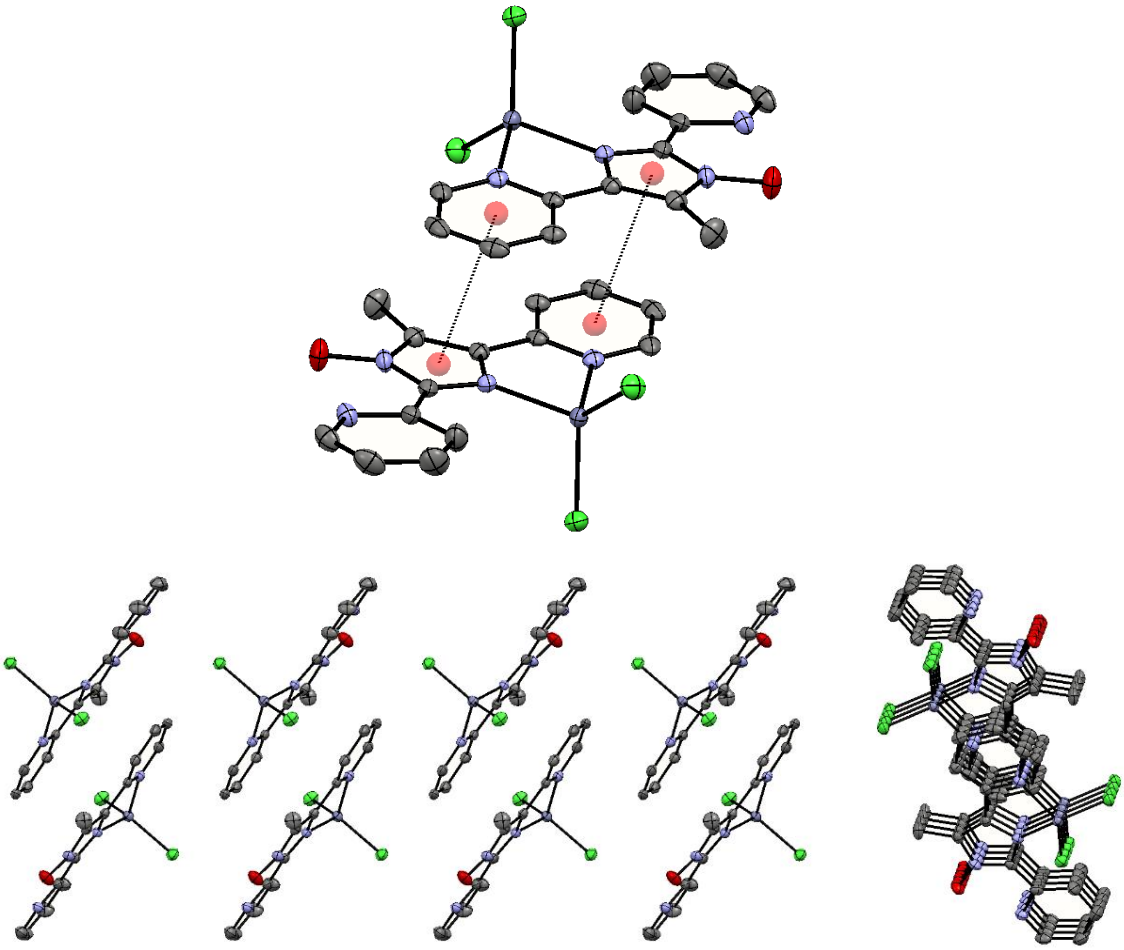


Figure S12. Supramolecular dimeric associates and supramolecular chains in the structure of **1**.

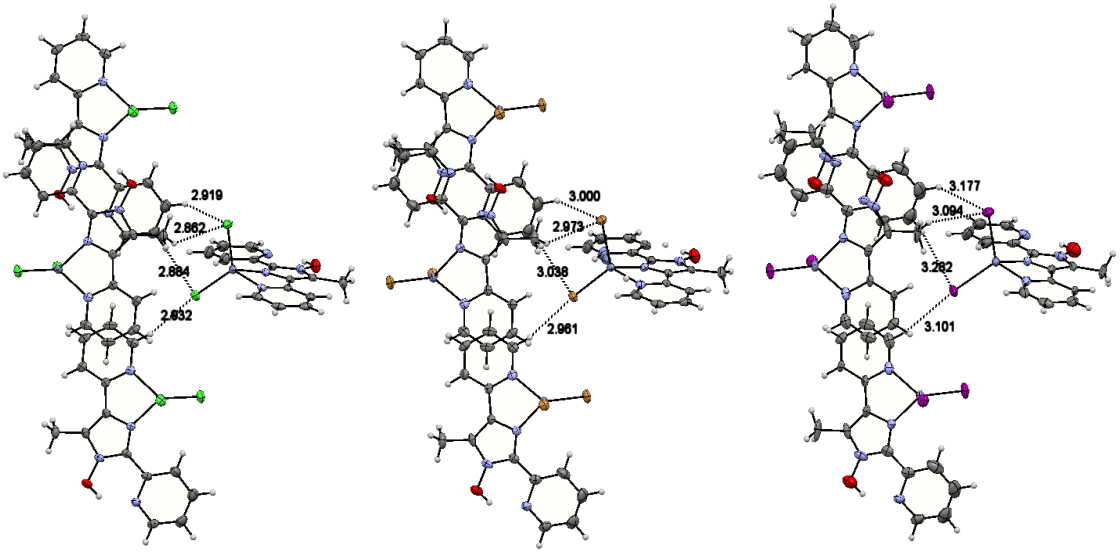


Figure S13. C–H···Hal contacts in the structures of **1**, **2** and **3**.

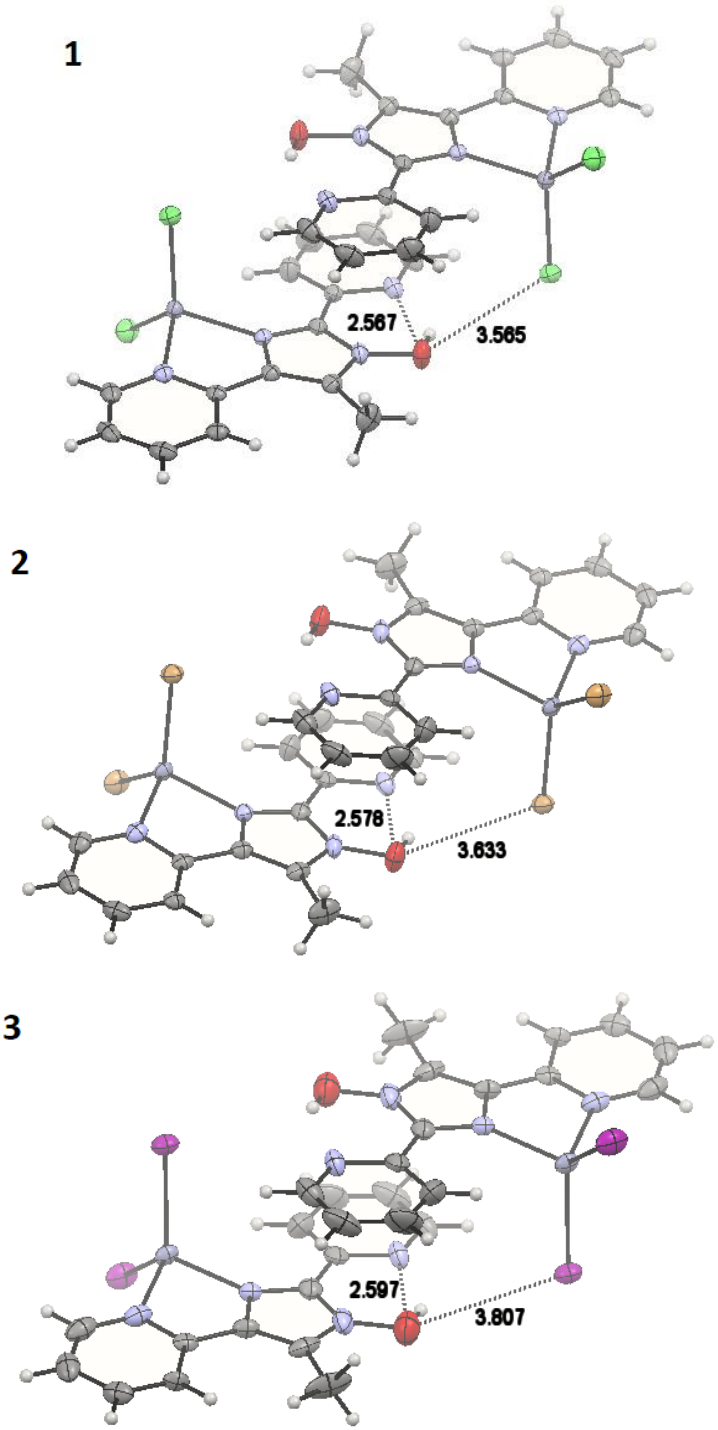


Figure S14. Intra- and intermolecular hydrogen bonds in the structures of **1**, **2** and **3**.

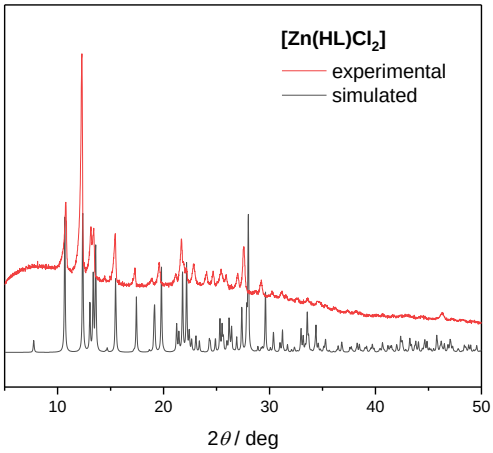


Figure S15. X-ray powder diffraction patterns of $[Zn(HL)Cl_2]$.

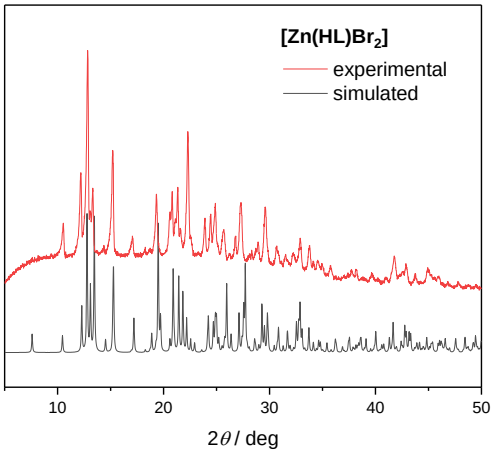


Figure S16. X-ray powder diffraction patterns of $[Zn(HL)Br_2]$.

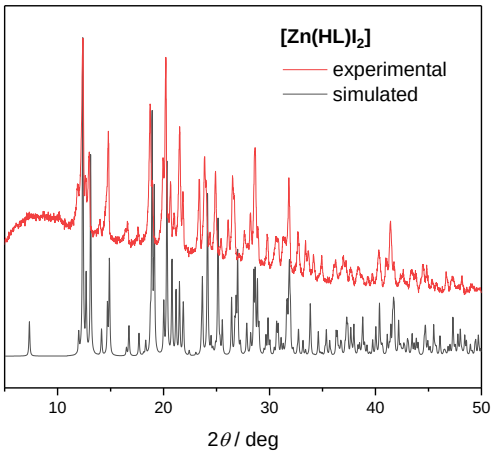


Figure S17. X-ray powder diffraction patterns of $[Zn(HL)I_2]$.

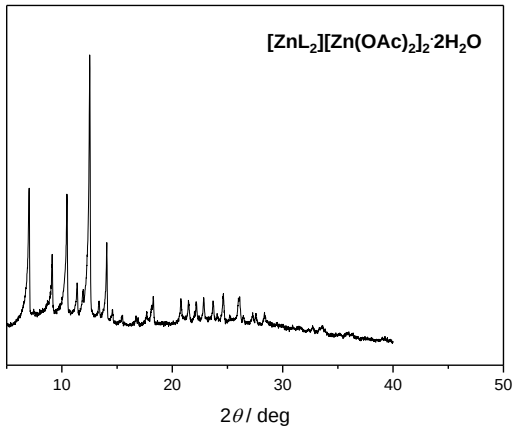


Figure S18. X-ray powder diffraction pattern of $[ZnL_2][Zn(OAc)_2]_2 \cdot 2H_2O$.

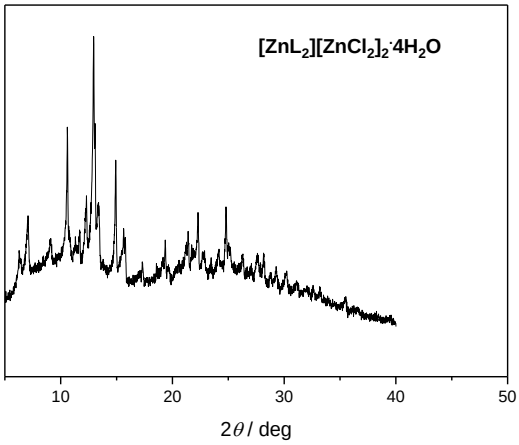


Figure S19. X-ray powder diffraction pattern of $[ZnL_2][ZnCl_2]_2 \cdot 4H_2O$.

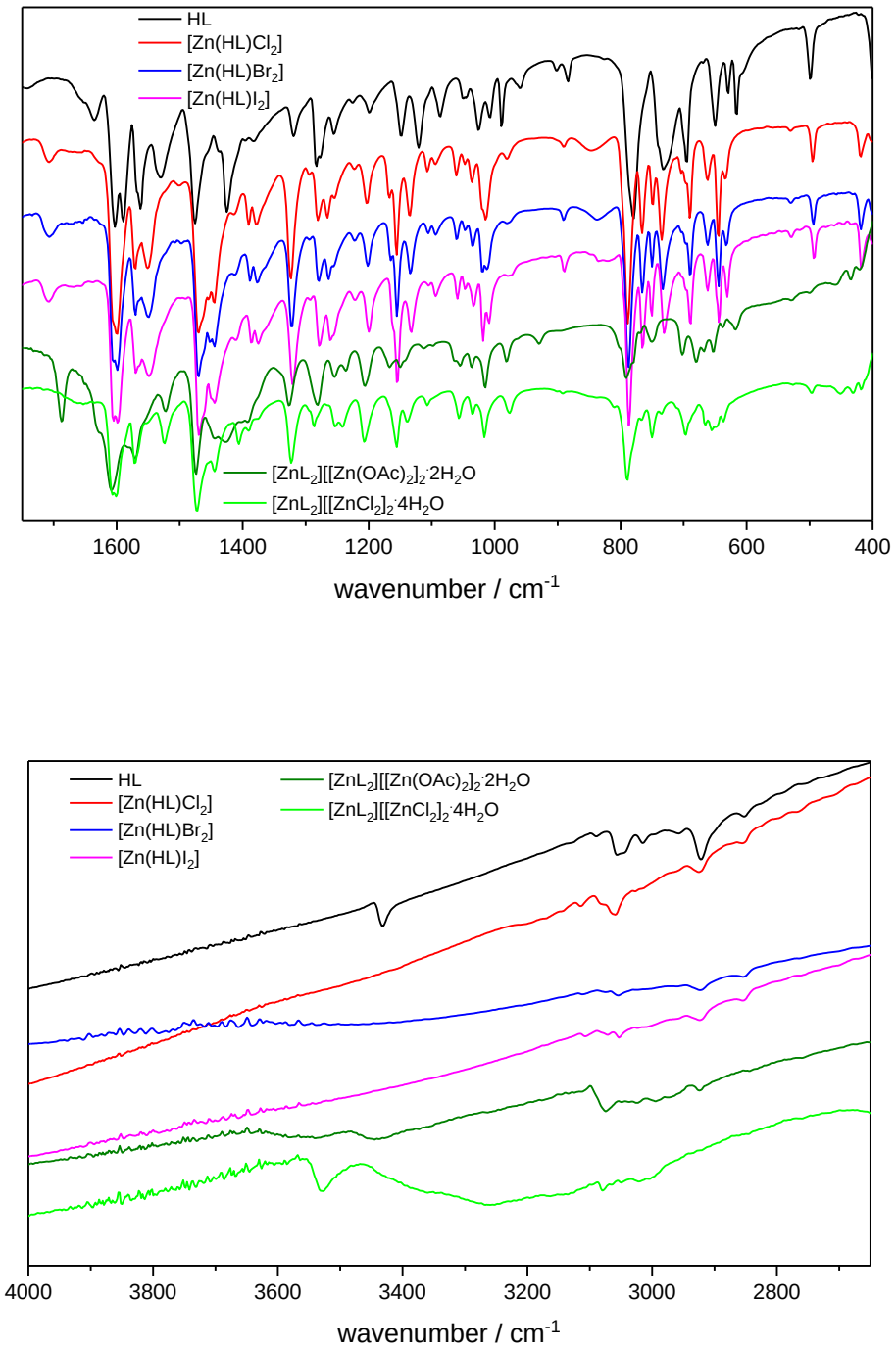


Figure S20. IR spectra of HL, $[Zn(HL)Cl_2]$, $[Zn(HL)Br_2]$, $[Zn(HL)I_2]$, $[ZnL_2][Zn(OAc)_2]_2{\cdot}2H_2O$ and $[ZnL_2][ZnCl_2]_2{\cdot}4H_2O$ in KBr (top) and fluorinated oil (bottom).

Table S2a. Photoluminescence lifetimes recorded for **$ZnHLCl_2$, $ZnHLBr_2$** and **$ZnHLI_2$** in the solid state.

Compound	T, K	λ_{ex}, nm[a]	λ_{det}, nm[b]	τ, ns[c]
$[Zn(HL)Cl_2]$	300	375	575	1.2, 3.5
			700	1.3, 4.0
	77	375	500	1.7, 3.6
			530	1.9, 3.7
			600	2.0, 4.3
$[Zn(HL)Br_2]$	300	375	535	0.7, 1.5
			700	0.9, 1.6
	77	375	500	2.1, 3.5
			560	1.5, 3.3
			650	1.6, 3.7
$[Zn(HL)I_2]$	300	375	560	0.2, 1.1
			700	0.2, 1.0, 2.6
	77	375	500	1.6, 3.3
			540	1.5, 3.2
			600	1.6, 3.5

a – excitation wavelength

b – detection wavelength

c – emission decay was analyzed with two or three components : $I = \sum_i A_i \exp\left(^{-t}/_{\tau_i}\right)$

Table S2b. Photoluminescence quantum yields (PLQY) recorded for **$ZnHLCl_2$, $ZnHLBr_2$** and **$ZnHLI_2$** in the solid state.

Compound	T, K	λ_{ex}, nm[a]	PLQY, %
$[Zn(HL)Cl_2]$	300	300	4
		400	11
	77	300	12
		400	25
$[Zn(HL)Br_2]$	300	300	4
		400	11
	77	300	9
		400	27
$[Zn(HL)I_2]$	300	300	3
		400	8
	77	300	5
		400	13

a – excitation wavelength

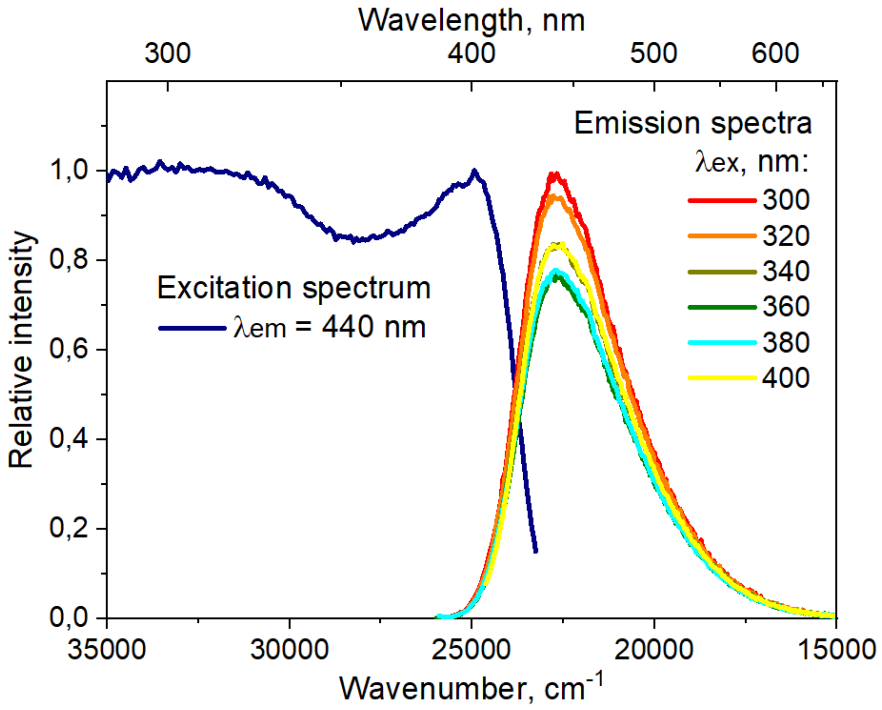


Figure S21. Excitation and emission spectra of **$[ZnL_2][Zn(OAc)_2]_2 \cdot 2H_2O$** in the solid state at 300 K.

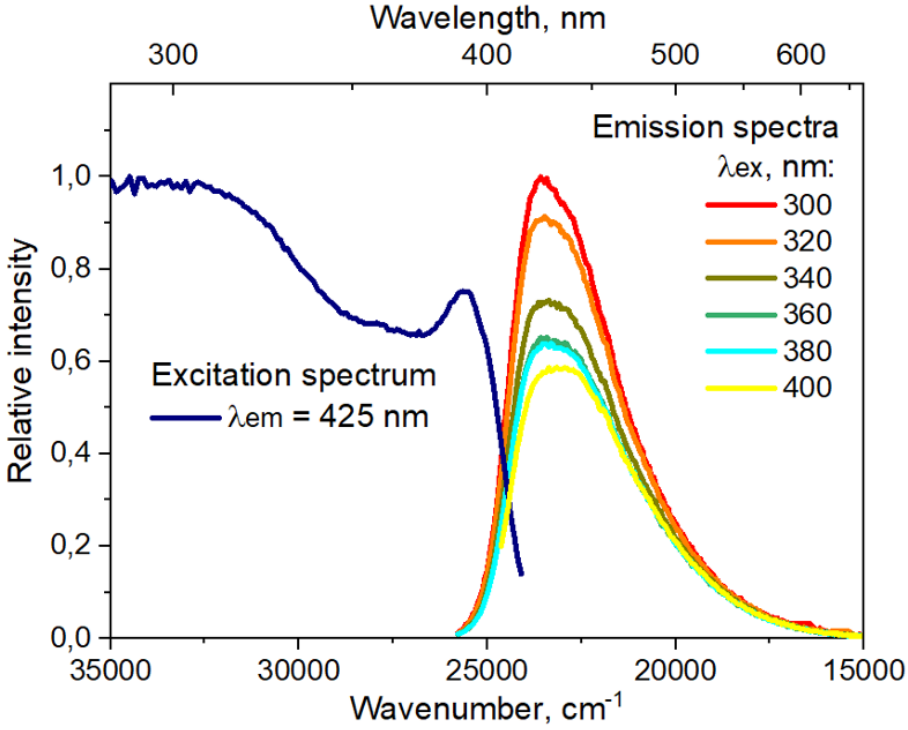


Figure S22. Excitation and emission spectra of **$[ZnL_2][ZnCl_2]_2 \cdot 4H_2O$** in the solid state at 300 K.

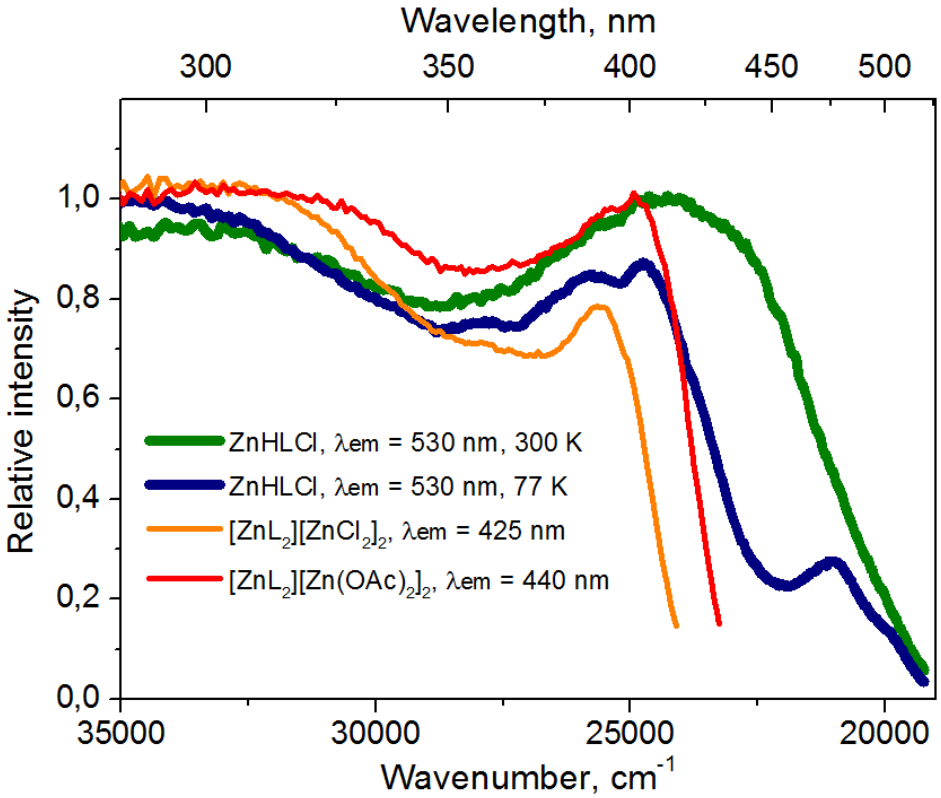


Figure S23. Comparison of the excitation spectra of ESIPT-capable complex **$ZnHLCl_2$** with non-ESIPT-capable complexes **$[ZnL_2][ZnCl_2]_2 \cdot 4H_2O$** and **$[ZnL_2][Zn(OAc)_2]_2 \cdot 2H_2O$** in the solid state. The absence of the peak at *ca.* 470 nm in the case of compounds **$[ZnL_2][ZnCl_2]_2 \cdot 4H_2O$** and **$[ZnL_2][Zn(OAc)_2]_2 \cdot 2H_2O$**, which is associated with the excitation of the proton-transferred species, supports the fact that proton transfer does not take place in **$[ZnL_2][ZnCl_2]_2 \cdot 4H_2O$** and **$[ZnL_2][Zn(OAc)_2]_2 \cdot 2H_2O$**.

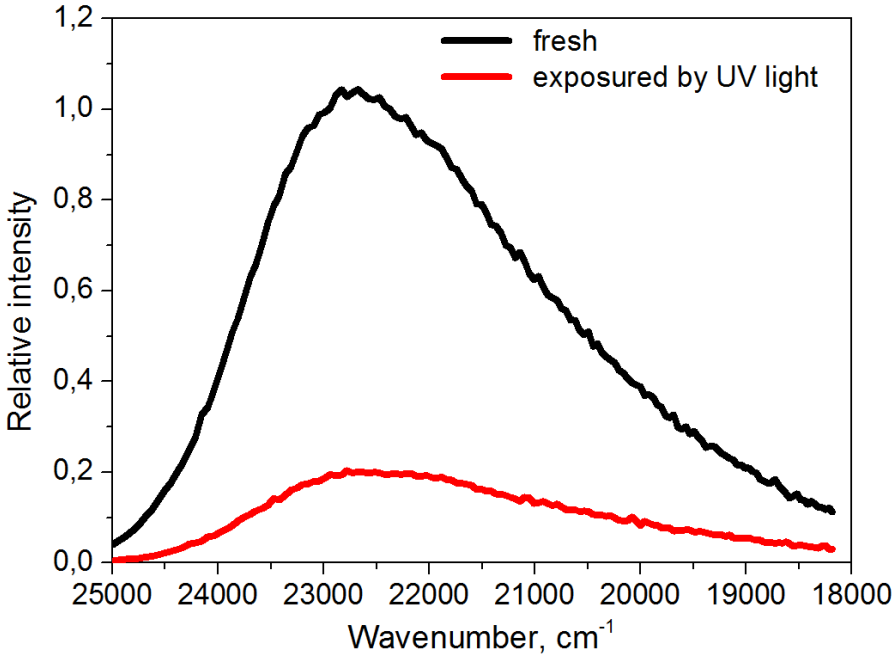


Figure S24. Comparison of the emission intensity of fresh and light-irradiated samples of **$[ZnL_2][Zn(OAc)_2]_2 \cdot 2H_2O$**, λ_{ex} = 300 nm.

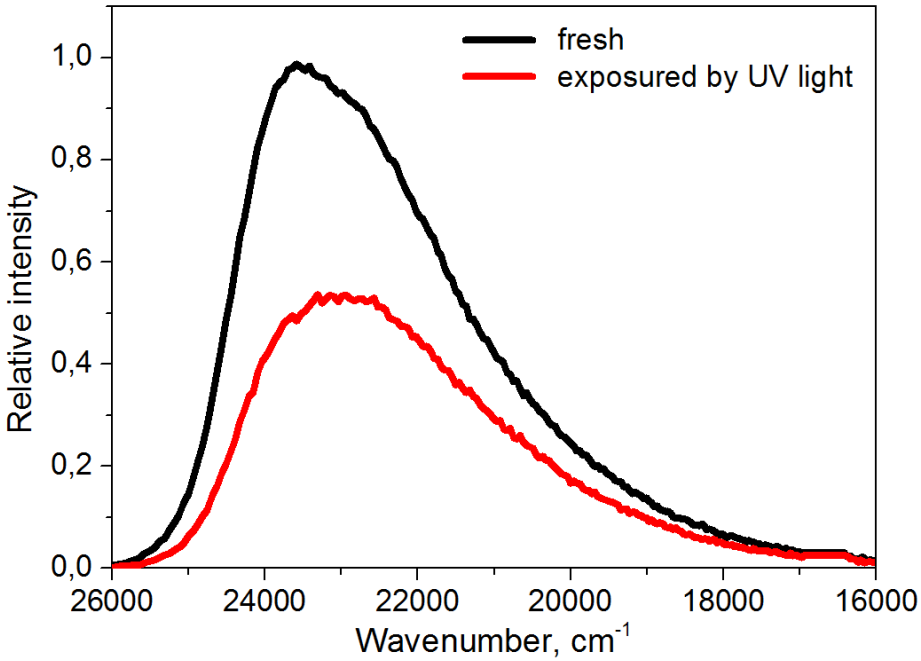


Figure S25. Comparison of the emission intensity of fresh and light-irradiated samples of **$[ZnL_2][ZnCl_2]_2 \cdot 4H_2O$**, λ_{ex} = 300 nm.

Table S3. Optimized geometry of the **ground state** of **$ZnHLCl_2$** (**normal form**, **S_0^N**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the M062X/6-31+g(d) level of theory **using the QM/MM method (QM region)**.

Cl	0.825694000000	-3.862487000000	0.840797000000
Cl	0.860198000000	-2.705945000000	-3.048448000000
Zn	0.352078000000	-2.470449000000	-0.869659000000
N	-1.624869000000	-1.592827000000	-0.662082000000
N	1.384673000000	1.668871000000	-0.178751000000
O	2.144111000000	2.779681000000	0.023539000000
H	3.071377000000	2.397088000000	0.119494000000
N	4.068468000000	1.004286000000	0.207530000000
C	3.576976000000	-1.350837000000	0.126029000000
H	2.849020000000	-2.149909000000	0.037855000000
N	0.776683000000	-0.410920000000	-0.380077000000
C	-0.329697000000	0.385206000000	-0.478963000000
C	0.035434000000	1.718729000000	-0.354596000000
C	1.815726000000	0.381064000000	-0.191224000000
C	3.202550000000	-0.009893000000	0.045135000000
C	5.346927000000	0.715598000000	0.453611000000
H	6.013682000000	1.560229000000	0.584438000000
C	5.814932000000	-0.588990000000	0.544366000000
H	6.858763000000	-0.775340000000	0.753585000000
C	4.910898000000	-1.634275000000	0.375487000000
H	5.230215000000	-2.665506000000	0.445290000000
C	-0.701125000000	3.013277000000	-0.354351000000
H	0.011559000000	3.839693000000	-0.346729000000
H	-1.342151000000	3.110885000000	0.526794000000
H	-1.328743000000	3.099373000000	-1.243589000000
C	-1.643759000000	-0.248892000000	-0.600794000000

C	-2.848594000000	0.455600000000	-0.589816000000
H	-2.848913000000	1.535699000000	-0.527055000000
C	-4.041879000000	-0.253150000000	-0.634597000000
H	-4.986063000000	0.280354000000	-0.606044000000
C	-4.012124000000	-1.644626000000	-0.678680000000
H	-4.917926000000	-2.237139000000	-0.689845000000
C	-2.772165000000	-2.270699000000	-0.688995000000
H	-2.680444000000	-3.350735000000	-0.715506000000

Table S4. Optimized geometry of the **ground state** of **$ZnHLCl_2$** (local minimum in the **tautomeric form**, **S_0^T**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the M062X/6-31+g(d) level of theory **using the QM/MM method (QM region)**.

Cl	0.775738000000	-3.832706000000	0.794024000000
Cl	0.862419000000	-2.694486000000	-3.114866000000
Zn	0.382329000000	-2.447386000000	-0.939736000000
N	-1.603480000000	-1.572254000000	-0.713366000000
N	1.326273000000	1.728743000000	-0.076356000000
O	2.035844000000	2.740983000000	0.284094000000
H	3.699823000000	2.009251000000	-0.012326000000
N	4.114242000000	0.993751000000	0.006614000000
C	3.520450000000	-1.295739000000	0.338944000000
H	2.759860000000	-2.065108000000	0.409664000000
N	0.780621000000	-0.361776000000	-0.448246000000
C	-0.368848000000	0.439095000000	-0.538406000000
C	-0.030507000000	1.755365000000	-0.344616000000
C	1.776102000000	0.415323000000	-0.155226000000
C	3.163381000000	0.004422000000	0.101424000000
C	5.422852000000	0.710120000000	0.283814000000
H	6.110503000000	1.540189000000	0.256674000000
C	5.819481000000	-0.583381000000	0.510674000000
H	6.866111000000	-0.782962000000	0.689654000000
C	4.878670000000	-1.622750000000	0.506064000000
H	5.179199000000	-2.649790000000	0.635424000000
C	-0.776846000000	3.040965000000	-0.302946000000
H	-0.064145000000	3.865705000000	-0.242426000000
H	-1.433986000000	3.098076000000	0.569324000000
H	-1.388116000000	3.161186000000	-1.198916000000
C	-1.655109000000	-0.226084000000	-0.660636000000
C	-2.878168000000	0.451907000000	-0.640426000000
H	-2.902287000000	1.532407000000	-0.587316000000
C	-4.053309000000	-0.284402000000	-0.663306000000
H	-5.008588000000	0.227819000000	-0.629716000000
C	-3.989970000000	-1.676222000000	-0.696056000000
H	-4.881761000000	-2.289741000000	-0.696996000000
C	-2.735121000000	-2.274573000000	-0.717746000000
H	-2.619622000000	-3.352583000000	-0.741496000000

Table S5. Optimized geometry of the **first singlet excited state** of **$ZnHLCl_2$** (**normal form**, **S_1^N**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the M062X/6-31+g(d) level of theory **using the QM/MM method (QM region)**.

Cl	0.765820000000	-3.851350000000	0.813668000000

Cl	0.854233000000	-2.692747000000	-3.054239000000
Zn	0.252724000000	-2.466490000000	-0.892939000000
N	-1.674414000000	-1.516269000000	-0.682558000000
N	1.390276000000	1.706888000000	-0.192659000000
O	2.203396000000	2.759990000000	0.007731000000
H	3.138708000000	2.287682000000	0.140765000000
N	4.026478000000	1.038870000000	0.254566000000
C	3.551372000000	-1.357624000000	0.149426000000
H	2.828048000000	-2.160273000000	0.039090000000
N	0.736563000000	-0.409694000000	-0.401544000000
C	-0.345017000000	0.418937000000	-0.505748000000
C	0.081778000000	1.787678000000	-0.378444000000
C	1.807769000000	0.361068000000	-0.192346000000
C	3.149936000000	-0.003470000000	0.064132000000
C	5.292041000000	0.747817000000	0.524826000000
H	5.956474000000	1.591691000000	0.678224000000
C	5.771260000000	-0.559809000000	0.620845000000
H	6.812718000000	-0.732362000000	0.855536000000
C	4.876382000000	-1.625292000000	0.426379000000
H	5.208838000000	-2.651905000000	0.500071000000
C	-0.631836000000	3.086553000000	-0.405280000000
H	0.092991000000	3.901971000000	-0.402943000000
H	-1.283663000000	3.195583000000	0.467519000000
H	-1.251898000000	3.153130000000	-1.301625000000
C	-1.652699000000	-0.141067000000	-0.638681000000
C	-2.841323000000	0.611443000000	-0.655612000000
H	-2.796976000000	1.692747000000	-0.622313000000
C	-4.061975000000	-0.038978000000	-0.697558000000
H	-4.984848000000	0.529917000000	-0.704380000000
C	-4.073766000000	-1.445049000000	-0.707985000000
H	-4.999167000000	-2.006823000000	-0.722763000000
C	-2.858958000000	-2.125837000000	-0.701333000000
H	-2.832856000000	-3.211066000000	-0.717779000000

Table S6. Optimized geometry of the **first singlet excited state** of **$ZnHLCl_2$** (**tautomeric form**, **S_1^T**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the M062X/6-31+g(d) level of theory **using the QM/MM method (QM region)**.

Cl	0.768662000000	-3.828544000000	0.787461000000
Cl	0.862806000000	-2.692947000000	-3.124254000000
Zn	0.386721000000	-2.444178000000	-0.949636000000
N	-1.600364000000	-1.569418000000	-0.720579000000
N	1.317994000000	1.737204000000	-0.061612000000
O	2.020436000000	2.735356000000	0.321418000000
H	3.789668000000	1.953758000000	-0.031057000000
N	4.120842000000	0.992160000000	-0.021981000000
C	3.512448000000	-1.287954000000	0.369470000000
H	2.747191000000	-2.053087000000	0.462880000000
N	0.781259000000	-0.354856000000	-0.457872000000
C	-0.374381000000	0.446692000000	-0.546788000000
C	-0.039863000000	1.760501000000	-0.343080000000
C	1.770508000000	0.420114000000	-0.149974000000
C	3.157854000000	0.006367000000	0.109575000000
C	5.433762000000	0.709247000000	0.259665000000

H	6.124402000000	1.537229000000	0.209953000000
C	5.820201000000	-0.582671000000	0.505971000000
H	6.867230000000	-0.784143000000	0.680639000000
C	4.874129000000	-1.621195000000	0.524827000000
H	5.171972000000	-2.647641000000	0.662693000000
C	-0.787601000000	3.044828000000	-0.295492000000
H	-0.074890000000	3.869325000000	-0.227416000000
H	-1.447042000000	3.096142000000	0.575502000000
H	-1.396532000000	3.169914000000	-1.192419000000
C	-1.656664000000	-0.222925000000	-0.669073000000
C	-2.882326000000	0.451283000000	-0.647538000000
H	-2.909843000000	1.531838000000	-0.595812000000
C	-4.054869000000	-0.288958000000	-0.667295000000
H	-5.011733000000	0.220208000000	-0.632995000000
C	-3.986744000000	-1.680837000000	-0.698435000000
H	-4.876520000000	-2.297357000000	-0.697909000000
C	-2.729759000000	-2.275227000000	-0.721749000000
H	-2.610860000000	-3.352935000000	-0.745100000000

Table S7. Optimized geometry of the **second singlet excited state** of **$ZnHLCl_2$** (**tautomeric form**, **S_2^T**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the M062X/6-31+g(d) level of theory **using the QM/MM method (QM region)**.

Cl	0.764481000000	-3.865582000000	0.818465000000
Cl	0.853504000000	-2.678844000000	-3.078942000000
Zn	0.399155000000	-2.448481000000	-0.892521000000
N	-1.586193000000	-1.574380000000	-0.672761000000
N	1.317573000000	1.776583000000	-0.157395000000
O	2.069383000000	2.786111000000	0.041026000000
H	3.769342000000	1.946039000000	0.111197000000
N	4.098232000000	0.982560000000	0.190765000000
C	3.502993000000	-1.326338000000	0.219365000000
H	2.754746000000	-2.104545000000	0.254385000000
N	0.783898000000	-0.356088000000	-0.394721000000
C	-0.370169000000	0.442383000000	-0.498928000000
C	-0.034127000000	1.777472000000	-0.361160000000
C	1.783782000000	0.441898000000	-0.178948000000
C	3.157000000000	0.033371000000	0.080046000000
C	5.396836000000	0.736560000000	0.421716000000
H	6.049122000000	1.589447000000	0.509160000000
C	5.819088000000	-0.627169000000	0.508470000000
H	6.863588000000	-0.848467000000	0.658570000000
C	4.877101000000	-1.615977000000	0.405755000000
H	5.175485000000	-2.654647000000	0.471964000000
C	-0.793231000000	3.056092000000	-0.348163000000
H	-0.086466000000	3.888297000000	-0.338187000000
H	-1.425313000000	3.137266000000	0.540824000000
H	-1.429562000000	3.139871000000	-1.230564000000
C	-1.646272000000	-0.223068000000	-0.617609000000
C	-2.875374000000	0.450131000000	-0.608361000000
H	-2.904543000000	1.530402000000	-0.552407000000
C	-4.046365000000	-0.289569000000	-0.646487000000
H	-5.004475000000	0.217455000000	-0.619314000000
C	-3.974230000000	-1.683732000000	-0.683162000000

H	-4.863020000000	-2.301783000000	-0.692838000000
C	-2.716095000000	-2.277637000000	-0.692290000000
H	-2.598283000000	-3.355681000000	-0.715083000000

Table S8. Optimized geometry of the **ground state** of **$ZnHLCl_2$** (**minor component**, **S_0^{minor}**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the M062X/6-31+g(d) level of theory **using the QM/MM method (QM region)**.

Cl	0.599908000000	-3.704082000000	0.684290000000
Cl	0.945568000000	-2.668690000000	-2.954056000000
Zn	1.615361000000	-2.297303000000	-0.830635000000
N	-1.649267000000	-1.605819000000	-0.464626000000
N	1.352632000000	1.783122000000	-0.152534000000
O	2.065994000000	2.846607000000	0.023328000000
N	3.385662000000	-1.271445000000	-0.153287000000
C	4.218337000000	0.927093000000	0.365884000000
H	3.980072000000	1.976854000000	0.471783000000
N	0.813308000000	-0.367075000000	-0.351830000000
C	-0.319396000000	0.380998000000	-0.449015000000
C	0.001877000000	1.743226000000	-0.332608000000
C	1.811407000000	0.493031000000	-0.175200000000
C	3.185278000000	0.057426000000	0.011828000000
C	4.602625000000	-1.770250000000	0.079496000000
H	4.713331000000	-2.842236000000	-0.033948000000
C	5.682027000000	-0.976134000000	0.446114000000
H	6.649096000000	-1.429561000000	0.618386000000
C	5.485297000000	0.396401000000	0.568705000000
H	6.311546000000	1.050361000000	0.825844000000
C	-0.773664000000	3.010688000000	-0.344728000000
H	-0.056687000000	3.833389000000	-0.283595000000
H	-1.457187000000	3.086987000000	0.507016000000
H	-1.355878000000	3.112908000000	-1.263948000000
C	-1.600310000000	-0.252864000000	-0.539910000000
C	-2.829455000000	0.420126000000	-0.655925000000
H	-2.834169000000	1.501048000000	-0.675599000000
C	-4.007068000000	-0.296161000000	-0.717525000000
H	-4.949058000000	0.238585000000	-0.773613000000
C	-3.993368000000	-1.701069000000	-0.703638000000
H	-4.900594000000	-2.286139000000	-0.763087000000
C	-2.777894000000	-2.328169000000	-0.573028000000
H	-2.639259000000	-3.399607000000	-0.513751000000
H	-0.798847000000	-2.136472000000	-0.225490000000

Table S9. Optimized geometry of the **first singlet excited state** of **$ZnHLCl_2$** (**minor component**, **S_1^{minor}**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the M062X/6-31+g(d) level of theory **using the QM/MM method (QM region)**.

Cl	0.757770000000	-3.694794000000	0.777121000000
Cl	0.994920000000	-2.656824000000	-2.981516000000
Zn	1.583194000000	-2.315583000000	-0.840273000000
N	-1.618148000000	-1.591515000000	-0.450163000000
N	1.353534000000	1.797367000000	-0.171740000000
O	2.041921000000	2.844722000000	-0.015180000000

N	3.378935000000	-1.271401000000	-0.175356000000
C	4.248814000000	0.909146000000	0.370934000000
H	4.053563000000	1.962024000000	0.504641000000
N	0.817351000000	-0.331832000000	-0.353107000000
C	-0.339980000000	0.432653000000	-0.443240000000
C	-0.029220000000	1.767083000000	-0.338545000000
C	1.830609000000	0.495320000000	-0.182273000000
C	3.199373000000	0.061230000000	0.002500000000
C	4.587421000000	-1.787558000000	0.059597000000
H	4.682579000000	-2.860153000000	-0.058786000000
C	5.680266000000	-1.015359000000	0.435016000000
H	6.639134000000	-1.485115000000	0.607457000000
C	5.506209000000	0.360966000000	0.570570000000
H	6.340151000000	1.000430000000	0.838174000000
C	-0.809000000000	3.030762000000	-0.335678000000
H	-0.125656000000	3.876536000000	-0.241127000000
H	-1.514056000000	3.060240000000	0.499503000000
H	-1.375897000000	3.136103000000	-1.262945000000
C	-1.639742000000	-0.212706000000	-0.533036000000
C	-2.851652000000	0.429110000000	-0.662654000000
H	-2.872435000000	1.509686000000	-0.709934000000
C	-4.047225000000	-0.299068000000	-0.725629000000
H	-4.995338000000	0.217721000000	-0.784479000000
C	-3.975931000000	-1.712204000000	-0.714299000000
H	-4.865098000000	-2.323851000000	-0.799143000000
C	-2.760620000000	-2.327716000000	-0.577725000000
H	-2.620947000000	-3.398881000000	-0.536995000000
H	-0.791801000000	-2.078595000000	-0.101289000000

Table S10. Optimized geometry of the **ground state** of **$ZnHLBr_2$** (**normal form**, **S_0^N**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the M062X/6-31+g(d) level of theory **using the QM/MM method (QM region)**.

Br	0.868164000000	-3.966194000000	0.909353000000
Br	0.915945000000	-2.670581000000	-3.162031000000
Zn	0.371061000000	-2.429764000000	-0.853635000000
N	-1.603133000000	-1.551249000000	-0.641524000000
N	1.404422000000	1.705075000000	-0.105190000000
O	2.162676000000	2.814973000000	0.111314000000
H	3.091717000000	2.435908000000	0.188252000000
N	4.101874000000	1.034280000000	0.229369000000
C	3.606965000000	-1.317890000000	0.105847000000
H	2.878671000000	-2.114500000000	0.003989000000
N	0.799248000000	-0.371649000000	-0.344542000000
C	-0.309792000000	0.424111000000	-0.421813000000
C	0.053447000000	1.755279000000	-0.271704000000
C	1.839045000000	0.418509000000	-0.147639000000
C	3.231671000000	0.024644000000	0.058443000000
C	5.384136000000	0.737341000000	0.449639000000
H	6.057684000000	1.576985000000	0.586073000000
C	5.851109000000	-0.570312000000	0.512728000000
H	6.898555000000	-0.762669000000	0.703765000000
C	4.941955000000	-1.611058000000	0.339904000000
H	5.255832000000	-2.646106000000	0.398031000000

C	-0.689748000000	3.046087000000	-0.242246000000
H	0.016682000000	3.875280000000	-0.175787000000
H	-1.360381000000	3.101875000000	0.620141000000
H	-1.288730000000	3.167851000000	-1.147639000000
C	-1.623640000000	-0.208959000000	-0.557401000000
C	-2.830815000000	0.491296000000	-0.542943000000
H	-2.834174000000	1.570520000000	-0.468741000000
C	-4.022642000000	-0.219321000000	-0.605503000000
H	-4.967408000000	0.313066000000	-0.577383000000
C	-3.991053000000	-1.609860000000	-0.672941000000
H	-4.896034000000	-2.204832000000	-0.704296000000
C	-2.748592000000	-2.231004000000	-0.687713000000
H	-2.651172000000	-3.308927000000	-0.735699000000

Table S11. Optimized geometry of the **ground state** of **$ZnHLBr_2$** (local minimum in the **tautomeric form**, **S_0^T**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the M062X/6-31+g(d) level of theory **using the QM/MM method (QM region)**.

Br	0.813652000000	-3.956640000000	0.858010000000
Br	0.922866000000	-2.652469000000	-3.226040000000
Zn	0.406414000000	-2.415025000000	-0.921330000000
N	-1.572607000000	-1.530839000000	-0.694000000000
N	1.371044000000	1.746336000000	0.008850000000
O	2.087732000000	2.747895000000	0.385040000000
H	3.758230000000	2.020455000000	0.025810000000
N	4.166453000000	1.001060000000	0.022210000000
C	3.564920000000	-1.287048000000	0.343600000000
H	2.800589000000	-2.051427000000	0.416930000000
N	0.818069000000	-0.334540000000	-0.404140000000
C	-0.330341000000	0.471056000000	-0.472800000000
C	0.011793000000	1.781710000000	-0.250460000000
C	1.818079000000	0.434732000000	-0.102750000000
C	3.210204000000	0.017108000000	0.124350000000
C	5.479476000000	0.703515000000	0.268660000000
H	6.175136000000	1.528544000000	0.234670000000
C	5.870932000000	-0.595290000000	0.478740000000
H	6.920884000000	-0.804467000000	0.631680000000
C	4.921734000000	-1.627671000000	0.491070000000
H	5.211466000000	-2.658638000000	0.629180000000
C	-0.734972000000	3.066201000000	-0.177510000000
H	-0.025482000000	3.884659000000	-0.041470000000
H	-1.432842000000	3.078583000000	0.664090000000
H	-1.304394000000	3.235114000000	-1.093740000000
C	-1.619663000000	-0.186230000000	-0.614390000000
C	-2.842031000000	0.492236000000	-0.591540000000
H	-2.864744000000	1.571945000000	-0.524330000000
C	-4.018982000000	-0.241418000000	-0.635900000000
H	-4.973229000000	0.273150000000	-0.602860000000
C	-3.959786000000	-1.632488000000	-0.694990000000
H	-4.853678000000	-2.244328000000	-0.718750000000
C	-2.705189000000	-2.230803000000	-0.721660000000
H	-2.588136000000	-3.307091000000	-0.771230000000

Table S12. Optimized geometry of the **first singlet excited state** of **$ZnHLBr_2$** (**tautomeric form**, **S_1^T**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the M062X/6-31+g(d) level of theory **using the QM/MM method (QM region)**.

Br	0.805773000000	-3.955046000000	0.849692000000
Br	0.923774000000	-2.649657000000	-3.236166000000
Zn	0.411395000000	-2.412689000000	-0.931986000000
N	-1.568306000000	-1.527663000000	-0.702476000000
N	1.366264000000	1.752455000000	0.024155000000
O	2.077019000000	2.738524000000	0.423162000000
H	3.853435000000	1.961289000000	0.001625000000
N	4.175647000000	0.996495000000	-0.008371000000
C	3.558858000000	-1.282454000000	0.376578000000
H	2.789363000000	-2.042211000000	0.474943000000
N	0.820717000000	-0.329010000000	-0.413641000000
C	-0.333314000000	0.478003000000	-0.481065000000
C	0.005827000000	1.785728000000	-0.248407000000
C	1.815048000000	0.437269000000	-0.097322000000
C	3.207094000000	0.016224000000	0.132785000000
C	5.493071000000	0.698848000000	0.241824000000
H	6.191894000000	1.521778000000	0.183490000000
C	5.873713000000	-0.598702000000	0.472901000000
H	6.924027000000	-0.810289000000	0.620401000000
C	4.918782000000	-1.629876000000	0.511679000000
H	5.205048000000	-2.660254000000	0.661220000000
C	-0.741428000000	3.069323000000	-0.169247000000
H	-0.031489000000	3.886242000000	-0.023262000000
H	-1.443189000000	3.075511000000	0.669384000000
H	-1.306630000000	3.244984000000	-1.087024000000
C	-1.619134000000	-0.182717000000	-0.623516000000
C	-2.843668000000	0.492651000000	-0.599460000000
H	-2.869124000000	1.572431000000	-0.533257000000
C	-4.018504000000	-0.244280000000	-0.641221000000
H	-4.974098000000	0.267752000000	-0.607485000000
C	-3.955379000000	-1.635424000000	-0.699122000000
H	-4.847700000000	-2.249668000000	-0.721795000000
C	-2.699054000000	-2.230498000000	-0.727488000000
H	-2.579210000000	-3.306550000000	-0.777286000000

Table S13. Optimized geometry of the **ground state** of **$ZnHLBr_2$** (**minor component**, **S_0^{minor}**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the M062X/6-31+g(d) level of theory **using the QM/MM method (QM region)**.

Br	0.713992000000	-3.802297000000	0.764890000000
Br	0.963526000000	-2.641173000000	-3.095504000000
Zn	1.676720000000	-2.244042000000	-0.847539000000
N	-1.607218000000	-1.561272000000	-0.450685000000
N	1.386909000000	1.831301000000	-0.100001000000
O	2.096366000000	2.897417000000	0.081530000000
N	3.446331000000	-1.201941000000	-0.216314000000
C	4.267714000000	0.986171000000	0.352952000000
H	4.020018000000	2.028587000000	0.501841000000
N	0.857694000000	-0.319263000000	-0.334030000000

C	-0.280234000000	0.426023000000	-0.408713000000
C	0.035044000000	1.786981000000	-0.268654000000
C	1.852415000000	0.544183000000	-0.150114000000
C	3.235293000000	0.117977000000	-0.005283000000
C	4.672643000000	-1.697228000000	-0.032121000000
H	4.786681000000	-2.764438000000	-0.189206000000
C	5.752659000000	-0.903812000000	0.336681000000
H	6.729029000000	-1.351281000000	0.472682000000
C	5.544588000000	0.461971000000	0.510580000000
H	6.370098000000	1.115517000000	0.774600000000
C	-0.747072000000	3.050635000000	-0.257022000000
H	-0.034367000000	3.874229000000	-0.164562000000
H	-1.442836000000	3.099602000000	0.586557000000
H	-1.315833000000	3.176611000000	-1.182351000000
C	-1.560425000000	-0.207864000000	-0.507893000000
C	-2.792005000000	0.461346000000	-0.617389000000
H	-2.799924000000	1.542271000000	-0.627987000000
C	-3.967511000000	-0.258128000000	-0.689196000000
H	-4.910474000000	0.275147000000	-0.745882000000
C	-3.951439000000	-1.663147000000	-0.686588000000
H	-4.858223000000	-2.250372000000	-0.752034000000
C	-2.733499000000	-2.286550000000	-0.560924000000
H	-2.588480000000	-3.357037000000	-0.509316000000
H	-0.752206000000	-2.089079000000	-0.228403000000

Table S14. Optimized geometry of the **first singlet excited state** of **$ZnHLBr_2$** (**minor component**, **S_1^{minor}**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the M062X/6-31+g(d) level of theory **using the QM/MM method (QM region)**.

Br	0.886794000000	-3.780615000000	0.857337000000
Br	1.014114000000	-2.628138000000	-3.125610000000
Zn	1.645494000000	-2.261271000000	-0.861017000000
N	-1.575946000000	-1.547547000000	-0.434130000000
N	1.386523000000	1.848266000000	-0.119157000000
O	2.070347000000	2.898591000000	0.040765000000
N	3.437138000000	-1.199352000000	-0.243888000000
C	4.297411000000	0.966664000000	0.361439000000
H	4.093677000000	2.010789000000	0.543022000000
N	0.860691000000	-0.281866000000	-0.334850000000
C	-0.302092000000	0.478767000000	-0.401708000000
C	0.002173000000	1.812409000000	-0.272669000000
C	1.870720000000	0.549164000000	-0.158522000000
C	3.247857000000	0.123285000000	-0.015786000000
C	4.653958000000	-1.714940000000	-0.057638000000
H	4.750418000000	-2.782362000000	-0.223779000000
C	5.747900000000	-0.946325000000	0.324134000000
H	6.715747000000	-1.411109000000	0.460915000000
C	5.563807000000	0.422459000000	0.515520000000
H	6.397502000000	1.059052000000	0.793876000000
C	-0.784185000000	3.071931000000	-0.247535000000
H	-0.105615000000	3.917743000000	-0.121937000000
H	-1.500957000000	3.075233000000	0.578066000000
H	-1.337786000000	3.200341000000	-1.180638000000

C	-1.600895000000	-0.168234000000	-0.501148000000
C	-2.815267000000	0.468959000000	-0.627516000000
H	-2.839770000000	1.549754000000	-0.665829000000
C	-4.008268000000	-0.263054000000	-0.701003000000
H	-4.957307000000	0.251592000000	-0.765153000000
C	-3.933865000000	-1.676032000000	-0.697018000000
H	-4.822472000000	-2.289969000000	-0.785886000000
C	-2.716231000000	-2.287165000000	-0.561770000000
H	-2.570400000000	-3.357087000000	-0.524742000000
H	-0.744361000000	-2.032821000000	-0.098381000000

Table S15. Optimized geometry of the **ground state** of **$ZnHLI_2$** (**normal form**, **S_0^N**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the M062X/6-31+g(d) level of theory **using the QM/MM method (QM region)**.

I	-0.831065000000	-4.189703000000	-1.018188000000
I	-0.929714000000	-2.675743000000	3.336445000000
Zn	-0.355745000000	-2.415383000000	0.819960000000
N	1.593346000000	-1.502155000000	0.599297000000
N	-1.482091000000	1.688156000000	0.045053000000
O	-2.267757000000	2.783996000000	-0.145718000000
H	-3.195342000000	2.394032000000	-0.149824000000
N	-4.186357000000	0.972260000000	-0.124531000000
C	-3.645363000000	-1.370100000000	-0.034898000000
H	-2.899436000000	-2.154593000000	0.017065000000
N	-0.832035000000	-0.375567000000	0.281323000000
C	0.264203000000	0.442101000000	0.326987000000
C	-0.127903000000	1.764872000000	0.177423000000
C	-1.892123000000	0.394607000000	0.108125000000
C	-3.288766000000	-0.022096000000	-0.015257000000
C	-5.476398000000	0.652465000000	-0.247995000000
H	-6.173700000000	1.480020000000	-0.328224000000
C	-5.925983000000	-0.663155000000	-0.271997000000
H	-6.983540000000	-0.873392000000	-0.370120000000
C	-4.988754000000	-1.687979000000	-0.168342000000
H	-5.286817000000	-2.729315000000	-0.199450000000
C	0.589168000000	3.070673000000	0.135943000000
H	1.228498000000	3.149086000000	-0.748338000000
H	1.215304000000	3.197210000000	1.022732000000
H	-0.135697000000	3.885855000000	0.103204000000
C	1.591104000000	-0.163829000000	0.466118000000
C	2.787685000000	0.553041000000	0.420146000000
H	2.773015000000	1.628143000000	0.301453000000
C	3.990811000000	-0.137097000000	0.506425000000
H	4.928659000000	0.405642000000	0.450401000000
C	3.981008000000	-1.523921000000	0.631028000000
H	4.895396000000	-2.103646000000	0.678563000000
C	2.748528000000	-2.162833000000	0.672745000000
H	2.666196000000	-3.239474000000	0.761209000000

Table S16. Optimized geometry of the **ground state** of **$ZnHLI_2$** (local minimum in the **tautomeric form**, **S_0^T**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the M062X/6-31+g(d) level of theory **using the QM/MM method (QM region)**.

I	-0.756456000000	-4.187570000000	-0.966630000000
I	-0.927218000000	-2.656003000000	3.398490000000
Zn	-0.386336000000	-2.404193000000	0.884650000000
N	1.567887000000	-1.484030000000	0.653290000000
N	-1.453148000000	1.725299000000	-0.068110000000
O	-2.199590000000	2.710184000000	-0.423740000000
H	-3.867855000000	1.958993000000	0.046190000000
N	-4.238061000000	0.942576000000	0.073630000000
C	-3.626334000000	-1.340540000000	-0.261510000000
H	-2.858718000000	-2.095914000000	-0.378400000000
N	-0.851077000000	-0.342687000000	0.344860000000
C	0.285023000000	0.486196000000	0.381810000000
C	-0.087752000000	1.787769000000	0.158070000000
C	-1.874081000000	0.406378000000	0.066810000000
C	-3.272089000000	-0.029364000000	-0.081200000000
C	-5.560897000000	0.620959000000	-0.072750000000
H	-6.264987000000	1.436777000000	0.008470000000
C	-5.947641000000	-0.686379000000	-0.233480000000
H	-7.004895000000	-0.913247000000	-0.285630000000
C	-4.983967000000	-1.705579000000	-0.309400000000
H	-5.263331000000	-2.743909000000	-0.420650000000
C	0.628653000000	3.089631000000	0.078750000000
H	1.297980000000	3.131140000000	-0.785190000000
H	1.222460000000	3.260705000000	0.979930000000
H	-0.103886000000	3.893078000000	-0.020970000000
C	1.588669000000	-0.142499000000	0.526550000000
C	2.799358000000	0.555380000000	0.470250000000
H	2.801409000000	1.631680000000	0.359300000000
C	3.989710000000	-0.156013000000	0.533740000000
H	4.936151000000	0.370426000000	0.467800000000
C	3.955681000000	-1.544466000000	0.648660000000
H	4.860585000000	-2.140070000000	0.680500000000
C	2.712246000000	-2.163087000000	0.704600000000
H	2.612795000000	-3.239144000000	0.788810000000

Table S17. Optimized geometry of the **first singlet excited state** of **$ZnHLI_2$** (**tautomeric form**, **S_1^T**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the M062X/6-31+g(d) level of theory **using the QM/MM method (QM region)**.

I	-0.747937000000	-4.187458000000	-0.959594000000
I	-0.926527000000	-2.652996000000	3.406523000000
Zn	-0.389241000000	-2.403074000000	0.892883000000
N	1.565540000000	-1.482137000000	0.659682000000
N	-1.449229000000	1.729579000000	-0.079486000000
O	-2.191143000000	2.702221000000	-0.453797000000
H	-3.941540000000	1.911176000000	0.068060000000
N	-4.243205000000	0.939909000000	0.096833000000
C	-3.624125000000	-1.336989000000	-0.284960000000
H	-2.854376000000	-2.089531000000	-0.420244000000
N	-0.852829000000	-0.338941000000	0.352969000000
C	0.287673000000	0.490922000000	0.388926000000
C	-0.082785000000	1.790321000000	0.157402000000
C	-1.871740000000	0.407891000000	0.063606000000

C	-3.269786000000	-0.029884000000	-0.087050000000
C	-5.569630000000	0.618286000000	-0.052014000000
H	-6.274197000000	1.433005000000	0.047664000000
C	-5.949791000000	-0.688040000000	-0.227888000000
H	-7.007040000000	-0.916628000000	-0.274867000000
C	-4.983348000000	-1.706740000000	-0.323606000000
H	-5.260927000000	-2.744640000000	-0.444052000000
C	0.633875000000	3.091613000000	0.073747000000
H	1.308788000000	3.127580000000	-0.786212000000
H	1.221771000000	3.269075000000	0.977766000000
H	-0.099168000000	3.893645000000	-0.036563000000
C	1.588733000000	-0.140138000000	0.534310000000
C	2.800945000000	0.555747000000	0.477462000000
H	2.804812000000	1.632258000000	0.367984000000
C	3.989946000000	-0.157890000000	0.538316000000
H	4.937279000000	0.366912000000	0.471757000000
C	3.953375000000	-1.546591000000	0.651520000000
H	4.857279000000	-2.143859000000	0.681652000000
C	2.708766000000	-2.163085000000	0.708513000000
H	2.607507000000	-3.239136000000	0.791726000000

Table S18. Optimized geometry of the **ground state** of **$ZnHLI_2$** (**minor component**, **S_0^{minor}**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the M062X/6-31+g(d) level of theory **using the QM/MM method (QM region)**.

I	-0.768892000000	-4.032322000000	-0.939552000000
I	-0.900065000000	-2.660589000000	3.247742000000
Zn	-1.689141000000	-2.257473000000	0.798440000000
N	1.592148000000	-1.513659000000	0.372194000000
N	-1.469620000000	1.822556000000	0.029044000000
O	-2.199526000000	2.877242000000	-0.137060000000
N	-3.480628000000	-1.237325000000	0.235783000000
C	-4.366382000000	0.938782000000	-0.268939000000
H	-4.149917000000	1.988483000000	-0.415933000000
N	-0.901918000000	-0.319679000000	0.262003000000
C	0.226472000000	0.445580000000	0.307049000000
C	-0.113141000000	1.800054000000	0.165383000000
C	-1.915091000000	0.528946000000	0.099089000000
C	-3.299828000000	0.086346000000	0.022354000000
C	-4.704880000000	-1.756902000000	0.115994000000
H	-4.787154000000	-2.827857000000	0.276581000000
C	-5.815927000000	-0.980926000000	-0.194014000000
H	-6.791733000000	-1.442166000000	-0.285123000000
C	-5.639555000000	0.389652000000	-0.367496000000
H	-6.489063000000	1.029338000000	-0.587426000000
C	0.649970000000	3.075824000000	0.132945000000
H	1.350206000000	3.118591000000	-0.707440000000
H	1.211003000000	3.231584000000	1.059443000000
H	-0.075245000000	3.886092000000	0.021993000000
C	1.519674000000	-0.160936000000	0.412018000000
C	2.740004000000	0.529369000000	0.521306000000
H	2.730644000000	1.610450000000	0.516815000000
C	3.926306000000	-0.170595000000	0.616970000000

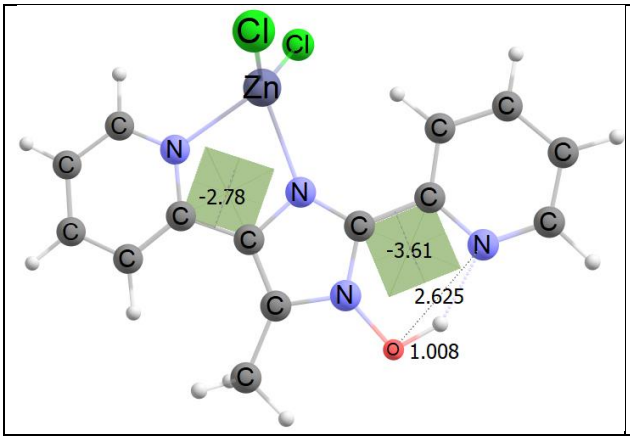
H	4.861515000000	0.376964000000	0.672469000000
C	3.933456000000	-1.575590000000	0.637385000000
H	4.849956000000	-2.146362000000	0.716820000000
C	2.727415000000	-2.220350000000	0.506388000000
H	2.595498000000	-3.293029000000	0.468471000000
H	0.748158000000	-2.055261000000	0.152084000000

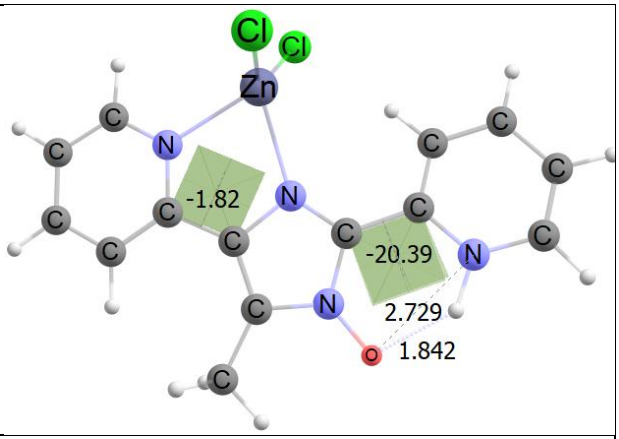
Table S19. Optimized geometry of the **first singlet excited state** of **$ZnHLI_2$** (**minor component**, **S_1^{minor}**) in Cartesian (XYZ) coordinates as calculated in Gaussian at the M062X/6-31+g(d) level of theory **using the QM/MM method (QM region)**.

I	-0.900558000000	-4.022685000000	-0.990893000000
I	-0.981731000000	-2.633426000000	3.289991000000
Zn	-1.653164000000	-2.269754000000	0.814181000000
N	1.555306000000	-1.498776000000	0.353809000000
N	-1.468542000000	1.842442000000	0.046129000000
O	-2.173129000000	2.880785000000	-0.105270000000
N	-3.464488000000	-1.237371000000	0.252159000000
C	-4.396572000000	0.918516000000	-0.268813000000
H	-4.227648000000	1.971565000000	-0.434336000000
N	-0.904057000000	-0.278850000000	0.261757000000
C	0.248428000000	0.503126000000	0.301789000000
C	-0.080762000000	1.830656000000	0.167072000000
C	-1.932463000000	0.536446000000	0.108017000000
C	-3.309708000000	0.090882000000	0.031412000000
C	-4.678726000000	-1.778324000000	0.129862000000
H	-4.740156000000	-2.850392000000	0.292988000000
C	-5.805738000000	-1.027137000000	-0.185754000000
H	-6.772261000000	-1.506422000000	-0.278858000000
C	-5.657360000000	0.347942000000	-0.366479000000
H	-6.517107000000	0.970778000000	-0.593839000000
C	0.686274000000	3.102448000000	0.122385000000
H	1.408255000000	3.101363000000	-0.699060000000
H	1.232127000000	3.259732000000	1.056699000000
H	-0.004822000000	3.935041000000	-0.022184000000
C	1.558658000000	-0.118270000000	0.402006000000
C	2.765701000000	0.535926000000	0.529173000000
H	2.776615000000	1.617570000000	0.553355000000
C	3.965645000000	-0.180828000000	0.626504000000
H	4.909908000000	0.344006000000	0.687838000000
C	3.910078000000	-1.595238000000	0.644228000000
H	4.806968000000	-2.195593000000	0.744844000000
C	2.701910000000	-2.222990000000	0.502897000000
H	2.565117000000	-3.294454000000	0.475676000000
H	0.735174000000	-1.997208000000	0.011720000000

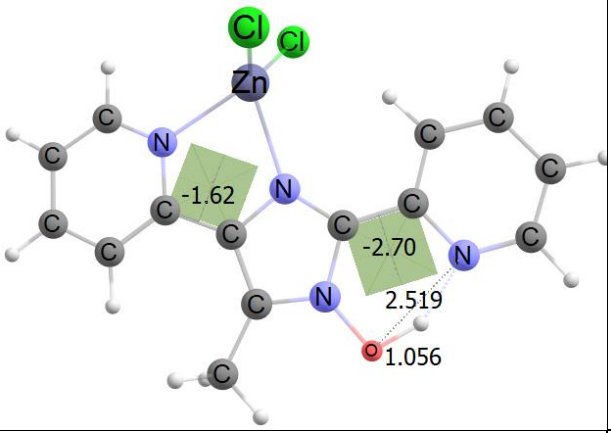
Table S20. Optimized geometries of the ground and excited states of **$ZnHLCl_2$**. Dihedral angles between the planes of aromatic heterocycles are shown for both major and minor components. In the case of the major component, O...H and O…N distances are also shown.

Normal form of the major component, ground state (S_0^N)	**Tautomeric form of the major component, ground state (S_0^T)**

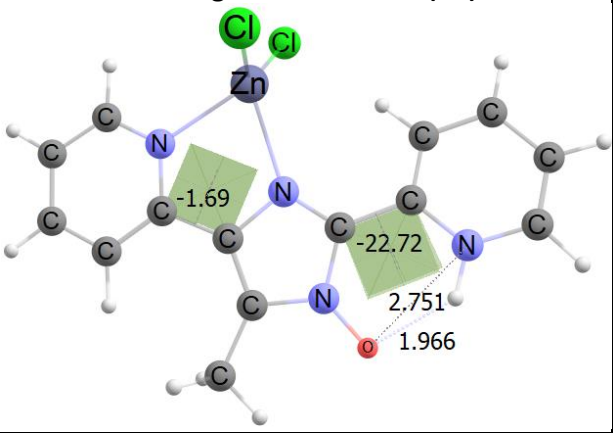




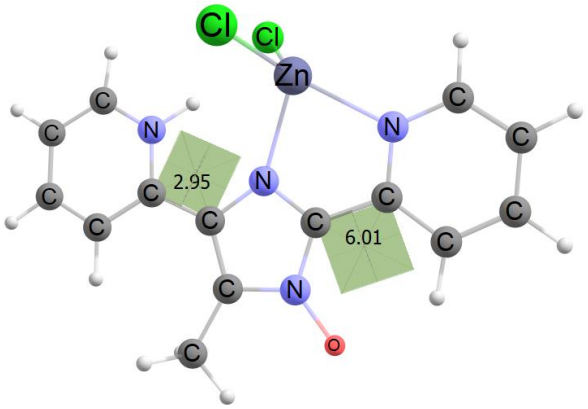
Normal form of the major component, first singlet excited state (S_1^N)



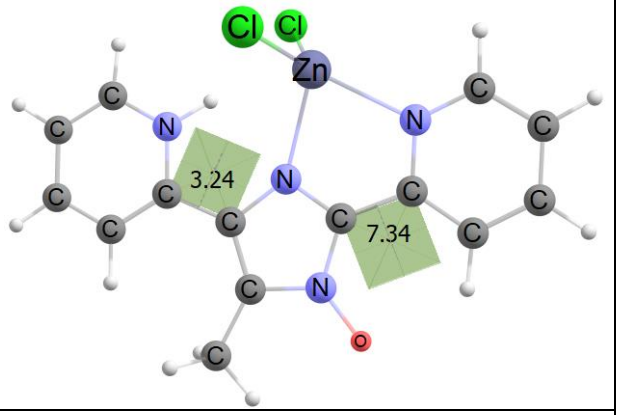
Tautomeric form of the major component, first singlet excited state (S_1^T)



Minor component, ground state (S_0^{minor})



Minor component, first singlet excited state (S_1^{minor})



Tautomeric form of the major component, second singlet excited state (S_2^T)

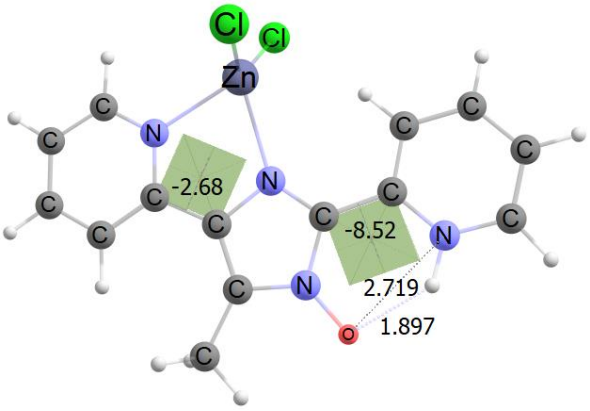


Table S21. Optimized geometries of the ground and excited states of **ZnHLBr$_2$**. Dihedral angles between the planes of aromatic heterocycles are shown for both major and minor components. In the case of the major component, O...H and O…N distances are also shown.

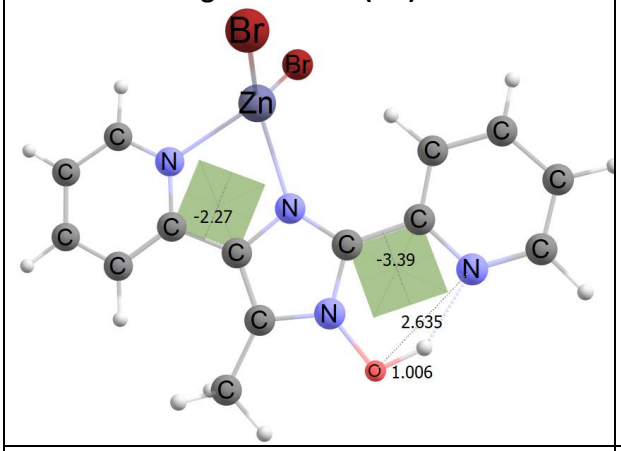
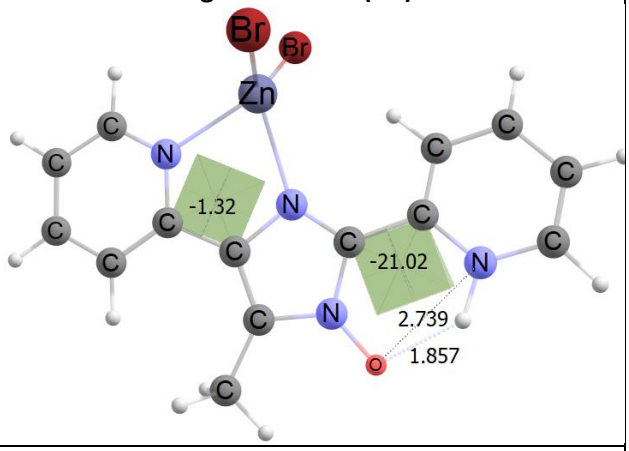
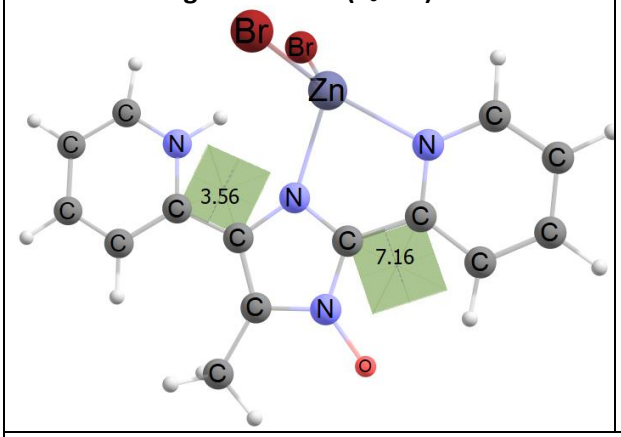
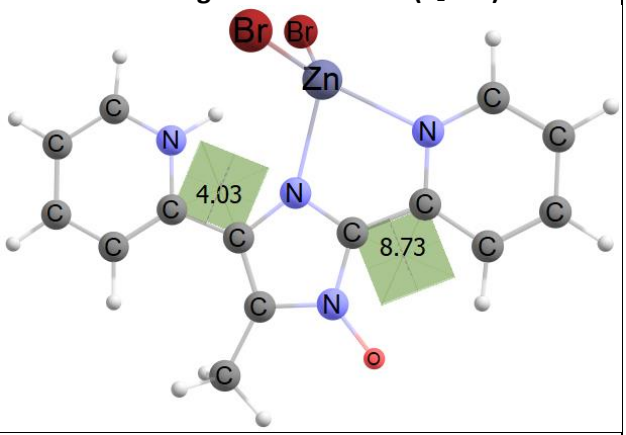
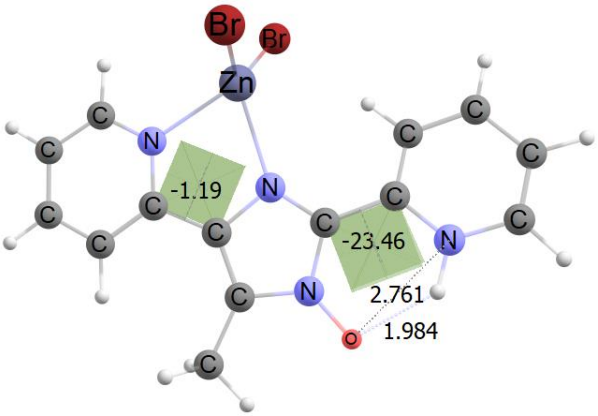
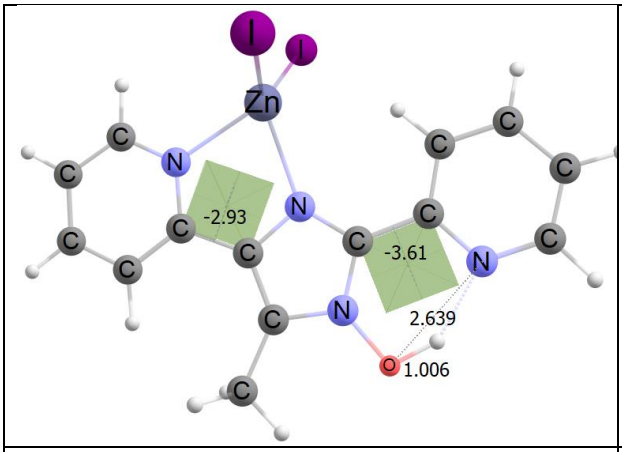
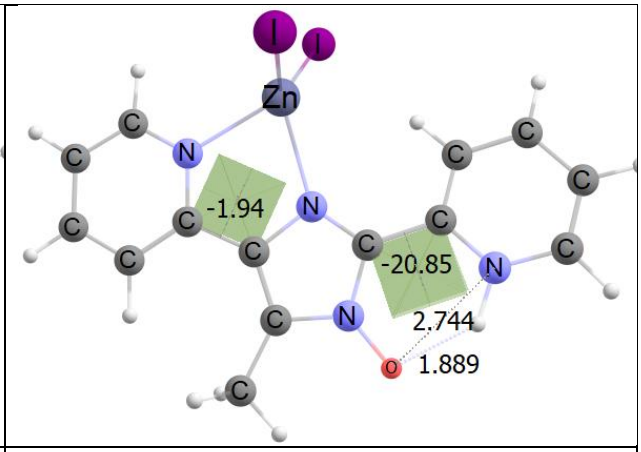
Normal form of the major component, ground state (S_0^N)	**Tautomeric form of the major component, ground state (S_0^T)**
	
Minor component, ground state (S_0^{minor})	**Minor component, first singlet excited state (S_1^{minor})**
	
Tautomeric form of the major component, first singlet excited state (S_1^T)	
	

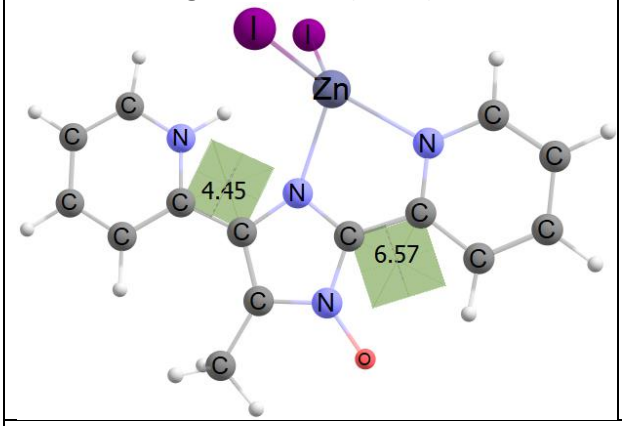
Table S22. Optimized geometries of the ground and excited states of **ZnHLI$_2$**. Dihedral angles between the planes of aromatic heterocycles are shown for both major and minor components. In the case of the major component, O...H and O…N distances are also shown.

Normal form of the major component, ground state (S_0^N)	**Tautomeric form of the major component, ground state (S_0^T)**

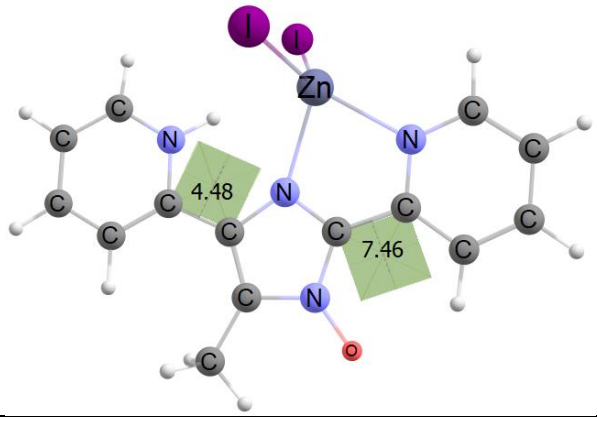




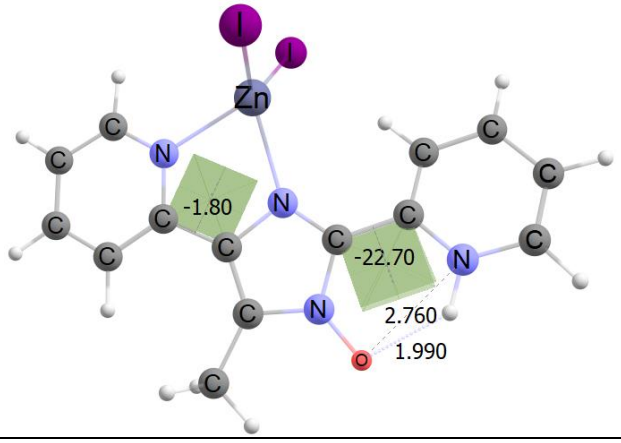
Minor component, ground state (S_0^{minor})



Minor component, first singlet excited state (S_1^{minor})



Tautomeric form of the major component, first singlet excited state (S_1^{T})



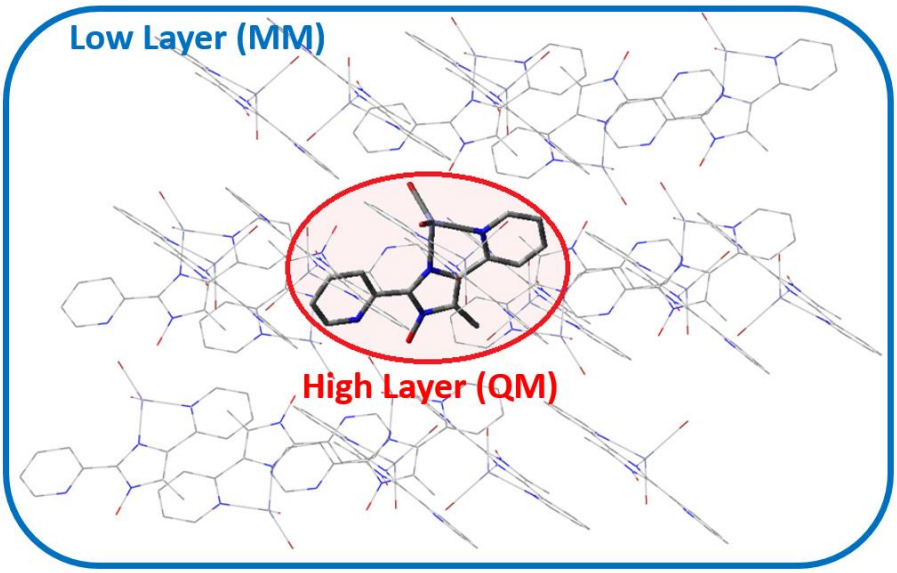


Figure S26. ONIOM model for the quantum chemical calculations of **$ZnHLBr_2$**.

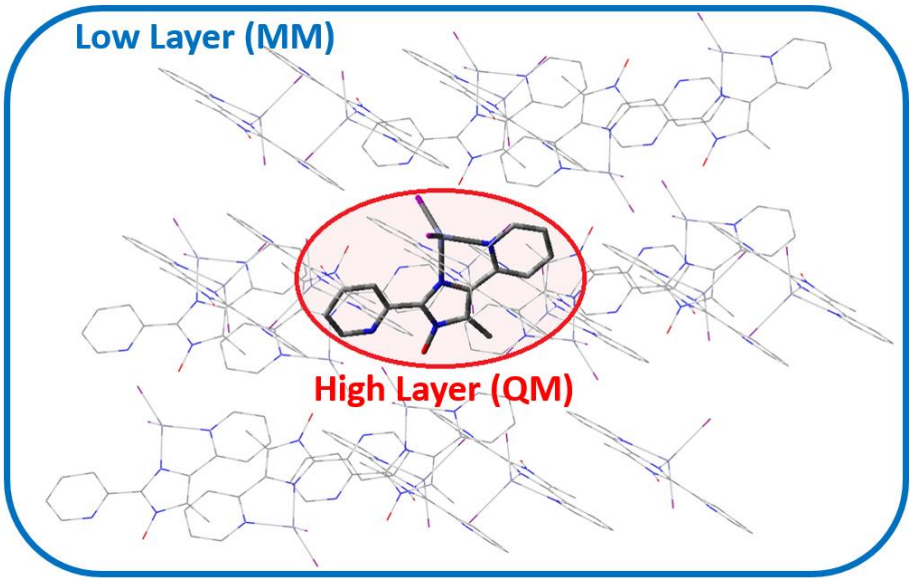


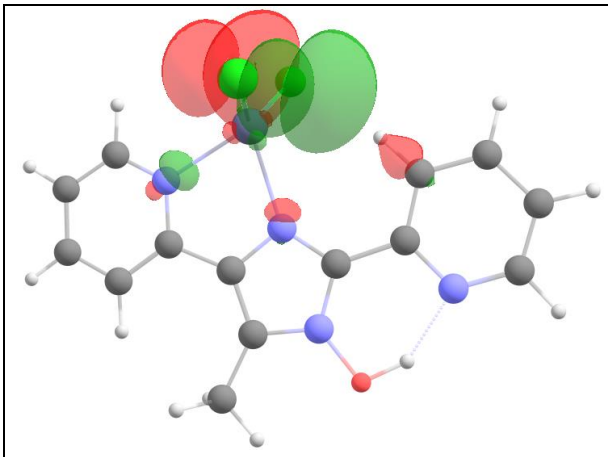
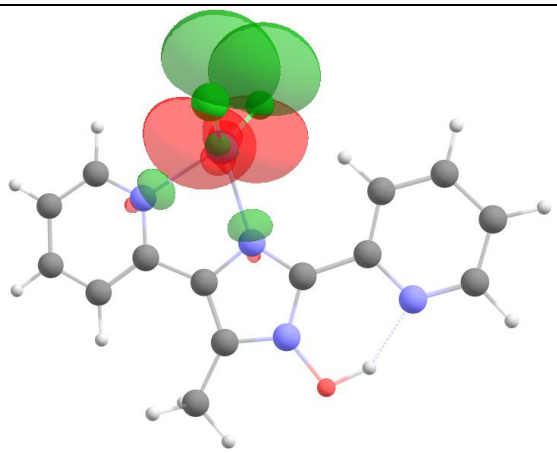
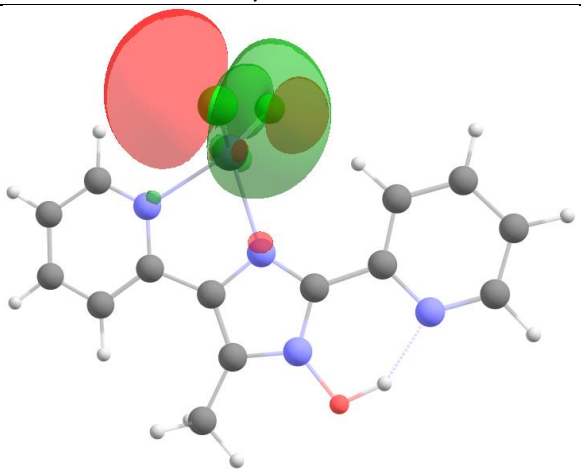
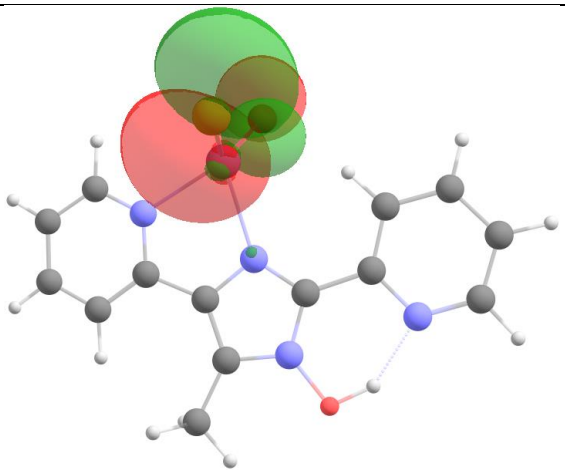
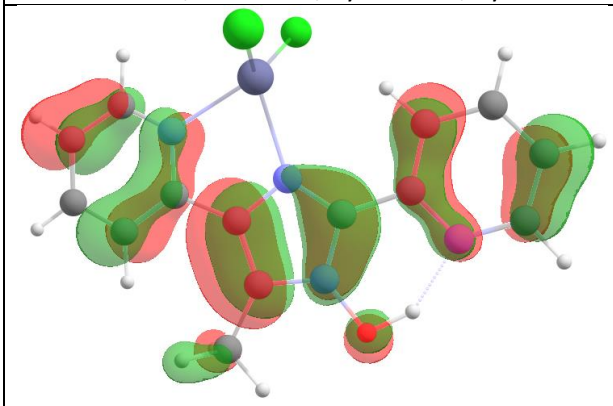
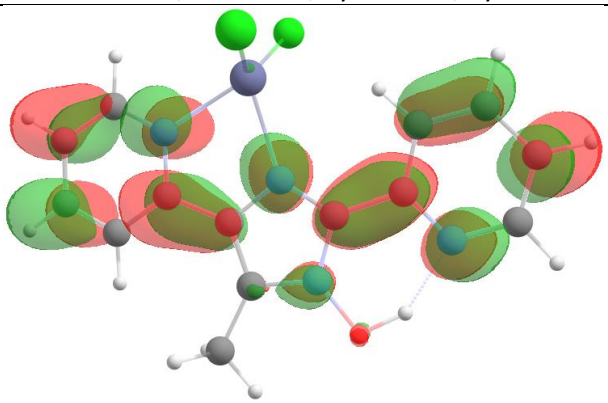
Figure S27. ONIOM model for the quantum chemical calculations of **$ZnHLI_2$**.

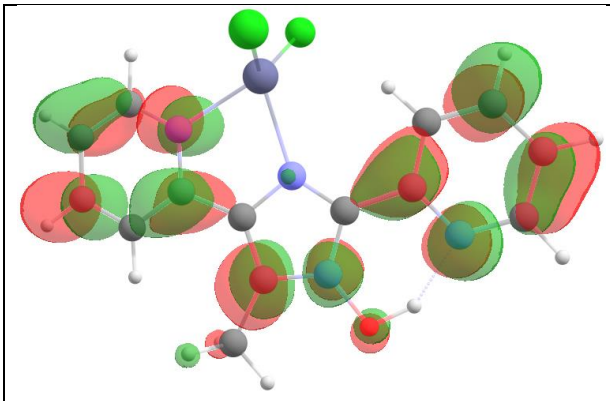
Table S23. Excited state properties of **$ZnHLCl_2$** at the relaxed ground state geometry (**normal form**, S_0^N, M062X/6-31+g(d) level of theory). Transitions with contribution >10% are shown.

State	Energy (eV)	Energy (nm)	Contributions (%)	Oscillator strength	Character
S1	4.2887	289	HOMO → LUMO (94.5%)	0.6168	IL
S2	4.8362	256	HOMO → LUMO+1 (81.6%)	0.1106	IL
S3	5.0363	246	HOMO-1 → LUMO (82.9%)	0.0064	XLCT
S4	5.0856	244	HOMO-2 → LUMO (53.8%) HOMO → LUMO+2 (26.8%)	0.0117	XLCT + IL
S5	5.1193	242	HOMO-2 → LUMO (25.5%) HOMO → LUMO+2 (55.5%)	0.0707	IL + XLCT
S6	5.2149	238	HOMO-3 → LUMO (62.8%)	0.0073	XLCT
S7	5.2953	234	HOMO → LUMO+3 (70.6%)	0.0747	IL

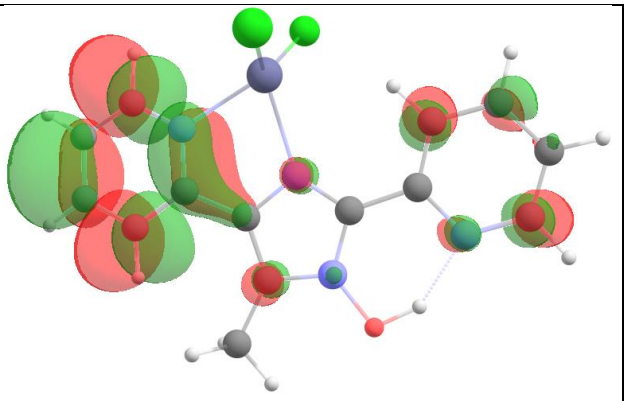
S8	5.3281	233	HOMO-4 → LUMO (55.3%) HOMO-3 → LUMO (15.5%)	0.0084	XLCT

Table S24. Isosurface contour plots of the molecular orbitals of **$ZnHLCl_2$** at the ground state geometry (**normal form**, **S_0^N**, M062X/6-31+g(d) level of theory). Orbital decomposition resulting from Mulliken population analysis.

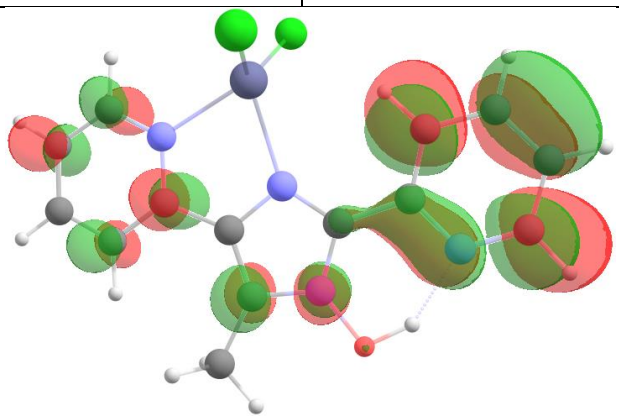
 **HOMO-4** $ZnCl_2$[a] 95.5%, Imid[b] 0.3%, Pyr-H[c] 2.4%, Pyr[d] 1.8%	 **HOMO-3** $ZnCl_2$ 96.1%, Imid 3.7%, Pyr-H 0.0%, Pyr 0.2%
 **HOMO-2** $ZnCl_2$ 98.0%, Imid 0.8%, Pyr-H 0.8%, Pyr 0.4%	 **HOMO-1** $ZnCl_2$ 99.4%, Imid 0.4%, Pyr-H 0.0%, Pyr 0.2%
 **HOMO** $ZnCl_2$ 0.4%, Imid 59.1%, Pyr-H 19.6%, Pyr 20.9%	 **LUMO** $ZnCl_2$ 0.6%, Imid 21.8%, Pyr-H 37.3%, Pyr 40.3%



LUMO+1
$ZnCl_2$ 0.2%, Imid 19.6%, Pyr-H 44.0%, Pyr 36.2%



LUMO+2
$ZnCl_2$ 0.0%, Imid 5.5%, Pyr-H 11.6%, Pyr 82.9%



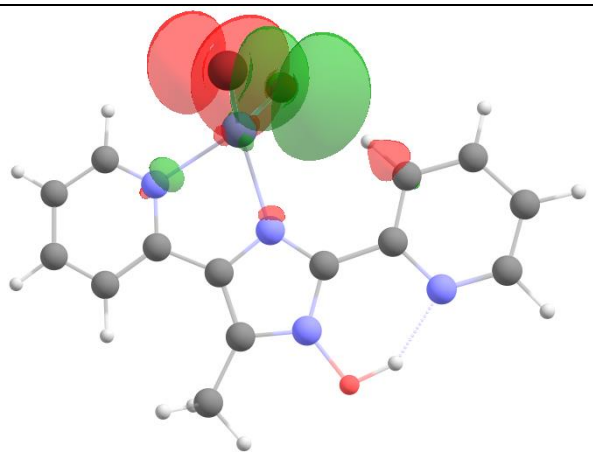
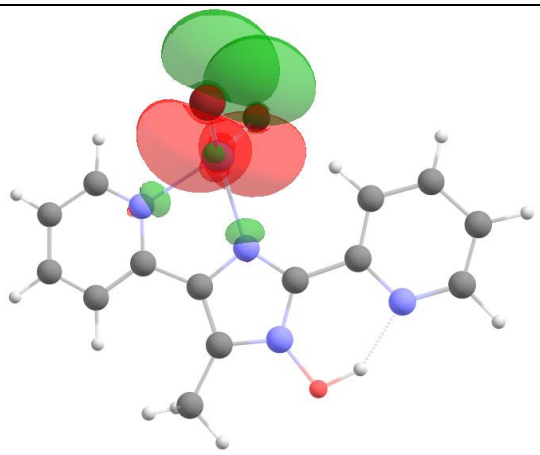
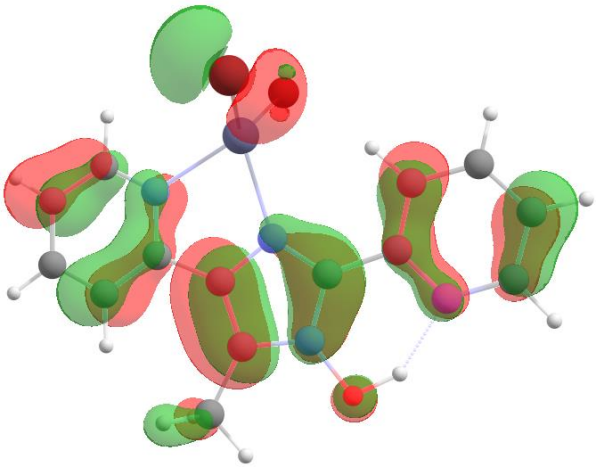
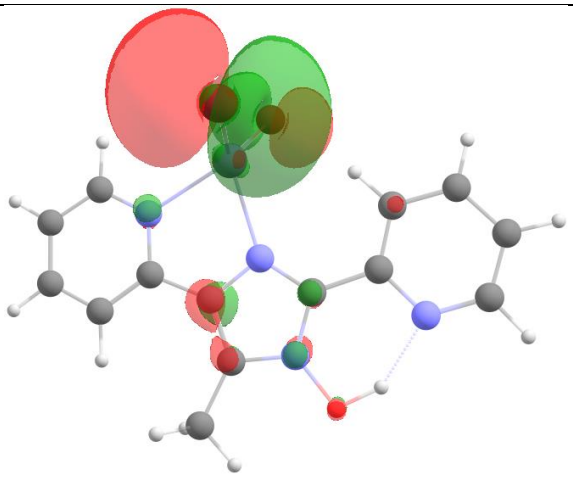
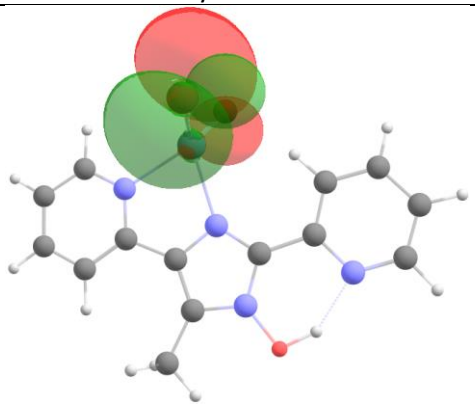
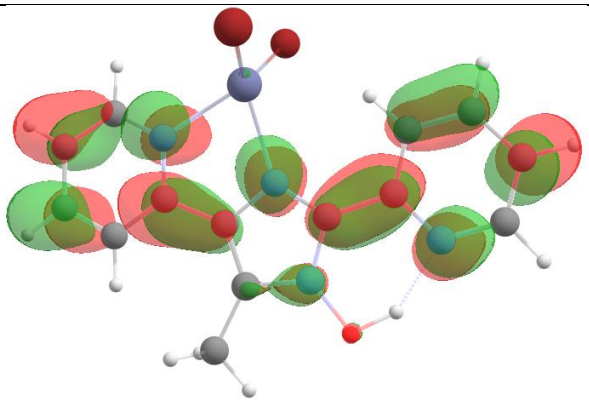
LUMO+3
$ZnCl_2$ 0.0%, Imid 9.6%, Pyr-H 76.8%, Pyr 13.6%

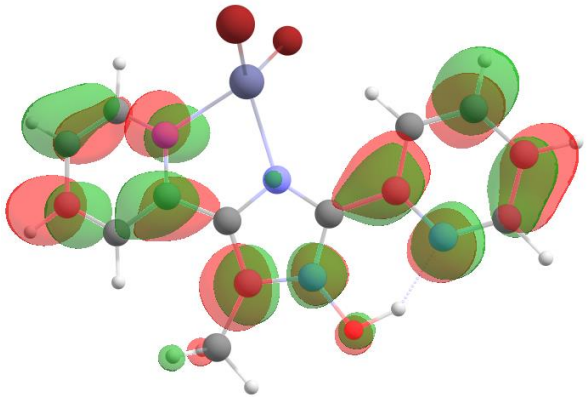
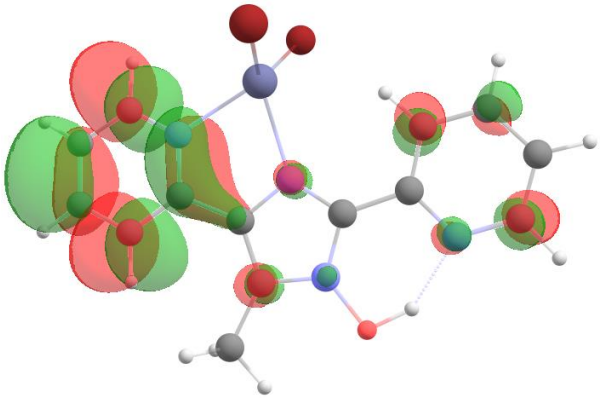
a – $ZnCl_2$ group
b – Imidazole ring
c – proton accepting pyridine ring
d – second pyridine ring

Table S25. Excited state properties of **$ZnHLBr_2$** at the relaxed ground state geometry (**normal form**, **S_0^N**, M062X/6-31+g(d) level of theory). Transitions with contribution >10% are shown.

State	Energy (eV)	Energy (nm)	Contributions (%)	Oscillator strength	Character
S1	4.2858	289	HOMO-2 → LUMO (78.7%) HOMO-1 → LUMO (13.9%)	0.5742	IL + XLCT
S2	4.5407	273	HOMO → LUMO (94.5%)	0.0023	XLCT
S3	4.6360	267	HOMO-2 → LUMO (13.8%) HOMO-1 → LUMO (80.7%)	0.0182	XLCT + IL
S4	4.7788	259	HOMO-3 → LUMO (87.0%)	0.0060	XLCT
S5	4.8405	256	HOMO-2 → LUMO+1 (67.2%)	0.1033	IL
S6	4.8885	254	HOMO-4 → LUMO (87.3%)	0.0091	XLCT
S7	5.1071	243	HOMO-2 → LUMO+2 (69.1%)	0.0617	IL
S8	5.2134	238	HOMO → LUMO+1 (92.7%)	0.0037	XLCT

Table S26. Isosurface contour plots of the molecular orbitals of **$ZnHLBr_2$** at the ground state geometry (**normal form**, **S_0^N**, M062X/6-31+g(d) level of theory). Orbital decomposition resulting from Mulliken population analysis.

 **HOMO-4** $ZnBr_2$[a] 96.4%, Imid[b] 0.2%, Pyr-H[c] 2.4%, Pyr[d] 1.0%	 **HOMO-3** $ZnBr_2$ 95.2%, Imid 2.6%, Pyr-H 1.3%, Pyr 0.9%
 **HOMO-2** $ZnBr_2$ 10.8%, Imid 52.6%, Pyr-H 17.8%, Pyr 18.8%	 **HOMO-1** $ZnBr_2$ 90.8%, Imid 5.2%, Pyr-H 2.5%, Pyr 1.5%
 **HOMO** $ZnBr_2$ 99.0%, Imid 1.0%, Pyr-H 0.0%, Pyr 0.0%	 **LUMO** $ZnBr_2$ 0.9%, Imid 20.2%, Pyr-H 36.9%, Pyr 42.0%

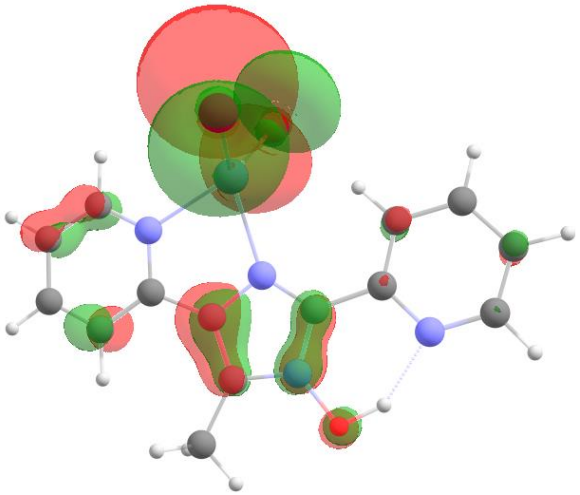
	
LUMO+1 $ZnBr_2$ 0.2%, Imid 20.5%, Pyr-H 43.7%, Pyr 35.6%	**LUMO+2** $ZnBr_2$ 0.0%, Imid 7.2%, Pyr-H 10.2%, Pyr 82.6%

a – $ZnBr_2$ group
b – Imidazole ring
c – proton accepting pyridine ring
d – second pyridine ring

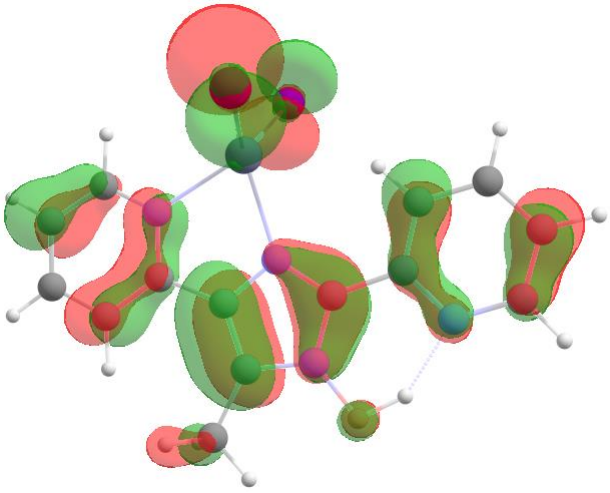
Table S27. Excited state properties of **$ZnHLI_2$** at the relaxed ground state geometry (**normal form**, **S_0^N**, M062X/6-31+g(d) level of theory). Transitions with contribution >10% are shown.

State	Energy (eV)	Energy (nm)	Contributions (%)	Oscillator strength	Character
S1	4.0132	309	HOMO → LUMO (96.2%)	0.0018	XLCT
S2	4.1082	302	HOMO-1 → LUMO (93.5%)	0.0130	XLCT
S3	4.2792	290	HOMO-4 → LUMO (22.5%) HOMO-2 → LUMO (67.7%)	0.1573	XLCT + IL
S4	4.2986	288	HOMO-4 → LUMO (49.5%) HOMO-2 → LUMO (26.5%)	0.3474	IL + XLCT
S5	4.3949	282	HOMO-3 → LUMO (88.1%)	0.0386	XLCT
S6	4.6731	265	HOMO → LUMO+1 (95.8%)	0.0012	XLCT
S7	4.7687	260	HOMO-5 → LUMO (25.7%) HOMO-4 → LUMO+1 (18.1%) HOMO-1 → LUMO+1 (35.5%)	0.0128	XLCT
S8	4.7715	260	HOMO-5 → LUMO (30.2%) HOMO-1 → LUMO+1 (55.1%)	0.0058	XLCT

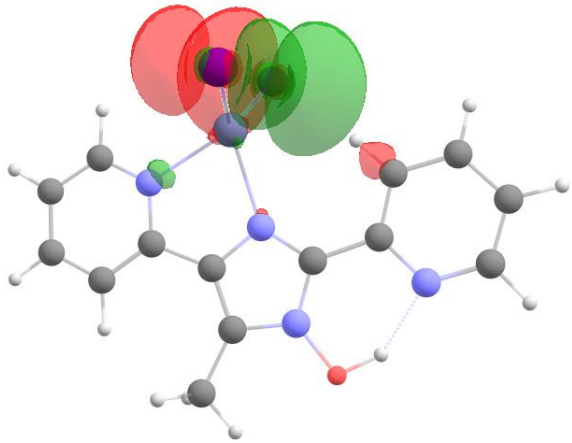
Table S28. Isosurface contour plots of the molecular orbitals of **$ZnHLI_2$** at the ground state geometry (**normal form**, **S_0^N**, M062X/6-31+g(d) level of theory). Orbital decomposition resulting from Mulliken population analysis.



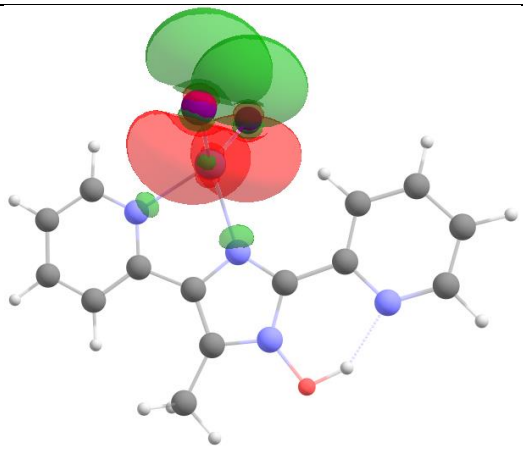
HOMO-5
ZnI_2[a] 77.2%, Imid[b] 12.9%, Pyr-H[c] 3.3%, Pyr[d] 6.6%



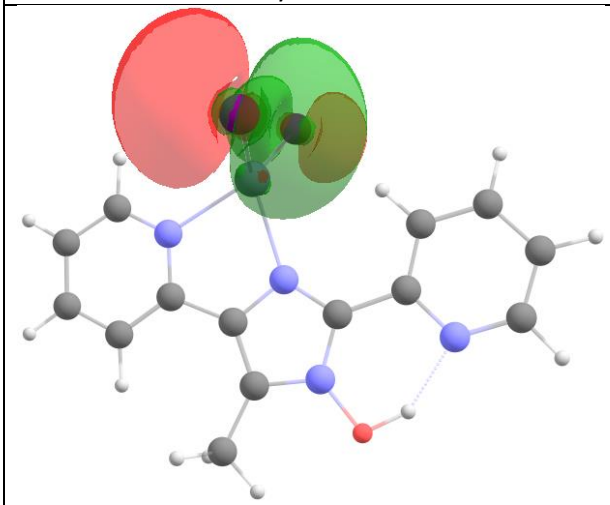
HOMO-4
ZnI_2 20.1%, Imid 48.0%, Pyr-H 16.6%, Pyr 15.3%



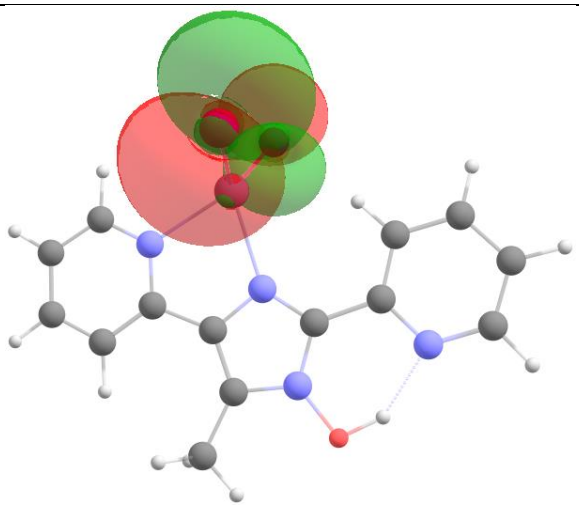
HOMO-3
ZnI_2 97.1%, Imid 0.0%, Pyr-H 2.6%, Pyr 0.3%



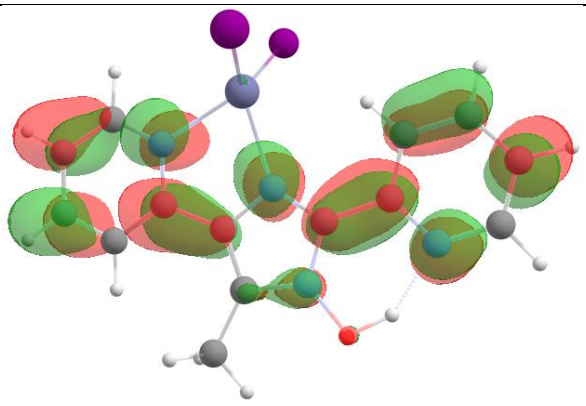
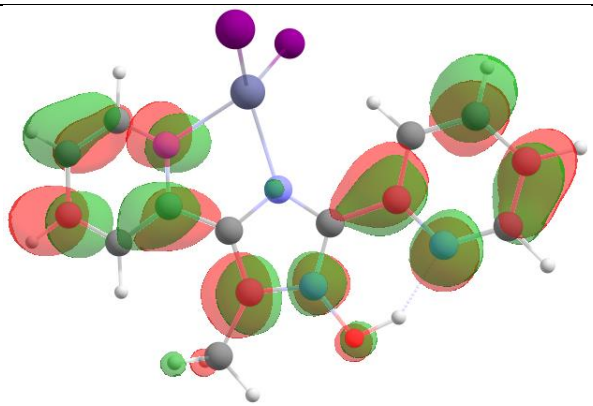
HOMO-2
ZnI_2 96.8%, Imid 2.0%, Pyr-H 0.0%, Pyr 1.2%



HOMO-1
ZnI_2 98.3%, Imid 0.6%, Pyr-H 0.8%, Pyr 0.3%



HOMO
ZnI_2 99.6%, Imid 0.0%, Pyr-H 0.0%, Pyr 0.4%

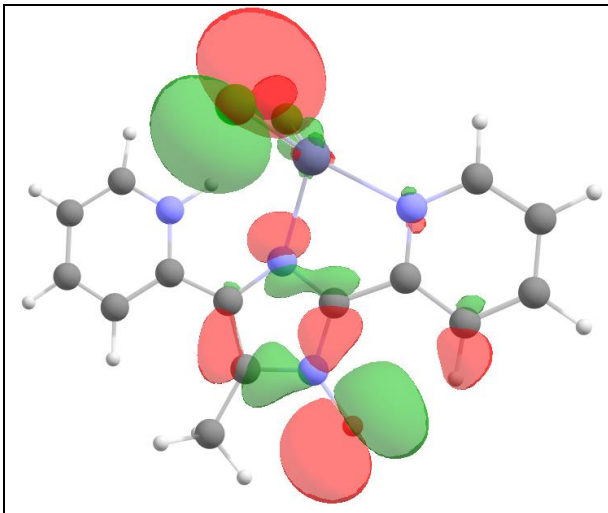
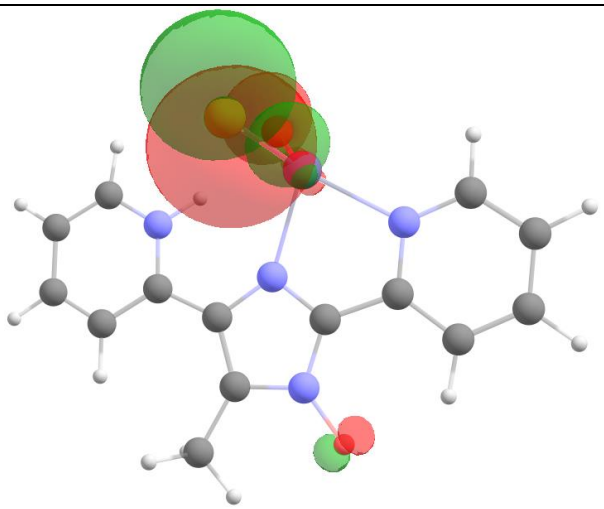
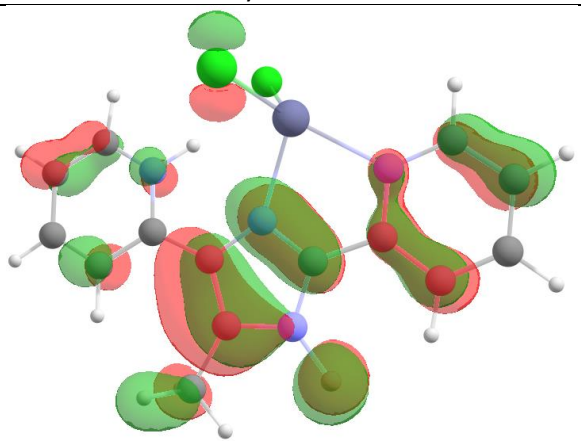
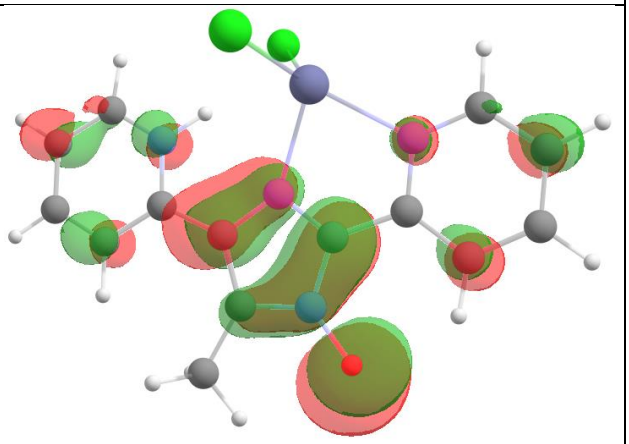
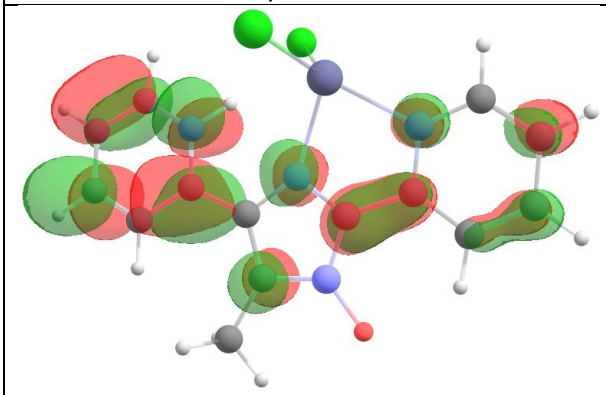
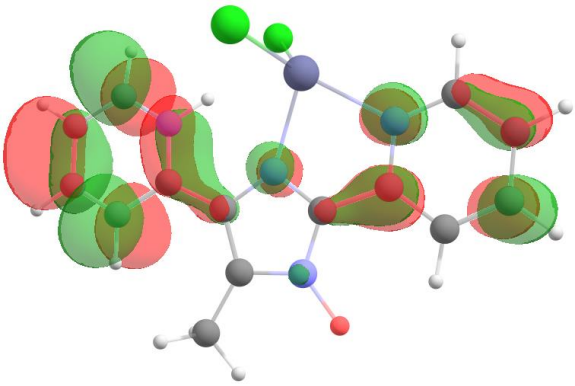
 **LUMO** ZnI_2 1.0%, Imid 22.1%, Pyr-H 36.0%, Pyr 40.9%	 **LUMO+1** ZnI_2 0.2%, Imid 20.1%, Pyr-H 43.7%, Pyr 36.0%

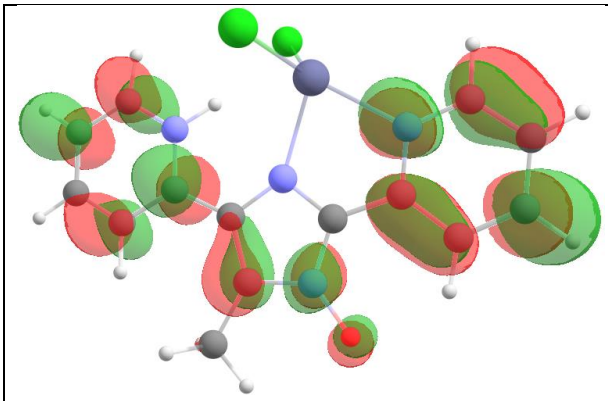
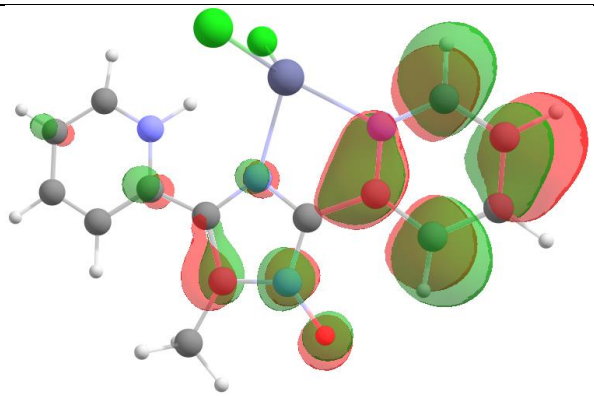
a – ZnI_2 group
b – Imidazole ring
c – proton accepting pyridine ring
d – second pyridine ring

Table S29. Excited state properties of **$ZnHLCl_2$** at the relaxed ground state geometry (**minor component**, **S_0^{minor}**, M062X/6-31+g(d) level of theory). Transitions with contribution >10% are shown.

State	Energy (eV)	Energy (nm)	Contributions (%)	Oscillator strength	Character
S1	2.9775	416	HOMO → LUMO (96.7%)	0.2897	IL
S2	3.7315	332	HOMO-1 → LUMO (89.0%)	0.1864	IL
S3	3.8365	323	HOMO → LUMO+1 (81.7%) HOMO → LUMO+2 (10.9%)	0.1238	IL
S4	4.2395	292	HOMO → LUMO+2 (81.9%)	0.2545	IL
S5	4.4849	276	HOMO-3 → LUMO (72.4%)	0.0011	XLCT + IL
S6	4.5707	271	HOMO → LUMO+3 (81.0%)	0.0126	IL
S7	4.6052	269	HOMO-2 → LUMO (92.5%)	0.0007	XLCT
S8	4.6831	265	HOMO-1 → LUMO+1 (76.6%) HOMO → LUMO+3 (11.2%)	0.0706	IL

Table S30. Isosurface contour plots of the molecular orbitals of **$ZnHLCl_2$** at the ground state geometry (**minor component**, **S_0^{minor}**, M062X/6-31+g(d) level of theory). Orbital decomposition resulting from Mulliken population analysis.

 **HOMO-3** $ZnCl_2$[a] 34.2%, Imid[b] 64.8%, Pyr1[c] 1.9%, Pyr2[d] 0.0%	 **HOMO-2** $ZnCl_2$ 98.3%, Imid 0.7%, Pyr1 0.5%, Pyr2 0.5%
 **HOMO-1** $ZnCl_2$ 2.6%, Imid 74.3%, Pyr1 13.8%, Pyr2 9.3%	 **HOMO** $ZnCl_2$ 0.4%, Imid 82.5%, Pyr1 7.9%, Pyr2 9.2%
 **LUMO** $ZnCl_2$ 0.5%, Imid 14.3%, Pyr1 13.4%, Pyr2 71.8%	 **LUMO+1** $ZnCl_2$ 0.4%, Imid 5.8%, Pyr1 22.1%, Pyr2 71.7%

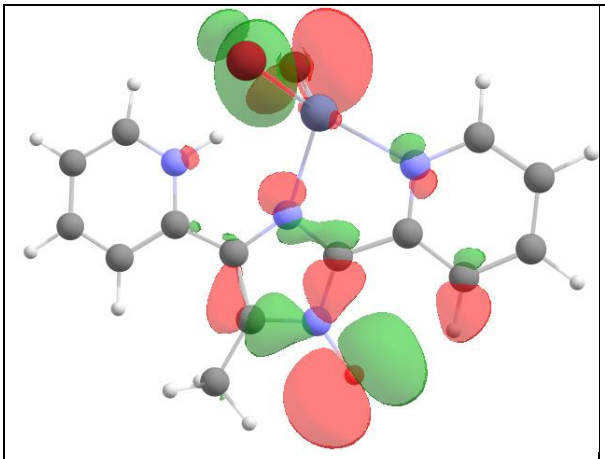
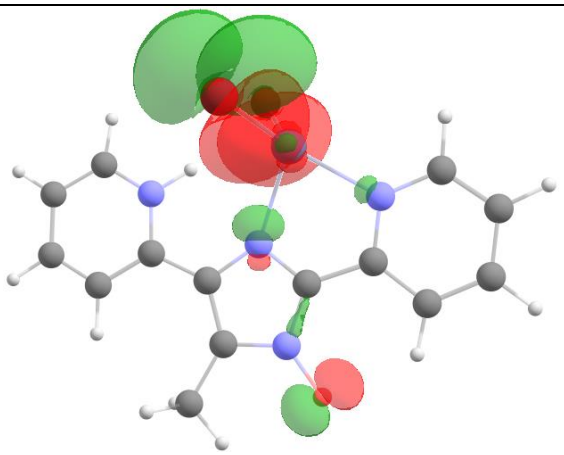
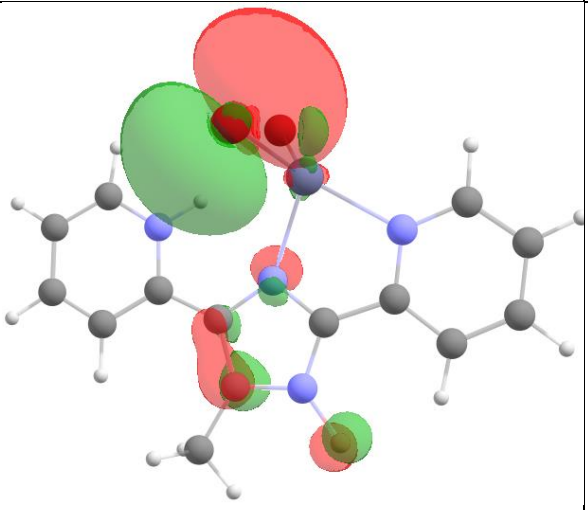
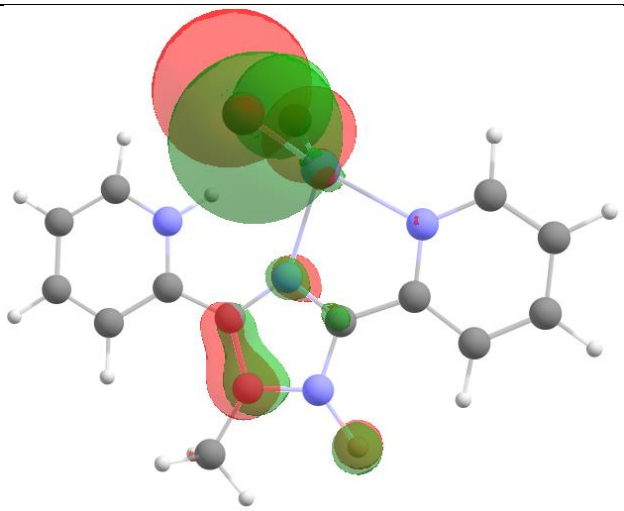
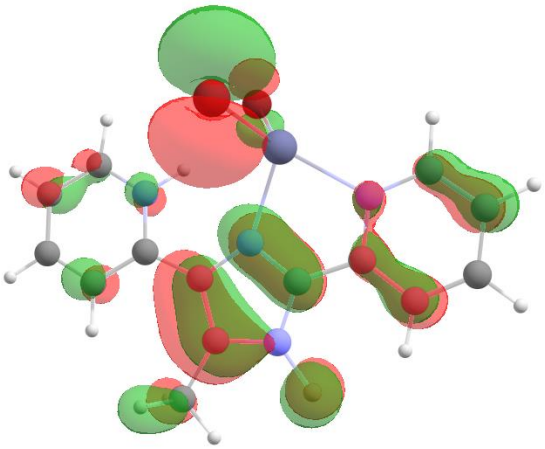
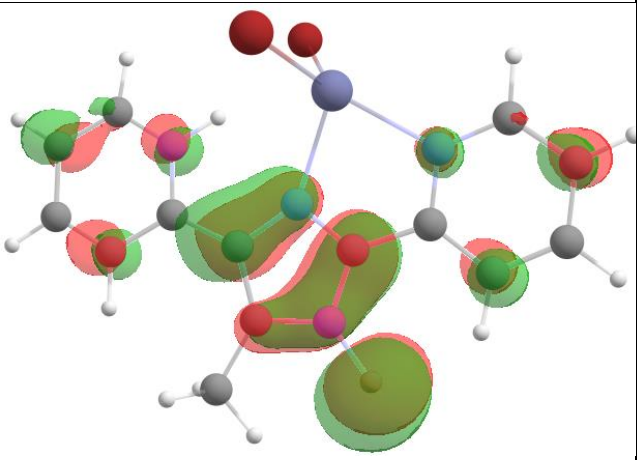
	
LUMO+2 $ZnCl_2$ 0.1%, Imid 13.9%, Pyr1 56.6%, Pyr2 29.4%	**LUMO+3** $ZnCl_2$ 0.0%, Imid 11.7%, Pyr1 84.3%, Pyr2 4.0%

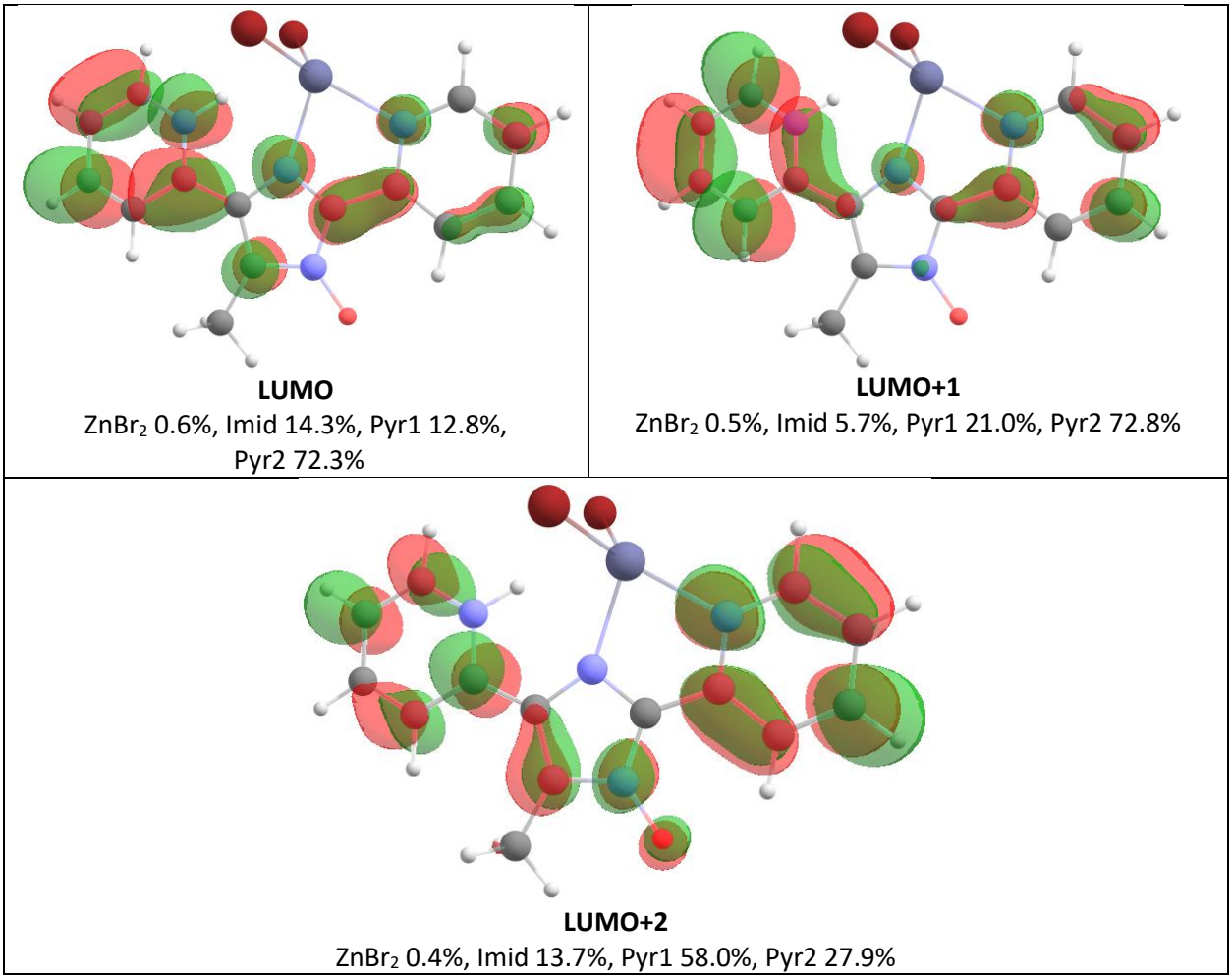
a – $ZnCl_2$ group
b – Imidazole ring
c – first pyridine ring (which is coordinated to Zn atom)
d – second pyridine ring (which is not coordinated to Zn atom)

Table S31. Excited state properties of **$ZnHLBr_2$** at the relaxed ground state geometry (**minor component**, **S_0^{minor}**, M062X/6-31+g(d) level of theory). Transitions with contribution >10% are shown.

State	Energy (eV)	Energy (nm)	Contributions (%)	Oscillator strength	Character
S1	2.9703	417	HOMO → LUMO (96.6%)	0.2764	IL
S2	3.7216	333	HOMO-1 → LUMO (78.2%)	0.1817	IL + XLCT
S3	3.8335	323	HOMO → LUMO+1 (82.4%)	0.1170	IL
S4	4.0906	303	HOMO-2 → LUMO (87.8%) HOMO-1 → LUMO (11.3%)	0.0001	XLCT
S5	4.2107	294	HOMO-3 → LUMO (50.4%) HOMO → LUMO+1 (37.4%)	0.0672	XLCT + IL
S6	4.2600	291	HOMO-3 → LUMO (43.1%) HOMO → LUMO+1 (45.4%)	0.1923	IL + XLCT
S7	4.4466	279	HOMO-5 → LUMO (20.6%) HOMO-4 → LUMO (68.9%)	0.0089	XLCT
S8	4.5786	271	HOMO → LUMO+2 (70.5%)	0.0130	XLCT

Table S32. Isosurface contour plots of the molecular orbitals of **$ZnHLBr_2$** at the ground state geometry (**minor component**, **S_0^{minor}**, M062X/6-31+g(d) level of theory). Orbital decomposition resulting from Mulliken population analysis.

 **HOMO-5** $ZnBr_2$[a] 32.0%, Imid[b] 63.8%, Pyr1[c] 2.5%, Pyr2[d] 1.7%	 **HOMO-4** $ZnBr_2$ 91.6%, Imid 8.1%, Pyr1 0.3%, Pyr2 0.0%
 **HOMO-3** $ZnBr_2$ 78.6%, Imid 19.0%, Pyr1 0.6%, Pyr2 1.8%	 **HOMO-2** $ZnBr_2$ 85.5%, Imid 11.4%, Pyr1 1.6%, Pyr2 1.5%
 **HOMO-1** $ZnBr_2$ 25.7%, Imid 55.8%, Pyr1 11.2%, Pyr2 7.3%	 **HOMO** $ZnBr_2$ 0.7%, Imid 82.4%, Pyr1 7.8%, Pyr2 9.1%



LUMO
$ZnBr_2$ 0.6%, Imid 14.3%, Pyr1 12.8%, Pyr2 72.3%

LUMO+1
$ZnBr_2$ 0.5%, Imid 5.7%, Pyr1 21.0%, Pyr2 72.8%

LUMO+2
$ZnBr_2$ 0.4%, Imid 13.7%, Pyr1 58.0%, Pyr2 27.9%

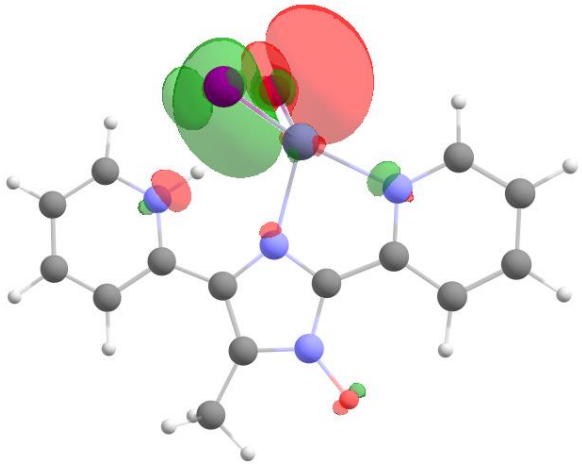
a – $ZnBr_2$ group
b – Imidazole ring
c – first pyridine ring (which is coordinated to Zn atom)
d – second pyridine ring (which is not coordinated to Zn atom)

Table S33. Excited state properties of **$ZnHLI_2$** at the relaxed ground state geometry (**minor component**, **S_0^{minor}**, M062X/6-31+g(d) level of theory). Transitions with contribution >10% are shown.

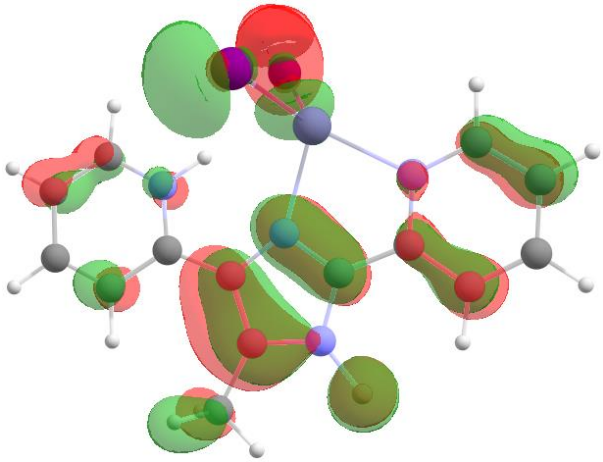
State	Energy (eV)	Energy (nm)	Contributions (%)	Oscillator strength	Character
S1	2.9503	420	HOMO → LUMO (96.5%)	0.2544	IL
S2	3.5335	351	HOMO-1 → LUMO (97.1%)	0.0167	XLCT
S3	3.6241	342	HOMO-4 → LUMO (13.2%) HOMO-2 → LUMO (80.8%)	0.0655	XLCT + IL
S4	3.7676	329	HOMO-4 → LUMO (60.4%) HOMO-2 → LUMO (12.5%) HOMO → LUMO+1 (19.3%)	0.0883	XLCT + IL
S5	3.8413	323	HOMO-4 → LUMO (11.4%) HOMO → LUMO+1 (66.5%)	0.1349	IL + XLCT

			HOMO → LUMO+2 (11.6%)		
S6	3.9636	313	HOMO-3 → LUMO (95.6%)	0.0048	XLCT
S7	4.1466	299	HOMO-5 → LUMO (95.9%)	0.0041	XLCT
S8	4.2430	292	HOMO → LUMO+2 (80.7%)	0.2301	IL

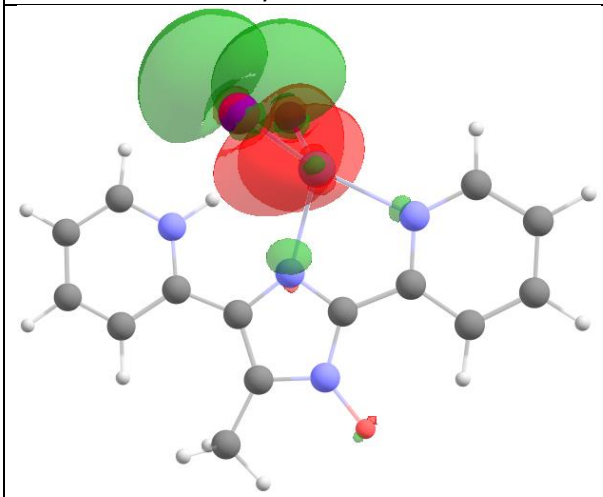
Table S34. Isosurface contour plots of the molecular orbitals of **$ZnHLI_2$** at the ground state geometry (**minor component**, **S_0^{minor}**, M062X/6-31+g(d) level of theory). Orbital decomposition resulting from Mulliken population analysis.



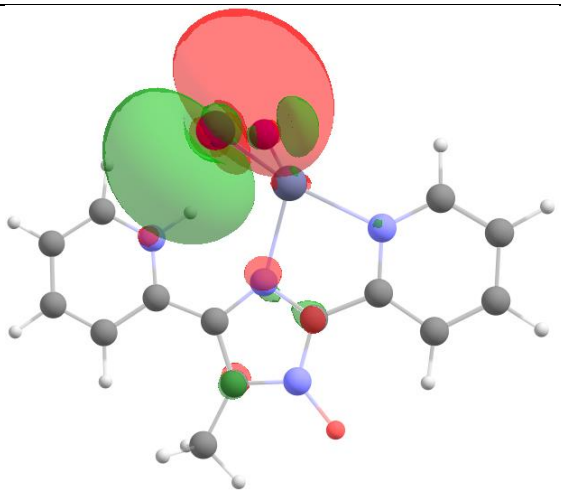
HOMO-5
ZnI_2[a] 93.3%, Imid[b] 2.0%, Pyr1[c] 1.3%, Pyr2[d] 3.4%



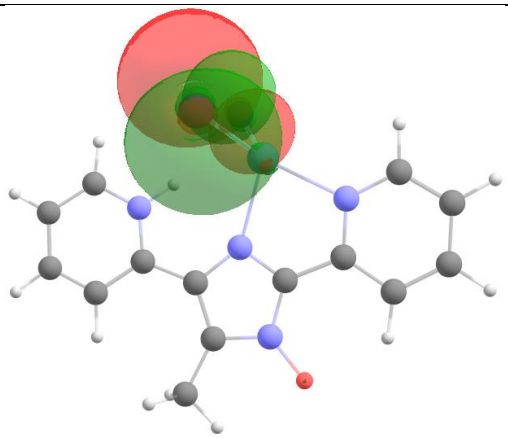
HOMO-4
ZnI_2 19.4%, Imid 61.2%, Pyr1 12.4%, Pyr2 7.0%



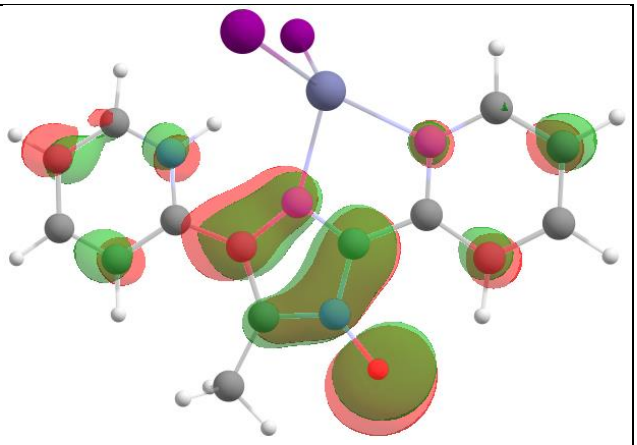
HOMO-3
ZnI_2 95.0%, Imid 2.1%, Pyr1 1.1%, Pyr2 1.8%



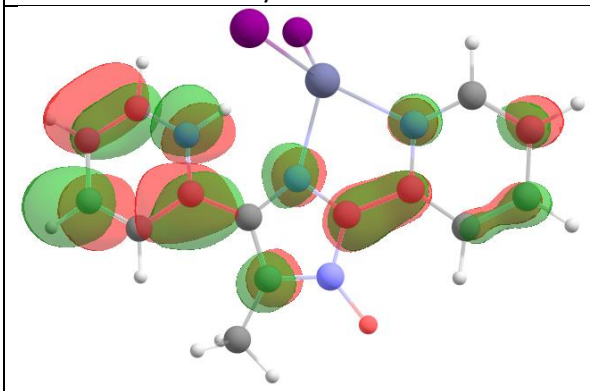
HOMO-2
ZnI_2 94.3%, Imid 4.6%, Pyr1 0.0%, Pyr2 1.1%



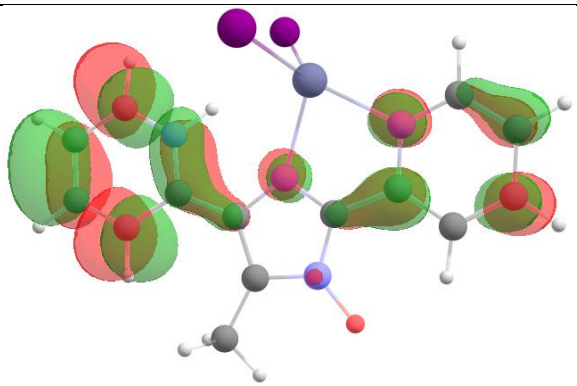
HOMO-1
ZnI_2 98.6%, Imid 0.6%, Pyr1 0.5%, Pyr2 0.3%



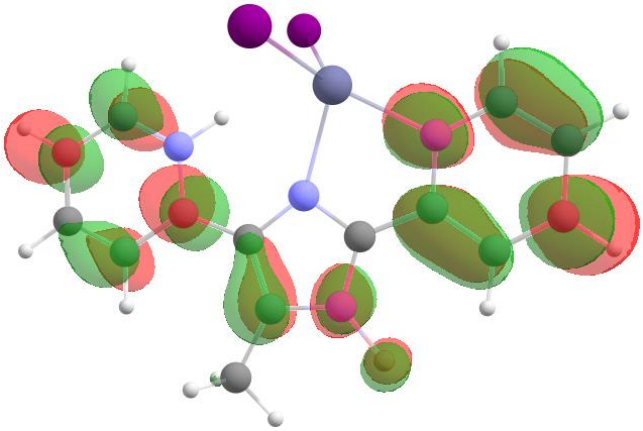
HOMO
ZnI_2 2.1%, Imid 81.6%, Pyr1 7.6%, Pyr2 8.7%



LUMO
ZnI_2 0.7%, Imid 14.6%, Pyr1 12.6%, Pyr2 72.1%



LUMO+1
ZnI_2 0.5%, Imid 5.9%, Pyr1 20.5%, Pyr2 73.1%



LUMO+2
ZnI_2 0.7%, Imid 14.1%, Pyr1 58.3%, Pyr2 26.9%

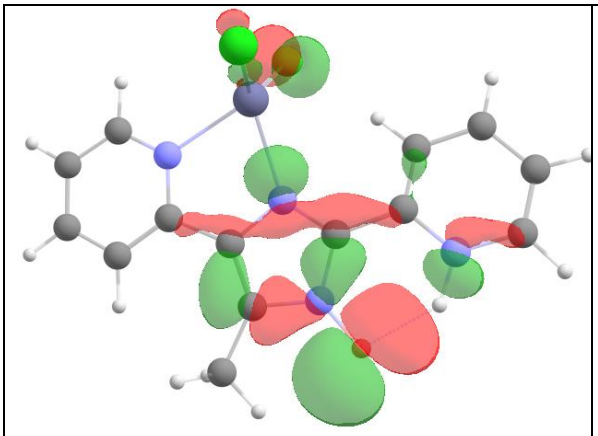
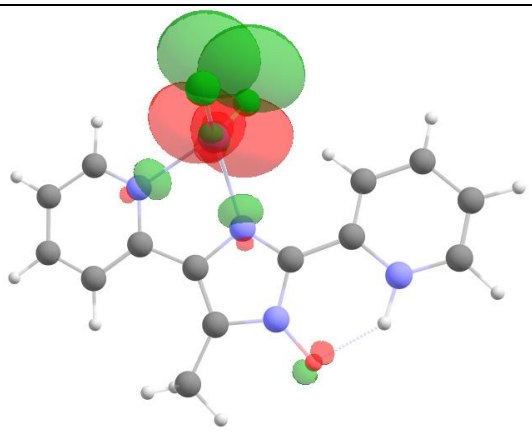
a – ZnI_2 group
b – Imidazole ring
c – first pyridine ring (which is coordinated to Zn atom)
d – second pyridine ring (which is not coordinated to Zn atom)

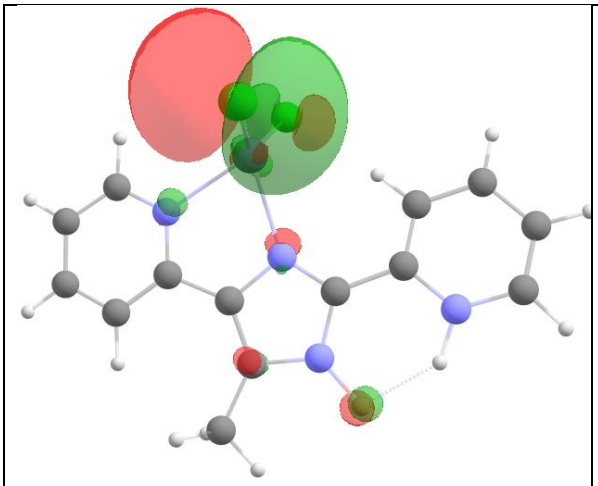
Table S35. Excited state properties of **$ZnHLCl_2$** at the relaxed ground state geometry (local minimum in the **tautomeric form**, **S_0^T**, M062X/6-31+g(d) level of theory). Transitions with contribution >10% are shown.

State	Energy (eV)	Energy (nm)	Contributions (%)	Oscillator strength	Character

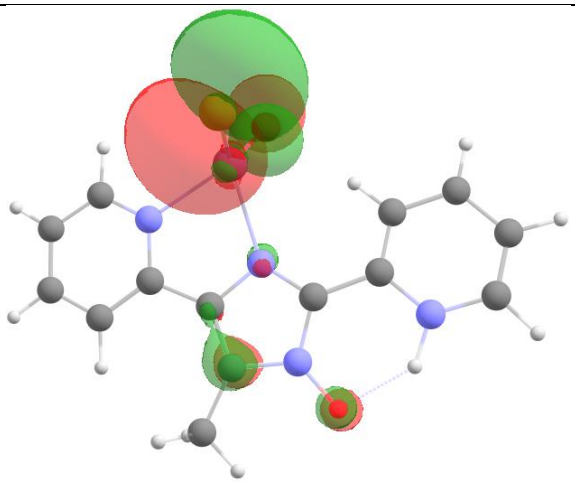
S1	2.6811	462	HOMO → LUMO (97.2%)	0.1371	IL
S2	3.6530	339	HOMO → LUMO+1 (97.1%)	0.0896	IL
S3	3.8499	322	HOMO-1 → LUMO (88.8%)	0.2914	IL
S4	4.2294	293	HOMO-7 → LUMO (49.9%) HOMO → LUMO+2 (15.8%)	0.0663	IL
S5	4.3625	284	HOMO-2 → LUMO (23.7%) HOMO → LUMO+2 (60.5%)	0.0944	IL + XLCT
S6	4.3792	283	HOMO-2 → LUMO (65.2%) HOMO → LUMO+2 (12.6%)	0.0228	IL + XLCT
S7	4.4522	278	HOMO-3 → LUMO (81.9%)	0.0053	XLCT
S8	4.6167	269	HOMO-7 → LUMO (10.8%) HOMO-4 → LUMO (83.6%)	0.0029	XLCT

Table S36. Isosurface contour plots of the molecular orbitals of **$ZnHLCl_2$** at the ground state geometry (local minimum in the **tautomeric form**, **S_0^T**, M062X/6-31+g(d) level of theory). Orbital decomposition resulting from Mulliken population analysis.

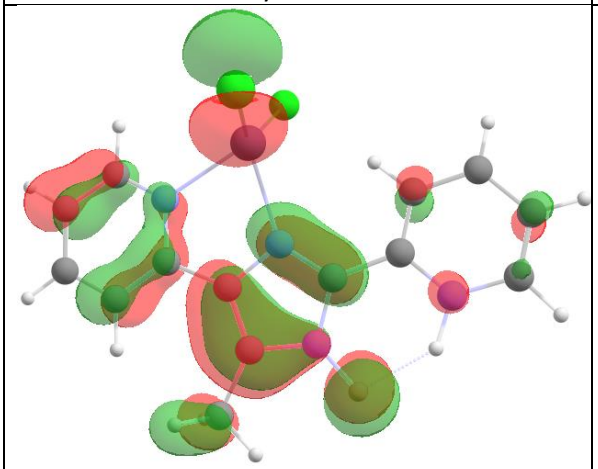
 **HOMO-7** $ZnCl_2$[a] 8.0%, Imid[b] 85.6%, Pyr-H[c] 5.5%, Pyr[d] 0.9%	 **HOMO-4** $ZnCl_2$ 94.7%, Imid 3.0%, Pyr-H 1.2%, Pyr 1.1%



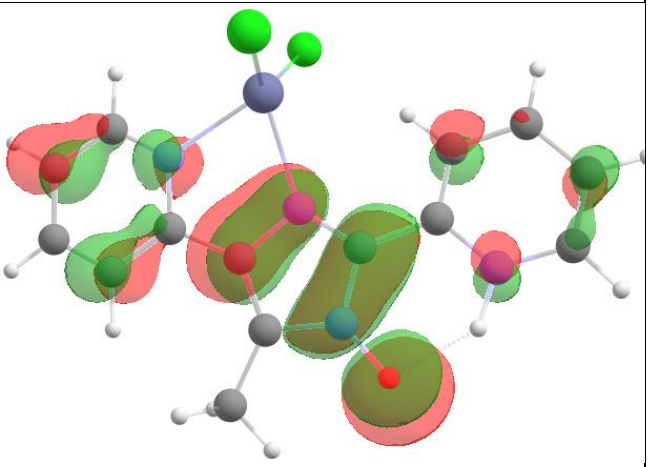
HOMO-3
$ZnCl_2$ 95.2%, Imid 3.6%, Pyr-H 0.4%, Pyr 0.8%



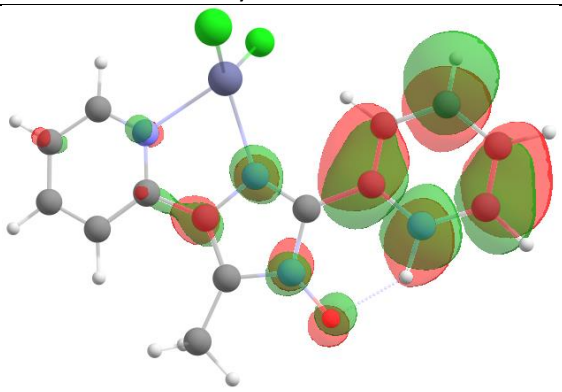
HOMO-2
$ZnCl_2$ 91.6%, Imid 6.0%, Pyr-H 0.0%, Pyr 2.4%



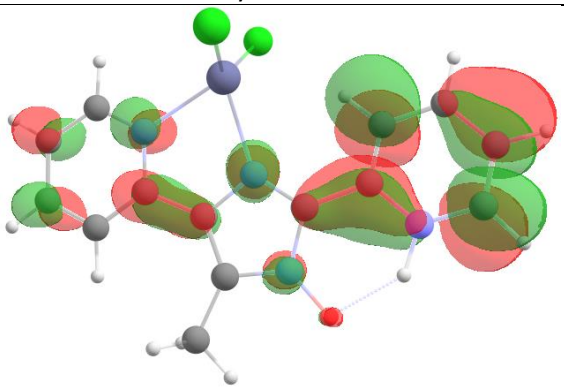
HOMO-1
$ZnCl_2$ 12.4%, Imid 69.2%, Pyr-H 4.9%, Pyr 13.5%



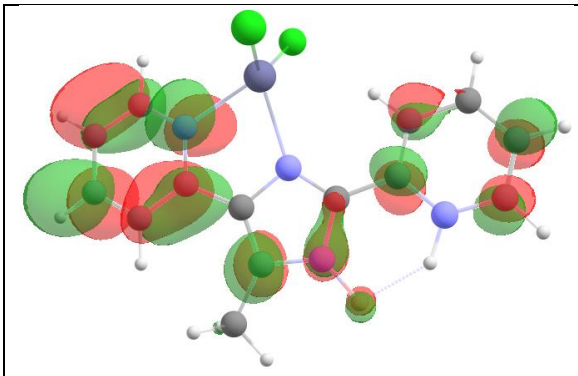
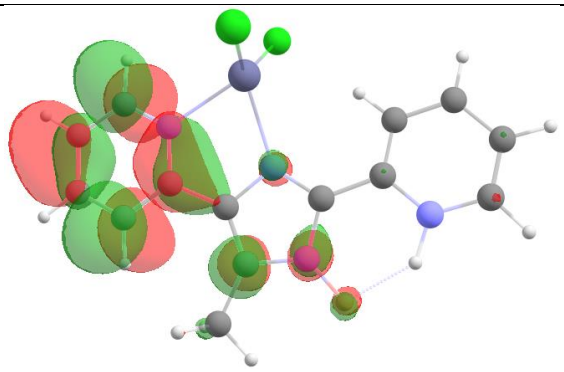
HOMO
$ZnCl_2$ 0.6%, Imid 79.8%, Pyr-H 7.7%, Pyr 11.9%



LUMO
$ZnCl_2$ 0.0%, Imid 15.3%, Pyr-H 81.2%, Pyr 3.5%



LUMO+1
$ZnCl_2$ 0.3%, Imid 10.7%, Pyr-H 75.3%, Pyr 13.7%

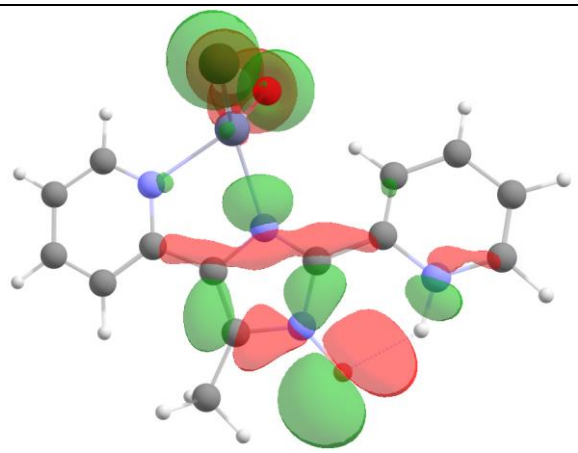
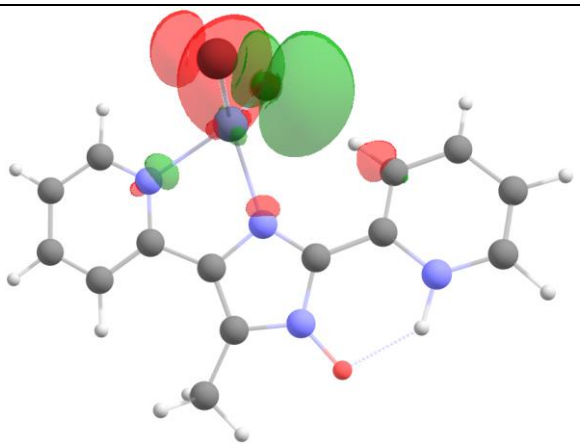
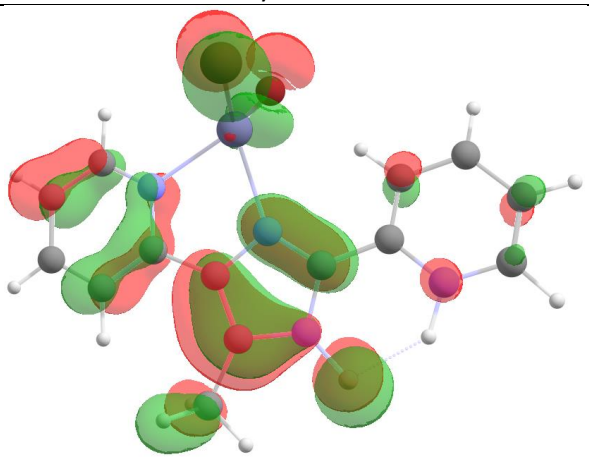
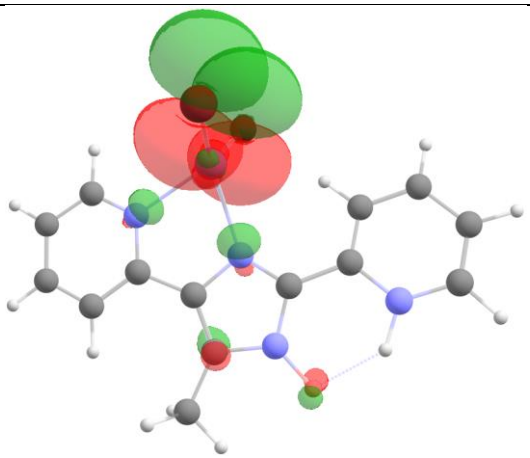
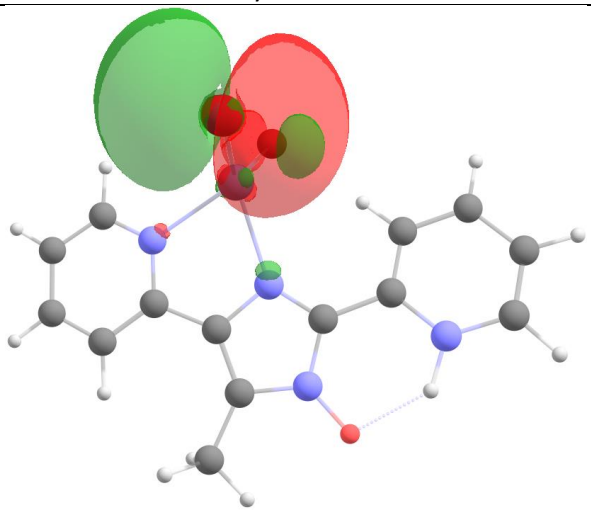
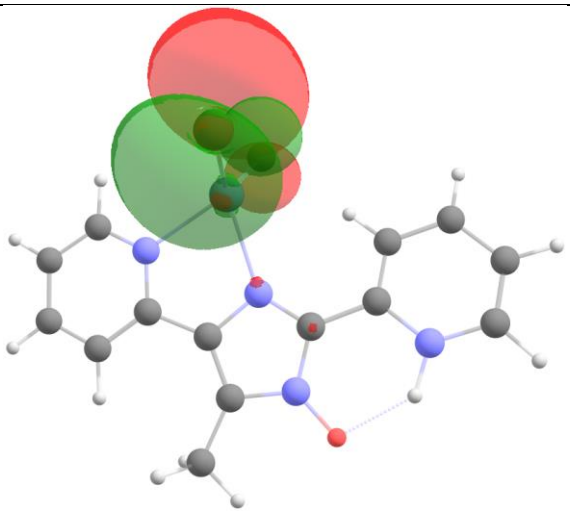
 **LUMO+2** $ZnCl_2$ 0.2%, Imid 12.0%, Pyr-H 16.3%, Pyr 71.5%	 **LUMO+3** $ZnCl_2$ 0.0%, Imid 13.3%, Pyr-H 2.7%, Pyr 84.0%

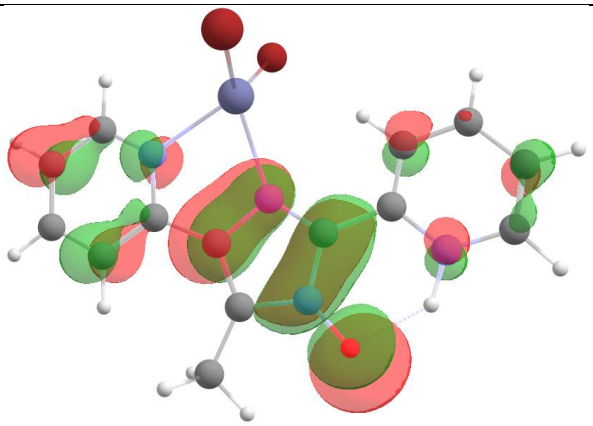
a – $ZnCl_2$ group
b – Imidazole ring
c – proton accepting pyridine ring
d – second pyridine ring

Table S37. Excited state properties of **$ZnHLBr_2$** at the relaxed ground state geometry (local minimum in the **tautomeric form**, **S_0^T**, M062X/6-31+g(d) level of theory). Transitions with contribution >10% are shown.

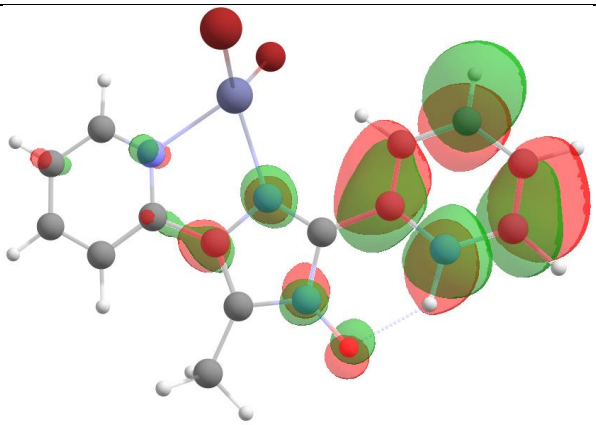
State	Energy (eV)	Energy (nm)	Contributions (%)	Oscillator strength	Character
S1	2.6639	465	HOMO → LUMO (97.1%)	0.1305	IL
S2	3.6480	340	HOMO → LUMO+1 (97.0%)	0.0822	IL
S3	3.7747	328	HOMO-4 → LUMO (28.0%) HOMO-1 → LUMO (57.7%)	0.1364	XLCT + IL
S4	3.8807	319	HOMO-4 → LUMO (28.9%) HOMO-2 → LUMO (25.0%) HOMO-1 → LUMO (38.9%)	0.0854	XLCT + IL
S5	3.9325	315	HOMO-4 → LUMO (29.3%) HOMO-2 → LUMO (64.1%)	0.0662	XLCT + IL
S6	4.0756	304	HOMO-3 → LUMO (79.4%)	0.0065	XLCT
S7	4.2085	295	HOMO-5 → LUMO (85.7%)	0.0026	XLCT
S8	4.2800	290	HOMO-7 → LUMO (28.7%) HOMO → LUMO+2 (42.3%)	0.0932	XLCT + IL

Table S38. Isosurface contour plots of the molecular orbitals of **ZnHLBr$_2$** at the ground state geometry (local minimum in the **tautomeric form**, **S_0^T**, M062X/6-31+g(d) level of theory). Orbital decomposition resulting from Mulliken population analysis.

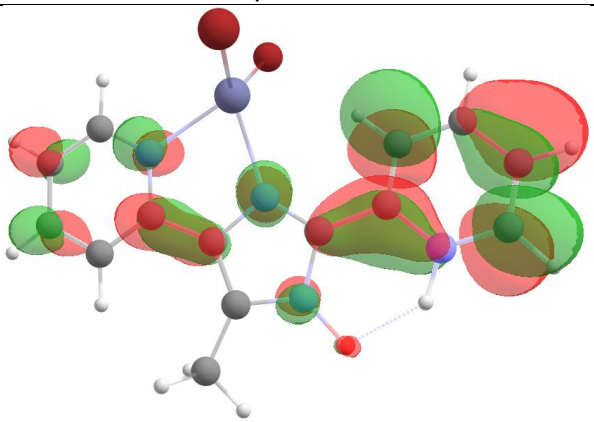
 **HOMO-7** $ZnBr_2$[a] 21.7%, Imid[b] 71.6%, Pyr-H[c] 4.8%, Pyr[d] 1.9%	 **HOMO-5** $ZnBr_2$ 95.8%, Imid 1.4%, Pyr-H 1.4%, Pyr 1.4%
 **HOMO-4** $ZnBr_2$ 12.9%, Imid 69.3%, Pyr-H 4.7%, Pyr 13.1%	 **HOMO-3** $ZnBr_2$ 92.8%, Imid 5.5%, Pyr-H 1.4%, Pyr 0.3%
 **HOMO-2** $ZnBr_2$ 97.5%, Imid 1.0%, Pyr-H 1.0%, Pyr 0.5%	 **HOMO-1** $ZnBr_2$ 97.0%, Imid 2.8%, Pyr-H 0.0%, Pyr 0.2%



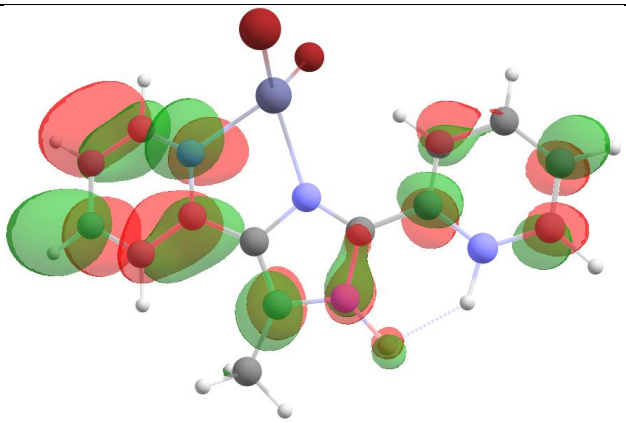
HOMO
$ZnBr_2$ 1.4%, Imid 79.8%, Pyr-H 7.4%, Pyr 11.4%



LUMO
$ZnBr_2$ 0.0%, Imid 15.1%, Pyr-H 81.3%, Pyr 3.6%



LUMO+1
$ZnBr_2$ 0.3%, Imid 9.7%, Pyr-H 76.1%, Pyr 13.9%



LUMO+2
$ZnBr_2$ 0.5%, Imid 11.9%, Pyr-H 16.4%, Pyr 71.2%

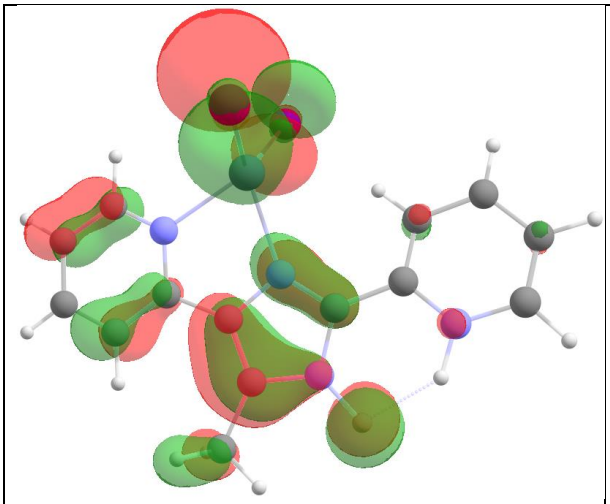
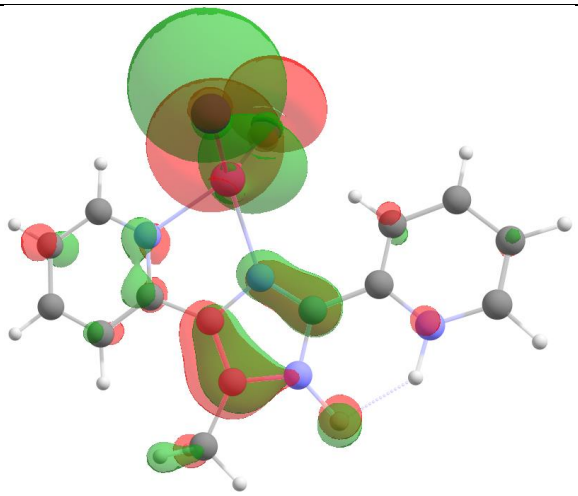
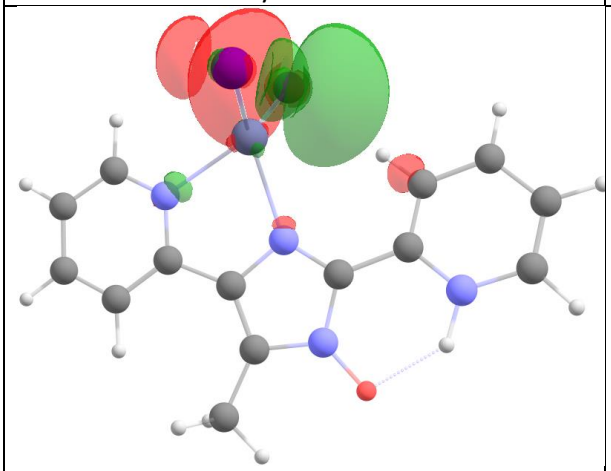
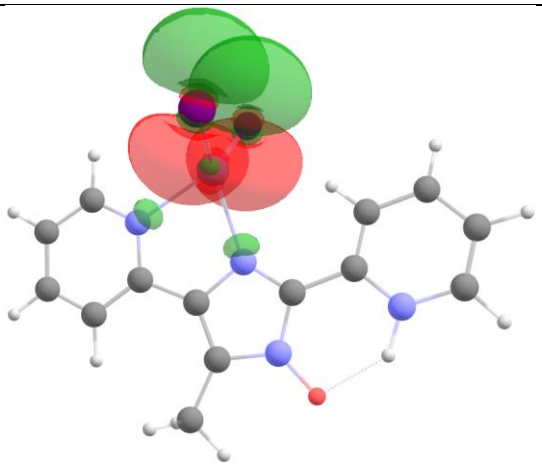
a – $ZnBr_2$ group
b – Imidazole ring
c – proton accepting pyridine ring
d – second pyridine ring

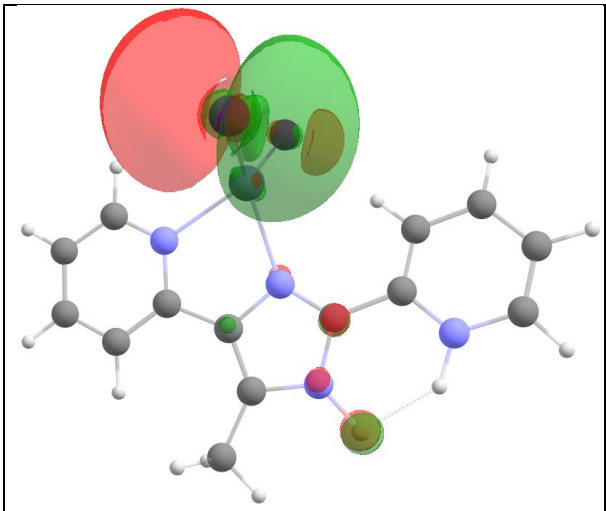
Table S39. Excited state properties of **$ZnHLI_2$** at the relaxed ground state geometry (local minimum in the **tautomeric form**, **S_0^T**, M062X/6-31+g(d) level of theory). Transitions with contribution >10% are shown.

State	Energy (eV)	Energy (nm)	Contributions (%)	Oscillator strength	Character
S1	2.6213	473	HOMO → LUMO (87.0%)	0.1244	IL + MLCT
S2	3.2553	381	HOMO-1 → LUMO (87.2%)	0.0039	MLCT
S3	3.3534	370	HOMO-2 → LUMO (93.5%)	0.0018	MLCT
S4	3.5466	350	HOMO-3 → LUMO (95.9%)	0.0027	MLCT
S5	3.6094	344	HOMO → LUMO+1 (87.9%)	0.0720	IL + MLCT
S6	3.6653	338	HOMO-4 → LUMO (97.0%)	0.0019	MLCT
S7	3.7797	328	HOMO-6 → LUMO (23.3%) HOMO-5 → LUMO (69.7%)	0.2233	IL + MLCT

S8	4.1399	299	HOMO-1 → LUMO+1 (81.5%)	0.0038	MLCT

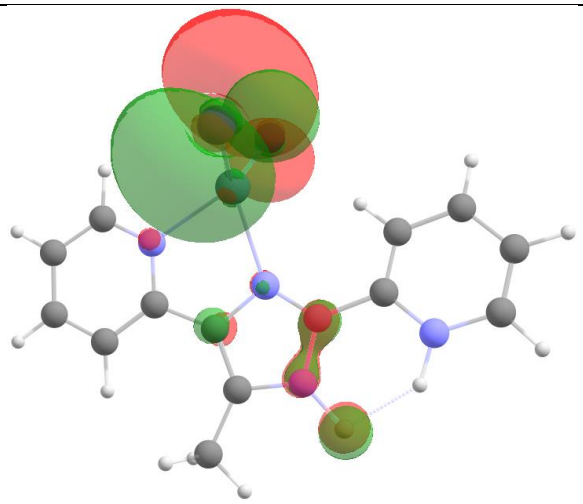
Table S40. Isosurface contour plots of the molecular orbitals of **$ZnHLI_2$** at the ground state geometry (local minimum in the **tautomeric form**, **S_0^T**, M062X/6-31+g(d) level of theory). Orbital decomposition resulting from Mulliken population analysis.

 **HOMO-6** ZnI_2[a] 29.1%, Imid[b] 55.2%, Pyr-H[c] 2.7%, Pyr[d] 13.0%	 **HOMO-5** ZnI_2 68.4%, Imid 23.8%, Pyr-H 2.9%, Pyr 4.9%
 **HOMO-4** ZnI_2 96.6%, Imid 1.0%, Pyr-H 1.3%, Pyr 1.1%	 **HOMO-3** ZnI_2 93.6%, Imid 4.0%, Pyr-H 1.4%, Pyr 1.0%



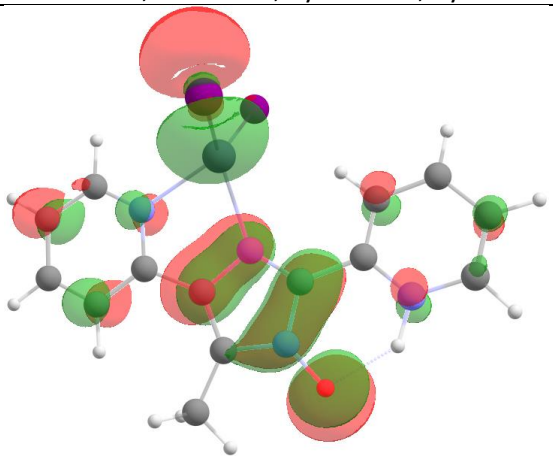
HOMO-2

ZnI_2 93.8%, Imid 4.0%, Pyr-H 1.1%, Pyr 1.1%



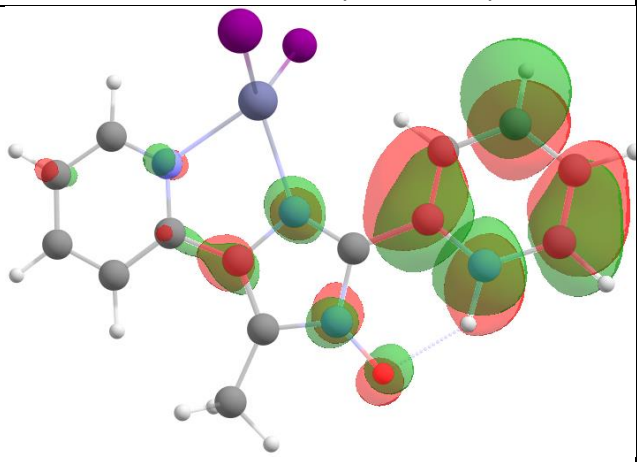
HOMO-1

ZnI_2 88.8%, Imid 9.3%, Pyr-H 0.6%, Pyr 1.3%



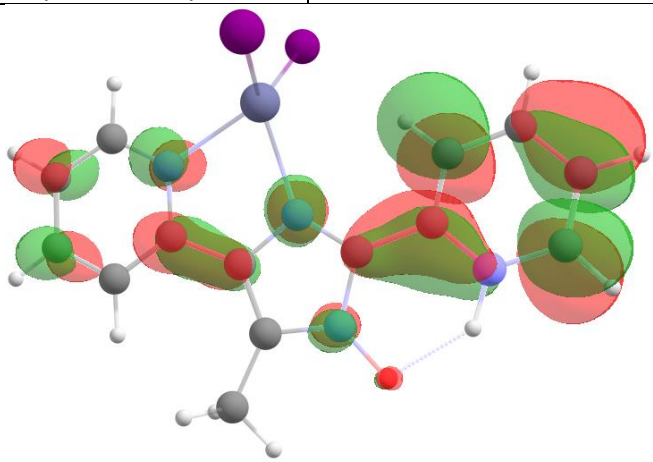
HOMO

ZnI_2 16.9%, Imid 68.7%, Pyr-H 5.7%, Pyr 8.7%



LUMO

ZnI_2 0.0%, Imid 16.5%, Pyr-H 79.7%, Pyr 3.8%



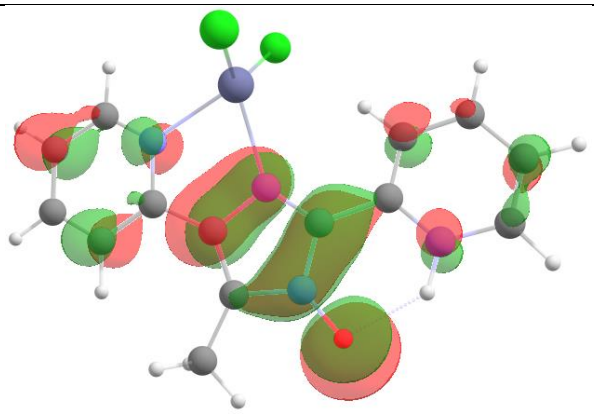
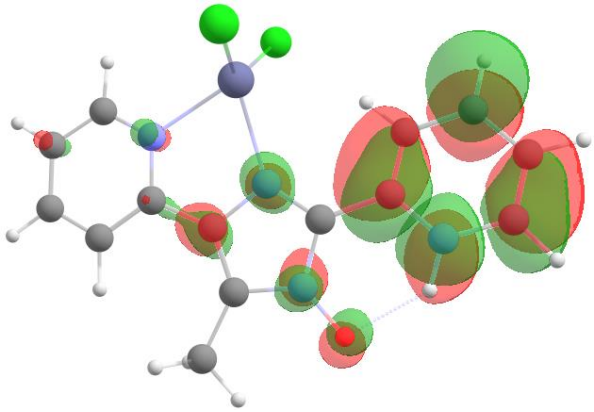
LUMO+1

ZnI_2 0.5%, Imid 9.6%, Pyr-H 76.5%, Pyr 13.4%

a – ZnI_2 group
b – Imidazole ring
c – proton accepting pyridine ring
d – second pyridine ring

Table S41. Isosurface contour plots of the molecular orbitals of **$ZnHLCl_2$** at the **first singlet excited state** geometry (**tautomeric form**, **S_1^T**, M062X/6-31+g(d) level of theory). Orbital decomposition resulting from Mulliken population analysis.

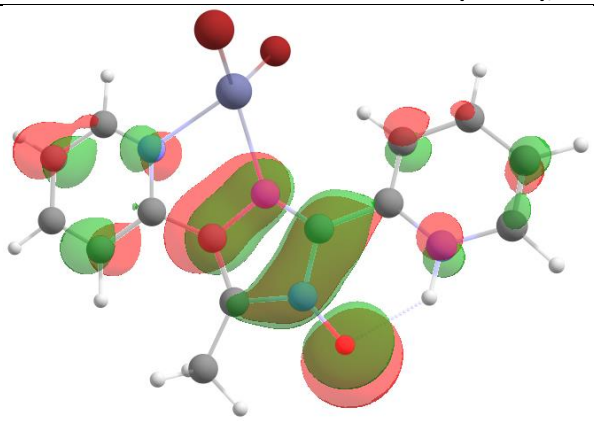
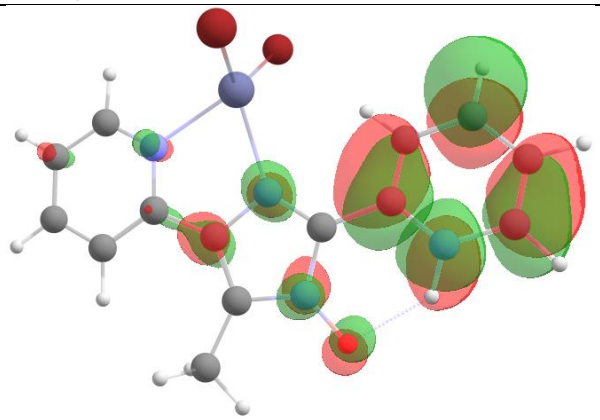
$S_1^T \rightarrow S_0^T$ is LUMO → HOMO transition (98.0%), λ = 509 nm, f = 0.1262

	
HOMO $ZnCl_2$[a] 0.6%, Imid[b] 81.3%, Pyr-H[c] 7.7%, Pyr[d] 10.4%	**LUMO** $ZnCl_2$ 0.0%, Imid 15.7%, Pyr-H 81.1%, Pyr 3.2%

a – $ZnCl_2$ group
b – Imidazole ring
c – proton accepting pyridine ring
d – second pyridine ring

Table S42. Isosurface contour plots of the molecular orbitals of **$ZnHLBr_2$** at the **first singlet excited state** geometry (**tautomeric form**, **S_1^T**, M062X/6-31+g(d) level of theory). Orbital decomposition resulting from Mulliken population analysis.

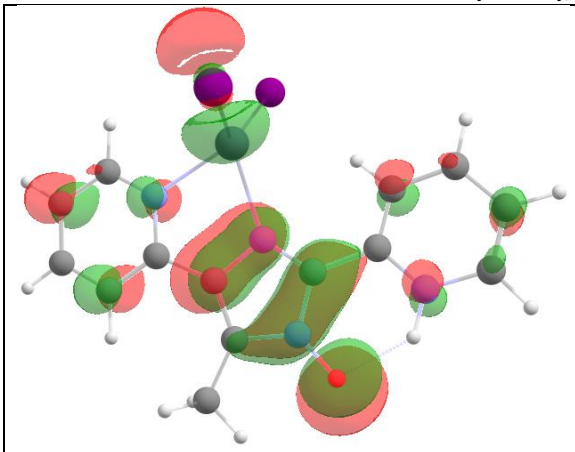
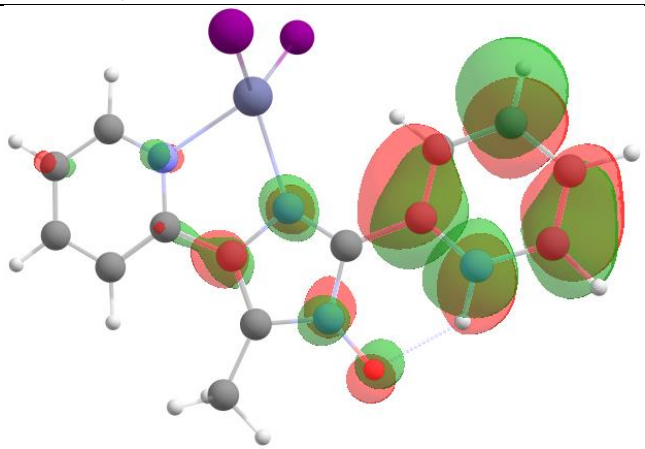
$S_1^T \rightarrow S_0^T$ is LUMO → HOMO transition (97.9%), λ = 510 nm, f = 0.1208

	
HOMO $ZnBr_2$[a] 1.2%, Imid[b] 81.3%, Pyr-H[c] 7.4%, Pyr[d] 10.1%	**LUMO** $ZnBr_2$ 0.0%, Imid 15.4%, Pyr-H 81.3%, Pyr 3.3%

a – $ZnBr_2$ group
b – Imidazole ring
c – proton accepting pyridine ring
d – second pyridine ring

Table S43. Isosurface contour plots of the molecular orbitals of **$ZnHLI_2$** at the **first singlet excited state** geometry (**tautomeric form**, **S_1^T**, M062X/6-31+g(d) level of theory). Orbital decomposition resulting from Mulliken population analysis.

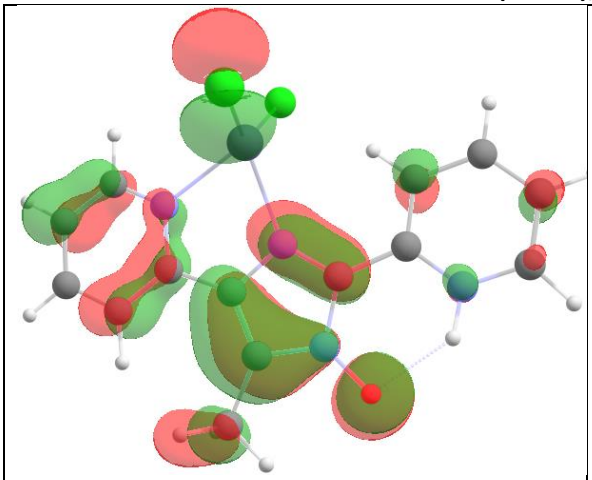
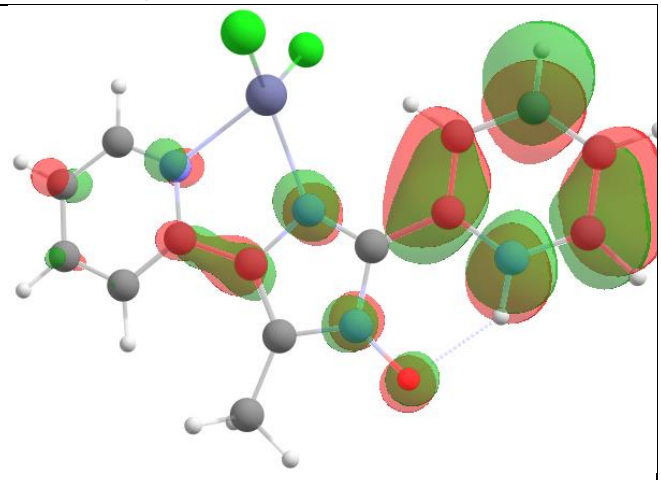
$S_1^T \rightarrow S_0^T$ is LUMO → HOMO transition (94.4%), λ = 507 nm, f = 0.1182

	
HOMO ZnI_2[a] 8.0%, Imid[b] 76.4%, Pyr-H[c] 6.7%, Pyr[d] 8.9%	**LUMO** ZnI_2 0.0%, Imid 16.9%, Pyr-H 79.7%, Pyr 3.4%

a – ZnI_2 group
b – Imidazole ring
c – first pyridine ring (which is coordinated to Zn atom)
d – second pyridine ring (which is not coordinated to Zn atom)

Table S44. Isosurface contour plots of the molecular orbitals of **$ZnHLCl_2$** at the **second singlet excited state** geometry (**tautomeric form**, **S_2^T**, M062X/6-31+g(d) level of theory). Orbital decomposition resulting from Mulliken population analysis.

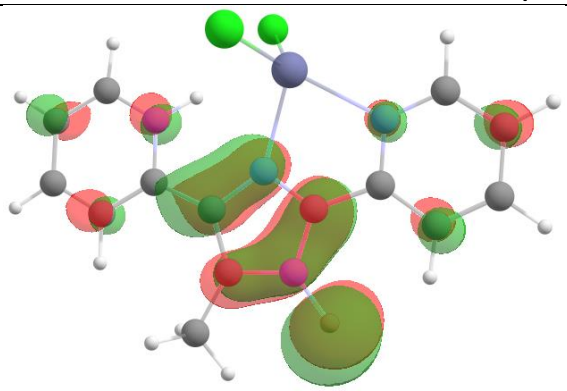
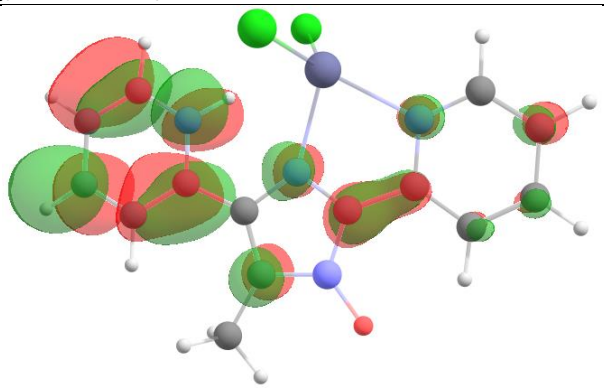
$S_2^T \rightarrow S_0^T$ is LUMO → HOMO-1 transition (98.3%), λ = 379 nm, f = 0.1276

	
HOMO-1 $ZnCl_2$[a] 10.3%, Imid[b] 71.9%, Pyr-H[c] 5.4%, Pyr[d] 12.4%	**LUMO** $ZnCl_2$ 0.0%, Imid 11.5%, Pyr-H 82.3%, Pyr 6.2%

a – $ZnCl_2$ group
b – Imidazole ring
c – proton accepting pyridine ring
d – second pyridine ring

Table S45. Isosurface contour plots of the molecular orbitals of **$ZnHLCl_2$** at the **first singlet excited state** geometry (**minor component**, **S_1^{minor}**, M062X/6-31+g(d) level of theory). Orbital decomposition resulting from Mulliken population analysis.

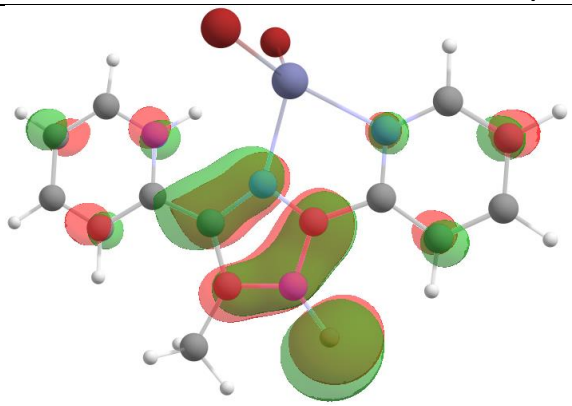
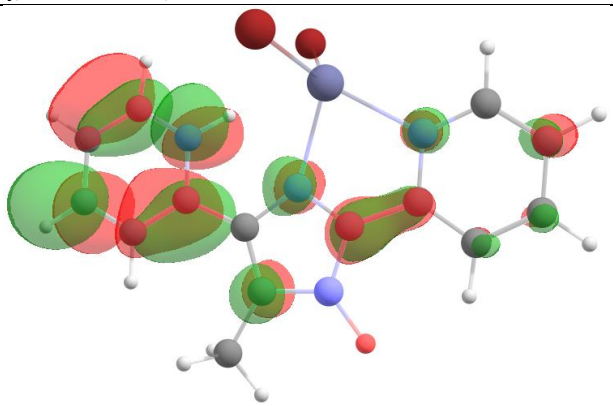
S_1^{minor} → S_0^{minor} is LUMO → HOMO transition (97.4%), λ = 491 nm, f = 0.1884

	
HOMO $ZnCl_2$[a] 0.5%, Imid[b] 85.4%, Pyr1[c] 6.4%, Pyr2[d] 7.7%	**LUMO** $ZnCl_2$ 0.4%, Imid 10.2%, Pyr1 7.4%, Pyr2 82.0%

a – $ZnCl_2$ group
b – Imidazole ring
c – first pyridine ring (which is coordinated to Zn atom)
d – second pyridine ring (which is not coordinated to Zn atom)

Table S46. Isosurface contour plots of the molecular orbitals of **$ZnHLBr_2$** at the **first singlet excited state** geometry (**minor component**, **S_1^{minor}**, M062X/6-31+g(d) level of theory). Orbital decomposition resulting from Mulliken population analysis.

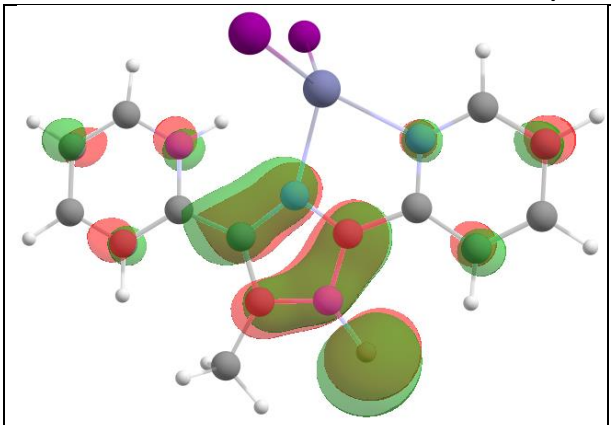
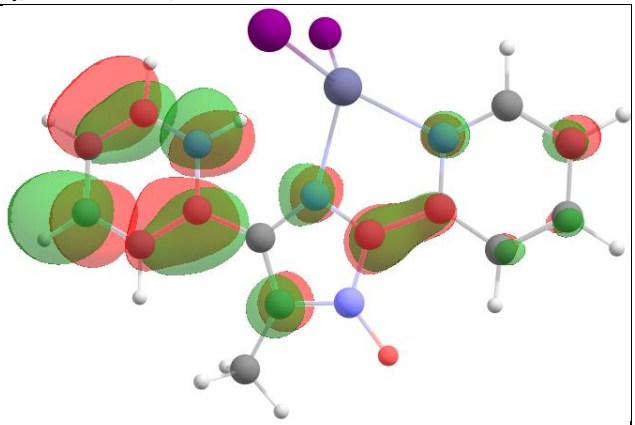
S_1^{minor} → S_0^{minor} is LUMO → HOMO transition (97.4%), λ = 493 nm, f = 0.1804

	
HOMO $ZnBr_2$[a] 0.7%, Imid[b] 85.3%, Pyr1[c] 6.3%, Pyr2[d] 7.7%	**LUMO** $ZnBr_2$ 0.5%, Imid 10.1%, Pyr1 7.1%, Pyr2 82.3%

a – $ZnBr_2$ group
b – Imidazole ring
c – first pyridine ring (which is coordinated to Zn atom)
d – second pyridine ring (which is not coordinated to Zn atom)

Table S47. Isosurface contour plots of the molecular orbitals of **$ZnHLI_2$** at the **first singlet excited state** geometry (**minor component**, **S_1^{minor}**, M062X/6-31+g(d) level of theory). Orbital decomposition resulting from Mulliken population analysis.

S_1^{minor} → S_0^{minor} is LUMO → HOMO transition (97.3%), λ = 494 nm, f = 0.1720

	
HOMO ZnI_2[a] 1.4%, Imid[b] 84.2%, Pyr-H[c] 6.2%, Pyr[d] 8.2%	**LUMO** ZnI_2 0.6%, Imid 10.0%, Pyr-H 7.2%, Pyr 82.2%

a – ZnI_2 group
b – Imidazole ring
c – first pyridine ring (which is coordinated to Zn atom)
d – second pyridine ring (which is not coordinated to Zn atom)

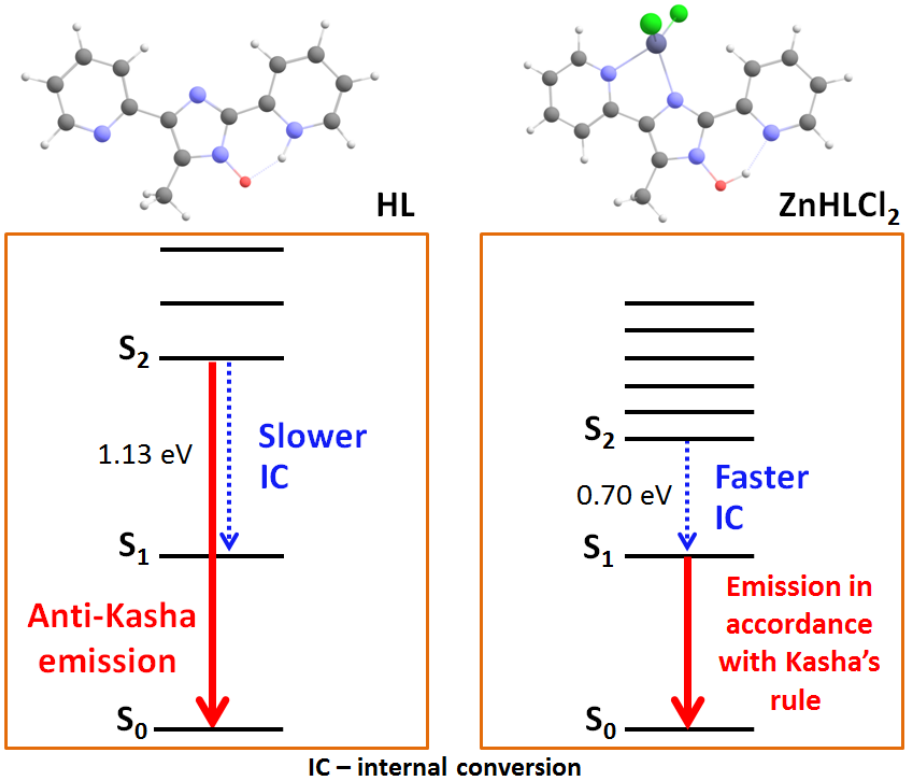


Figure S28. Comparison of the emission mechanisms of the free ligand **HL** and the complex **$ZnHLCl_2$**.