Supporting Information

Synthesis, Structures and Photophysical Properties of Tetra- and Hexanuclear Zinc-Hydroxido-Acetato-Clusters Supported by Tridentate Salicylaldiminato Ligands

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Content

1. Characterization of compounds - Infrared Spectroscopy

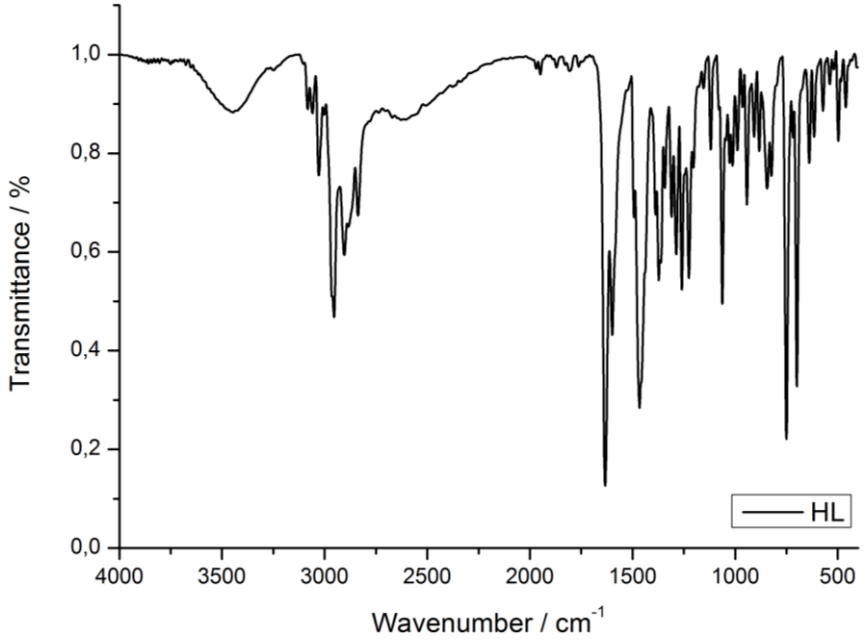


Figure S1: FTIR spectrum of **HL** (KBr pellet).

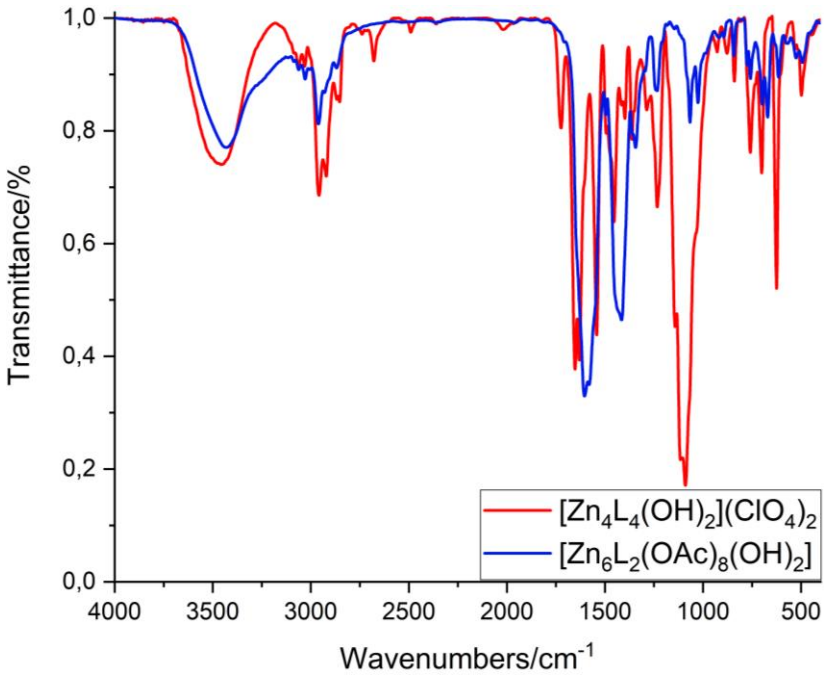


Figure S2: FTIR spectra of $[Zn_6L_2(OH)_2(OAc)_8]$ (**1**, KBr pellet) and $[Zn_4L_4(OH)_2](ClO_4)_2$ (**2**, KBr pellet).

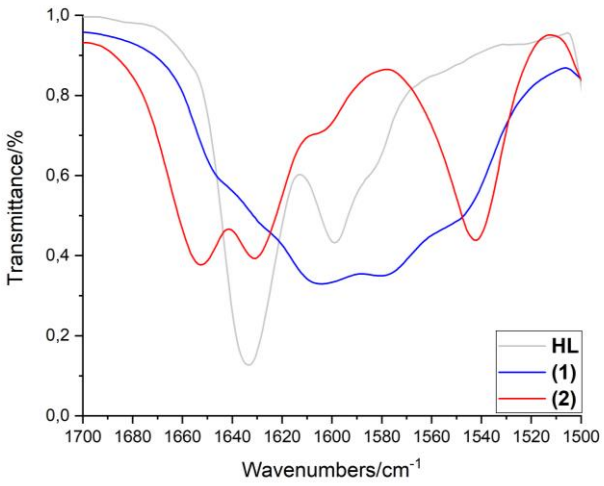


Figure S3. Overlay of the FTIR spectra of the ligand (**HL**) and the zinc complexes **1** and **2** (1700-1500 cm^{-1}).

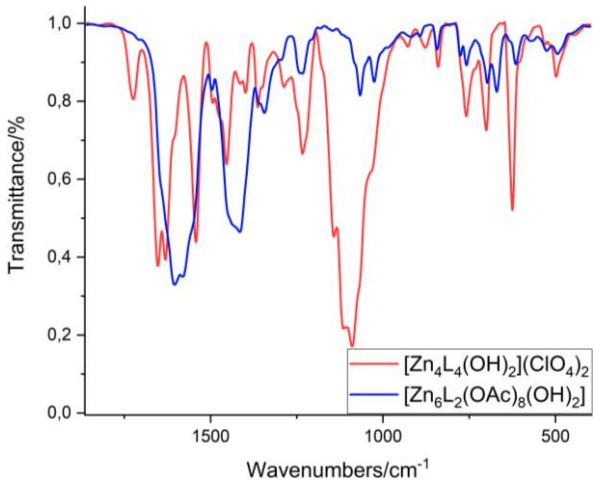


Figure S4. Overlay of the FTIR spectra of the zinc complexes **1** and **2** (1750-450 cm^{-1}).
2)

2. Packing diagram for HL.

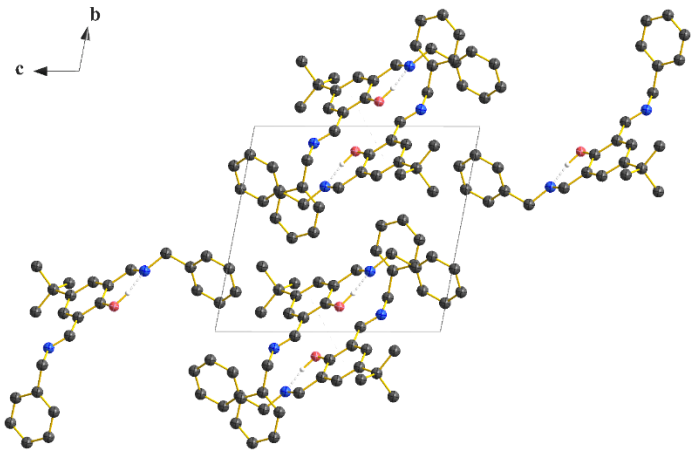


Figure S5: Packing diagram of **HL** showing intermolecular π-π stacking (offset face-to-face) interactions between adjacent ligand molecules.

3. Determination of Coordination Geometries utilizing SHAPE

The coordination geometries of the zinc complexes were examined utilizing the SHAPE program. According to SHAPE, deviations from ideal coordination geometry are represented by a symmetry factor, that increases upon increasing distortions from the ideal geometry, for which the deviation factor is zero.

Table S1. Shape symmetry factors for complex 1

Six-Coordinated Zinc atoms in **1** (Zn1, Zn4) ----------

HP-6 1 D6h Hexagon
PPY-6 2 C5v Pentagonal pyramid
OC-6 3 Oh Octahedron
TPR-6 4 D3h Trigonal prism
JPPY-6 5 C5v Johnson pentagonal pyramid J2

Structure [ML6]		HP-6	PPY-6	OC-6	TPR-6	JPPY-6
Zn1	,	31.959,	24.957,	0.828,	13.389,	28.438
Zn4	,	31.206,	25.671,	0.721,	13.226,	29.216

Five-Coordinated Zinc atoms in **1** (Zn2, Zn5) ----------

PP-5 1 D5h Pentagon
vOC-5 2 C4v Vacant octahedron
TBPY-5 3 D3h Trigonal bipyramid
SPY-5 4 C4v Spherical square pyramid
JTBPY-5 5 D3h Johnson trigonal bipyramid J12

Structure [ML5]		PP-5	vOC-5	TBPY-5	SPY-5	JTBPY-5
Zn2	,	29.426,	1.717,	4.444,	0.440,	6.940
Zn5	,	31.065,	3.507,	1.552,	1.849,	4.376

Four-Coordinated Zinc atoms in **1** (Zn3, Zn6) ----------

SP-4 1 D4h Square
T-4 2 Td Tetrahedron
SS-4 3 C2v Seesaw
vTBPY-4 4 C3v Vacant trigonal bipyramid

Structure [ML4]		SP-4	T-4	SS-4	vTBPY-4
Zn3	,	28.540,	0.502,	6.311,	2.797
Zn6	,	29.538,	0.350,	6.655,	3.021

Shape symmetry factors for complex 2

Zn-Polyeder

PP-5 1 D5h Pentagon

vOC-5 2 C4v Vacant octahedron
TBPY-5 3 D3h Trigonal bipyramid
SPY-5 4 C4v Spherical square pyramid
JTBPY-5 5 D3h Johnson trigonal bipyramid J12

Structure [ML5]		PP-5	vOC-5	TBPY-5	SPY-5	JTBPY-5
Zn1	,	28.490,	5.477,	2.372,	3.635,	4.374
Zn2	,	31.065,	3.507,	1.552,	1.849,	4.376
Zn3	,	28.969,	5.073,	2.693,	3.047,	4.619
Zn4	,	29.457,	5.271,	2.085,	3.327,	4.307

4. Characterization of compounds - NMR spectroscopy

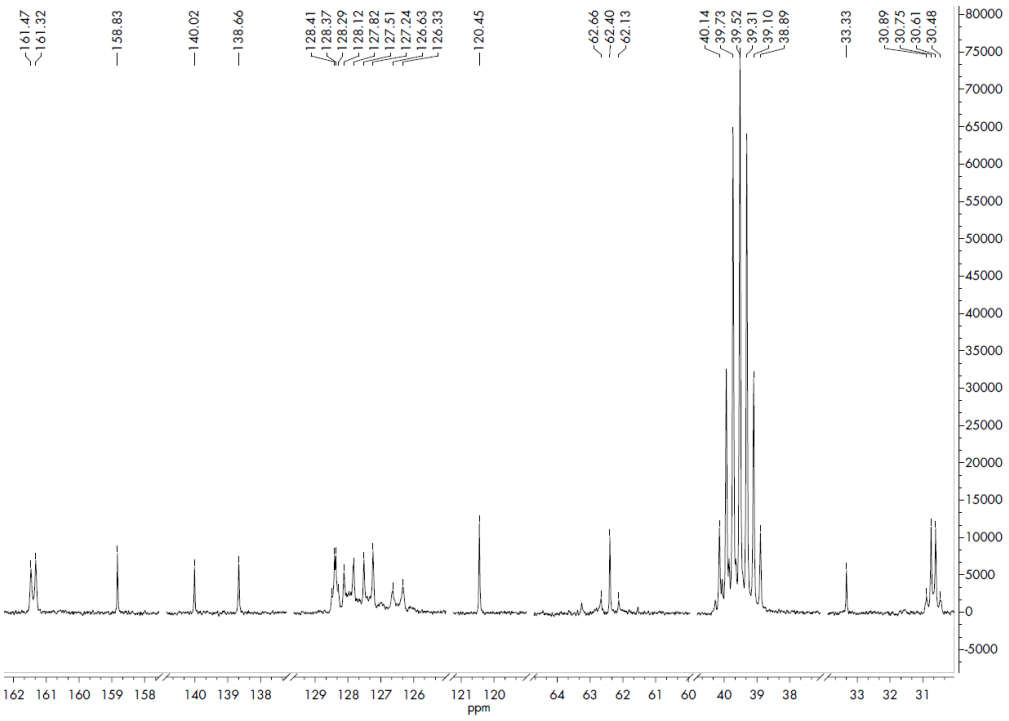


Figure S6: ^{13}C-NMR spectrum of **HL** recorded in dimethylsulfoxide-d^6 at 363 K; multiplicity of C-H coupling displayed; parts of the spectrum without signals cut out for better observation of the multiplicities.

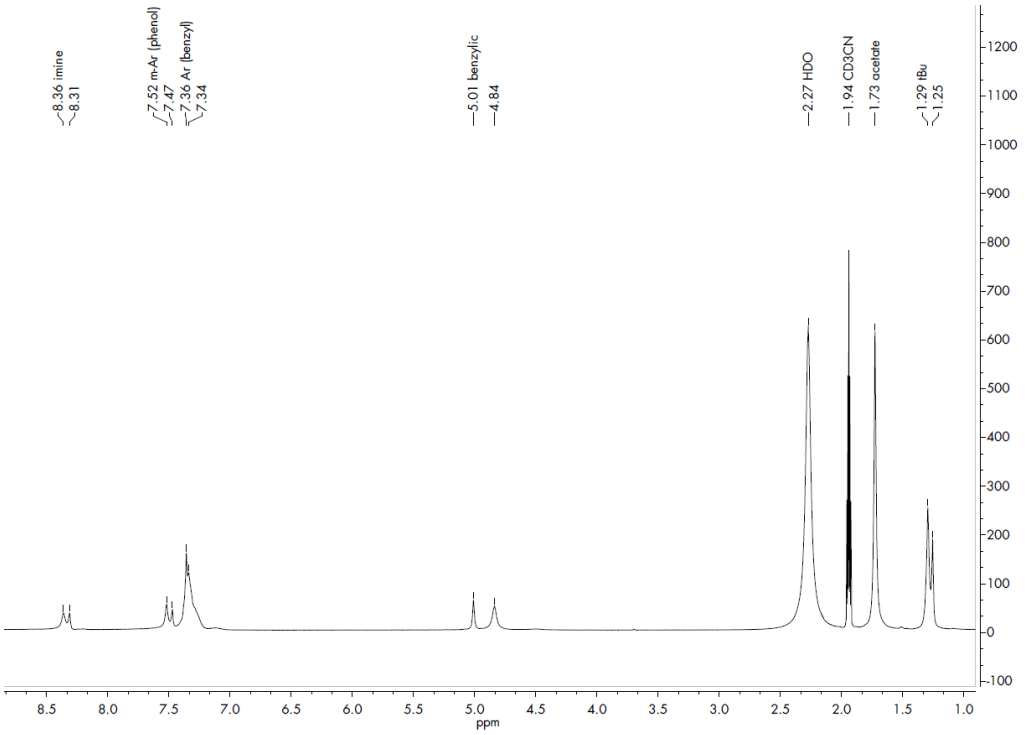


Figure S7: ^{1}H-NMR spectrum of $[Zn_6L_2(OH)_2(OAc)_8]$ recorded in CD_3CN at ambient temperature.

5. UV/vis spectroscopy & Fluorescence spectroscopy

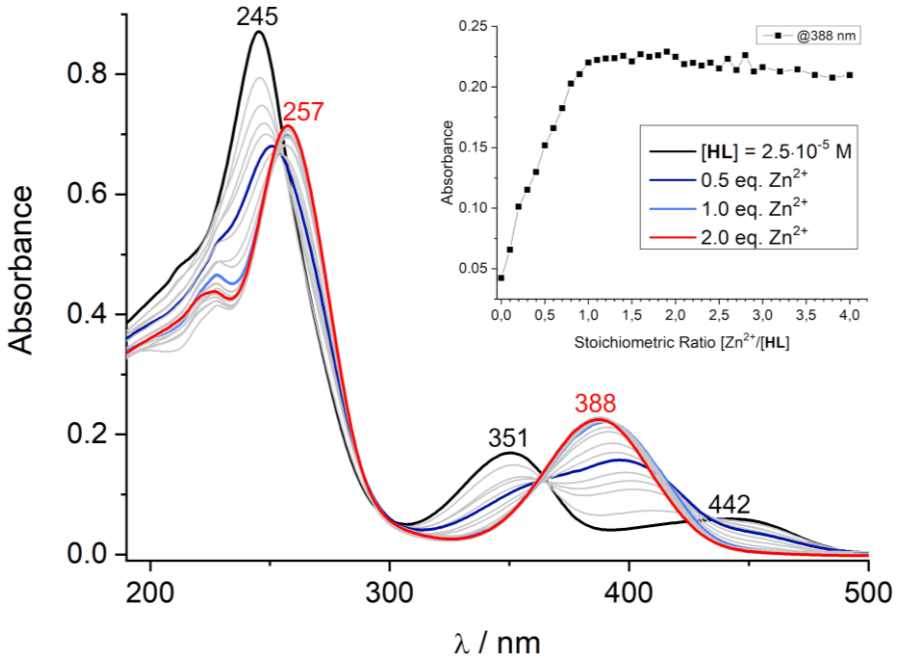


Figure S8. Spectrophotometric titration of **HL** with $Zn(ClO_4)_2 \cdot 6\ H_2O$ in CH_2Cl_2/MeOH (3:2/v:v) at a 10^{-5} M concentration and constant ionic strength (10^{-2} M N(*n*-Bu)$_4PF_6$, T = 295 K). The blue curve corresponds to a final Zn^{2+}/**HL** molar ratio of 1:1. The inset shows the evolution of selected absorbance values versus the $[Zn^{2+}]$/[**HL**] molar ratio.

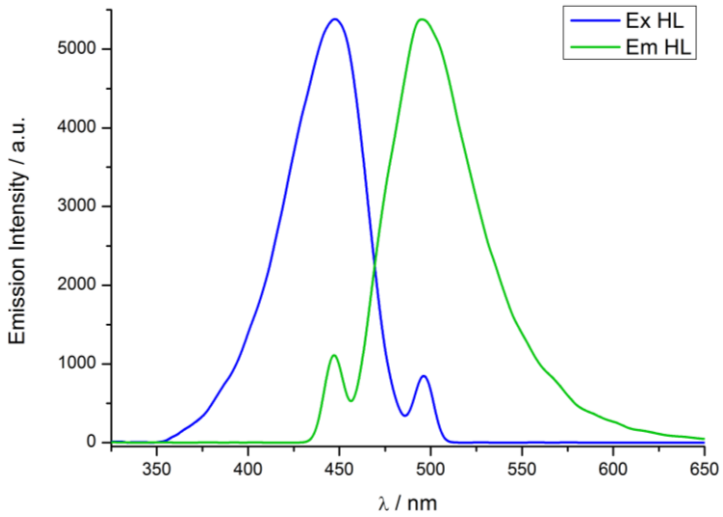


Figure S9. Excitation (blue) and emission spectrum (green) of **HL** in acetonitrile (c(HL) = $1 \cdot 10^{-5}$ M, 298 K). MeCN; $1 \cdot 10^{-5}$M; λ_{Ex} = 447 nm; λ_{Em} = 497 nm

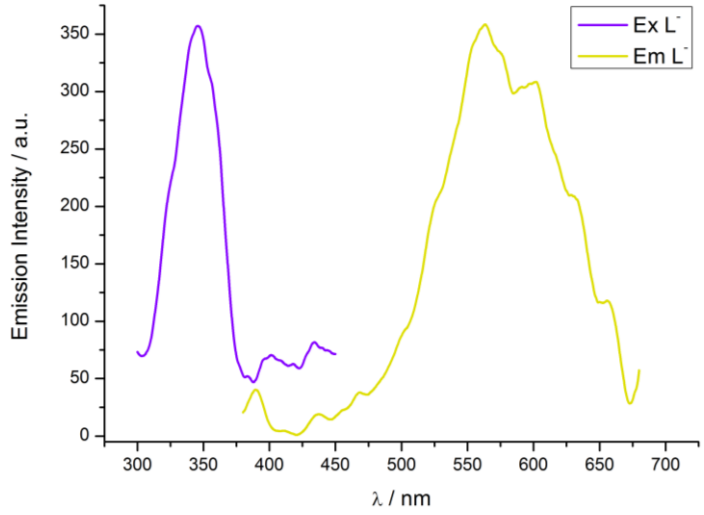


Figure S10: Excitation (violet) and emission spectrum (yellow) of $\mathbf{L}^-$ in acetonitrile in the presence of base (c(HL) = $1 \cdot 10^{-5}$ M, c(NEt_3) = $1 \cdot 10^{-5}$ M, 298 K). MeCN; c(HL) = $1 \cdot 10^{-5}$M; c(NEt_3) = $1 \cdot 10^{-5}$M; λ_{Ex} = 346 nm; λ_{Em} = 563 nm

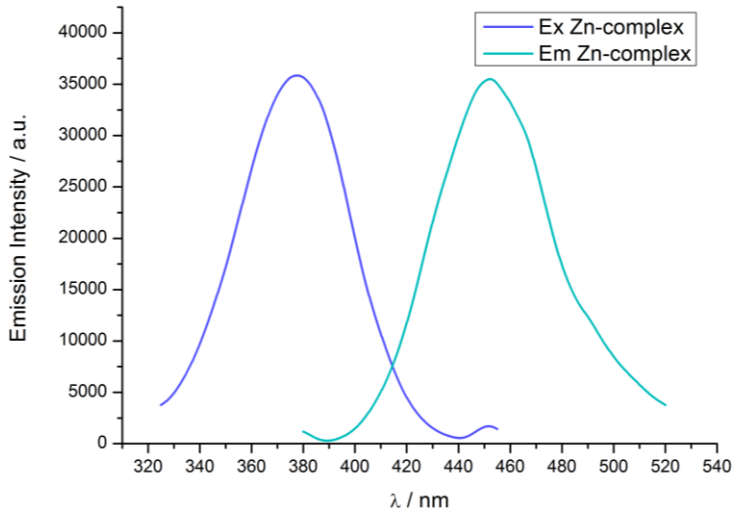
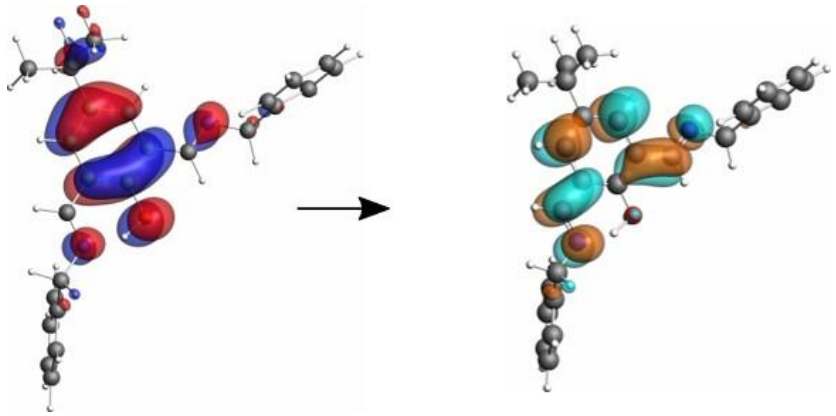


Figure S11. Excitation (azure) and emission spectrum (turquoise) of **[$Zn_6L_2(OH)_2(OAc)_8$]** in acetonitrile (c(**complex**) = $1 \cdot 10^{-5}$ M, 298 K). λ_{Ex} = 378 nm; λ_{Em} = 452 nm.

6. Characterization of compounds – DFT calculations

a)



b)

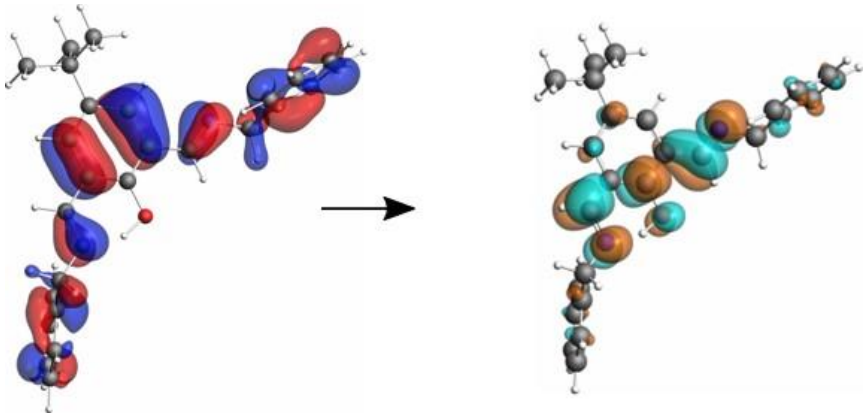
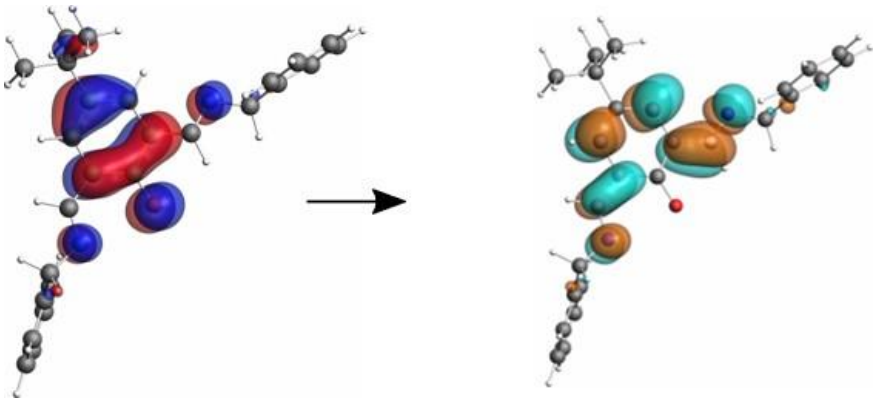


Figure S12: Major contributions to the observed UV-Vis bands of **HL** with the single orbital transition contribution in parentheses. a) HOMO→LUMO: 334 nm (97%). b) HOMO-1→LUMO+1: 245 nm (67%).

a)



b)

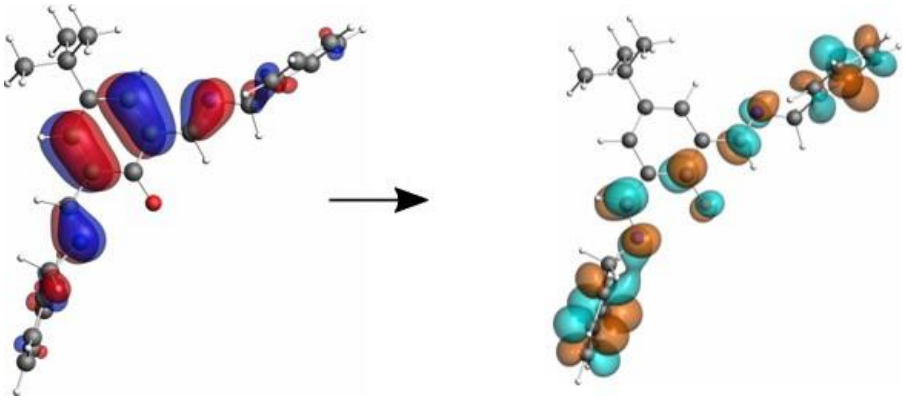


Figure S13: Major contributions to the observed UV-Vis bands of **HL**$^{-}$ with the single orbital transition contribution in parentheses. a) HOMO→LUMO: 409 nm (98%). b) HOMO-2→LUMO+1: 229 nm (36%).

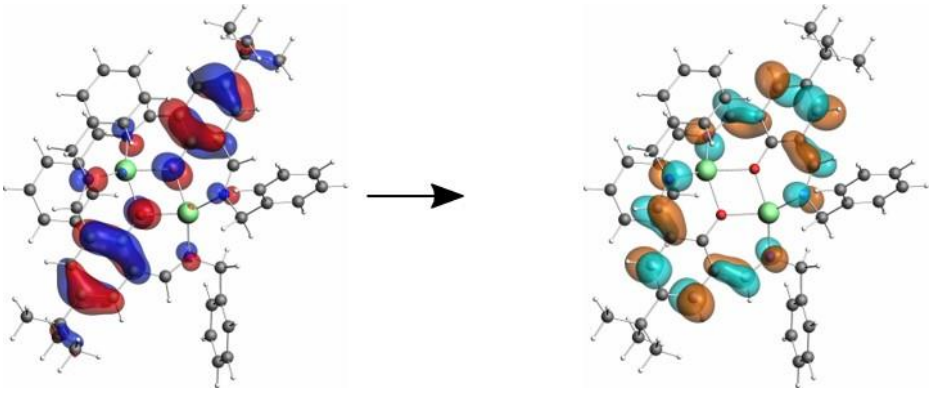


Figure S14: Major contributions to the observed UV-Vis bands of $[Zn_2L_2]^{2+}$ with the single orbital transition contribution in parentheses. a) HOMO→LUMO: 348 nm (57%).

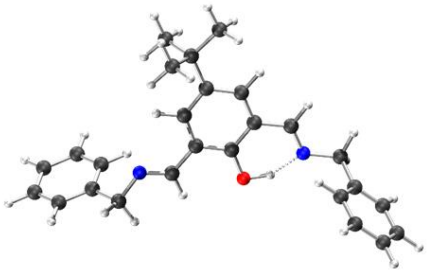


Figure S15: PBE-D3(BJ) optimized structure of **HL** used for the simulation of UV-Vis spectra (pristine) and basis for the other used structures.

Calculated atomic coordinates have been deposited at the open access data base zenode, see https://doi.org/10.5281/zenodo.7837334

7. Determination of detection limit (LOD value)

The fluorescence intensity of HL at 454 nm as a function of the Zn^{2+} ion concentration was found to be linear in the range from $1 \cdot 10^{-6}$ to $1 \cdot 10^{-7}$ M. The limit of detection (c_{LOD} value; $c_{LOD} = 3\sigma_{bl}/b$, where σ_{bl} is the standard deviation of the blank measurements and b the slope of the regression line according to the IUPAC defnition)) is a measure for the lowest concentration that can be measured. The fluorescence titration carried out between HL and Zn^{2+} provides a value of 0.24(4) ppm.

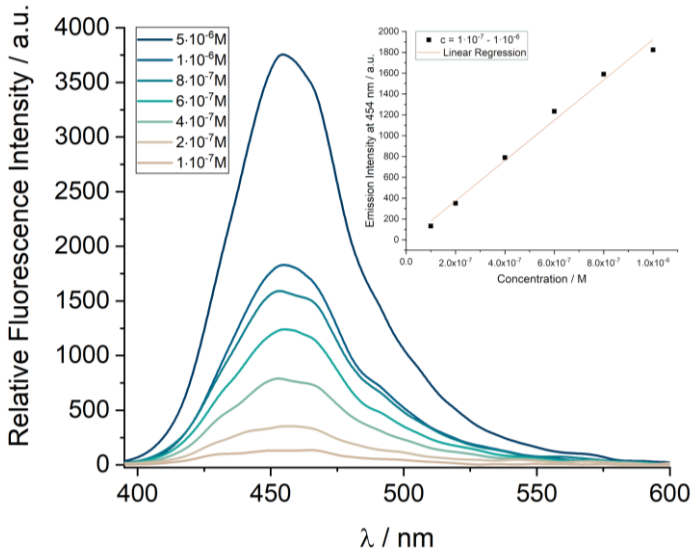


Figure S16: Fluorescence spectra **HL** as a function of Zn^{2+} ion concentration.