

Dalton Transactions

Electronic Supplementary Information

Synthesis, structure and spectral properties of *O, N, N* coordinating
ligands and their neutral Zn(II) complexes: a combined
experimental and theoretical study[†]

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Table S1 Selected Parameters for the Vertical Excitation (UV-vis Absorptions) and the Emission of HL¹; Electronic Excitation Energies (eV) and Oscillator Strengths (*f*), Configurations of the Low-Lying Excited States of HL¹; Calculation of the S₀–S₁ Energy Gaps Based on Optimized Ground-State Geometries (UV-vis Absorption) and the Optimized Excited-State Geometries (Fluorescence) (THF used as solvent)

Process	Electronic Transitions	Composition	Excitation energy	Oscillator strength (<i>f</i>)	CI	λ _{exp} (nm)
Absorbance	S ₀ → S ₁	HOMO → LUMO	2.6913eV (460 nm)	0.3835	0.70491	468
	S ₀ → S ₃	HOMO – 1 → LUMO HOMO → LUMO + 1	3.4268eV (361 nm)	0.3388	0.63760 –0.29451	360
Emission	S ₁ → S ₀	HOMO → LUMO	3.4882eV (530 nm)	0.2674	0.70633	533

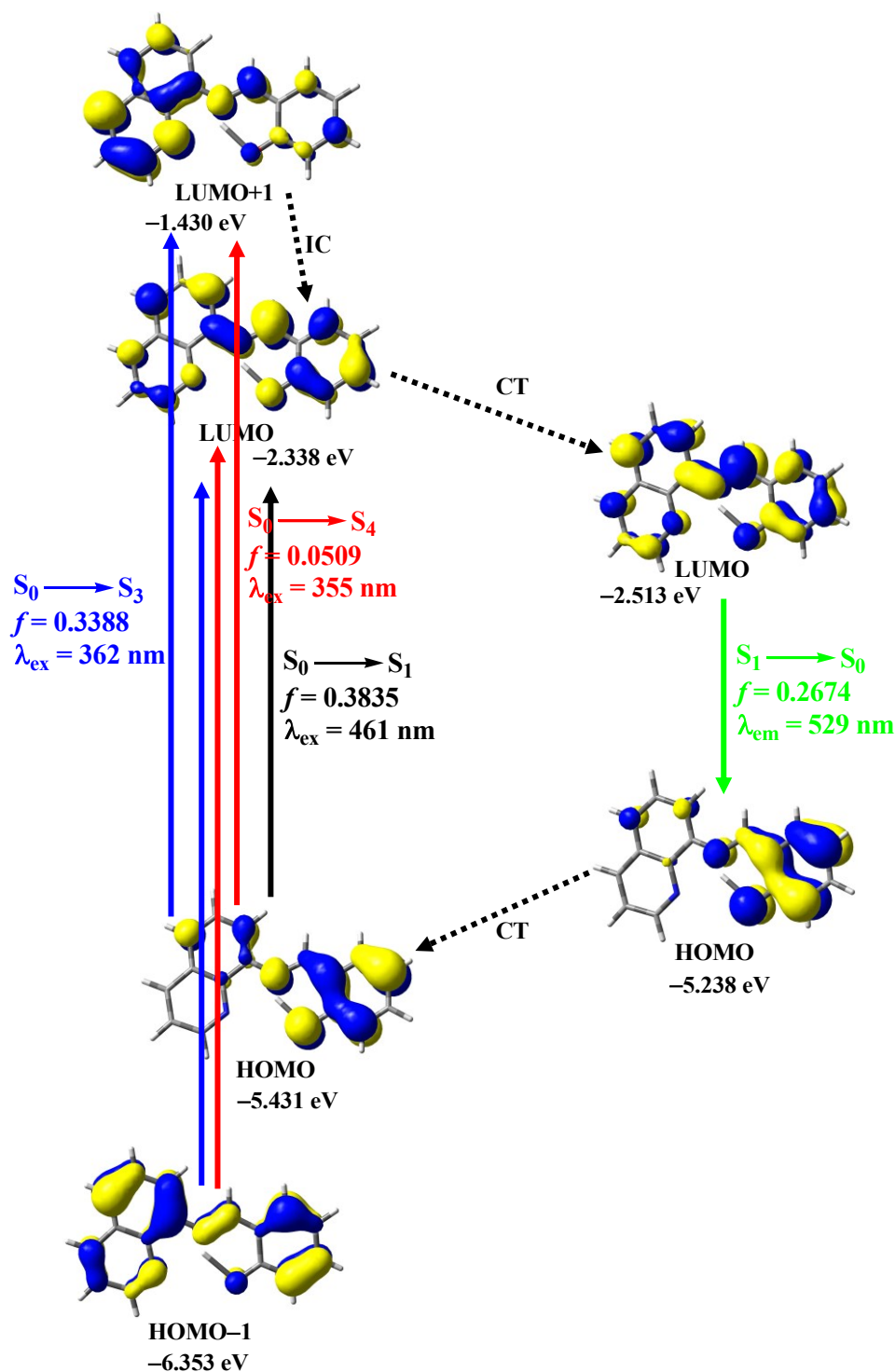


Fig. S1 Frontier molecular orbitals involved in the UV-vis absorption and emission of HL¹. IC stands for internal conversion and CT stands for conformation transformation. Excitation and radiative decay process are marked as solid lines and the non-radiative processes are marked by dotted lines.

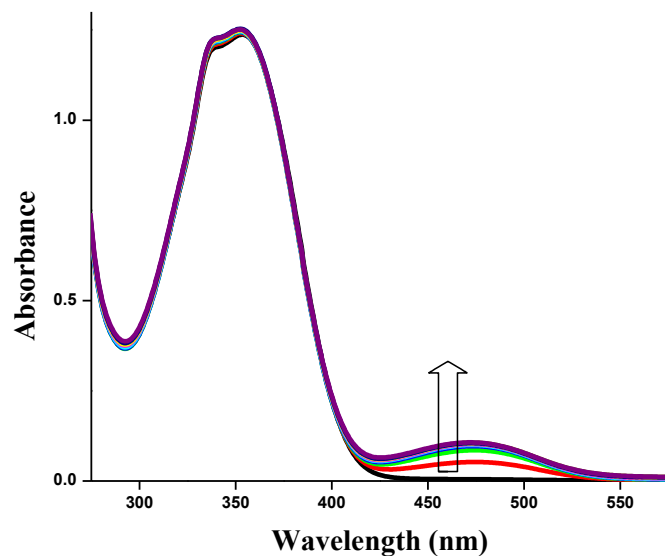


Fig. S2 Spectrophotometric titrations of HL¹ (0.1 mM) with various numbers of equivalent of Zn(ClO₄)₂·6H₂O in THF at room temperature ([Zn²⁺] = 0, 0.01, 0.02, 0.03, 0.04, 0.05 mM).

With increasing concentration of Zn²⁺ ion the characteristic absorbance of the ligand (HL¹) at 344 nm gradually decreases while the band at 468 nm gradually increases through an isosbestic point at 410 nm respectively. UV-vis titration study has been confirmed the formation of 1:2 complexes between Zn(II) and ligand. Absorption titration spectrum is given above.

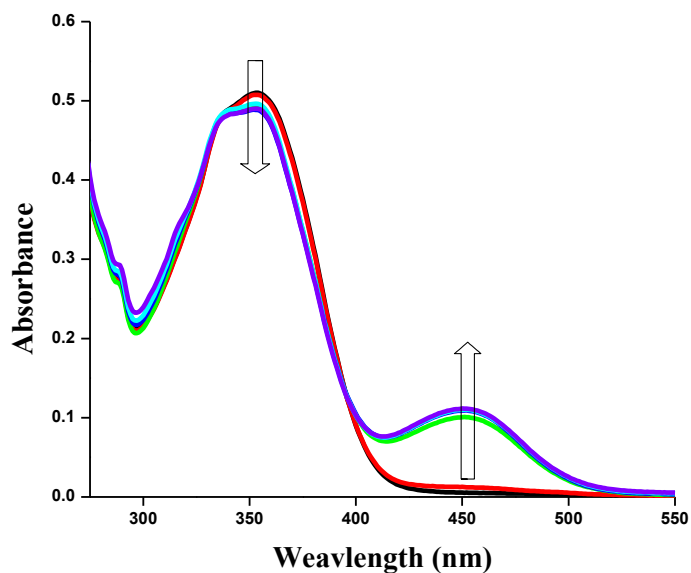


Fig. S3 Spectrophotometric titrations of HL³ (0.1 mM) with various numbers of equivalent of Zn(ClO₄)₂·6H₂O in THF at room temperature ([Zn²⁺] = 0, 0.01, 0.04, 0.05 mM).

With increasing concentration of Zn²⁺ ion the characteristic absorbance of the ligand (HL³) at 360 nm gradually decreases while the band at 450 nm gradually increases through an isosbestic point at 395 nm respectively. UV-vis titration study has been confirmed the formation of 1:2 complexes between Zn(II) and ligand. Absorption titration spectrum is given above.

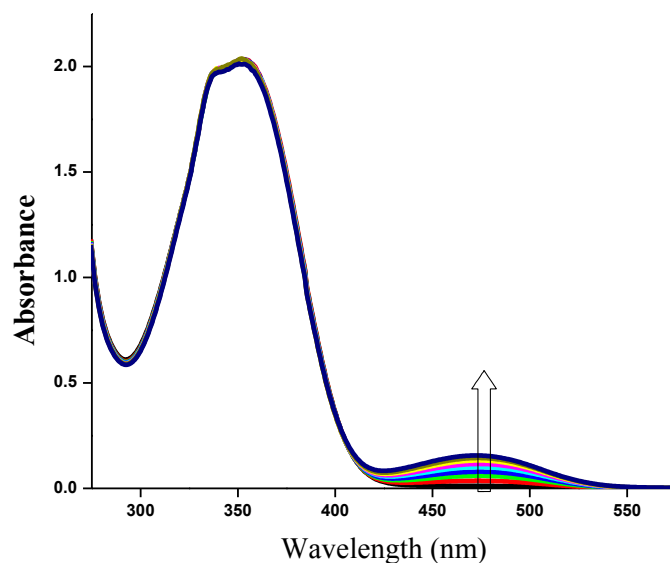


Fig. S4 Spectrophotometric titrations of HL⁴ (0.1 mM) with various numbers of equivalent of Zn(ClO₄)₂·6H₂O in THF at room temperature ([Zn²⁺] = 0, 0.01, 0.02, 0.03, 0.04, 0.05 mM).

With increasing concentration of Zn²⁺ ion the characteristic absorbance of the ligand (HL⁴) at 357 nm gradually decreases while the band at 473 nm gradually increases through an isosbestic point at 408 nm respectively. UV-vis titration study has been confirmed the formation of 1:2 complexes between Zn(II) and ligand. Absorption titration spectrum is given above.

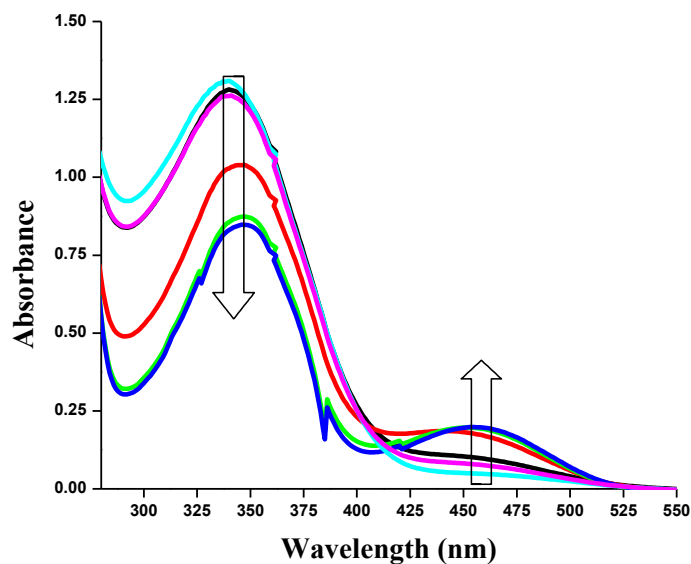


Fig. S5 Spectrophotometric titrations of HL⁵ (0.1 mM) with various numbers of equivalent of Zn(ClO₄)₂·6H₂O in THF at room temperature ([Zn²⁺] = 0, 0.01, 0.02, 0.03, 0.04, 0.05 mM).

With increasing concentration of Zn²⁺ ion the characteristic absorbance of the ligand (HL⁵) at 337 nm gradually decreases while the band at 454 nm gradually increases through an isosbestic point at 410 nm respectively. UV-vis titration study has been confirmed the formation of 1:2 complexes between Zn(II) and ligand. Absorption titration spectrum is given above.

Table S2 Main calculated optical transition for complex 4 with composition in terms of molecular orbital contribution of the transition, Vertical excitation energies and Oscillator strength in THF

Excitation	Composition	Excitation energy	Oscillator strength (<i>f</i>)	CI	Assign	λ_{exp} (nm)
1	HOMO - 1 → LUMO	2.5201eV (491 nm)	0.2773	0.50875	ILCT	473
	HOMO → LUMO + 1			-0.42459	ILCT	
2	HOMO - 1 → LUMO + 1	2.5327eV (489 nm)	0.1829	0.64360	ILCT	
	HOMO → LUMO			-0.19465	ILCT	
3	HOMO - 4 → LUMO	3.4909eV (355 nm)	0.1487	0.57825	ILCT	351
	HOMO - 2 → LUMO			-0.33841	ILCT	
4	HOMO - 5 → LUMO	3.5361eV (350 nm)	0.2968	0.56625	ILCT	
	HOMO - 3 → LUMO			-0.2843	ILCT	
	HOMO - 2 → LUMO + 1			0.18359	ILCT	

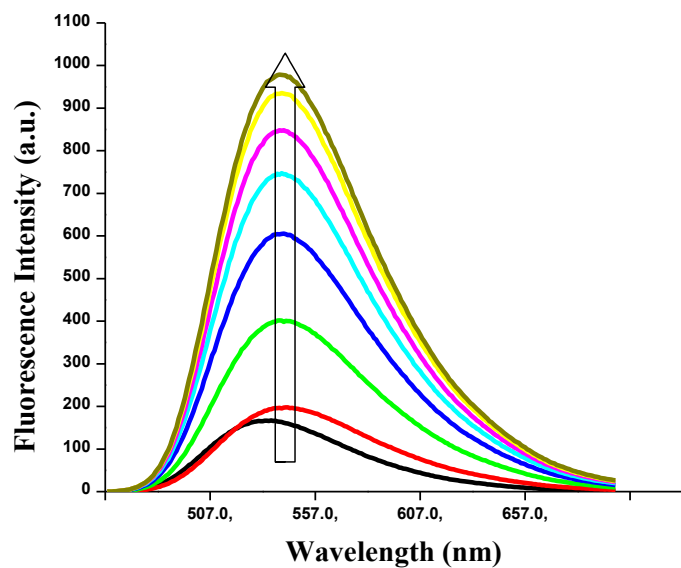


Fig. S6 Fluorescence emission spectra of HL¹ upon addition of Zn(II) in THF, $\lambda_{\text{ex}} = 466$ nm at room temperature ($[\text{HL}^1] = 0.1 \text{ mM}$, $[\text{Zn(II)}] = 0, 0.007, 0.014, 0.021, 0.028, 0.035, 0.042$ and 0.05 mM).

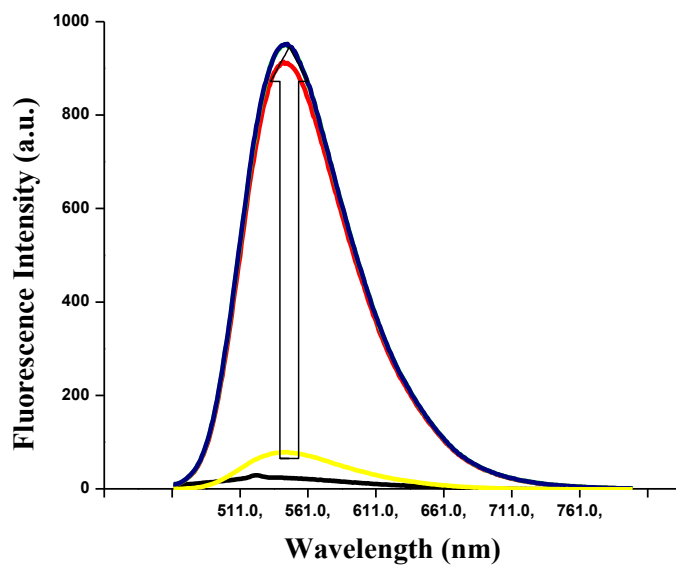


Fig. S7 Fluorescence emission spectra of HL³ upon addition of Zn(II) in THF, $\lambda_{\text{ex}} = 450$ nm at room temperature ($[\text{HL}^3] = 0.1 \text{ mM}$, $[\text{Zn(II)}] = 0, 0.02, 0.04, \text{ and } 0.05 \text{ mM}$).

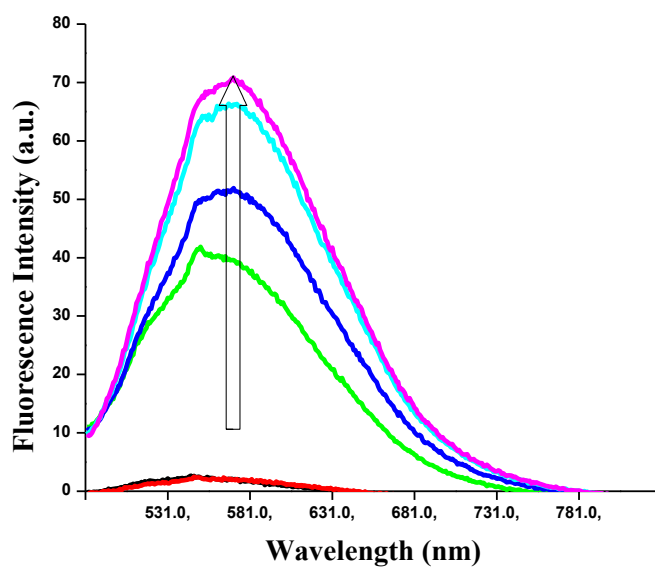


Fig. S8 Fluorescence emission spectra of HL⁴ upon addition of Zn(II) in THF, $\lambda_{\text{ex}} = 473$ nm at room temperature ([HL⁴] = 0.1mM, [Zn(II)] = 0, 0.02, 0.03, 0.04, 0.045 and 0.05 mM).

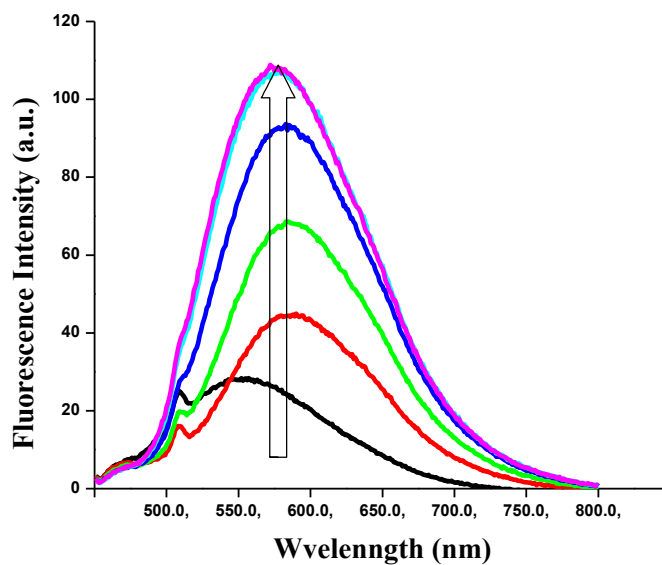


Fig. S9 Fluorescence emission spectra of HL⁵ upon addition of Zn(II) in THF, $\lambda_{\text{ex}} = 454$ nm at room temperature ([HL⁵] = 0.1mM, [Zn(II)] = 0, 0.01, 0.02, 0.03, 0.045 and 0.05 mM).