Supporting Information

Design and Synthesis of Solution-Processed Redox-Active Bis(Formazanate) Zinc Complex for Resistive Switching Applications

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Contents

Table S1. Crystal data and structure refinement for Complex 1(CCDC 2286211).	
Empirical formula	$C_{49}H_{46}Cl_2N_{18}O_5Zn$
Formula weight	1103.31
Temperature/K	100.15
Crystal system	Triclinic
Space group	P-1
a (Å)	14.417(4)
b (Å)	14.593(4)
c (Å)	15.448(4)
α (°)	109.695(7)
β (°)	116.709(7)
γ (°)	96.843(7)
Volume (Å^3)	2588.0(13)
Z	2
ρ_{calc}g.cm^{-3}	1.416
μ, mm^{-1}	0.643
F(000)	1140.0
Crystal size (mm^3)	0.35 × 0.32 × 0.26
Radiation	MoK_α (λ = 0.71073)
2Θ range for data collection (°)	5.602 to 49.996
Index ranges	$-17 \le h \le 17$, $-17 \le k \le 17$, $-18 \le l \le 18$
Reflections collected	18273
Independent reflections	8976 [R_{int} = 0.0409, R_{sigma} = 0.0628]
Data/restraints/parameters	8976/6/749
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0544, wR_2 = 0.1245
Final R indexes [all data]	R_1 = 0.0749, wR_2 = 0.1361
Largest diff. peak/hole (e Å^{-3})	0.81/-0.55

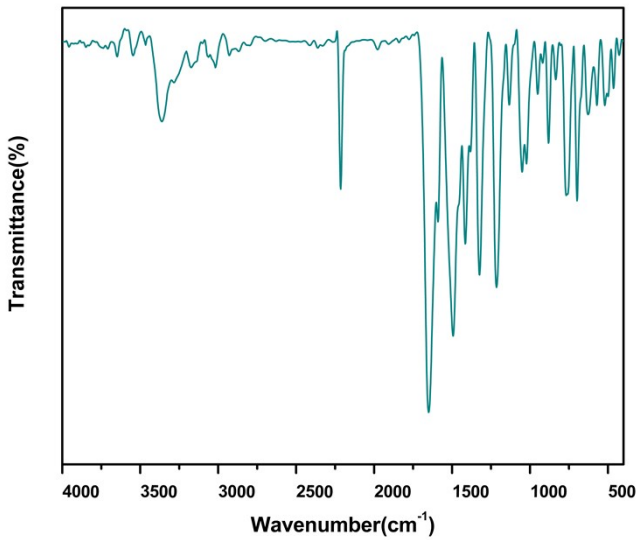


Figure S1. FT-IR spectrum of Ligand (LH).

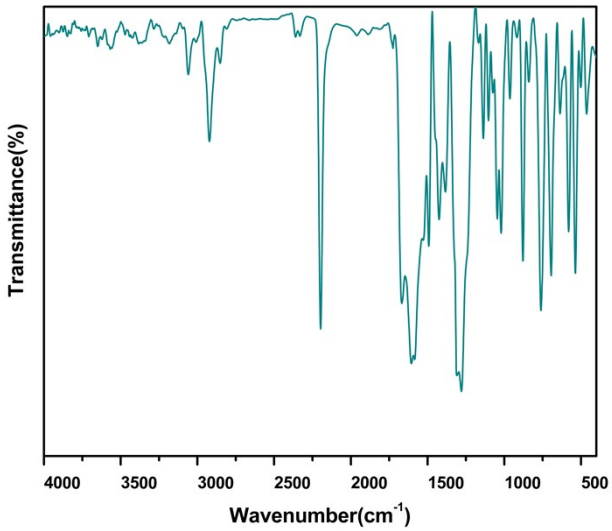


Figure S2. FT-IR Spectrum of complex **1**, $[Zn^{II}L_2]$

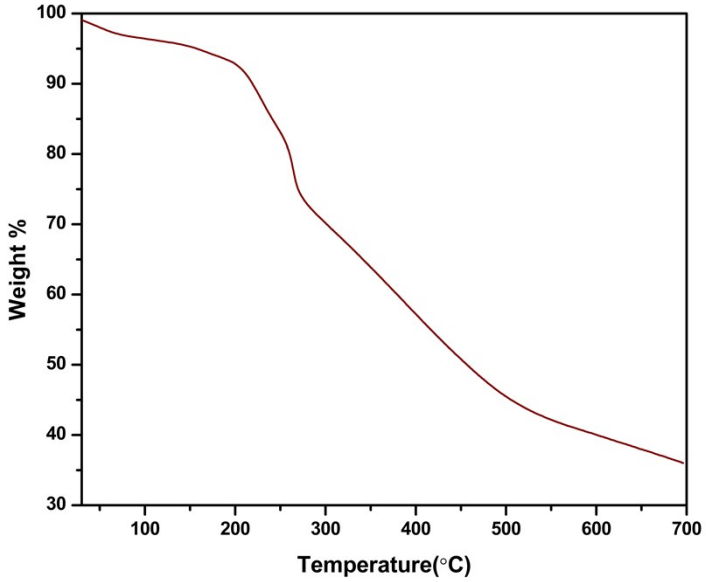


Figure S3. Thermogravimetric analysis of Complex 1.

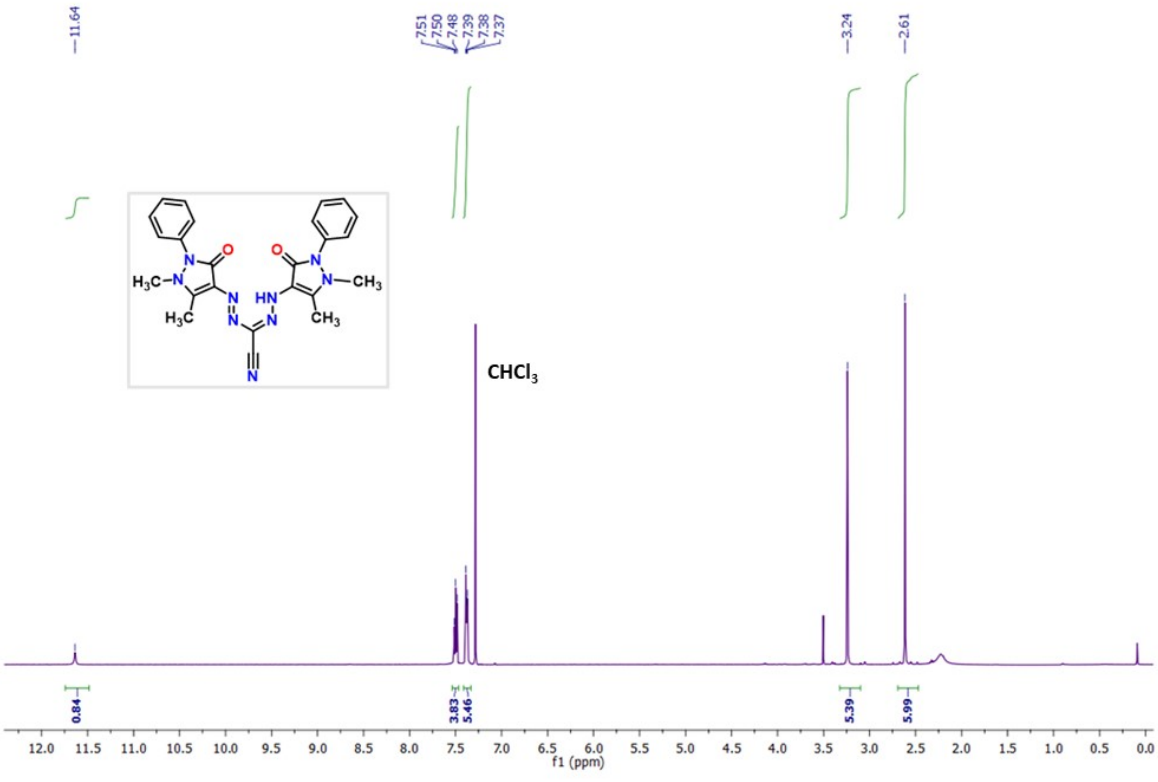


Figure S4. ^{1}H NMR (500 MHz, $CDCl_3$) of Ligand (LH).

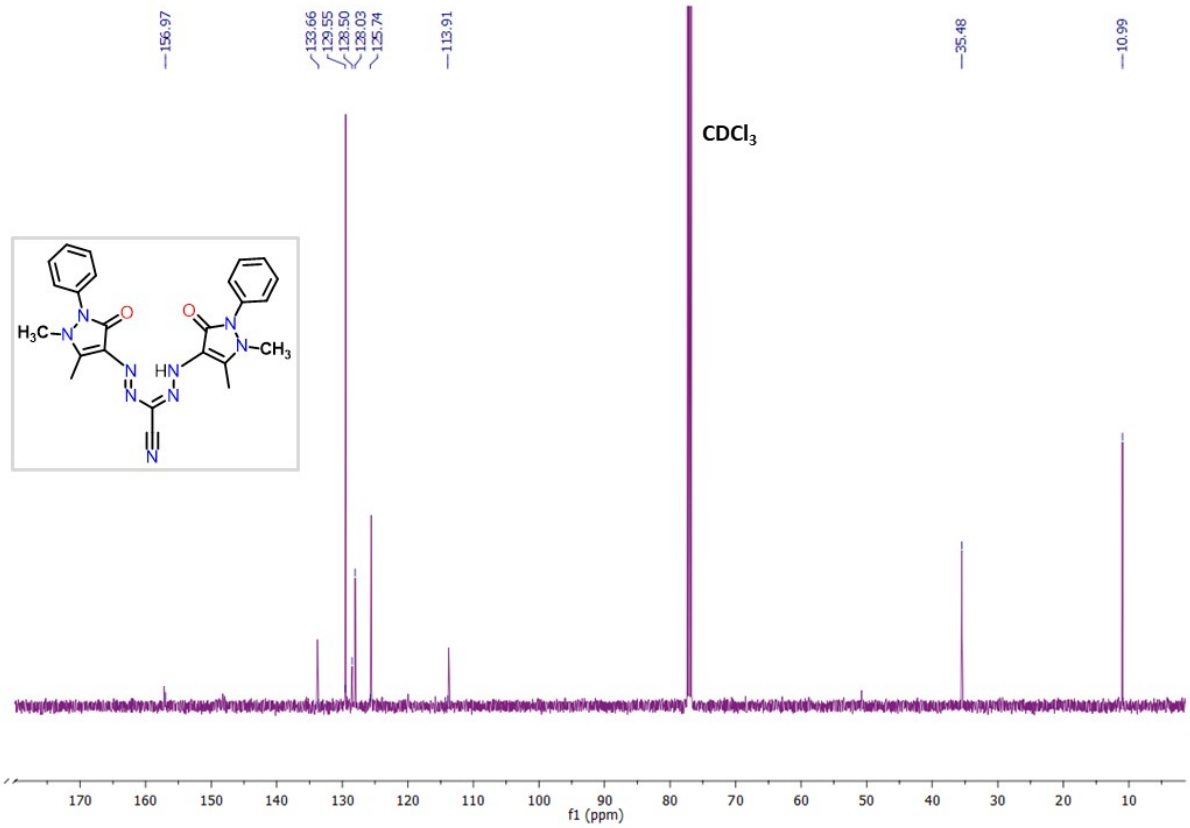


Figure S5. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of Ligand (LH).

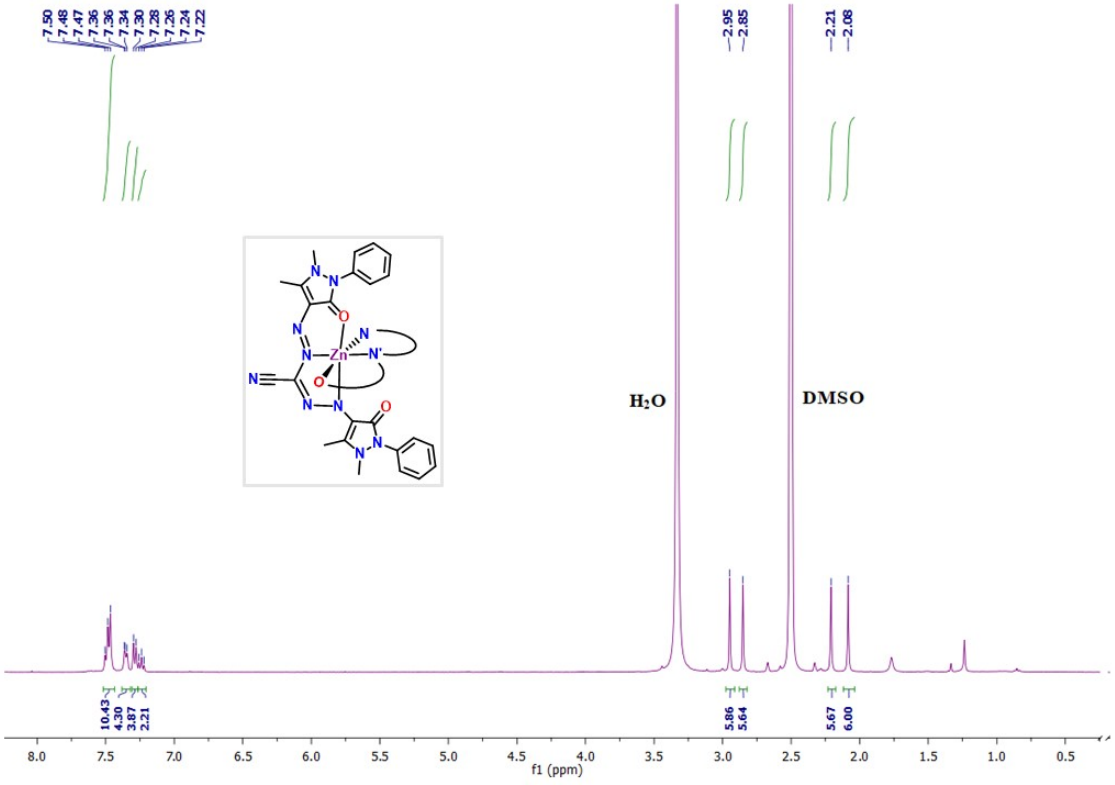


Figure S6. ^{1}H NMR (400 MHz, DMSO) of Complex 1, $[Zn^{II}L_2]$.

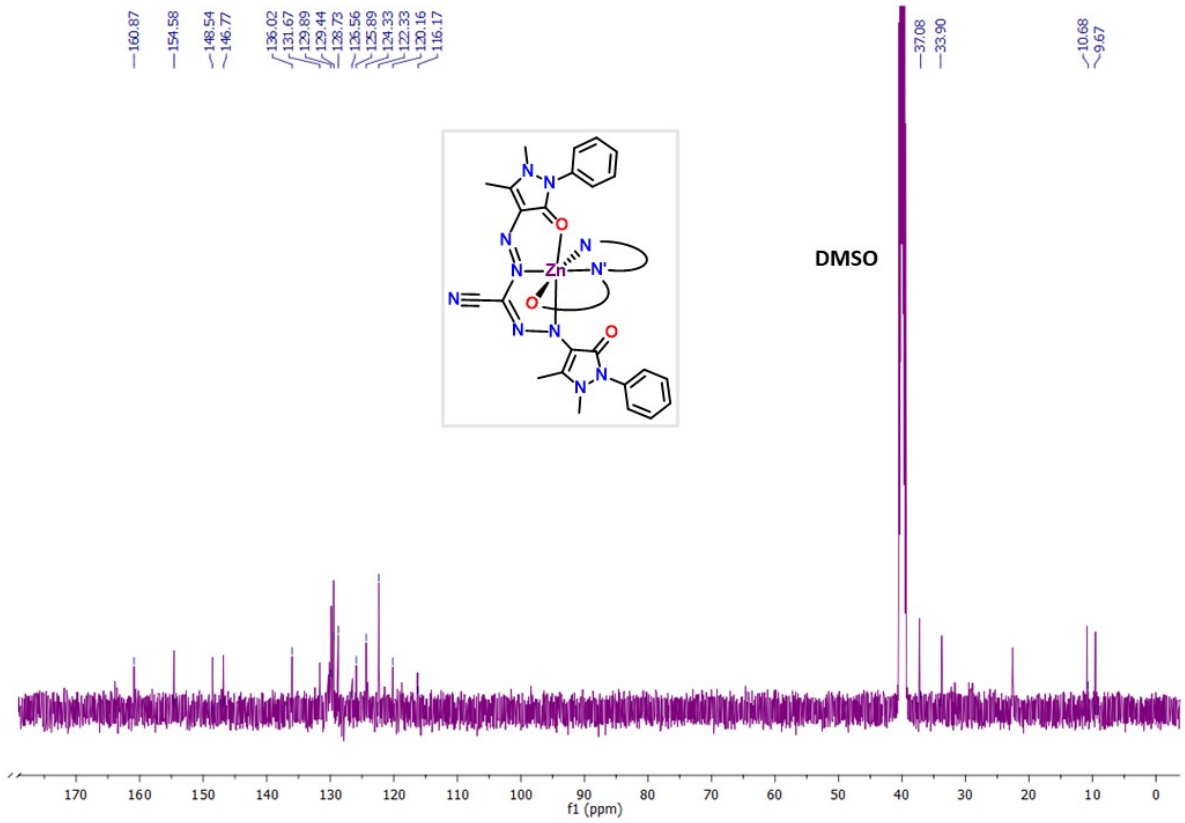


Figure S7. $^{13}C\{^{1}H\}$ (126 MHz, DMSO) NMR of Complex 1, $[Zn^{II}L_2]$.

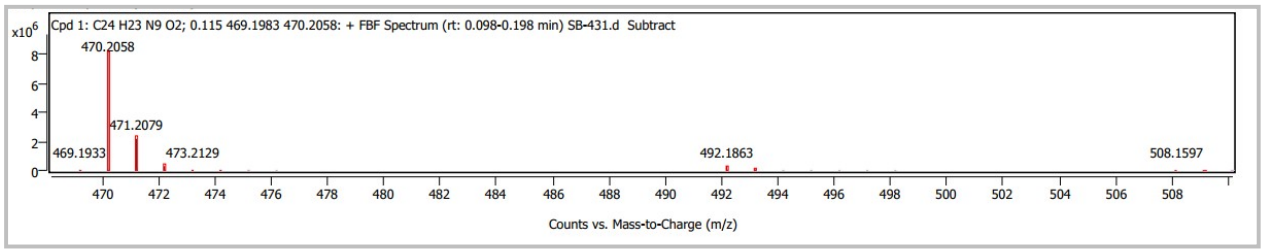


Figure S8. ESI-MS analysis for Ligand (LH): Exact mass calcd for $[C_{24}H_{23}N_9O_2+H]^+$: 470.2008. The exact mass found: 470.2058. Difference: **+1.06** ppm.

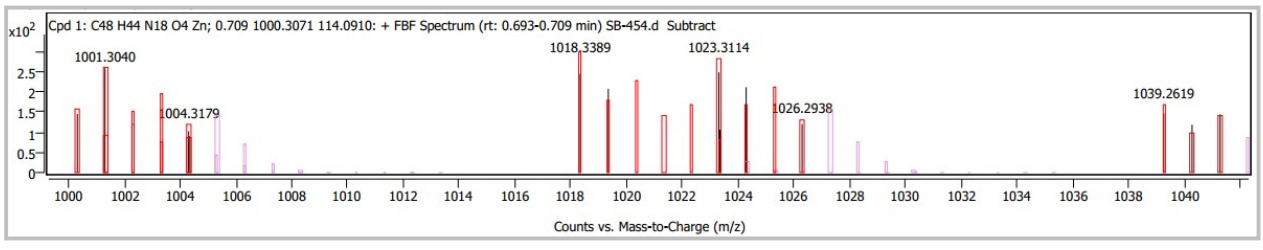
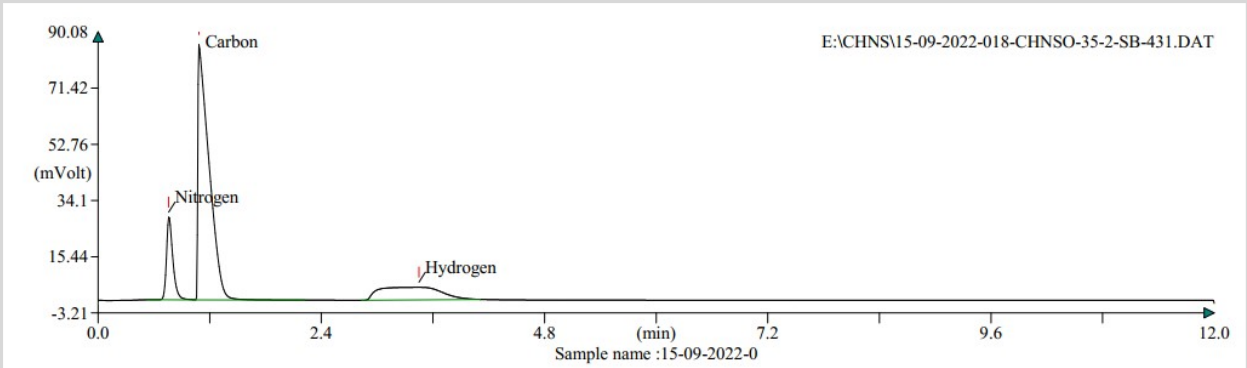
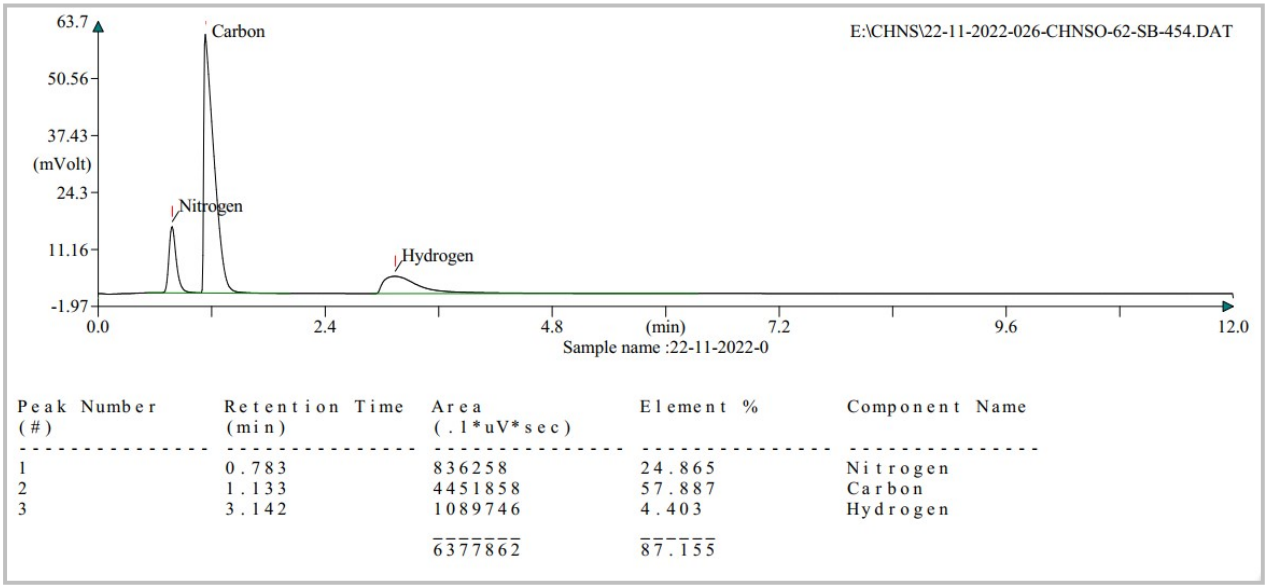


Figure S9. ESI-MS analysis for Complex 1, $[Zn^{II}L_2]$: Exact mass calcd for $[C_{48}H_{44}N_{18}O_4Zn+H]^+$: 1001.3084. The exact mass found: 1001.3040. Difference: **-4.39** ppm.



Peak Number (#)	Retention Time (min)	Area (.1*uV*sec)	Element %	Component Name
1	0.758	1308225	26.962	Nitrogen
2	1.083	7043890	61.134	Carbon
3	3.450	1945331	5.260	Hydrogen
		10297450	93.357	

Figure S10. Elemental analysis of Ligand (LH): Anal. Calcd. (%) for $C_{24}H_{23}N_9O_2$: C, 61.40; H, 4.94; N, 26.85. Found: C, 61.13; H, 5.26; N, 26.96.



Peak Number (#)	Retention Time (min)	Area (.1*uV*sec)	Element %	Component Name
1	0.783	836258	24.865	Nitrogen
2	1.133	4451858	57.887	Carbon
3	3.142	1089746	4.403	Hydrogen
		6377862	87.155	

Figure S11. Elemental analysis of Complex 1, $[Zn^{II}L_2]$: Anal. Calcd. (%) for $C_{48}H_{44}N_{18}O_4Zn$: C, 57.52; H, 4.42; N, 25.15. Found: C, 57.88; H, 4.40; N, 24.86.

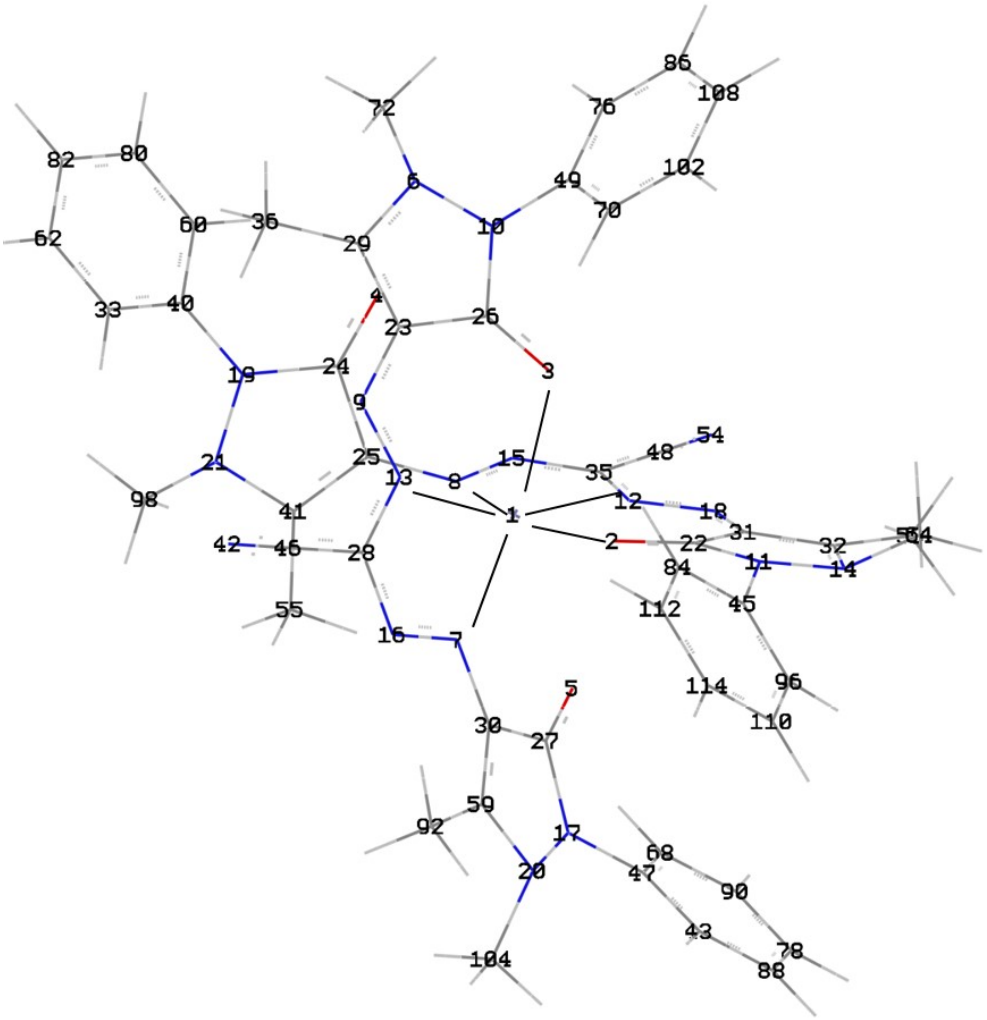


Figure S12. DFT optimized structure of complex **1.**

Table S2. The Natural Population Analysis (NPA) charges (au) on the metal (Zn) and NNC(**CN**)NNCCO backbone of coordinating ligand moieties of complex **1**.

Atom	**NPA Charges (au)**	
Zn = 1.55316 au	**L1**	**L2**
N	-0.41336	-0.40135
N	-0.14815	-0.19676
C	0.09465	0.09312
C	0.23977	0.23239
N	-0.32424	-0.32099
N	-0.28135	-0.32327
N	-0.20817	-0.20337
C	-0.03992	-0.04877
C	0.54189	0.54127
O	-0.65831	-0.66137

Table S3. Second-order perturbation energy E_2 (eV), off-diagonal Fock matrix elements *F(i,j)* and acceptor – donor energy values $(E_j - E_i)$ (a.u.) of selected donor-acceptor NBO-NBO* interactions in metal-complex, as computed at BP86+D3/TZVPP+SDD method.

Donor NBO (i)	Acceptor NBO(j)	E_2 (eV)	E_j - E_i (au)	F(i,j)
		Ligand-to-Metal		
LP(1)O2	LP*(1)Zn	0.51	0.53	0.071
LP(2)O2	LP*(1)Zn	0.62	0.27	0.055
LP(1)N8	LP*(1)Zn	1.57	0.34	0.100
LP(1)N12	LP*(1)Zn	1.26	0.34	0.090
		Ligand-to-Ligand (within)		
LP(2)O4	π*(C60-C80)	0.02	0.19	0.009
LP(1)N8	π*(N8-N15)	0.03	0.27	0.012
LP(1)N8	π*(C25-C41)	0.21	0.33	0.036
LP(1)N11	π*(O2-C22)	1.77	0.23	0.086
LP(1)N11	π*(C45-C96)	0.69	0.24	0.056
LP(1)N14	π*(C31-C32)	0.97	0.27	0.07
LP(1)N15	π*(C25-C41)	0.03	0.28	0.012
LP(1)N18	π*(C48-N54)	0.05	0.37	0.019
LP(1)N19	π*(O4-C24)	1.51	0.24	0.081
LP(1)N19	π*(C33-C40)	0.81	0.23	0.059
LP(1)N21	π*(C25-C41)	0.86	0.28	0.067
LP(1)C35	π*(N8-N15)	7.45	0.06	0.093
LP(1)C35	π*(N12-N18)	6.74	0.05	0.083
LP(1)C35	π*(C48-N54)	2.67	0.2	0.098
π(O2-C22)	π*(O2-C22)	0.09	0.3	0.022
π(O2-C22)	π*(C31-C32)	0.15	0.32	0.029
π(O4-C24)	π*(O4-C24)	0.08	0.3	0.022
π(O4-C24	π*(C25-C41)	0.16	0.31	0.03
π(N8-N15)	π*(N8-N15)	0.07	0.25	0.019
π(N8-N15)	π*(C25-C41)	0.28	0.31	0.04
π(N12-N18)	π*(C31-C32)	0.57	0.3	0.056
π(C25-C41)	π*(O4-C24)	1.01	0.23	0.065
π(C25-C41)	π*(N8-N15)	0.31	0.19	0.033
π(C25-C41)	π*(C25-C41)	0.06	0.24	0.017
π(C31-C32)	π*(O2-C22)	1.20	0.21	0.069
π(C31-C32)	π*(N12-N18)	0.91	0.19	0.056
π(C31-C32)	π*(C31-C32)	0.09	0.23	0.02
π(C33-C40)	π*(C60-C80)	0.57	0.23	0.05
π(C33-C40)	π*(C62-C82)	0.65	0.23	0.053
π(C45-C96)	π*(C84-C112)	0.58	0.24	0.051

π(C45-C96)	π*(C110-C114)	0.62	0.24	0.052
π(C60-C80)	π*(C33-C40)	0.69	0.22	0.053
π(C60-C80)	π*(C62-C82)	0.62	0.22	0.051
π(C62-C82)	π*(C33-C40)	0.63	0.22	0.051
π(C62-C82)	π*(C60-C80)	0.65	0.23	0.052
π(C84-C112)	π*(C45-C96)	0.71	0.21	0.053
π(C84-C112)	π*(C110-C114)	0.63	0.22	0.051
π(C110-C114)	π*(C45-C96)	0.65	0.22	0.051
π(C110-C114)	π*(C84-C112)	0.64	0.23	0.052

- **Molecular orbital energy levels Band gap (E_g) calculated from UV-visible spectrum**

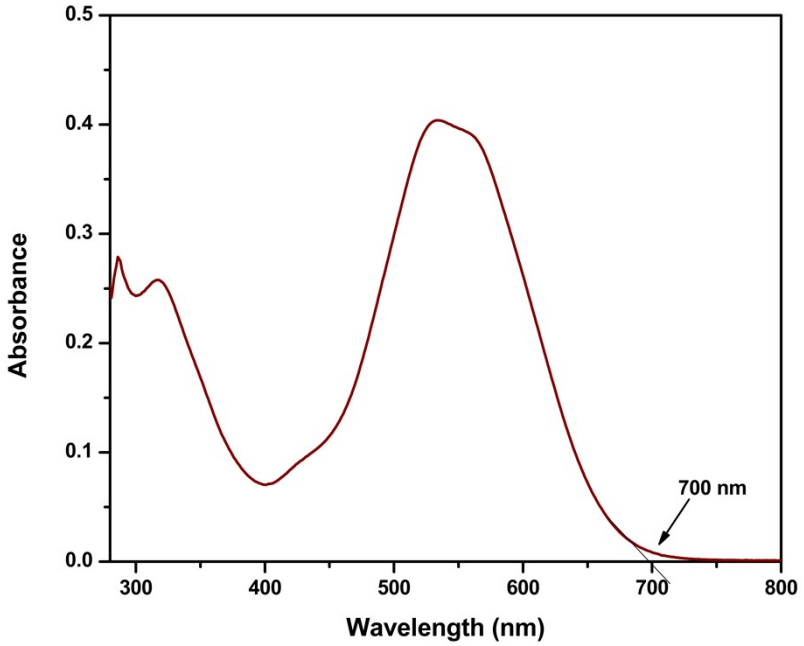


Figure S13. UV-vis absorption spectrum for the Complex **1** (L_2Zn) in $CHCl_3$ exhibiting onset optical absorbance.

$$E_g = hc/\lambda_{onset}$$

where, E_g is the optical band gap of the complex **1**, h is the Planck constant (6.63×10^{-34} m^2kg/s), c is the speed of light (3×10^8 m/s), λonset is the onset optical absorbance wavelength.

$$E_g\ (eV) = 1240/(\text{wavelength in nm}) = 1240/700 = 1.77\ eV$$

Table S4: Calculated TD-DFT electronic transition wavelength (nm), oscillator strength (f_{osc}), major compositions in terms MO contributions and electronic transition character for the ligand (LH) and complex **1** (Zn-L_2)

S. no.	Wavelength (nm)	f_{osc}	Major composition	Transition Character
LH				
1.	548	0.3030	HOMO+(HOMO-1)+(HOMO-2)+(HOMO-3)	n + π → π*
2.	468	0.8003	HOMO+(HOMO-1)+(HOMO-2)+(HOMO-3)	n + π → π*
Complex 1				
1.	606	0.0294	(HOMO-2) → LUMO	n + π → π* inter-ligand
2.	582	0.1642	(HOMO-1) + (HOMO-2) → (LUMO+1)	n + π → π* intra-ligand
3.	562	0.4206	HOMO + (HOMO-3) + (HOMO-5) → LUMO	n + π → π* intra-ligand
4.	506	0.1009	(HOMO-4) + (HOMO-5) → (LUMO+1)	n + π → π* inter-ligand, intra-ligand
5.	492	0.2087	(HOMO-5) → LUMO + (LUMO+1)	n + π → π* inter-ligand, intra-ligand
6.	475	0.5523	(HOMO-1) + (HOMO-2) → (LUMO+1)	π → π* intra-ligand
9.	464	0.2422	(HOMO-6) → LUMO + (LUMO+1)	π → π* inter-ligand, intra-ligand
10	412	0.1468	HOMO → (LUMO+4) (HOMO+10) → LUMO	π → π* inter-ligand, intra-ligand