Supplementary Information

Controlled Fluorescent Properties of Zn (II) Salen-type Complex based on Ligand Design

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Content

Experimental Section

Materials and Physical Methods.

All materials were reagent grade obtained from commercial sources and used without further purification, and solvents were dried by standard procedures. IR spectra were recorded on a Nicolet-360 FT-IR spectrophotometer in KBr pellets. Elemental (C, H, and N) analyses were performed on a Perkin-Elmer 2400 II analyzer. Absorbance spectra were obtained with a Shimadzu UV-3600/Hitachi U-3501 spectrophotometer; the luminescent spectra for the liquid state were recorded at room temperature on Hitachi F-7000 FL Spectrophotometer with a xenon arc lamp ashen light source. In the measurements of emission spectra, the pass width is Ex=2.5 nm, Em=5nm.In all measurements, the sample concentration 1×10^{-6}M was maintained. Only freshly prepared solutions were used for the spectroscopic study, and all experiments have been carried out at room temperature (298 K). Fluorescence lifetime was measure using Fluorolog-Tau-3 picoseconds level fluorescence spectroscopy. Average fluorescence lifetime ($\langle\tau_f\rangle$) is calculated using 3 exponentials.

Fluorescence quantum yields (φ) of the compound **1** were estimated at room temperature in various solvents by a relative method using Rhodamine B alcohol solution (Φ=0.71) as the standard using the following equation

$$\frac{\varphi_S}{\varphi_R} = \frac{I_S}{I_R} \times \frac{A_R}{A_S} \times \frac{\eta^2{}_S}{\eta^2{}_R}$$

Where *I* is the area under the emission spectral curve, *A* denote absorbance at the wavelength of exciting light, *η* is the refractive index of the medium, φ is the fluorescence quantum yield, and the subscripts *S* and *R* stand in the recognition of the respective parameters of studied sample and reference, respectively.

X-ray Data Collection and Structure Refinement.

All of the crystals were collected from solution directly and were not washed with solvent. Single-crystal X-ray diffraction data were collected on a Rigaku RAXIS-RAPID CCD diffract meter equipped with a graphite- monochromatic Mo Kα radiation (λ =0.71073Å) using an ω scan mode at 93(2) or 153(2)K. Unit-cell parameters were determined from automatic centering of reflections and refined by least-squares method. Crystallographic data of compounds **1-2** are given in Table S1. Selected and all bond distances and angles are given in Tables S2, Tables S3, respectively. All non-hydrogen atoms were located by direct methods and subsequent difference Fourier syntheses. The hydrogen atoms bound to carbon were located by geometrical calculations, and their positions and thermal parameters were fixed during structure refinement. All non-hydrogen atoms were refined by full-matrix least-squares techniques with I>2σ (I). All calculations were performed by SHELXTL 97 program.

Synthesis of Ligands.

N, N'- bis (2, 4-dihydroxybenzaldehyde)-2, 3-diamino maleonitrile (H_2L1). 2, 4-dihydroxybenzaldehyde (2.76g, 20mmol) and

DMN (1.08 g, 10mmol) were added to absolute ethanol (40mL), a drop of concentrated HC1 was added as the catalyst, and the mixture was refluxed for 8 h. The resulting red solution was cooled to room temperature to give red solid, which was filtered off, washed with ether, and dried, under vacuum. Yield 2.18g, 62.7%. Anal. found (calcd) for $C_{18}H_{12}N_4O_4$: C, 62.06 (62.10); H, 3.42 (3.48); N, 16.07 (16.09). ATR-FTIR (ν_{max}/cm^{-1}): 521w, 840s, 1376m, 1462m, 1509m, 1626w, 2210s, 2240s, 3308m, 3199m, 3400m.

N, N'- bis (2, 3-dihydroxybenzaldehyde)-2, 3-diamino maleonitrile (H_2L2). It was carried out following a procedure similar to that described above for **H_2L1**, using in this case (2.76g, 20mmol) of 2,3-dihydroxybenzaldehyde instead of 2, 4-dihydroxybenzaldehyde. The red solid material was filtered off, washed with ether (2×3 ml), and dried under vacuum. Yield 2.36g, 67.8%. Anal. found (calcd) for $C_{18}H_{12}N_4O_4$: C, 62.22 (62.10); H, 3.50 (3.48); N, 16.20 (16.09). ATR-FTIR (νmax/cm-1): 726s, 1197m, 1200m, 1276s, 1381m, 1458s, 1558s, 1590m, 1624w, 2218m, 3428m, 3525w, 3531w.

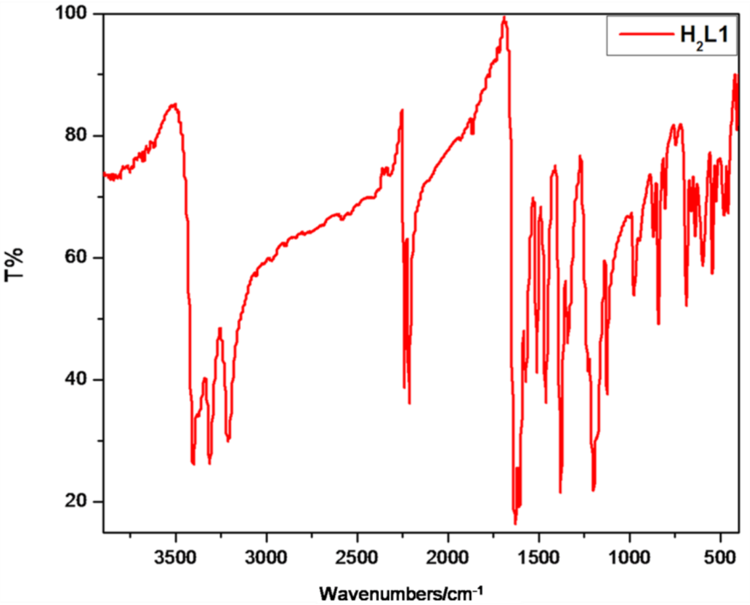
Preparation of complexes 1 - 2.

[ZnL1 (CH_3OH)]·2CH_3OH (1). H_2L1 (35mg, 0.1mmol) was dissolved in 5ml methanol solution and stirring at room temperature for half an hour. Then a methanol solution (5mL) of Zn (CH_3COO)$_2$ (0.1mmol, 22.0mg) was added to the above solution with stirring at room temperature for half an hour. Garnet rod like single crystals suitable for x-ray diffraction were obtained by slow evaporation for 5 days (Yield: 44.69mg, 88%). Anal. found (calcd) for $C_{21}H_{22}N_4O_7Zn$: C, 49.54 (49.67); H, 4.66 (4.37); N, 11.11 (11.03). ATR-FTIR (ν_{max}/cm^{-1}): 418w, 527w, 844w, 1373m, 1434m, 1526s, 1579m, 2216w.

[ZnL2]·H_2O (2). **H_2L2** (18mg, 0.05mmol) was dissolved in 5ml methanol, then a methanol solution (5mL) of Zn (CH_3COO)$_2$ (0.05mmol, 11.0mg) was added to the above solution. The following steps is same with complex **1.** Dark red single crystals suitable for x-ray diffreaction appeared after a week by slow evaporation of the solvent. (Yield: 18.26mg, 85%). Anal. found (calcd) for $C_{18}H_{12}ZnN_4O_5$: C, 50.17 (50.31); H, 2.88 (2.81); N, 12.98 (13.04). ATR-FTIR (ν_{max}/cm^{-1}): 566w, 729m, 1182m, 1294w, 1291m, 1313m, 1391m, 1440s, 1603w, 1576s, 1652w, 2219m.

IR spectra

(a)



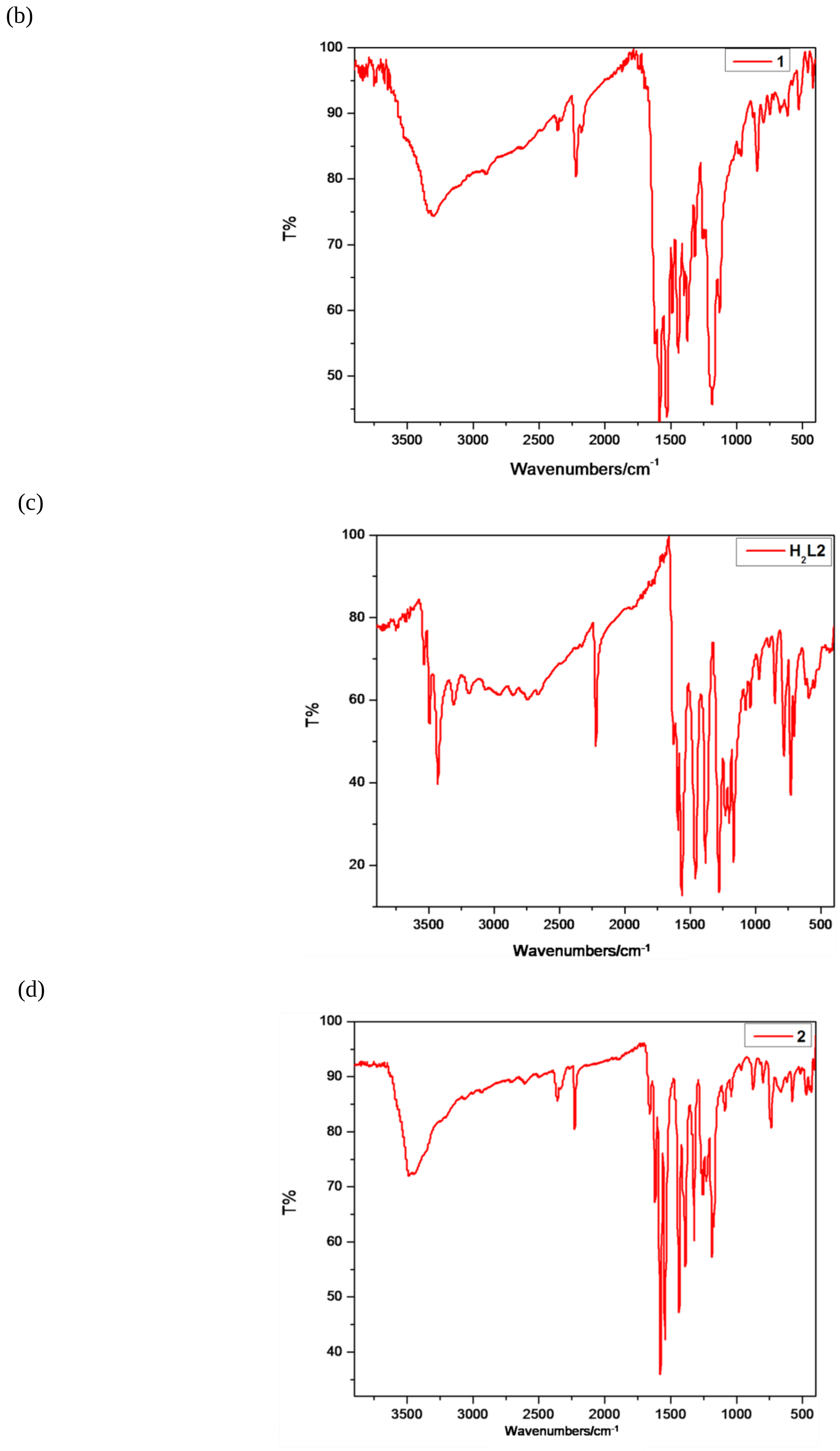


Figure S1 IR spectra of of ligand H_2L1, H_2L2, and their relevant complexes **1**, **2**.

Crystal structure of complex 1

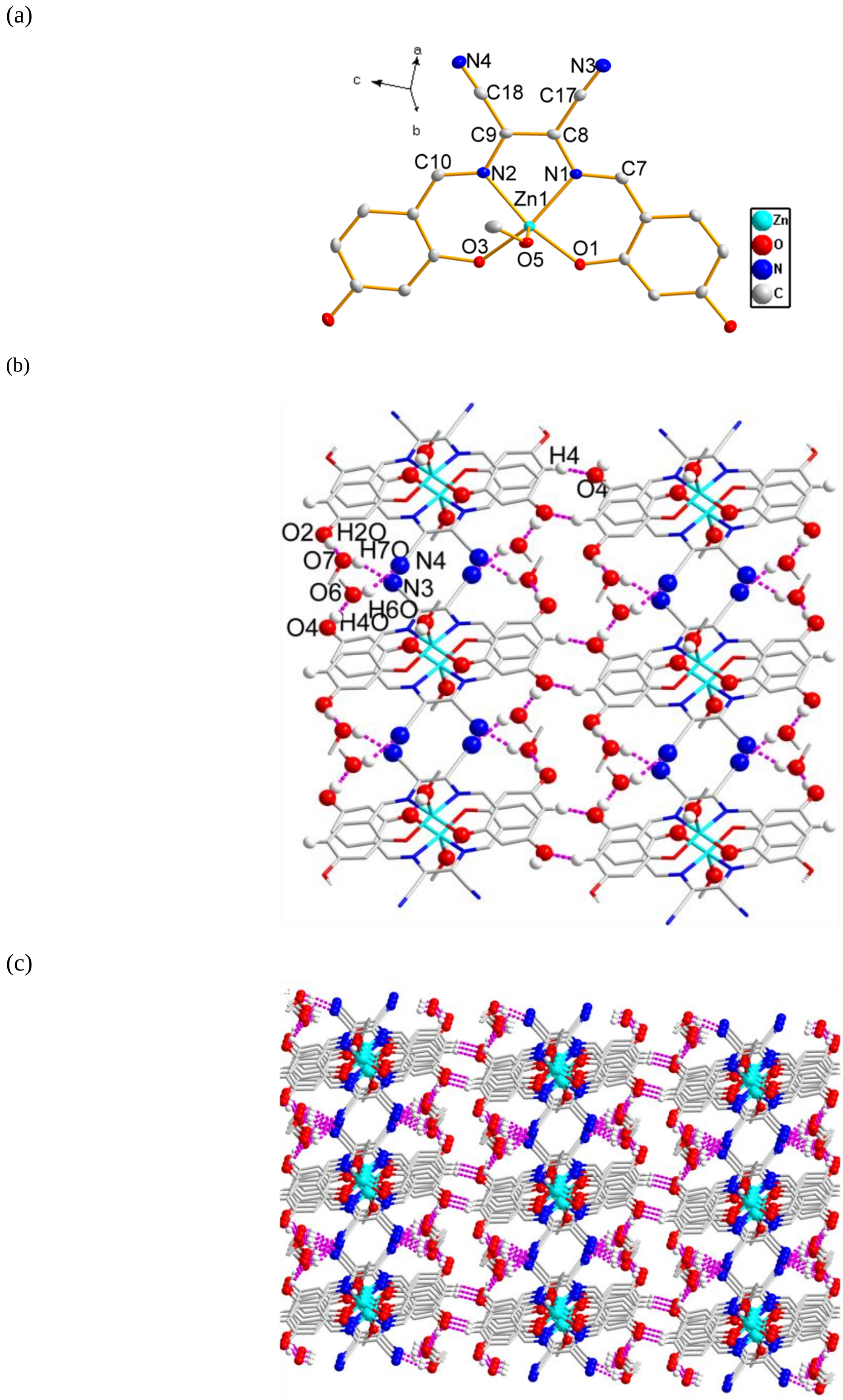
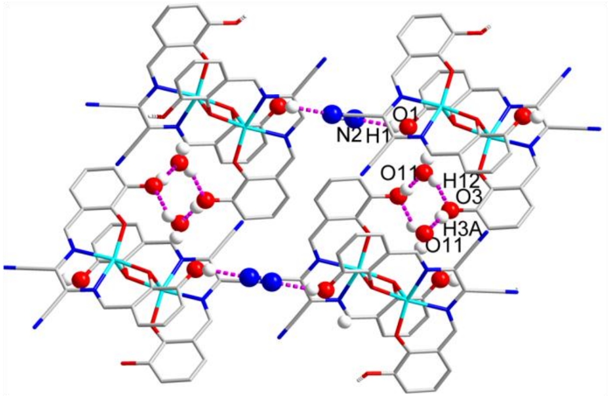


Figure S2 (a) A thermal ellipsoid picture of **1** (50 % probability ellipsoids). The hydrogen atoms are omitted for clarity. (b) 2D layer linked by hydrogen bonds. N3…H7O–O7: 2.171Å, 2.958Å, 155.8°; O7…H2O–O2: 1.954Å, 2.713Å, 164°; N4A…H6OA–O6A: 2.193Å, 2.948Å, 149.5°; O6A…H4O–O4: 1.875Å, 2.695Å, 175.2°, O4…H4–C4: 2.725Å, 3.500Å, 139.3°. (c) 3D supramolecular structure of complex **1.**

Crystal structure of complex 2

(a)



(b)

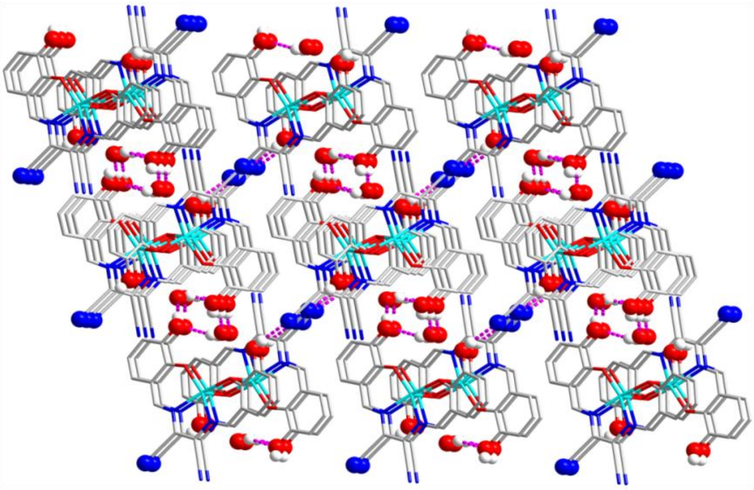


Figure S3 (a) 2D layer of complex **2** linked by hydrogen bonds O11…H3A–O3: 1.804Å, 175.94°, 2.622Å; O3…H12–O11: 2.280Å, 2.979Å, 152.97°, N2…H1–O1: 2.579 Å, 3.432 Å, 152.83°.(b) 3D supramolecular structure of complex **2.**

Time-resolved fluorescence decay of the complex 1

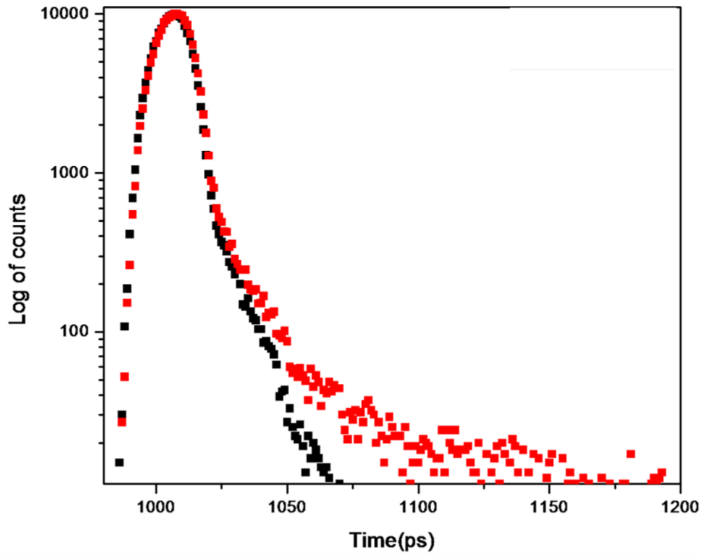


Figure S4 Time-resolved fluorescence decay of the complex **1** (1.0×10^{-6}mol) in THF. The fluorescence was monitored at 365 nm.

UV-Vis absorption and fluorescence spectra of H_2L1 and complex 1

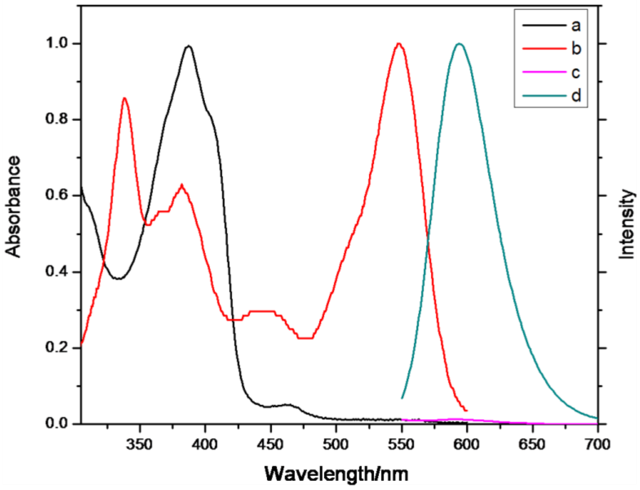


Figure S5 UV-Vis absorption and fluorescence (λ_{exc} = 365 nm) spectra of **H_2L1** (a, c) and its complex **1** (b, d) (1.0×10^{-6}mol L^{-1}) in THF solvent.

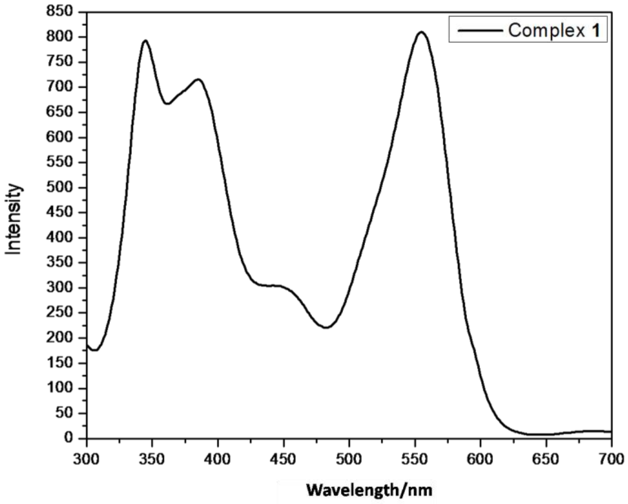


Figure S6 Fluorescence excitation spectra of **1** inTHF solvent (1.0×10^{-6} mol L^{-1}, λ_{em} = 593 nm).

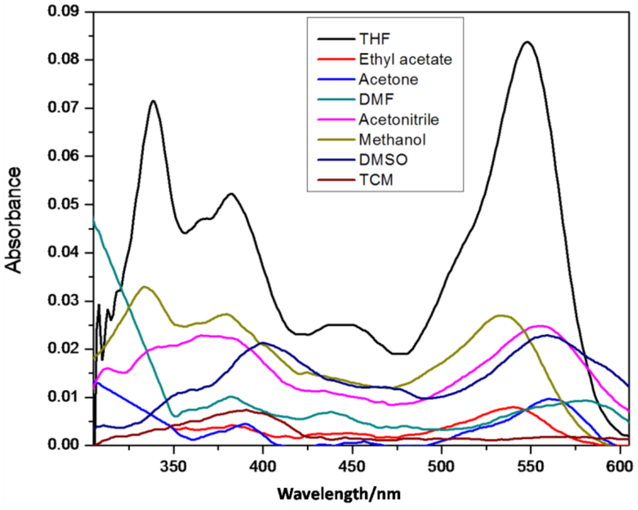
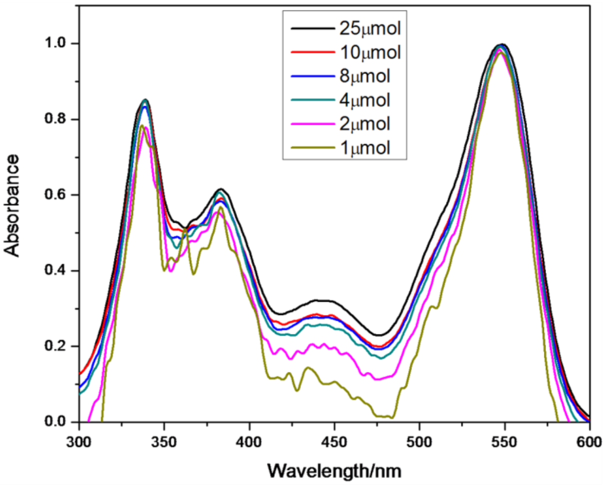


Figure S7 The UV-Vis absorption spectra of complex **1** in various solvents.

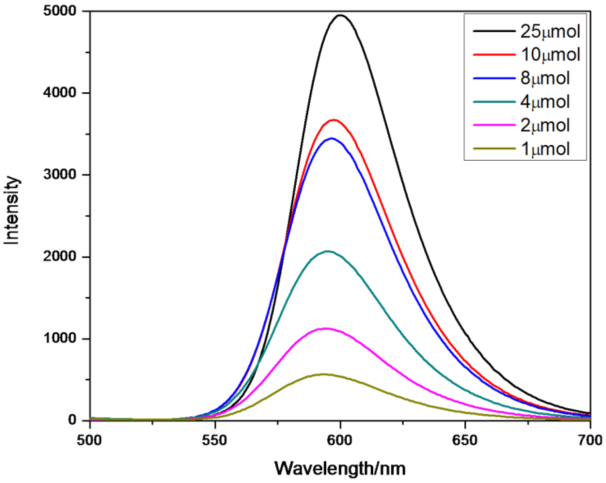
(a)



(b)

Figure S8 Concentration dependence (1.0-25 μmol range) of UV-Vis absorption spectra of **1** in THF solutions (a). Visual color changes (1.0-25 μmol range) from right to left (b).

(a)



(b)

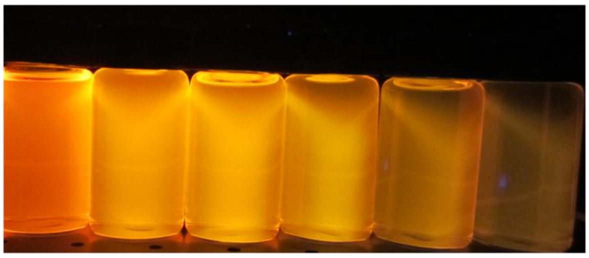


Figure S9. Concentration dependence (1.0-25 μmol range) of fluorescence spectra of **1** (λ_{exc} = 365 nm) in THF solutions (a). Fluorescence of **1** (1.0-25μmol range, from right to left) upon irradiation with a 365 nm UV lamp (b).

UV-Vis absorption spectra of ligand H_2L2 and complex 2

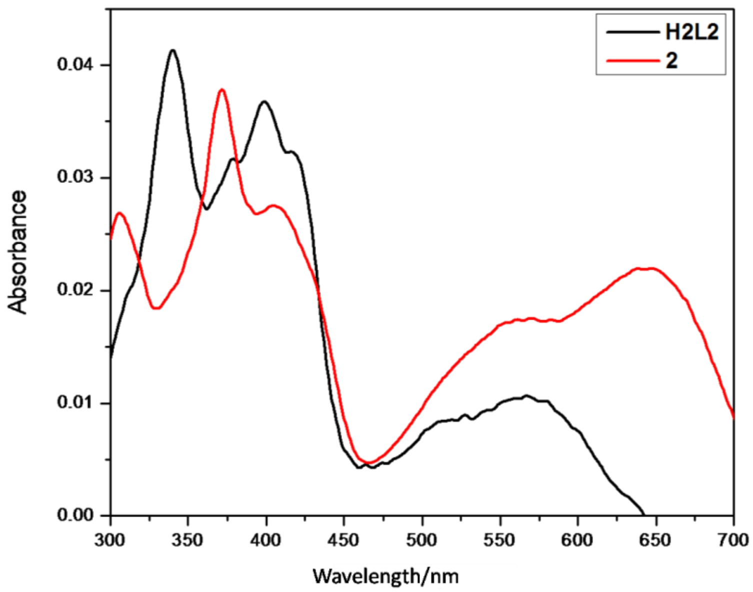


Figure S10 UV-Vis absorption spectra of ligand **H_2L2** and its relevant complex **2** in THF solvent (1.0 ×10^{-6} mol L^{-1}).

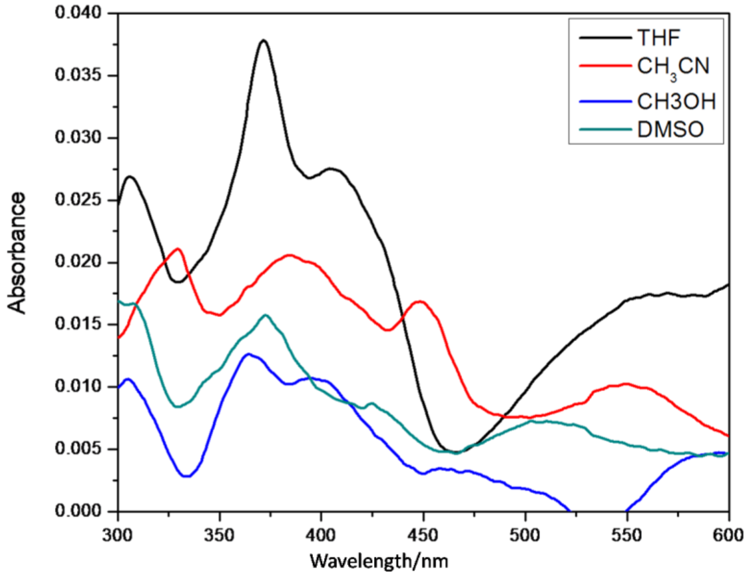


Figure S11 The UV-Vis absorption spectra of complex **2** in various solvents

^{1}HNMR spectra

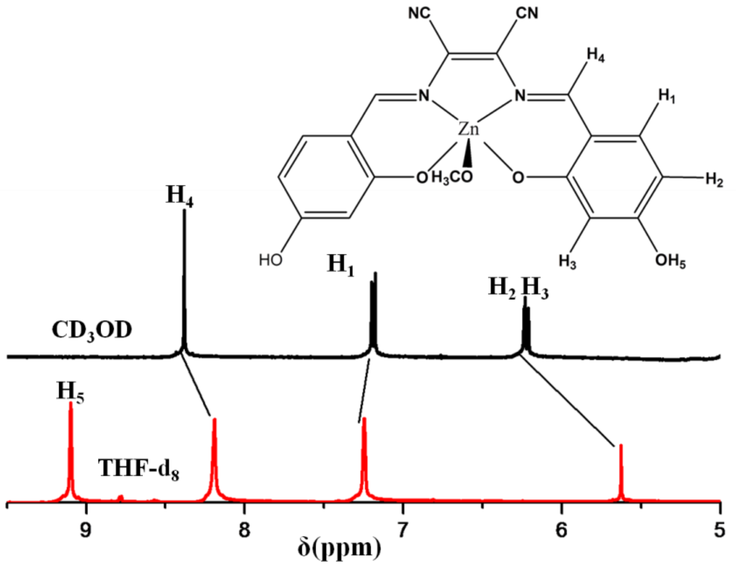


Figure S12 ^{1}HNMR spectra of complex **1** in CD_3OD and THF-d_8 solvents.

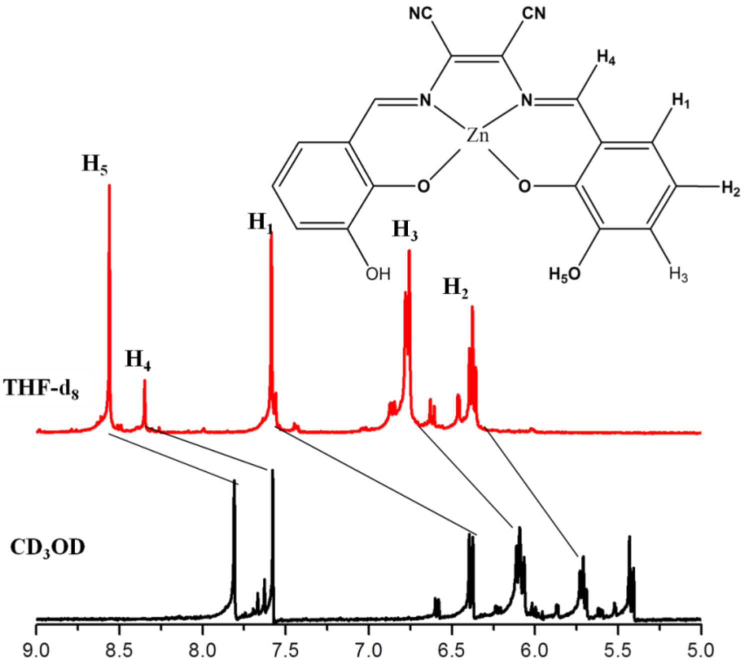


Figure S13 ^{1}HNMR spectra of complex **2** in CD_3OD and THF-d_8 solvents.

Tables of bond lengths (Å) and angles (°) for complexes 1 and 2

Table S1. Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

Compound **1**							
Zn(1)-O(1)	1.9569(15)	Zn(1) -O(3)	1.9788(15)	Zn(1) -O(5)	2.0326(17)	Zn(1) -N(1)	2.0768(18)
Zn(1)-N(2)	2.0952(18)	O(1)-Zn(1)-O(3)	94.88(6)	O(1)-Zn(1)-O(5)	100.91(7)	O(3)-Zn(1)-O(5)	103.26(7)
O(3)-Zn(1)-N(1)	154.92(7)	O(1)-Zn(1)-N(1)	89.35(7)	O(5)-Zn(1)-N(1)	100.16(7)	O(1)-Zn(1)-N(2)	157.41(7)
O(3)-Zn(1)-N(2)	87.88(7)	O(5)-Zn(1)-N(2)	100.25(7)	N(1)-Zn(1)-N(2)	79.21(7)		
Compound **2**							
N(3)-Zn(1)	2.080(2)	N(4)-Zn(1)	2.073(2)	O(2)-Zn(1)	1.9454(19)	O(6)-Zn(1)	2.0006(17)
O(6)-Zn(1)’	2.1347(18)	O(2)-Zn(1)-O(6)	99.49(7)	O(2)-Zn(1)-N(4)	89.15(8)	O(6)-Zn(1)-N(4)	167.11(8)
O(2)-Zn(1)-N(3)	158.88(8)	O(6)-Zn(1)-N(3)	88.73(8)	O(2)-Zn(1)-O(6)’	98.06(7)	O(6)-Zn(1)-O(6)’	85.51(7)
N(3)-Zn(1)-O(6)’	101.98(8)						

Table S2. Bond Lengths (Å) and Angles (deg) in the Zn (II) Coordination Spheres in **1**

Atom 1,2	d 1,2(Å)	Atom 1,2	d 1,2(Å)
Zn1 - N1	2.0767	C2 - C3	1.3767
Zn1 - O5	2.0322	C3 - C4	1.4125
Zn1 - O3	1.9787	C4 - C5	1.3568
Zn1 - O1	1.9566	C5 - C6	1.4289
O1 - C1	1.2971	C6- C7	1.3973
O2 - C3	1.3496	C8 - C9	1.3723
O3 - C16	1.3210	C9 - C18	1.4369
O4 - C14	1.3486	C10 - C11	1.4076
O5 - C19	1.4242	C11 - C16	1.4385
N1 - C8	1.3777	C11 - C12	1.4271
N1 - C7	1.3197	C12 - C13	1.3590
N2 - C9	1.3838	C13 - C14	1.4082
N2 - C10	1.3134	C14 - C15	1.3840
N3 - C17	1.1475	C15 - C16	1.3945
N4 - C18	1.1438	O6' - C20'	1.4244
C1 - C6	1.4491	O7_a - C21_a	1.4207
C1 - C2	1.4062	O7'_b - C21'_b	1.4207
C1 - O1	1.2971		
Atoms 1,2,3	Angle 1,2,3 [deg]	Atoms 1,2,3	Angle 1,2,3 [deg]
O1- Zn1 - N2	157.41	O3- Zn1 - O5	103.25
O1- Zn1 - N1	89.35	O3- Zn1 - N1	154.94
O1- Zn1 - O5	100.91	O3- Zn1 – N2	87.88
O1- Zn1 - O3	94.89	O5- Zn1 - N2	100.25
O5- Zn1 - N1	100.16	N1 -Zn1 - N2	79.22
C1- O1 - Zn1	128.51	C16- O3 - Zn1	128.93
C7- N1 - Zn1	124.48	C7- N1 - C8	122.71
C8- N1 - Zn1	112.32	C10- N2 - Zn1	125.56
C10- N2 - C9	122.41	C7- C6 - C1	124.77

C9- N2 - Zn1	111.66	C5- C6 - C1	118.15
O1- C1 - C6	123.80	N1- C7 - C6	125.18
O1- C1 - C2	118.67	C9- C8 - C17	121.10
C2- C1 - C6	117.53	C9- C8 - N1	117.95
C3- C2 - C1	121.99	N1- C8 - C17	120.93
O2- C3 - C4	116.54	C8- C9 - C18	120.98
O2- C3 - C2	122.62	C8- C9 - N2	117.63
C2- C3 - C4	120.84	N2- C9 - C18	121.39
C5- C4 - C3	118.85	N2- C10 - C11	124.78
C4- C5 - C6	122.57	C10- C11 - C16	125.21
C10- C11 - C12	117.04	C13- C12 - C11	122.74
C12- C11 - C16	117.63	C12- C13 - C14	118.75
O4- C14 - C13	117.35	O3- C16 - C15	118.39
O4- C14 - C15	121.93	C15- C16 - C11	118.62
C15- C14 - C13	120.70	N3- C17 - C8	176.03
C14- C15 - C16	121.51	N4- C18 - C9	176.91
O3- C16 - C11	122.98		