Supporting Information

A new cyclic supermolecular Zn(II) complex derived from N_2O_2 oxime chelate ligand with luminescence mechanochromism

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Experimental

Materials and physical measurements

All chemicals were obtained from commercial suppliers and used without any further purification. Elemental analyses were carried out on an Elemental Vario EL analyzer. The IR spectra were obtained in KBr discs on a Therrno Mattson FTIR spectrometer in the 4000–400 cm^{-1} region. Fluorescence spectra were generated on a Hitachi RF-5301 spectrophotometer equipped with quartz cuvettes of 1 cm path length. ^1H NMR and ^{13}C NMR spectra were measured on the Bruker 400 MHz instruments using TMS as an internal standard and $CDCl_3$ and C_2D_6OS as solvent at room temperature. X-ray single crystal structures were obtained on a Rapid Auto Version 3.0 Rigaku RAXIS-RAPID detector. The melting points of the compounds were determined on a Beijing XT4-100x microscopic melting point apparatus.

Procedure for experiment

Preparation of H_2L.

To an ethanol solution (30 mL) of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) (1.70 g, 6.12 mmol) was added an ethanol solution (10 mL) of 1,2-bis(aminooxy)ethane (0.282 g, 3.06 mmol). The mixture solution was stirred at 65 °C for 8 h, after cooling to room temperature, the reaction mixture was filtered, washed successively with ethanol and ethanol / hexane (1:4), respectively. The precipitate was dried under vacuum, and obtained pale-yellow solid 1.65 g. Yield: 87.1%, m.p. 137-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 1.58 (s, 3H), 4.66 (t, J = 8 Hz, 2H), 7.32 (m, 4H), 7.42 (m, 4H), 7.65 (d, J = 8Hz, 2H). ^{13}C NMR (400 MHz, C_2D_6OS): 14.6, 15.7, 21.3, 60.3, 65.5, 73.0, 129.4, 135.8, 150.0, 170.9. IR: 3442, 3058, 2932, 2879, 1617, 1593, 1557, 1499, 1456, 1405, 1361, 1308, 1220, 1053, 970, 846, 746, 694. Anal. Calcd. for $C_{36}H_{32}N_6O_4$ (%):C 70.57, H 5.26, N 13.72. Found: C 70.50, H 5.37, N 13.61.

Preparation of the Zn(II) complexes

Preparation of the crystal [ZnL(CH_3OH)]: a solution of Zn(II) acetate dihydrate (11.0 mg, 0.05 mmol) in methanol (4 mL) was added dropwise to a solution of H_2L (30.1 mg, 0.05 mmol) in methanol (6 mL), which made the color of the mixing solution turned to colorless immediately, then the mixture was allowed to stand at room temperature for about one week. When the solvent was partially evaporated, several colorless block-shaped single crystals suitable for X-ray crystallographic analysis were obtained. ^{1}H NMR (400 MHz, C_2D_6OS): 1.57 (s, 3H), 3.13 (d, J = 5.2

Hz, 3H), 4.06 (t, J = 12.4 Hz, 2H), 7.32 (m, 4H), 7.12 (m, 4H), 7.35 (d, J = 8Hz, 2H), 8.07 (d, J = 7.6 Hz, 1H). ^{13}C NMR (400 MHz, C_2D_6OS): 15.6, 49.1, 70.6, 95.0, 119.5, 124.7, 127.5, 128.8, 129.1, 134.6, 140.0, 147.7, 162.2, 165.9. IR: 3592, 3435, 3056, 1955, 1597, 1569, 1506, 1480, 1434, 1367, 1356, 1272, 1089, 1068, 1045, 1018, 908, 869, 779, 760, 712, 693, 610, 568, 507, 453. Anal. Calcd. for [ZnL(CH_3OH)] (%): C 62.76, H 4.84, N 11.87. Found: C 62.67, H 4.81, N 11.91.

Preparation of the powder of the Zn(II) complex (unground sample): the powder of the Zn(II) complex was synthesized according to an analogous method as the crystal sample. a solution of Zn(II) acetate dihydrate (104.4 mg, 0.47 mmol) in methanol (4 mL) was added dropwise to a solution of H_2L (261.2 mg, 0.43 mmol) in methanol (6 mL), which made the color of the mixing solution turned to colorless immediately, then the powder of the Zn(II) complex was obtained after two days. IR: 3436, 3058, 2924, 2834, 1958, 1600, 1568, 1501, 1456, 1434, 1373, 1354, 1241, 1088, 1070, 1049, 1015, 912, 870, 779, 759, 715, 696, 612, 571, 508, 454. Anal. Calcd. for the unground sample ZnL·2 CH_3OH (%): C 61.67, H 5.18, N 11.35. Found: C 61.71, H 5.13, N 11.39.

Preparation of the ground sample: the powder Zn(II) complex was ground in agate mortar to obtain the ground sample. IR: 3594, 3436, 3058, 2926, 1958, 1598, 1569, 1506, 1479, 1434, 1370, 1351, 1273, 1089, 1070, 1045, 1015, 908, 870, 780, 760, 712, 693, 612, 568, 508, 452. Anal. Calcd. for the ground sample [ZnLCH_3OH]·CH_3OH (%): C 61.67, H 5.18, N 11.35. Found: C 61.70, H 5.14, N 11.38.

X-ray structure determination of [ZnL(CH_3OH)]

The single crystals of the complex [ZnL(CH_3OH)] with approximate dimensions of 0.35×0.32×0.28 mm were placed on a Bruker Smart diffractmeter equipped with Apex CCD area detector. The diffraction data were collected using a graphite monochromated Mo Kα radition (λ = 0.71073 Å) at 293(2) K. The structures were solved by using the program SHELXS-97 and Fourier difference techniques, and refined by full-matrix least-squares method on F^2 using SHELXL-97. All hydrogen atoms were added theoretically.

Recovery experiment

To a ground sample (0.3065g) of the Zn(II) complex was added methanol solution (1.5 mL), then the mixture was allowed to stand at room temperature for about 20 min.

Captions:

Scheme 1 The synthetic route of H_2L.

Fig. S1 ^1H NMR of H_2L.

Fig. S2 ^{13}C NMR of H_2L

Fig. S3 IR spectra of H_2L.

Fig. S4 ^1H NMR of ZnL.

Fig. S5 ^{13}C NMR of ZnL.

Fig. S6. TGA-DTG analyses of the unground sample.

Fig. S7 TGA-DTG analyses of the ground sample.

Fig. S8 TGA-DTG analyses of the crystal sample.

Fig. S9 IR spectra of the unground sample (red), the ground sample (blue) and the crystal sample (black).

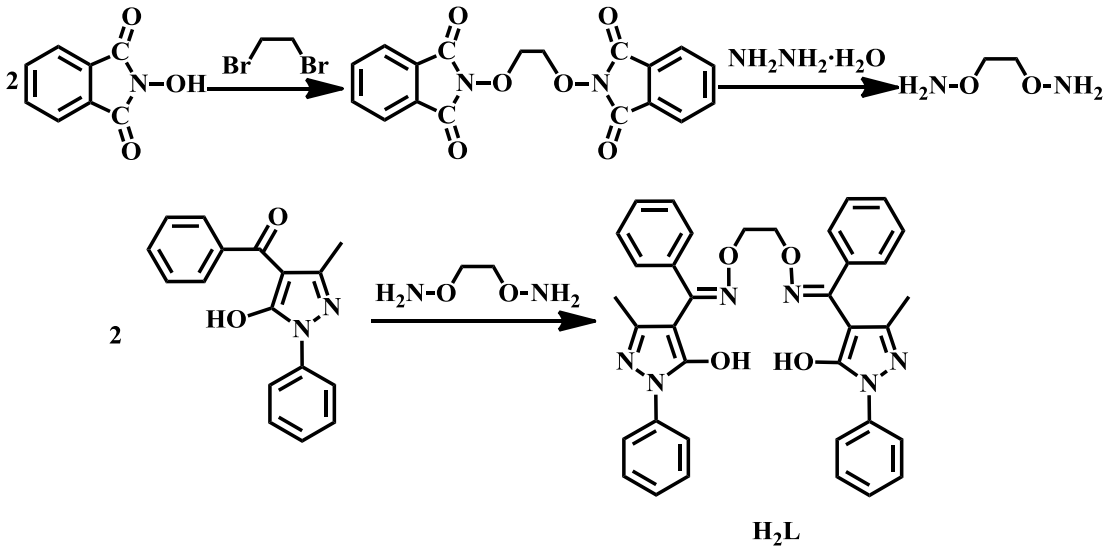
Fig. S10 Powder X-ray diffraction patterns of the unground sample (red), the ground sample (blue) and the crystal Zn(II) sample (black).

Fig. S11 Powder X-ray diffraction pattern of the recovered ground sample.

Fig. S12 The Fluorescence emission of H_2L (10mM) upon addition of Zn(II) (0.2 equivalent, 0.2 equivalent, 0.5 equivalent, 1.0 equivalent, 2.0 equivalent, 4.0 equivalent) in MeOH.

Table S1 Crystal data and structure refinement for [ZnL(CH_3OH)].

Table S2 Selected bond distances [Å] and bond angles [°] for [ZnL(CH_3OH)].



Scheme 1 The synthetic route of H_2L.

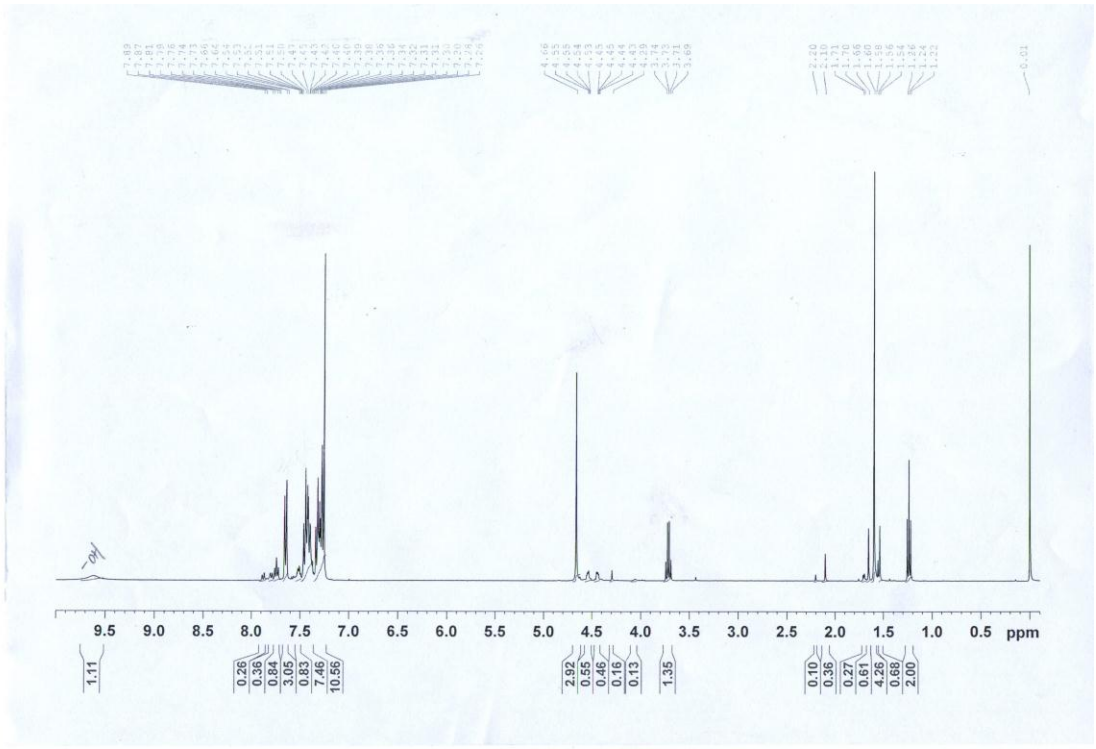


Fig. S1 ^{1}H NMR of H_2L.

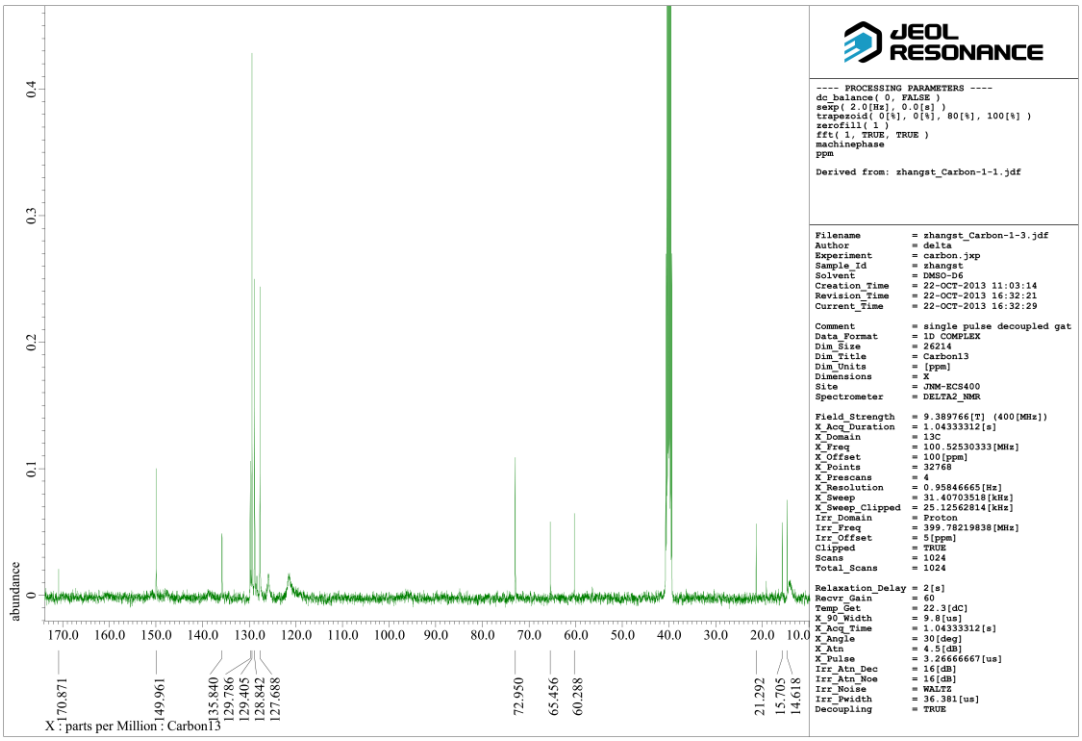


Fig. S2 ^{13}C NMR of H_2L

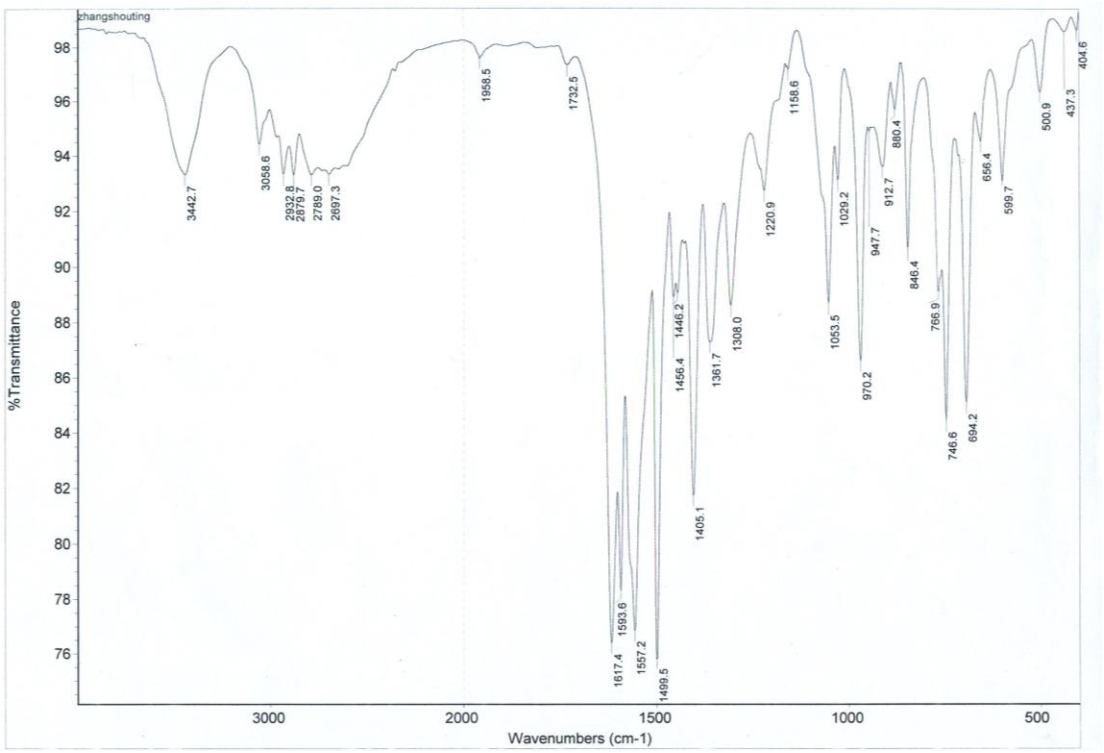


Fig. S3. IR spectra of H_2L.

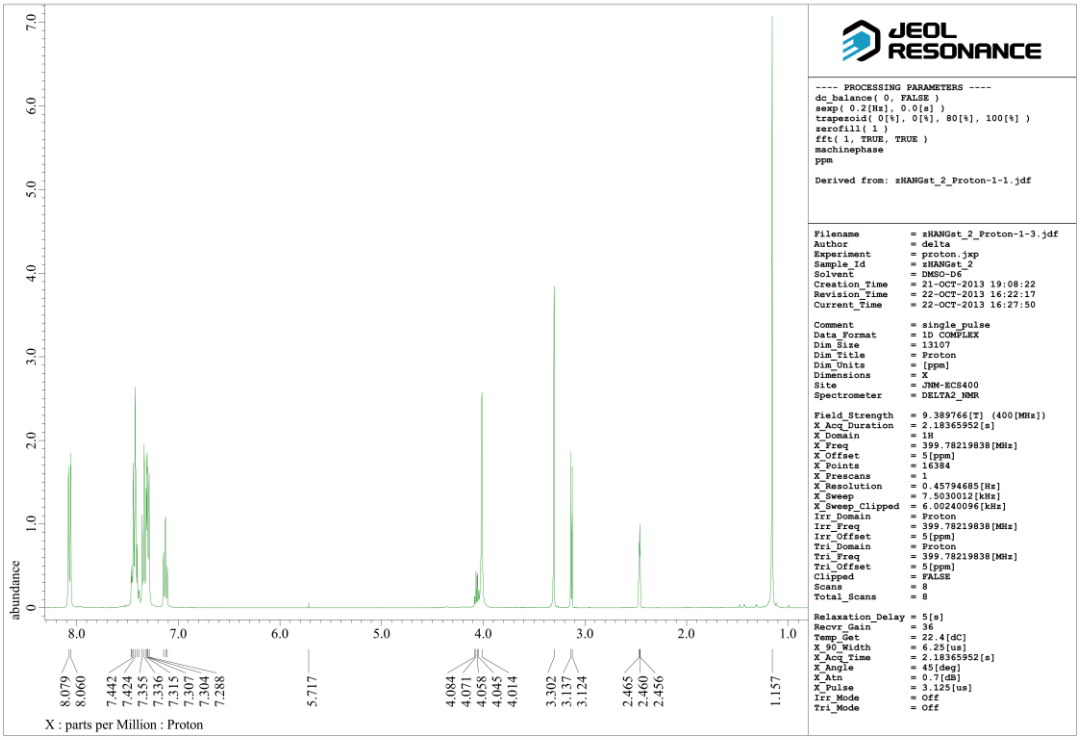


Fig. S4 ^{1}H NMR of ZnL.

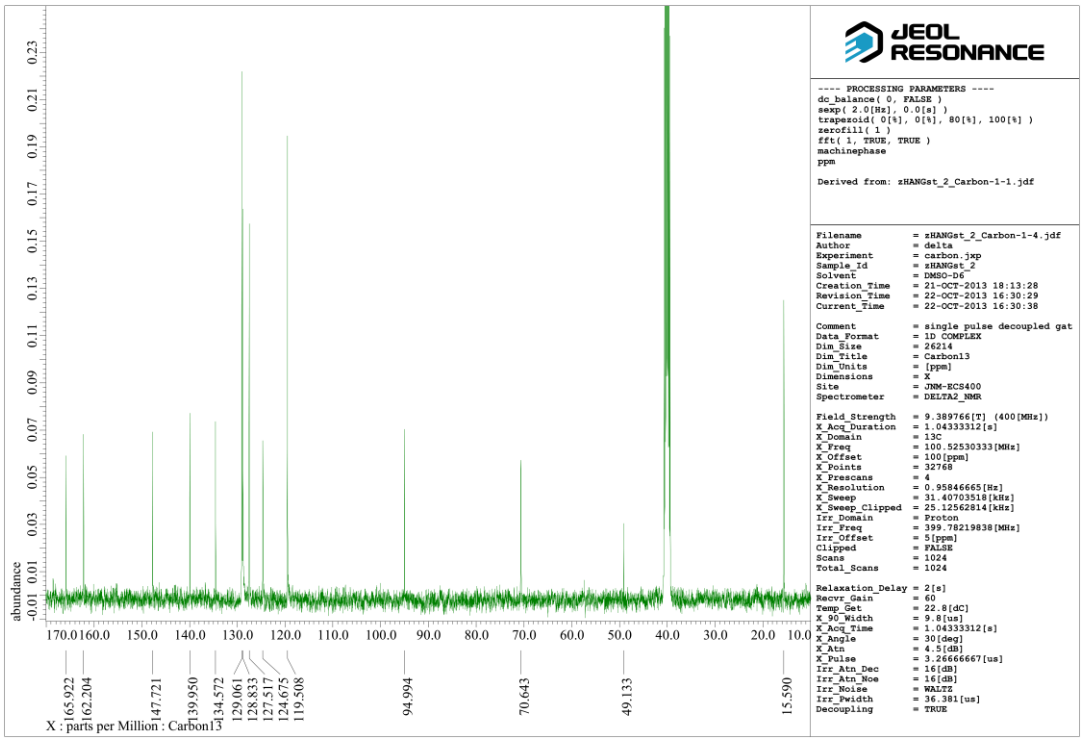


Fig. S5 ^{13}C NMR of ZnL.

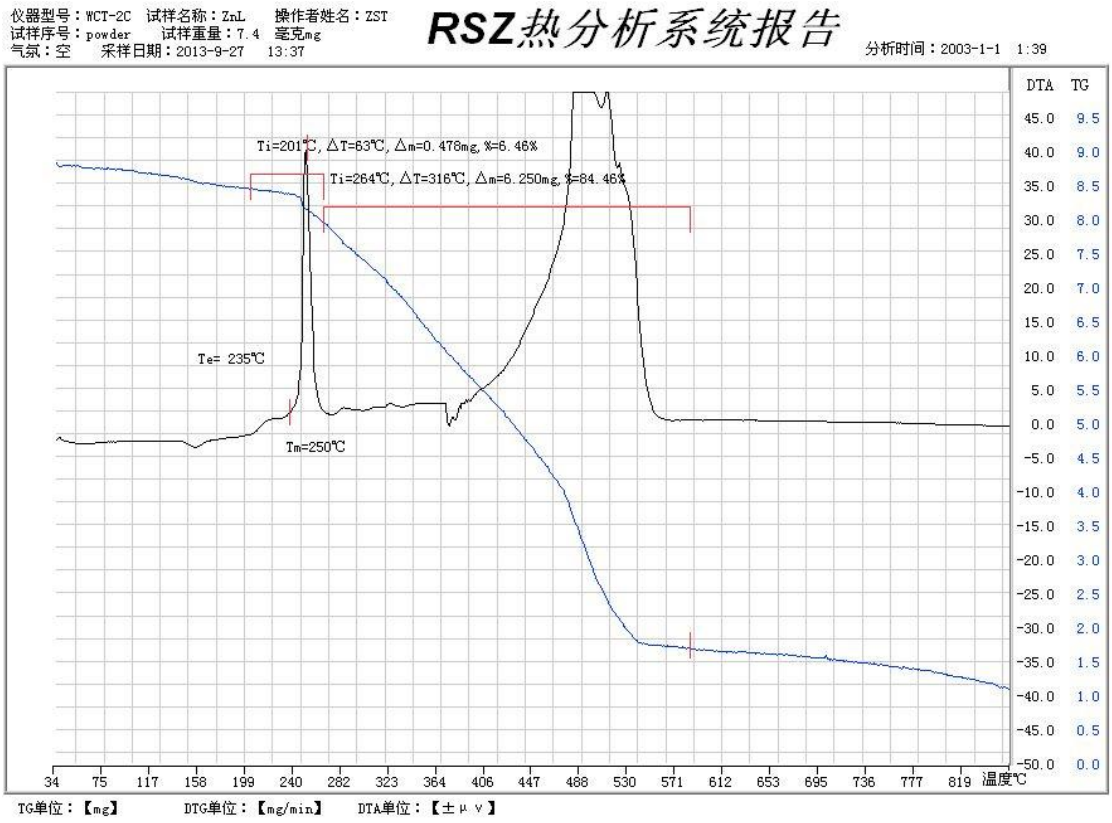


Fig. S6 TGA-DTG analyses of the unground sample.

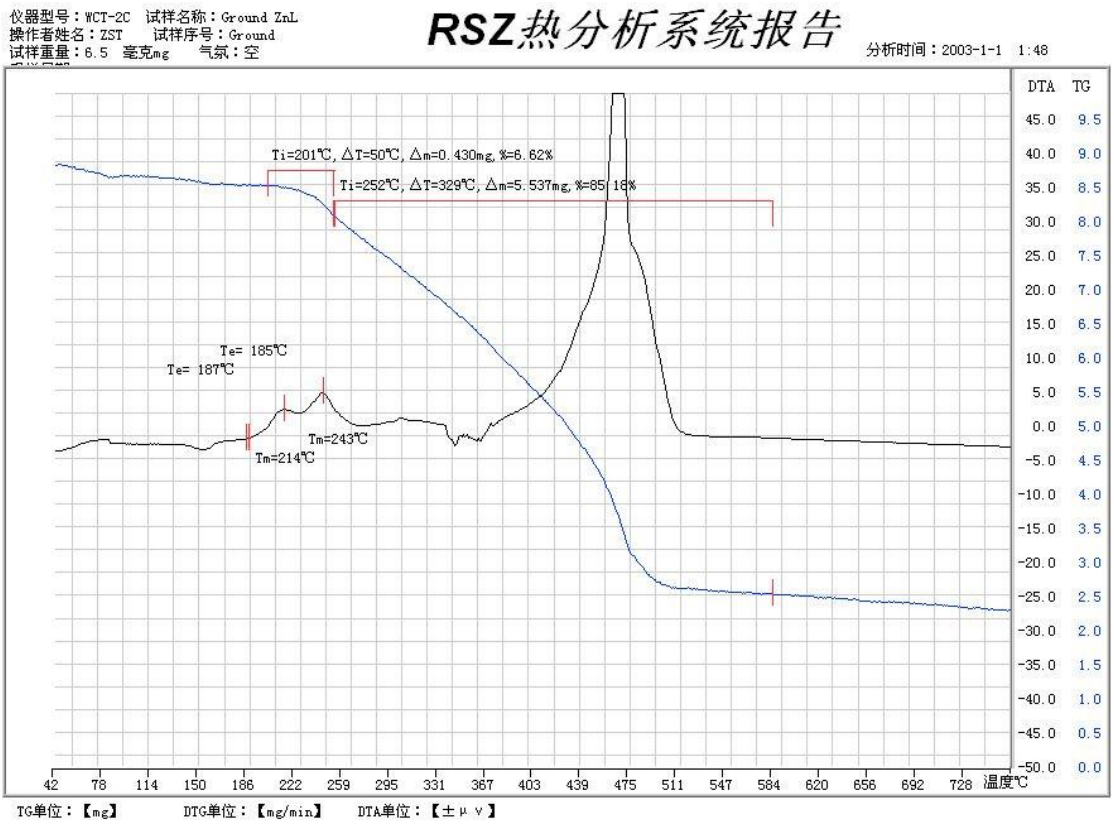


Fig. S7 TGA-DTG analyses of the ground sample.

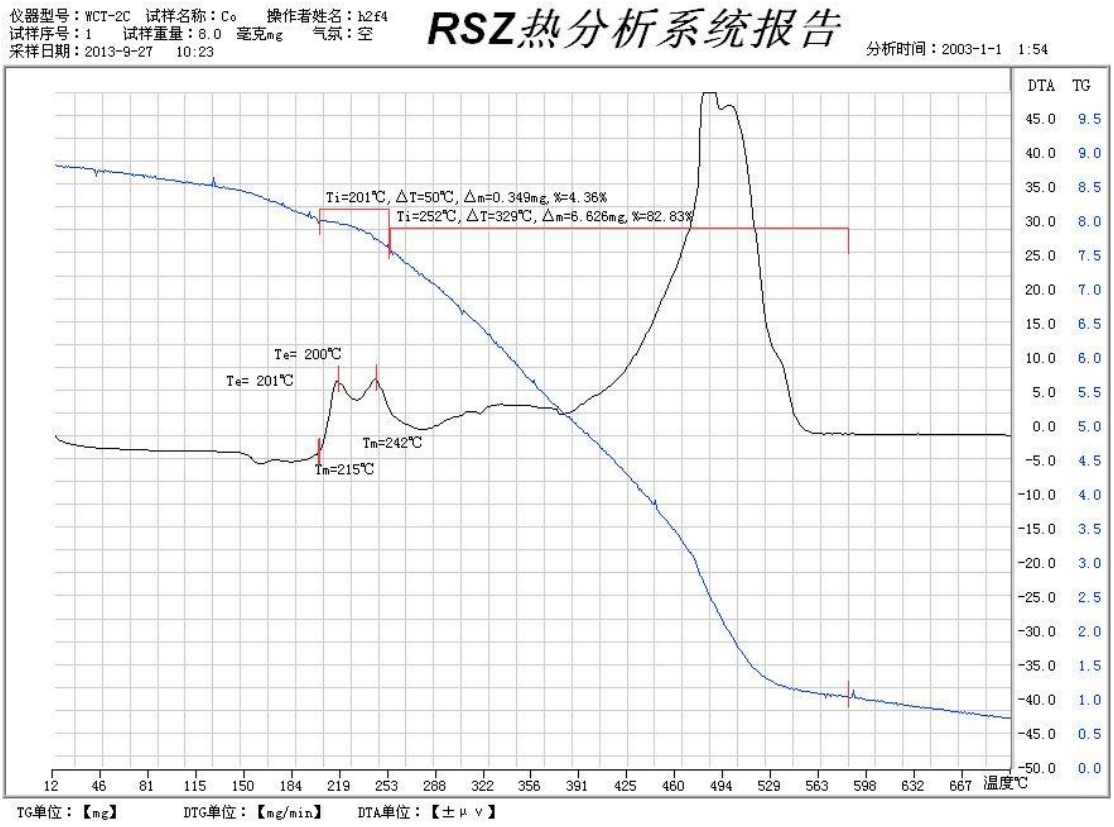


Fig. S8 TGA-DTG analyses of the crystal sample.

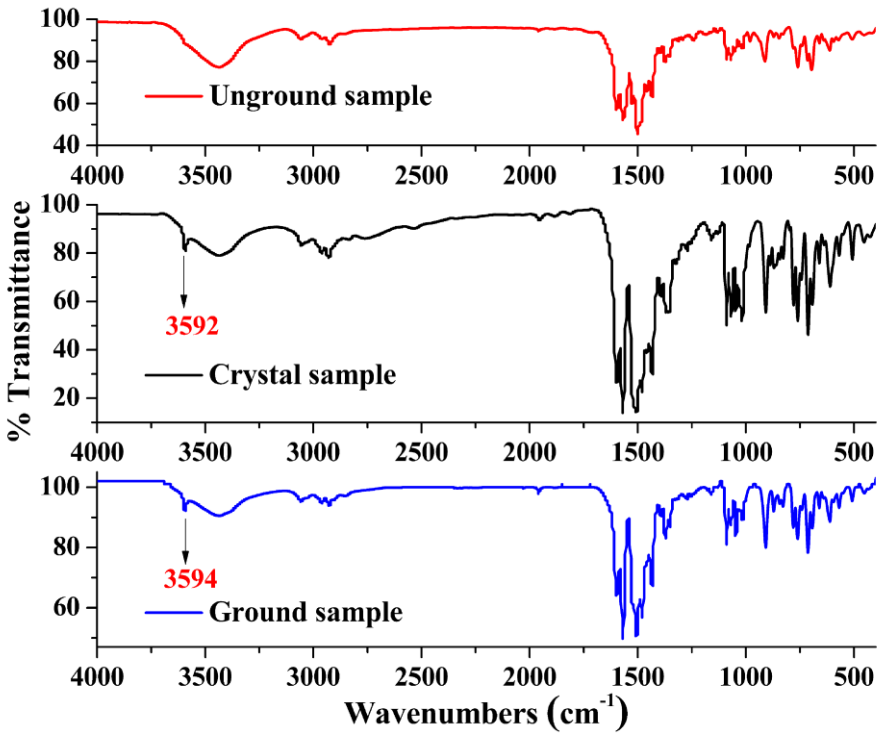


Fig. S9 IR spectra of the unground sample (red), the ground sample (blue) and the crystal sample (black).

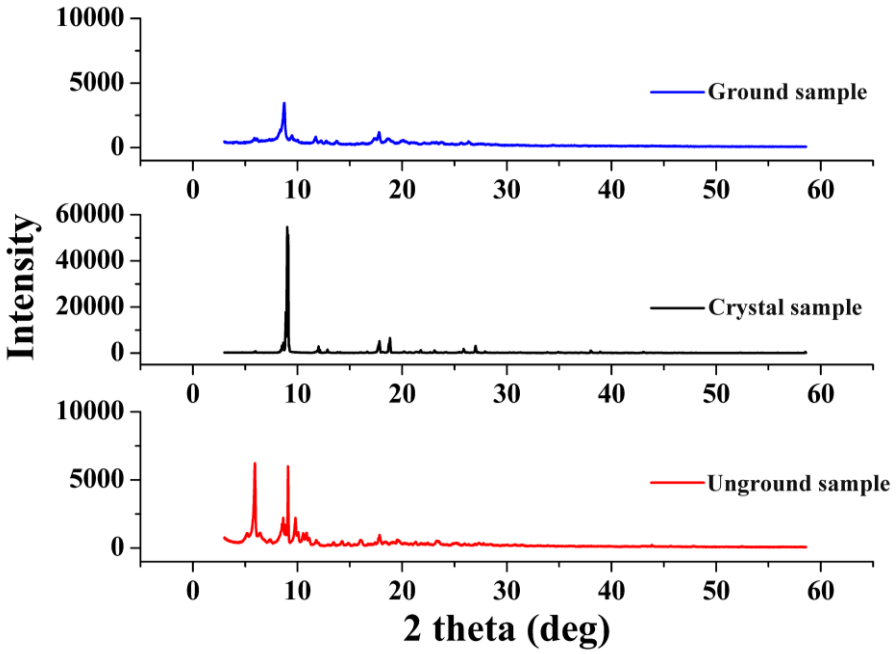


Fig. S10 Powder X-ray diffraction patterns of the unground sample (red), the ground sample (blue) and the crystal Zn(II) sample (black).

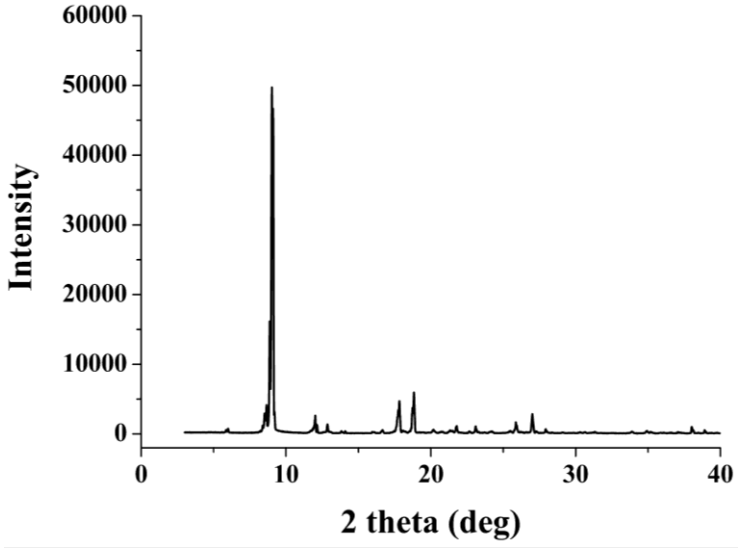


Fig. S11. Powder X-ray diffraction pattern of the recovered ground sample.

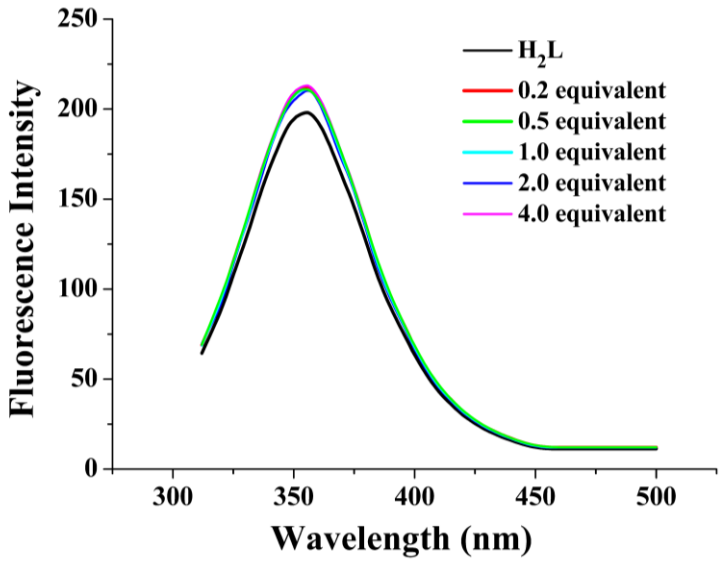


Fig. S12 The Fluorescence emission of H_2L (10mM) upon addition of Zn(II) (0.2 equivalent, 0.2 equivalent, 0.5 equivalent, 1.0 equivalent, 2.0 equivalent, 4.0 equivalent) in MeOH.

Table S1 Crystal data and structure refinement for [ZnL(CH_3OH)].

	Zn(II) complex
Empirical formula	$C_{37}H_{34}N_6O_5Zn$
Formula weight	708.07
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, Space group	Triclinic, *P*-1
Unit cell dimensions	0.35×0.32×0.28
a (Å)	10.6014(8)
b (Å)	10.6656(8)
c (Å)	15.898(2)
α (º)	104.972(9)
β (º)	105.000(9)
γ (º)	91.803(6)
Volume ($Å^3$)	1668.0(3)
Z, Calculated density(Mg/m^3)	2, 1.410
F (000)	736
Crystal size (mm)	0.35×0.32×0.28
θ range for data collection (º)	2.9584 to 28.5666
Limiting indices	-13≤ h ≤13, -13≤ k ≤13, -19 ≤ l≤ 19
Reflections collected / unique	6683 / 458 [R(int) = 0.0399]
Completeness to θ	97.86 %(theta = 26.32º)
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Final *R* indices [I>2σ(I)]	R_1 = 0.0399, wR_2 = 0.0768
R indices (all data)	R_1 = 0.0520, wR_2 = 0.0849

$\omega = 1/[s^2(F_0^2)+(0.0202P)^2+0.5349P]$, where $P = (F_0^2+2F_c^2)/3$

Table S2 Selected bond distances [Å] and bond angles [º] for [ZnL(CH_3OH)].

Bond	Dist.	Bond	Dist.	Bond	Dist.
Zn(1)-O(1)	2.0204(2)	C(11)-N(3)	1.311(3)	O(3)-N(4)	1.436(2)
Zn(1)-O(4)	1.9406(2)	C(20)-N(4)	1.303(3)	N(5)-N(6)	1.393(2)
Zn (1)-O(5)	2.0682(2)	C(6)-N(1)	1.429(3)	C(1)-C(2)	1.382(4)
Zn (1)-N(3)	2.0583(2)	C(7)-N(1)	1.368(3)	C(1)-C(6)	1.381(3)
Zn (1)-N(4)	2.1986(2)	C(9)-N(2)	1.316(3)	C(2)-C(3)	1.379(4)
O(1)-C(7)	1.269(2)	C(28)-N(5)	1.325(3)	C(3)-C(4)	1.372(4)
O(4)-C(30)	1.282(2)	C(30)-N(6)	1.371(3)	C(18)-C(19)	1.506(4)
C(7)-C(8)	1.420(3)	C(31)-N(6)	1.422(3)	O(3)-C(19)	1.425(3)
C(27)-C(30)	1.410(3)	O(2)-N(3)	1.436(2)	N(1)-N(2)	1.399(2)
Bond	Angles	Bond	Angles	Bond	Angles
O(1)-Zn(1)-O(5)	86.61(7)	O(4)-Zn(1)-N(4)	88.15(7)	C(37A)-O(5)-Zn(1)	128.6(3)
O(1)-Zn(1)-N(3)	89.96(7)	O(5)-Zn(1)-N(4)	86.20(7)	C(37B)-O(5)-Zn(1)	125.5(9)
O(1)-Zn(1)-N(4)	172.48(7)	N(3)-Zn(1)-O(5)	138.34(8)	O(2)-N(3)-Zn(1)	114.61(1)
O(4)-Zn(1)-O(1)	96.26(7)	N(3)-Zn(1)-N(4)	93.95(7)	C(11)-N(3)-Zn(1)	129.84(2)
O(4)-Zn(1)-O(5)	108.91(7)	C(7)-O(1)-Zn(1)	122.49(14)	O(3)-N(4)-Zn(1)	123.47(1)
O(4)-Zn(1)-N(3)	112.73(8)	C(30)-O(4)-Zn(1)	122.35(14)	C(20)-N(4)-Zn(1)	125.72(2)

Symmetry transformations used to generate equivalent atoms: -x,-y,-z