Supporting information

Assembly of Zn-metal organic frameworks based on N-rich ligand: selective sorption for CO_2 and luminescence sensing of nitro explosives

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S1. Materials and measurements

All chemical materials were purchased from commercial sources and used without further purification. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. XRPD patterns were recorded on a Siemens D5005 diffractometer with Cu Kα (λ = 1.5418 Å) radiation in the range of 3−60° at a rate of 5°/min. The UV-Vis absorption spectra were examined on a Shimadzu UV-2550 spectrophotometer in the wavelength range of 200-800 nm. The C, H, and N elemental analyses were conducted on a Perkin-Elmer 2400CHN elemental analyzer. TG curves were performed on a Perkin–Elmer TG-7 analyzer heated from room temperature to 1000 ºC at a ramp rate of 5 °C/min under nitrogen. The photoluminescence spectra were measured on a Perkin-Elmer FLS-920 Edinburgh Fluorescence Spectrometer.

S2. X-ray crystallography

Single-crystal X-ray diffraction data for **1–2** were recorded by using a Bruker Apex CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å) at 293 K. Absorption corrections were applied by using a multi-scan technique. All the structures were solved by Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program within WINGX. Non-hydrogen atoms were refined with anisotropic temperature parameters.

The Selected bond lengths [Å] and angles [˚] for **1−2** are summarized in Table S1and Table S2.

S3. Gas sorption experiments

The N_2 and CO_2 sorption measurements were performed on automatic volumetric adsorption equipment (Belsorp mini II). Before gas adsorption measurements, the samples were immersed in CH_2Cl_2 for 24 h, and the extracts were decanted. Fresh CH_2Cl_2 was subsequently added, and the crystals were allowed to stay for an additional 24 h to remove the nonvolatile solvates (DMA). After the removal of dichloromethane by decanting, the samples were activated by drying under a dynamic vacuum at room temperature overnight. Before the measurement, the samples were dried again by using the ‘outgas’ function of the surface area analyzer for 12 h at 90 ºC.

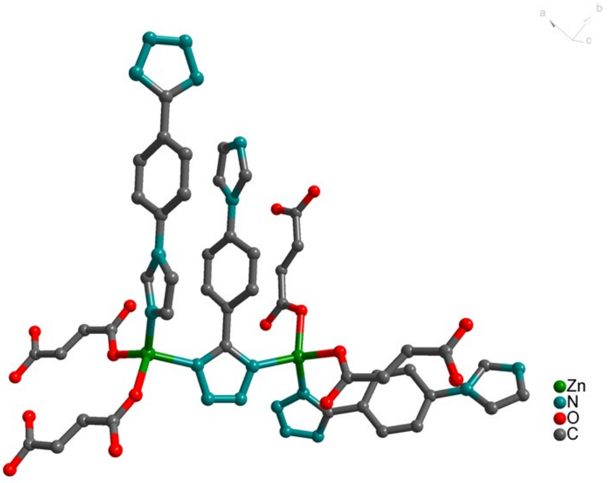

Fig. S1 The representations of 1D chain of compound **1** along the *c* axis.

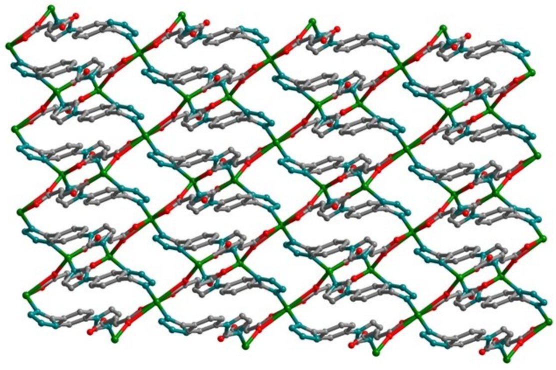

Fig. S2 The view of the 3D framework of compound **1** along *b* axis.

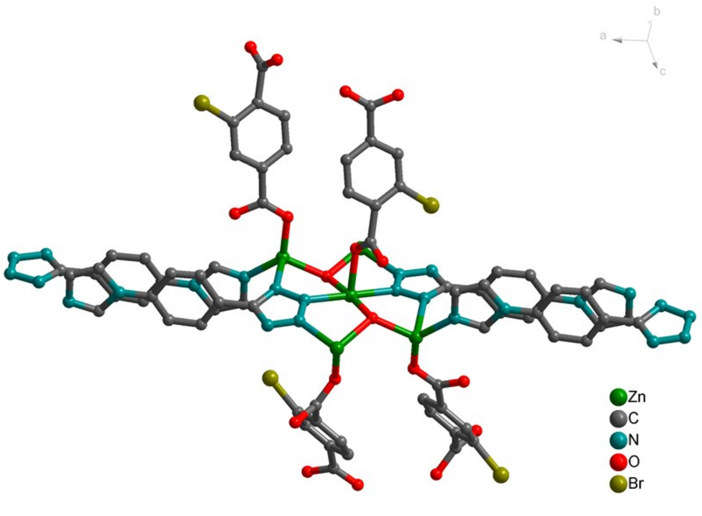

Fig. S3 View of the coordination environment around Zn(II) and the building unit in framework **2**.

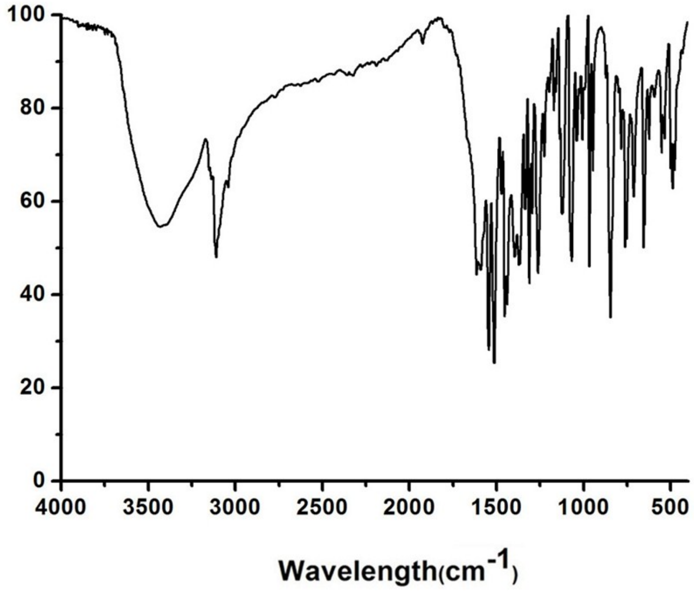

Fig. S4 FT-IR spectra of **1**.

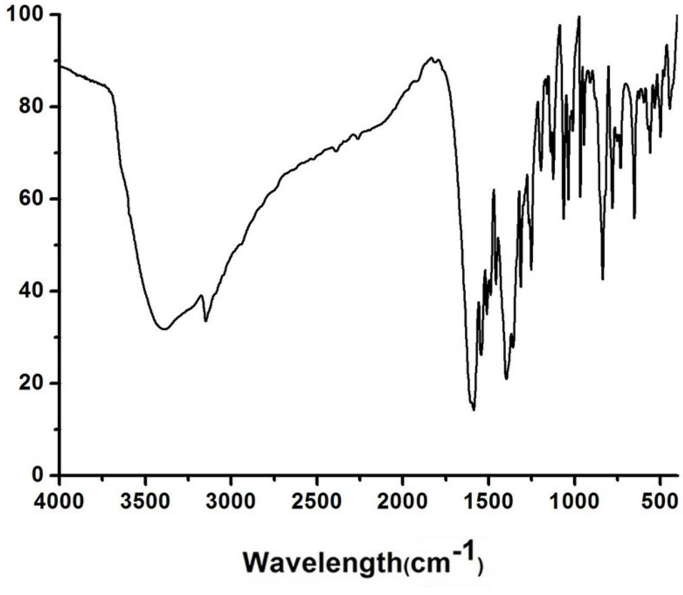

Fig. S5 FT-IR spectra of **2**.

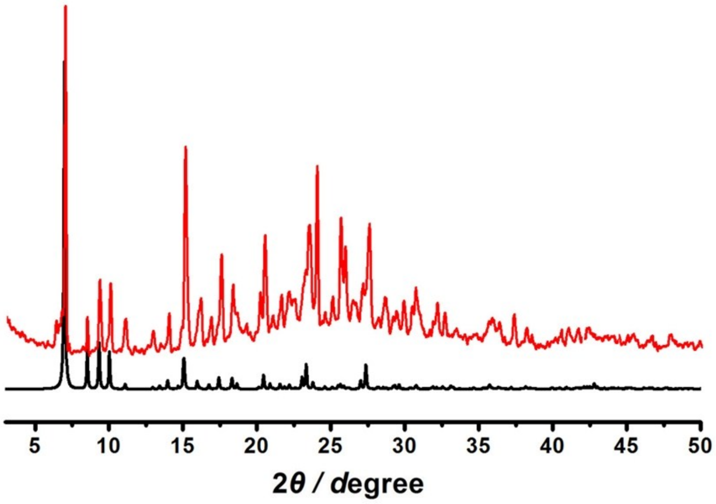

Fig. S6 X-ray powder diffraction patterns of **1**: simulated (black) and as-synthesized (red).

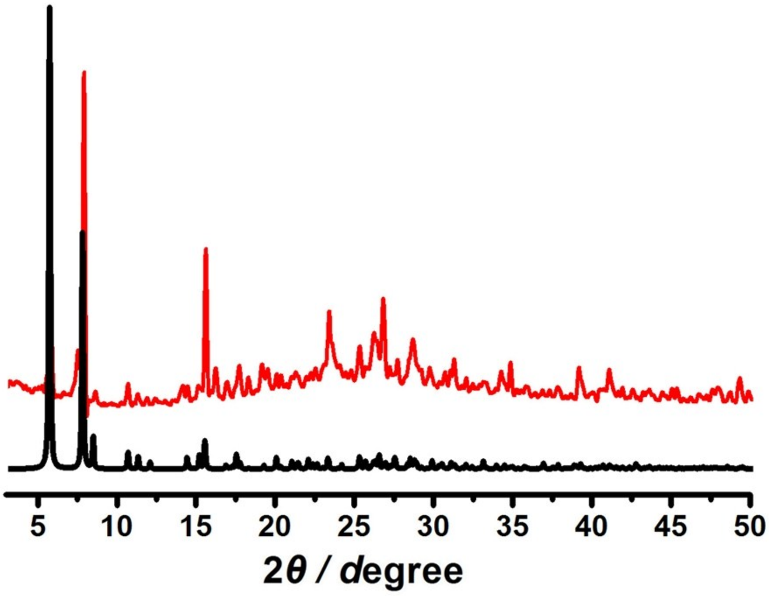

Fig. S7 X-ray powder diffraction patterns of **2**: simulated (black) and as-synthesized (red).

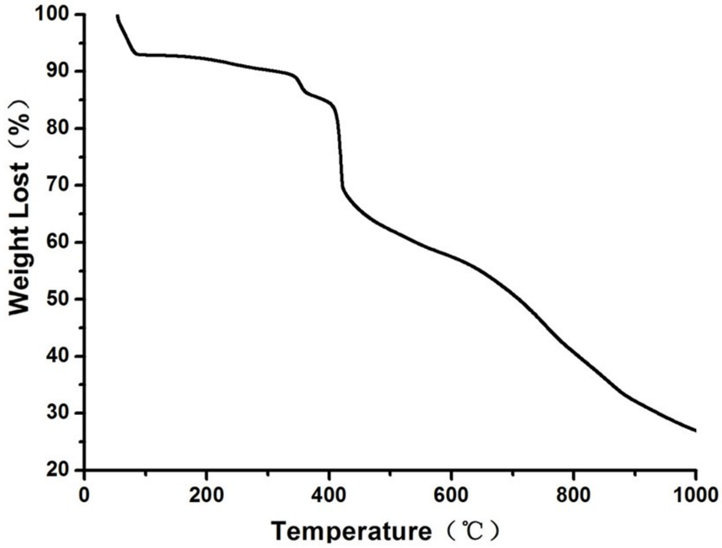

Fig. S8 TG curves of compound **1.**

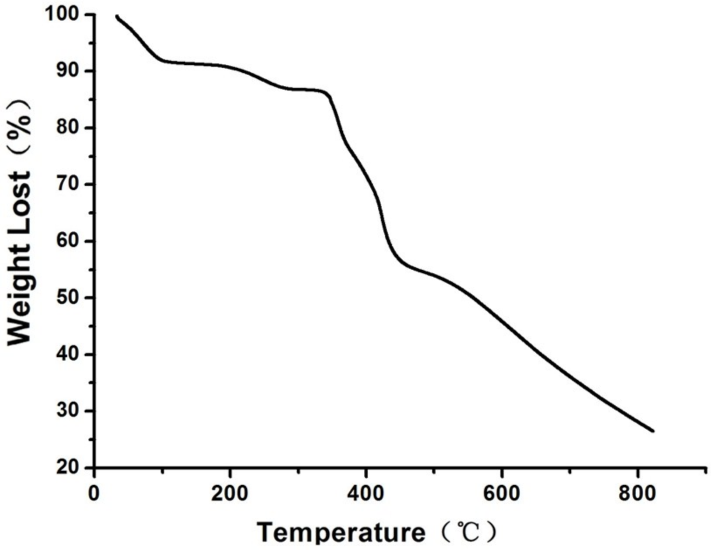

Fig. S9 TG curves of compound **2.**

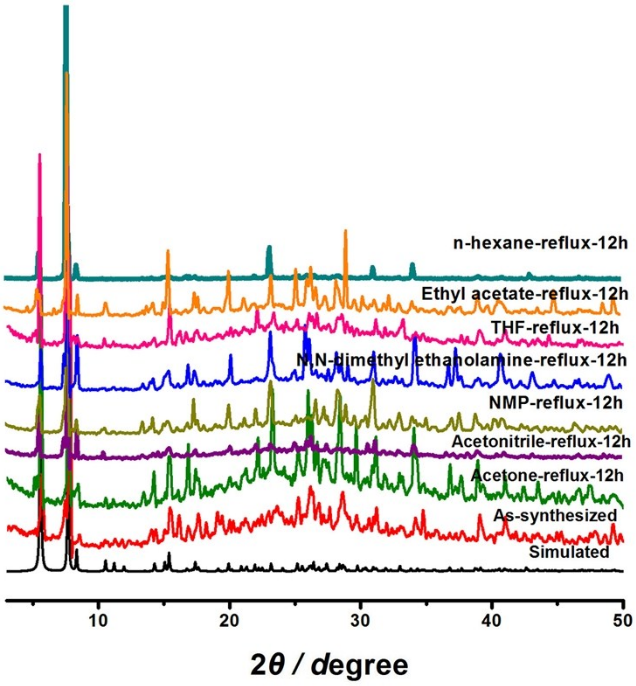

Fig. S10 X-ray powder diffraction patterns of **2**: simulated (black), as-synthesized (red), acetone (green), after soaking in acetonitrile (purple), NMP (dark yellow), N,N-dimethyl ethanolamine (blue), THF (pink), ethyl acetate (orange) and n-hexane (dark cyan).

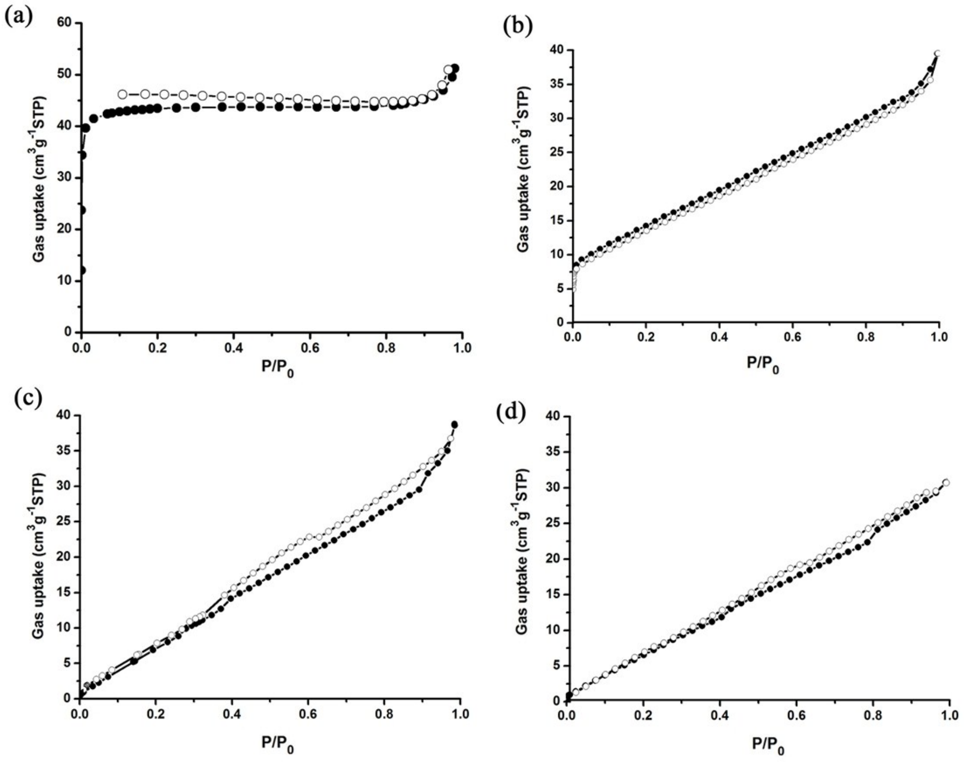

Fig. S11 (a) The nitrogen sorption isotherms of **1a** at 77 K, after (b) water, (c) HCl (0.005 M) and (d) NaOH (0.005 M) treatment.

S4. Heat of adsorption calculation for gas uptake

1. The isosteric heat of adsorption values were calculated using the Clausius–Clapeyron equation:

$\ln(P_1/P_2)= \Delta H_{abs} \times (T_2 - T_1) / R\ T_1\ T_2$ (1)

Where P_i = pressure for isotherm i

T_i = temperature for isotherm i

R = 8.315 J / (K*mol)

The equation can be applied to calculate the enthalpy of adsorption of a gas as a function of the quantity of gas adsorbed.

2. The isosteric heat of adsorption values were calculated using the virial equation (1):

$\ln(p) = \ln(n) + (a_0 + a_1 \times n + a_2 \times n_2) + b$ (1)

where p is pressure, n is amount adsorbed, T is temperature, and a0, a1, a2 and b1 are temperature independent empirical parameters. The isosteric heat of adsorption was estimated from the following equation (2) as a function of methane uptake.

$Qst = -R \times (a_0 + a_1 \times n + a_2 \times n_2)$ (2)

Table S1. Virial fit parameters for **1**.

Equation y=ln(x)+1/k*(a_0+a_1*x+a_2*x^2+a_3*x^3+a_4*x^4+a_5*x^5)+(b_0+b_1*x+b_2*x^2)		
Adj. R-Square	0.96902	
	Value	Standard Error
a_0	-4267.89431	578.97046
a_1	-1.16255	24.48297
a_2	0.76692	0.49691
a_3	-0.01297	0.00967
a_4	7.24221E-5	5.9139E-5
a_5	0	0
b_0	17.21349	2.06577
b_1	-0.04601	0.08831
b_2	0	0

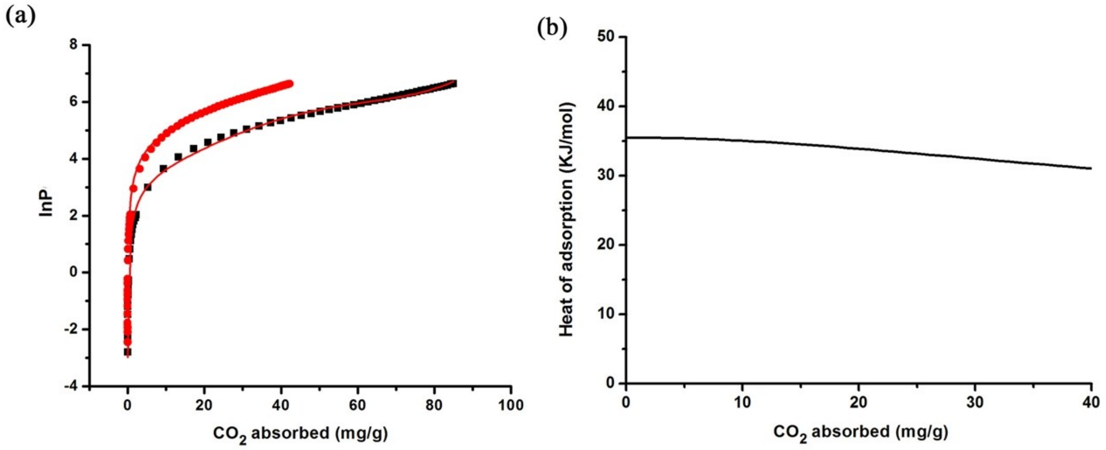

Fig. S12 (a) Virial analysis of the sorption data for **1** (square, black: 273 K, circle, red: 298 K). (b) Heats of adsorption for CO_2 of **1** estimated by virial equation.

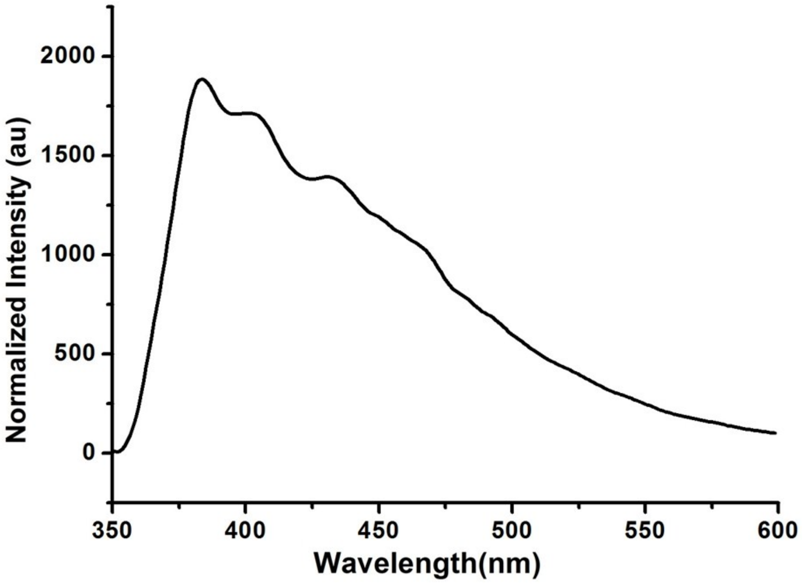

Fig. S13 Emission spectra of the fma ligand.

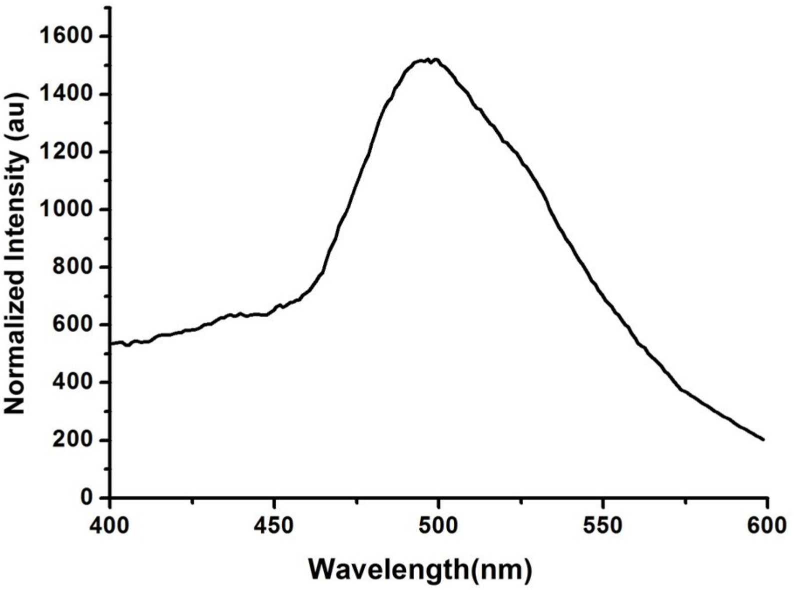

Fig. S14 Emission spectra of the Br-bdc ligand.

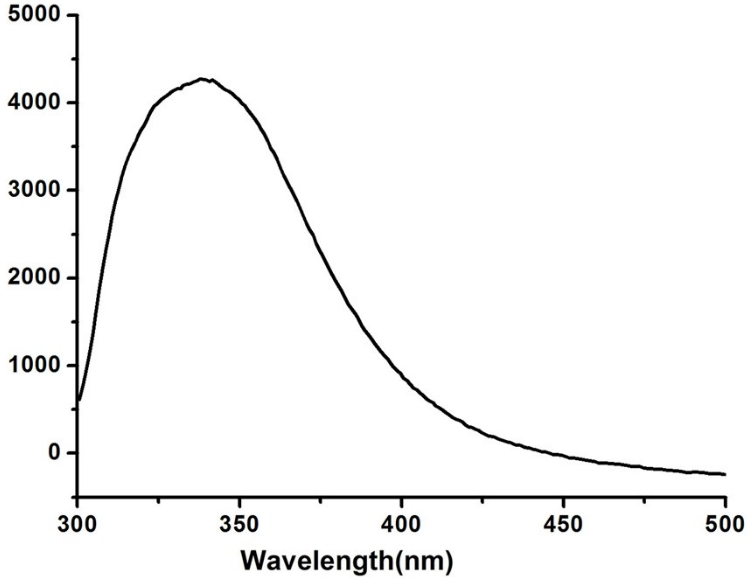

Fig. S15 Emission spectra of the HL ligand.

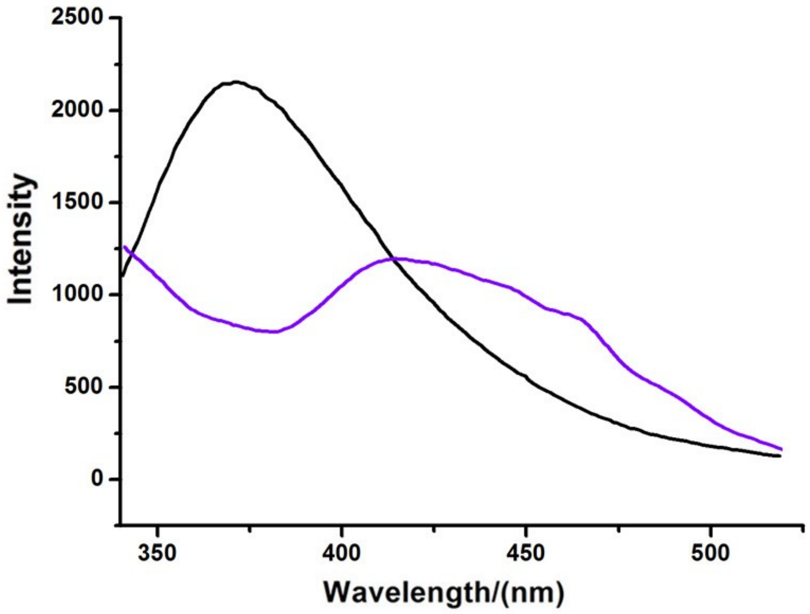

Fig. S16 Luminescence spectra of the compound **1**(black) and **2** (purple) at room temperature.

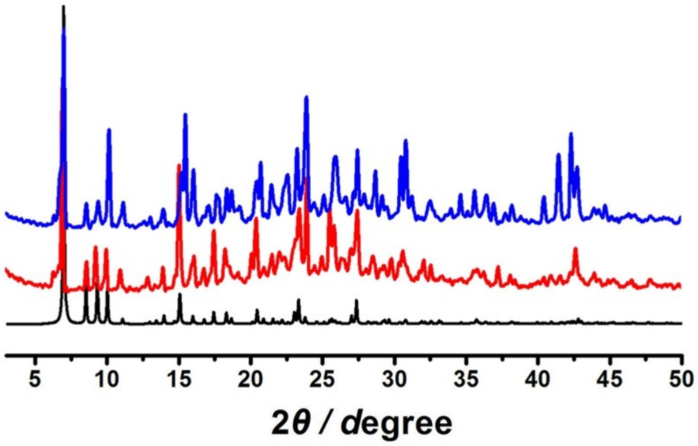

Fig. S17 X-ray powder diffraction patterns of **1**: simulated (black), as-synthesized (red) and after 5 cycles of quenching NB (blue).

Table S2 Selected bond lengths [Å] and angles [˚] for **1**.

Zn(1)-O(2)	1.955(3)	O(2)#1-Zn(1)-N(6)#2	120.10(14)
Zn(1)-O(2)#1	1.955(3)	O(2)-Zn(1)-N(6)#3	120.10(14)
Zn(1)-N(6)#2	2.001(4)	O(2)#1-Zn(1)-N(6)#3	111.03(14)
Zn(1)-N(6)#3	2.001(4)	N(6)#2-Zn(1)-N(6)#3	103.9(2)
Zn(2)-O(4)#4	1.915(4)	O(4)#4-Zn(2)-O(1)	105.98(15)

Zn(2)-O(1)	1.972(3)	O(4)#4-Zn(2)-N(1)	122.03(18)
Zn(2)-N(1)	1.984(4)	O(1)-Zn(2)-N(1)	101.96(15)
Zn(2)-N(3)#5	2.015(4)	O(4)#4-Zn(2)-N(3)#5	118.16(18)
O(2)-Zn(1)-O(2)#1	91.47(18)	O(1)-Zn(2)-N(3)#5	101.20(14)
O(2)-Zn(1)-N(6)#2	111.03 (14)	N(1)-Zn(2)-N(3)#5	104.37(16)

Table S3 Selected bond lengths [Å] and angles [˚] for **2**.

Zn(1)-O(2)	1.941(4)	O(2)-Zn(1)-N(1)	95.30(17)
Zn(1)-O(5)	1.988(3)	O(5)-Zn(1)-N(1)	90.59(13)
Zn(1)-N(1)	2.264(4)	N(6)#1-Zn(1)-N(1)	90.09(15)
Zn(1)-N(6)#1	2.028(4)	O(2)-Zn(1)-N(4)#2	87.10(16)
Zn(1)-N(4)#2	2.368(4)	O(5)-Zn(1)-N(4)#2	88.79(12)
Zn(2)-O(4)#3	2.083(4)	N(1)-Zn(1)-N(4)#2	177.60(16)
Zn(2)-O(3)#4	2.096(4)	O(4)#3-Zn(2)-O(3)#4	177.23(14)
Zn(2)-N(2)#5	2.112(4)	O(4)#3-Zn(2)-N(2)#5	90.89(15)
Zn(2)-N(3)	2.113(4)	O(3)#4-Zn(2)-N(2)#5	87.61(16)
Zn(2)-O(5)#6	2.134(3)	O(4)#3-Zn(2)-N(3)	91.64(15)
Zn(2)-O(5)#5	2.148(3)	N(2)#5-Zn(2)-N(3)	177.42(16)
O(3)-Zn(2)#4	2.096(4)	O(4)#3-Zn(2)-O(5)#6	94.37(14)
O(2)-Zn(1)-O(5)	109.21(17)	O(3)#4-Zn(2)-O(5)#6	88.03(14)
O(2)-Zn(1)-N(6)#1	129.71(18)	N(3)-Zn(2)-O(5)#6	87.92(14)
O(5)-Zn(1)-N(6)#1	120.71(16)	O(5)#6-Zn(2)-O(5)#5	173.82(6)