Electronic Supporting Information（ESI）

Selective gas adsorption and fluorescent sensing response of a Zn(II) metal-organic framework constructed by the mixed-ligand strategy

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Contents

S1. Materials and measurements

All the reagents and solvents for the synthesis were purchased from commercial sources and used as received. All solvents were analytical grade and without further purification.

IR spectra was measured on a FTS6000 (Bio-rad) FT-IR spectrometer using KBr pellets in the 4000–400 cm^{-1} range. Thermogravimetric analyses (TGA) was carried out on a Rigaku standard TG-DTA analyzer with a heating rate of 10 °C min^{-1}, with an empty Al_2O_3 crucible used as a reference. The room-temperature powder X-ray diffraction spectra (PXRD) was recorded on a Rigaku D/Max-2500 diffractometer at 60 kV, 300 mA with a Cu-target tube and a graphite monochromator. All fluorescence measurements were performed on a Varian Cary Eclipse fluorescence spectrometer equipped with a plotter unit. Simulation of the PXRD pattern was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge via the internet at http://www.iucr.org.

S2.Experimental section

Synthesis of $[H_2N(CH_3)_2]\cdot Zn(NDC)(atz)\cdot H_2O$ (1)

A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (0.27 mmol), NDC (0.15 mmol), Hatz (0.30 mmol) and 7.5 mL DMF/EtOH (v/v = 4:1) was sealed in a 25 ml Teflon-lined reaction vessel and heated to 120 °C for 72 hours. The reaction vessel was cooled to room temperature and colorless crystals were collected with ca 40% yield based on NDC.

S3. X-ray crystallography

The single crystal X-ray data collection was collected on a Rigaku SCX-mini diffractometer for **1**. The determination of unit cell parameters and data collection were performed with Mo-Kα radiation (λ= 0.71073 Å). The structure was solved by using the SHELXS(2016/6) program and refined anisotropically by a full-matrix least-squares technique based on F^2.[S1] All non-hydrogen atoms were located successfully from Fourier maps. It should be noted that the guest molecules in the channels of **1** are highly disordered and could not be modeled properly, so the diffused electron densities resulting from them were removed by the SQUEEZE routine in PLATON and the results were appended in the CIF file.[S2] These residual electron densities were assigned to some dimethylammonium ions and solvent molecules. So SQUEEZE removed the solvent molecules per unit cell. So the tentative formula of **1** is given in the above. Table

S1 shows crystallographic crystal data and structure processing parameters, while the selected bond length and angle data are presented in Table S2. CCDC 1031993 (**1**) contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic Data for **1.**

	1
Formula	$C_{15}H_{16}N_6O_4Zn$
*M*r (g mol^{-1})	409.73
Space group	$P2_1$/c
Crystal system	monoclinic
a (Å)	10.370(2)
b (Å)	10.025(2)
c (Å)	19.575(4)
α(°)	90
β(°)	92.13(3)
γ(°)	90
V (Å^3)	2033.6(7)
Z	4
Dc (g cm^{-3})	1.338
F(000)	840
θ range /°	3.0-27.8
reflns collected	13505
independent reflns	237
R1a(I > 2σ (I))	0.1057 (2199)
wR2b(I >2σ (I))	0.2574 (4650)

$^aR_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$; $^bwR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2]^{1/2}$.

Table S2 Selected bond distances (Å) and angles (°).

complex **1**			
Zn(1)-O(4)	1.990(6)	Zn(1)-N(2)	2.034(7)
Zn(1)-N(1)	2.045(7)	Zn(1)-O(2)	2.088(6)
Zn(1)-O(1)	2.414(7)	Zn(1)-C(47)	2.603(9)
O(4)-Zn(1)-N(2)	100.7(3)	O(4)-Zn(1)-N(1)	100.1(3)
N(2)-Zn(1)-N(1)	108.8(3)	O(4)-Zn(1)-O(2)	147.7(3)
N(2)-Zn(1)-O(2)	99.4(3)	N(1)-Zn(1)-O(2)	97.0(3)
O(4)-Zn(1)-O(1)	92.4(2)	N(2)-Zn(1)-O(1)	143.8(3)
N(1)-Zn(1)-O(1)	101.7(3)	O(2)-Zn(1)-O(1)	57.2(2)
O(4)-Zn(1)-C(47)	120.3(3)	N(2)-Zn(1)-C(47)	123.7(3)
N(1)-Zn(1)-C(47)	100.7(3)	O(2)-Zn(1)-C(47)	28.7(3)
O(1)-Zn(1)-C(47)	28.5(2)		

symmetry codes: #1: x-1, y, z; #2: -x+1, y-1/2, -z+3/2; #3: x-1, y, z-1.

S4. Structural characteristics of complex 1.

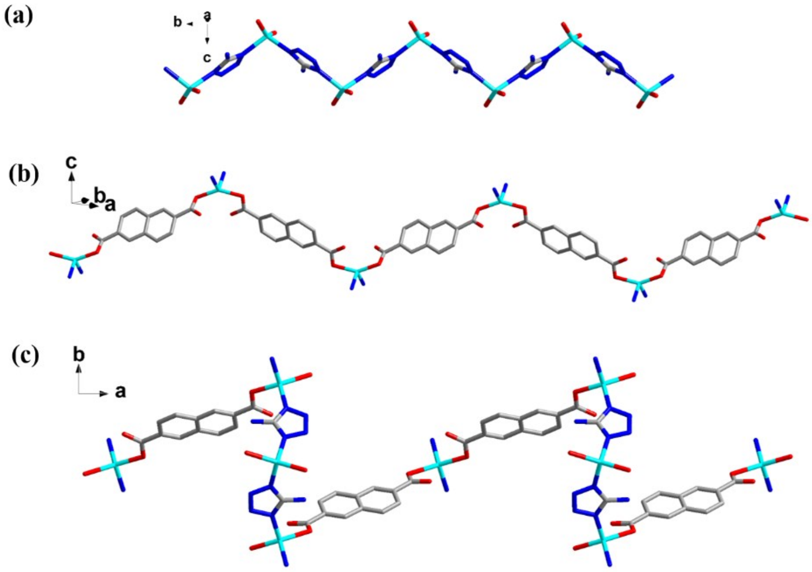

Fig. S1 Three different types of 1D chains in complex **1**.

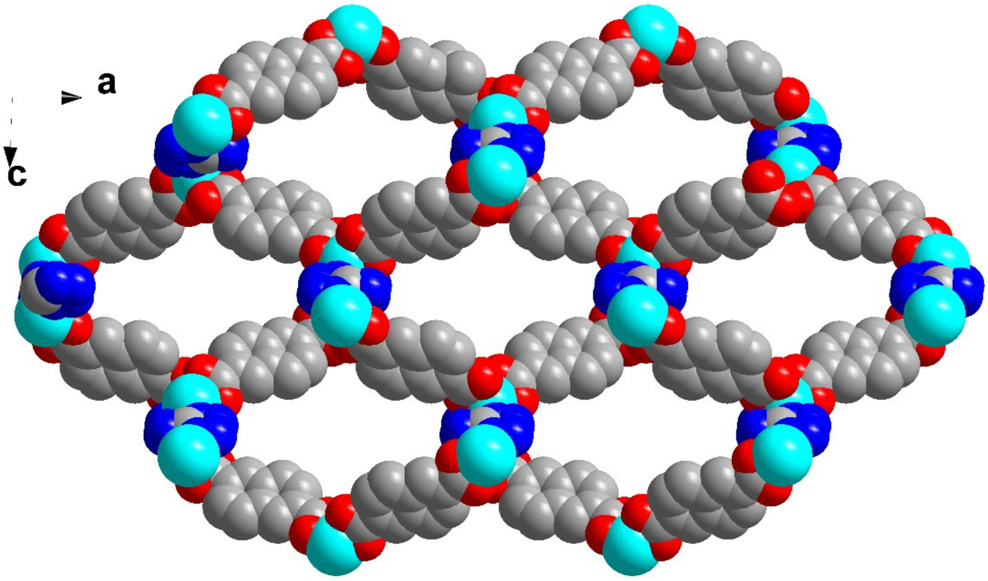

Fig. S2 The Space-filling diagram of complex **1**, viewed along *b* axis.

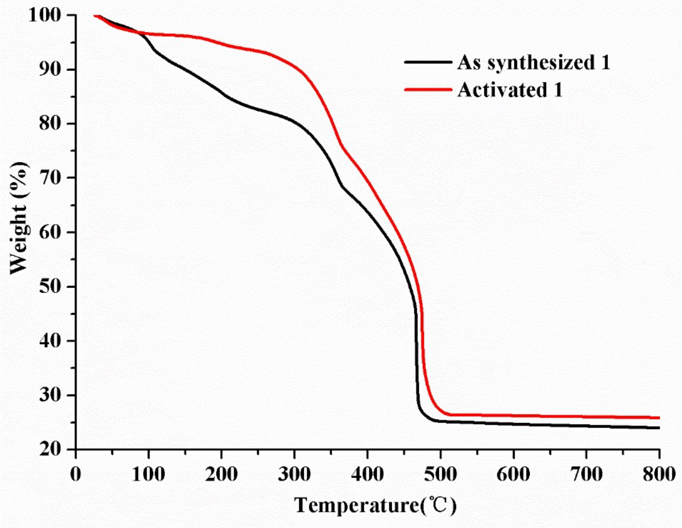

Fig. S3 TGA curves for complex **1.** Black line: **1** washed with C_2H_5OH. Red line: Activated **1**.

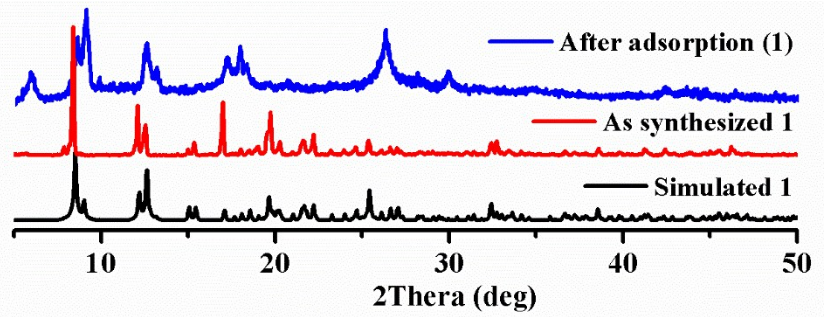

Fig. S4 PXRD patterns of complex **1**.

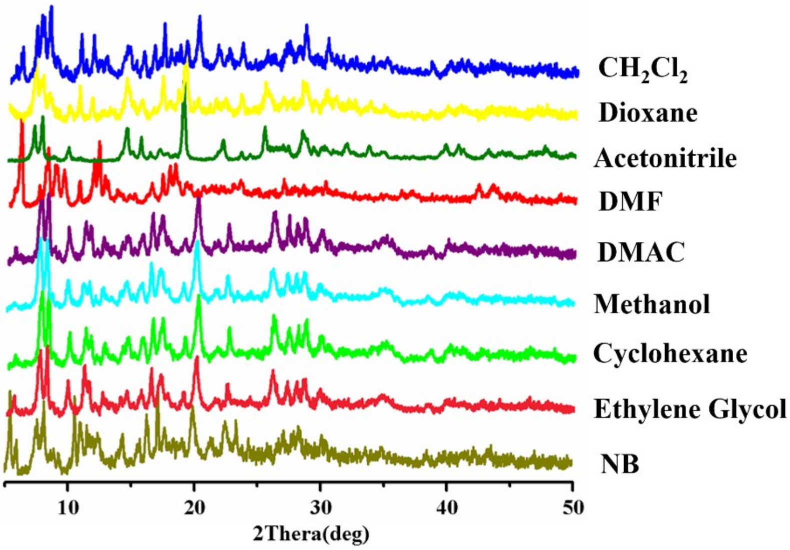

Fig. S5 PXRD patterns of complex **1** dispersed in different organic solvents.

S5. Adsorption property

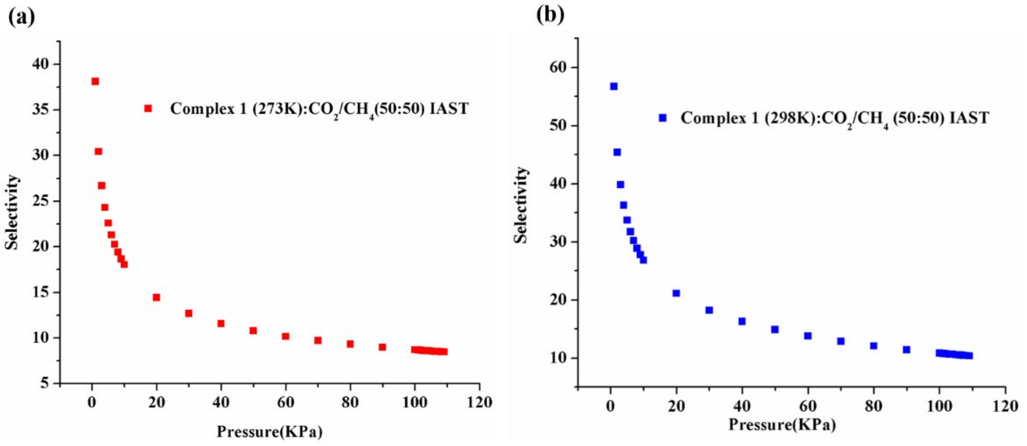

Fig. S6 IAST adsorption selectivities for CO_2 and CH_4 mixtures (50:50) at 273 K (a) and 298K (b), respectively.

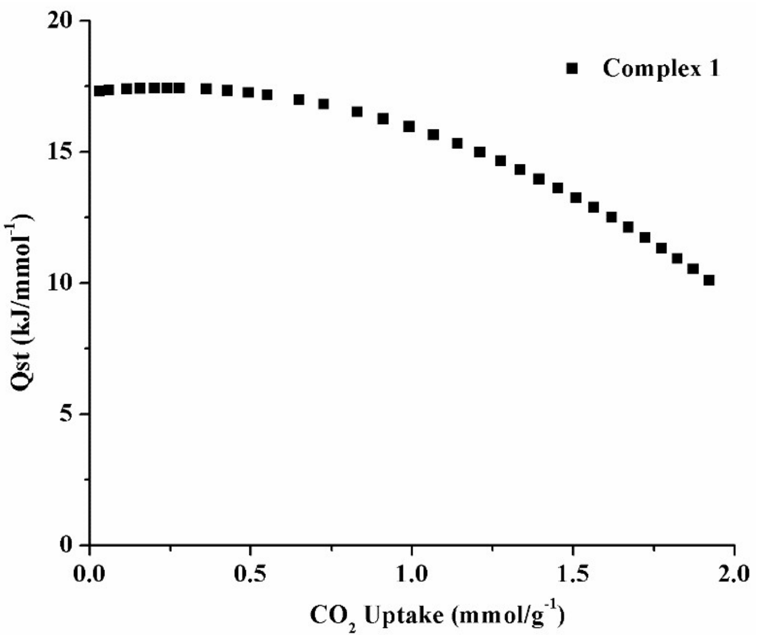

Fig. S7 Q_{st} of CO_2 adsorption of complex **1**.

S6. Fluorescence property

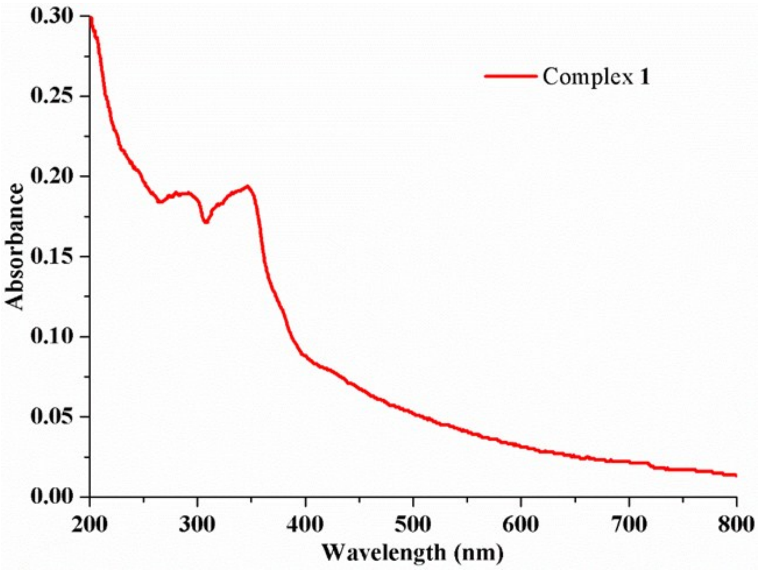

Fig. S8 Scattering solid UV-vis absorption spectrum of **1**.

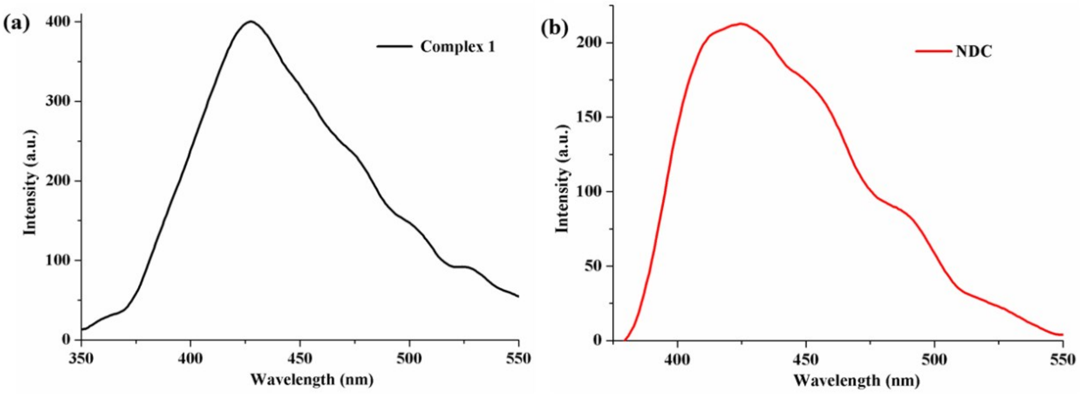

Fig. S9 Solid-state emission spectra of (a) complex **1** and (b) NDC ligand; λ_{ex} = 320 nm.

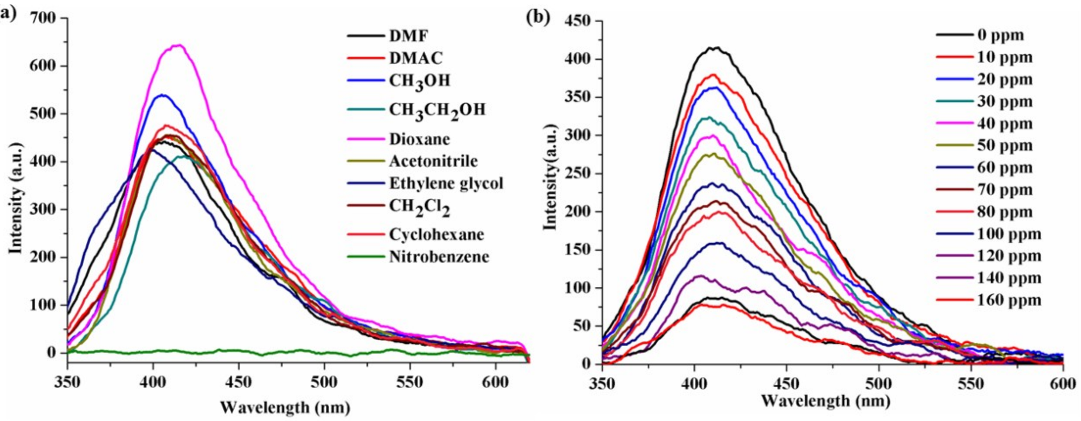

Fig. S10 (a) Fluorescent intensities of **1** dispersed in different solvents (λ_{ex} = 320 nm). (b) Fluorescent titration of **1** dispersed in DMF (1 mg/ml) upon increasing addition of NB (λ_{ex} = 320 nm).

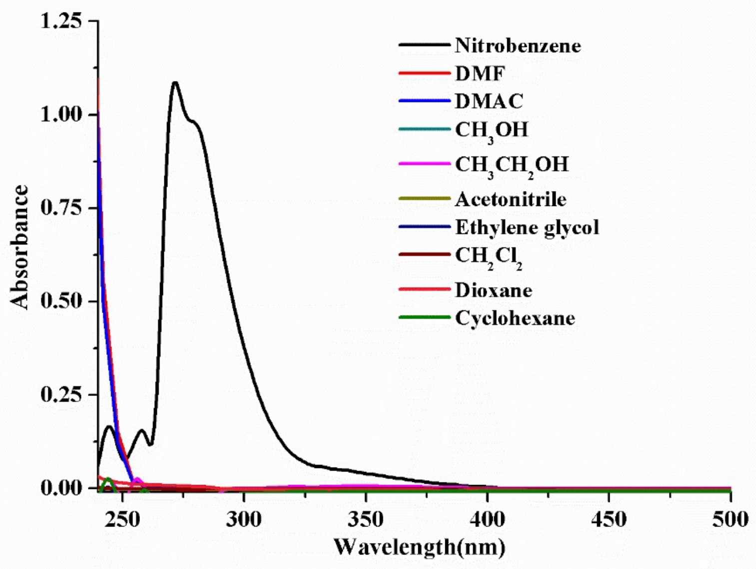

Fig. S11 UV−vis spectra of all the tested organic solvents.

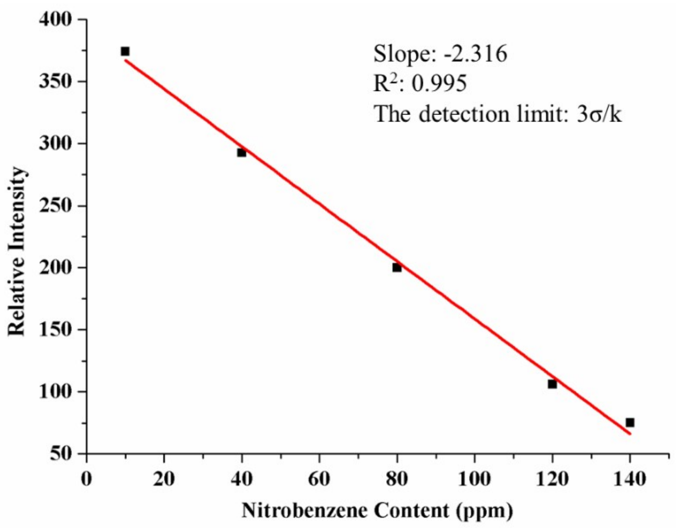

Fig. S12 Fitting plot of the detection limit of complex **1** to nitrobenzene.

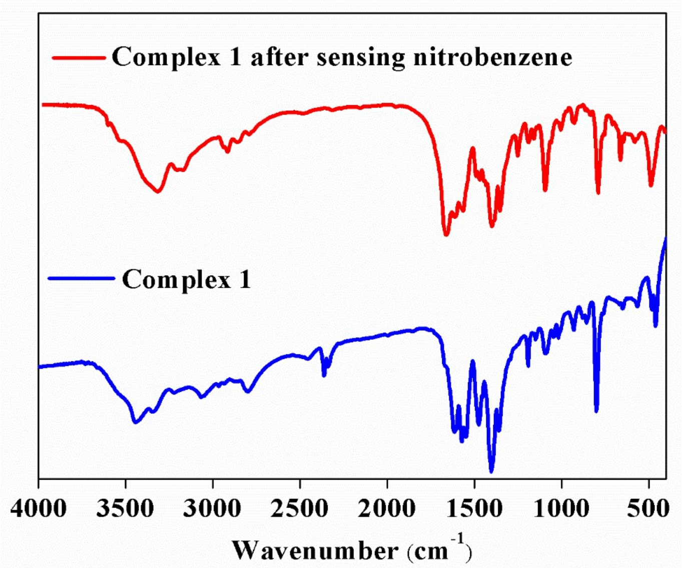

Fig. S13 IR spectra of complex **1** before and after sensing nitrobenzene.

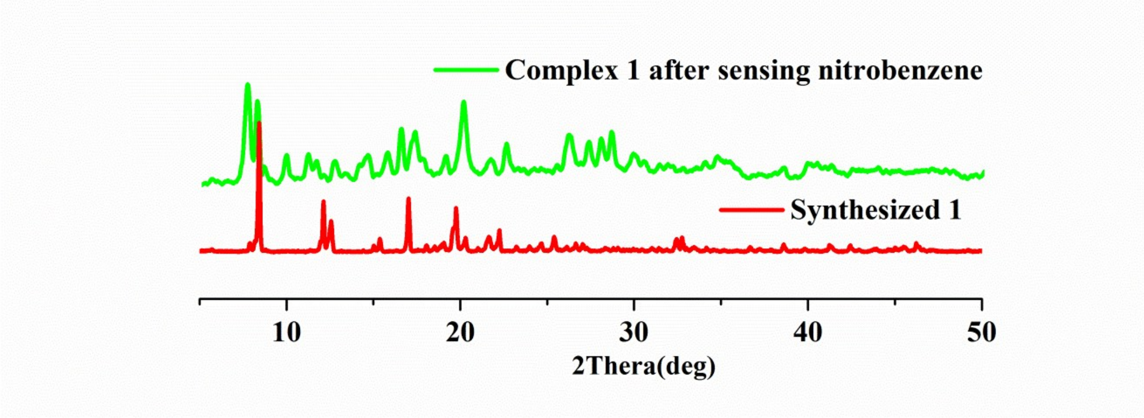

Fig. S14 PXRD patterns of complex **1** before and after sensing nitrobenzene.

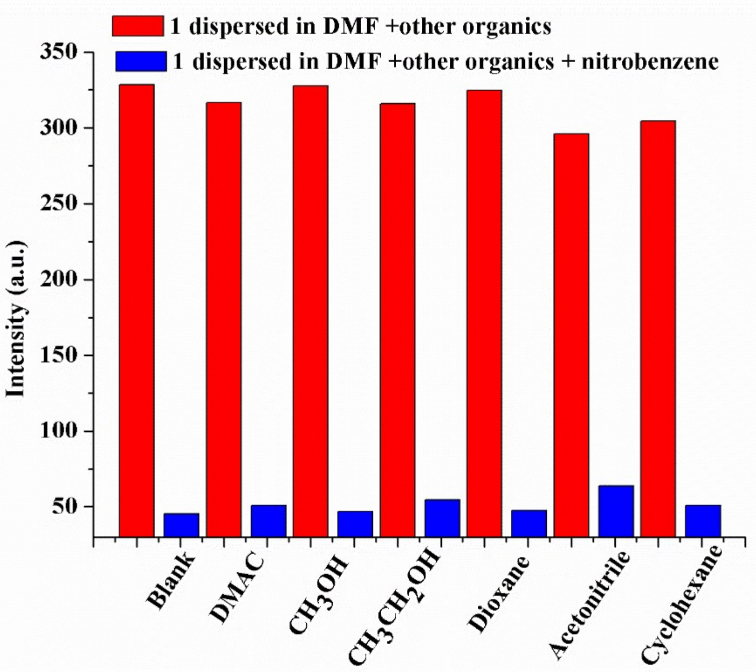

Fig. S15 Emission intensities of complex **1** dispersed in DMF with the addition of different organic solvents (red) and subsequent addition of nitrobenzene (blue).

References

S1. Sheldrick, G. M. *SHELXL97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, **1997**.

S2. Spek, A. L. J. Appl. Crystallogr. **2003**, *36*, 7-13.