Electronic Supporting Information (ESI)

A Metal-Organic Framework as a "Turn on" Fluorescent Sensor for Aluminum Ions

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Section 1. Experimental Section

1. Synthesis of HO-H_3BTC ligand

Synthesis procedure for HO-H_3BTC was shown in Fig. S1. CH_3CN (260 mL) was added to the mixture of 2,6-bis(hydroxymethyl)-4-cresol (10 g) and K_2CO_3 (16.37 g), then CH_3I (10.16 g) was slowly added with constant stirring. The reaction mixture was heated to reflux at 80 °C for 36 h. After reaction, the mixture was filtered and the solvent of filtrate was removed in vacuo. Finally, the pure product (**1**) was obtained (7.0 g). ^{1}H NMR (300 MHz, DMSO): 7.08 (2H), 5.02 (2H), 4.47 (4H), 3.62 (3H), 2.25 (3H) (Fig. S2).

A mixture of (**1**) (5.0 g) obtained from above step, NaOH (0.55 g) and 165 mL H_2O were added in a 500 mL flask equipped with magnetic stirrer and oil bath. 20.3 g $KMnO_4$ was added in several batches to the solution while stirring and without heating. The resultant brown slurry was heated to 80 °C for 72 h. The resultant was filtered to remove the large amount of MnO_2, and the filtrate was acidified with hydrochloric acid. Under vacuum state, the solvent H_2O was removed, and then CH_3OH was added in the obtaining product. Finally, removal of CH_3OH in vacuo yields the product (**2**) methoxy-BTC (3.3 g). ^{1}H NMR (300 MHz, D_2O): 8.12 (2H), 3.71 (3H) (Fig. S2).

A mixture of methoxy-BTC (3 g) and 48% HBr (63 mL) was placed in a 250 mL bottom flask. The reaction mixture was heated to reflux at 150 °C for 48 h. When the reaction was complete, the hydrobromic acid was removed under reduced pressure, and the residue was mixed with small amount of water. The

2-hydroxy-benzene-l,3,5-tricarboxylic acid (HO-H_3BTC 2.4 g) was collected followed by filtration. ^{1}H NMR (300 MHz, DMSO): 8.45 (2H) (Fig. S2). ESI-MS (m/z):225.0 (M - 1) (Fig. S3).

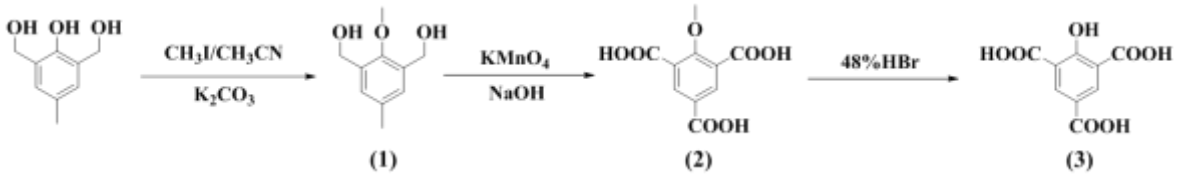
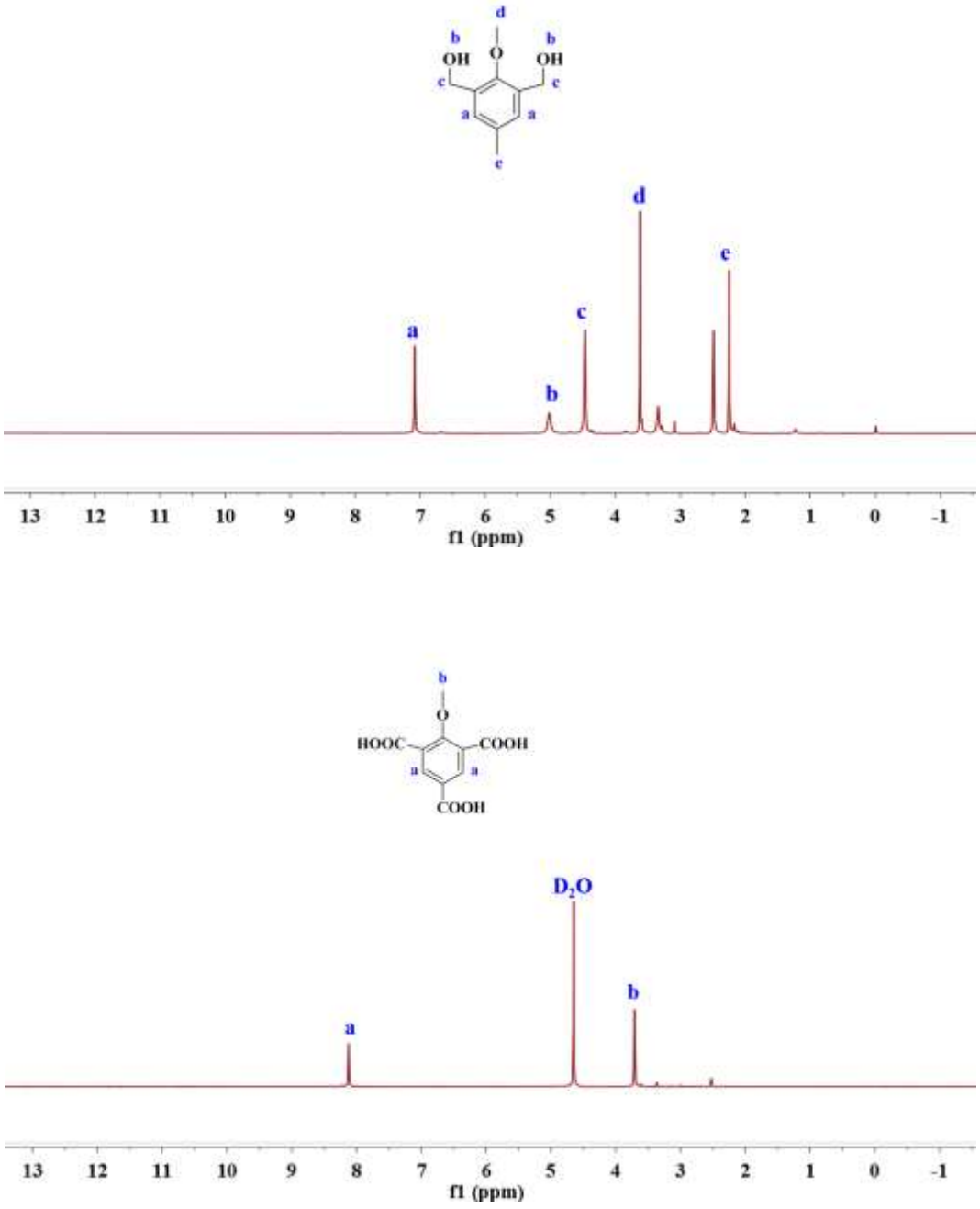


Fig. S1 Synthesis procedure for HO-H_3BTC.



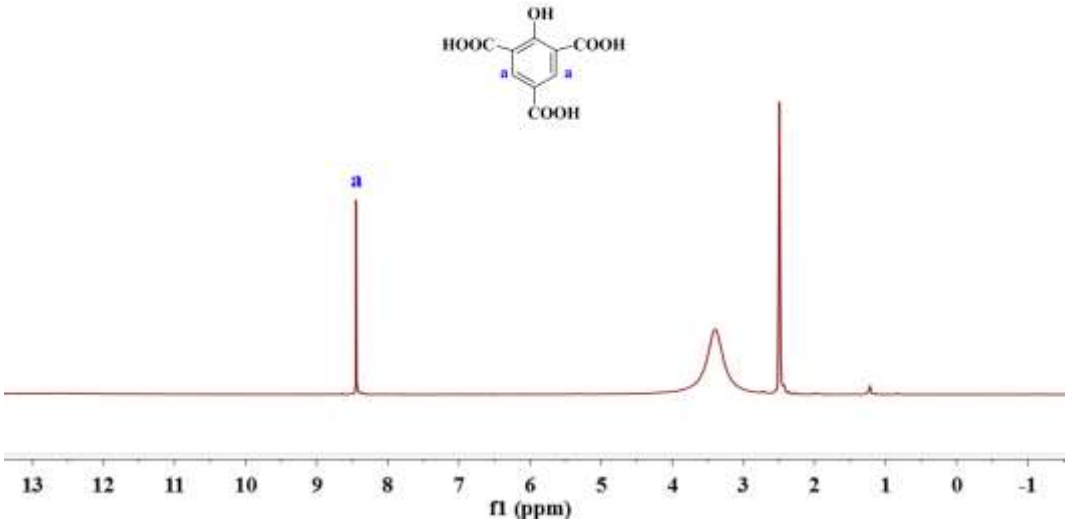


Fig. S2 ^{1}H NMR spectroscopy of every step in the process of synthesizing HO-H_3BTC ligand.

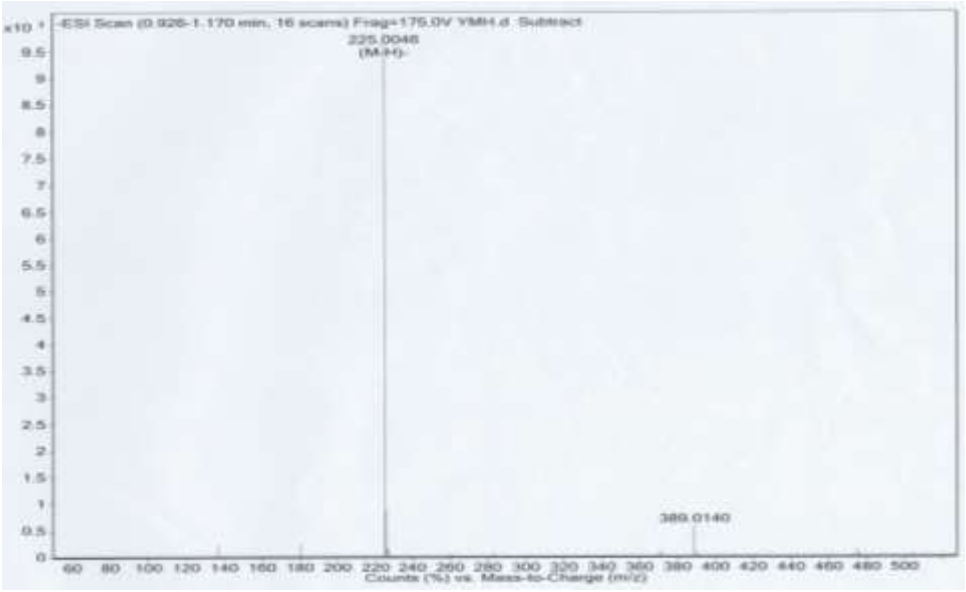


Fig. S3 The mass spectra (MS) of HO-H_3BTC ligand.

Section 2. Supplementary Tables and Figures

Table S1. Crystal data and structure refinement parameters for **NUM-2**

	NUM-2	
Formula	$C_{14}H_{12}NO_{10}Zn_2$	
*M*r (g mol^{-1})	485.03	
Space group	$P2_1/c$	
Crystal system	Monoclinic	
a (Å)	10.997(2)	
b (Å)	14.914(3)	
c (Å)	14.368(3)	
β(°)	109.31(3)	
V (Å^3)	2224.0(8)	
Z	4	
F(000)	972.0	
Dc (gcm^{-3})	1.449	
μ (mm^{-1})	2.200	
R_{int}	0.0399	
Limiting indices	$-13 \le h \le 13$ $-17 \le k \le 17$ $-17 \le l \le 17$	
GOF on F^2	1.058	
R_1, wR_2 [$I>2\sigma(I)$]^a	0.0537	0.0632
R_1, wR_2 [all data]^b	0.1279	0.1333

^{a} $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^{b} $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2\}^{1/2}$

Table S2 Selected bond lengths (Å) for **NUM-2**

Zn(1)-O(10)#1	1.965(4)	Zn(2)-O(2)	2.040(4)
Zn(1)-O(5)#2	1.968(4)	Zn(2)-O(7)	2.071(5)
Zn(1)-O(3)	1.989(4)	Zn(2)-O(6)	2.130(4)
Zn(1)-O(1)#2	2.043(3)	Zn(2)-O(9)	2.155(4)
Zn(1)-O(1)	2.048(3)	Zn(2)-N(1)	2.161(5)
Zn(2)-O(8)#3	2.034(4)		

#1 x,-y+1/2,z-1/2 #2 -x+1,-y,-z #3 x-1,y,z

Table S3 Selected angles (°) for **NUM-2**

O(10)#1-Zn(1)-O(5)#2	115.15(19)	O(8)#3-Zn(2)-O(6)	92.34(17)
O(10)#1-Zn(1)-O(3)	109.17(18)	O(2)-Zn(2)-O(6)	91.39(17)
O(5)#2-Zn(1)-O(3)	90.71(16)	O(7)-Zn(2)-O(6)	86.73(18)
O(10)#1-Zn(1)-O(1)#2	105.06(16)	O(8)#3-Zn(2)-O(9)	82.71(16)
O(5)#2-Zn(1)-O(1)#2	85.12(14)	O(2)-Zn(2)-O(9)	82.86(17)
O(3)-Zn(1)-O(1)#2	143.82(17)	O(7)-Zn(2)-O(9)	174.67(19)
O(10)#1-Zn(1)-O(1)	105.17(15)	O(6)-Zn(2)-O(9)	87.94(19)
O(5)#2-Zn(1)-O(1)	138.65(18)	O(8)#3-Zn(2)-N(1)	91.80(18)
O(3)-Zn(1)-O(1)	84.31(14)	O(2)-Zn(2)-N(1)	85.16(18)
O(1)#2-Zn(1)-O(1)	75.70(14)	O(7)-Zn(2)-N(1)	90.5(2)
O(8)#3-Zn(2)-O(2)	164.95(15)	O(6)-Zn(2)-N(1)	175.31(18)
O(8)#3-Zn(2)-O(7)	97.68(17)	O(9)-Zn(2)-N(1)	94.8(2)
O(2)-Zn(2)-O(7)	97.08(18)		

#1 x,-y+1/2,z-1/2 #2 -x+1,-y,-z #3 x-1,y,z

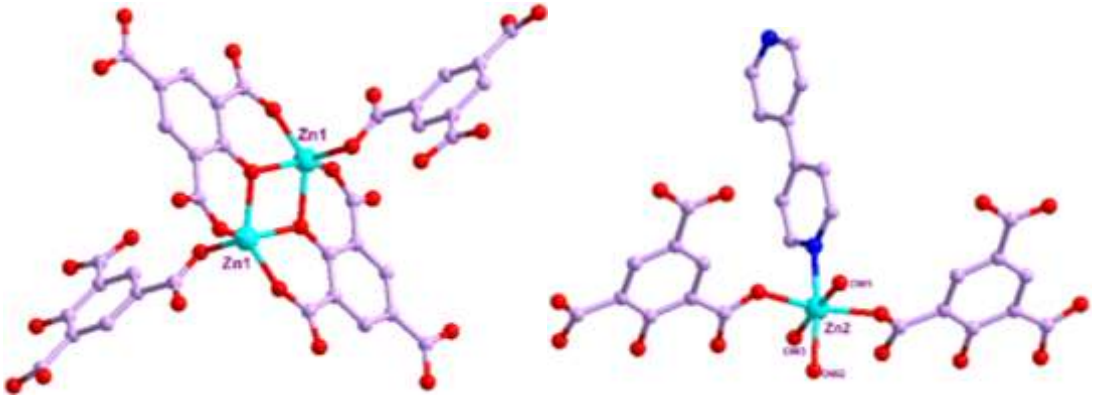


Fig. S4 The coordination environment of Zn1 and Zn2.

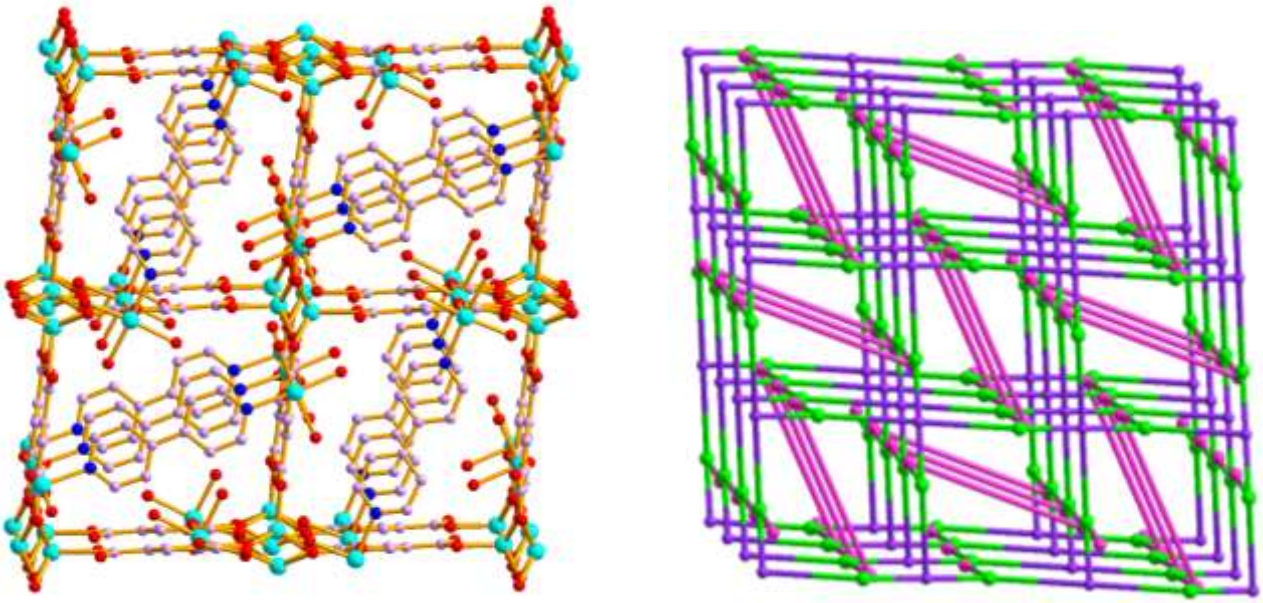


Fig. S5 (a) The 3D structure of **NUM-2**; (b) The framework topology of (3,4)-connected network with Point (Schlafli) symbol $\{6\cdot7^5\}_2\{6^2\cdot8\}_2\{7^4\cdot8^2\}$.

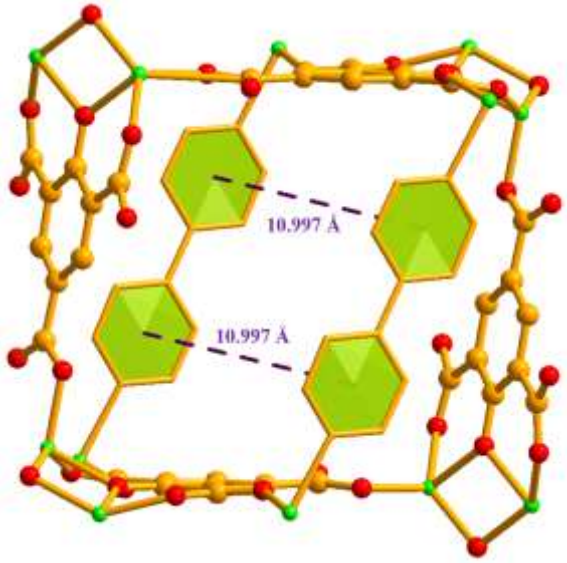


Fig. S6 The distance of pyridine rings between the two 4,4'-BPY ligands.

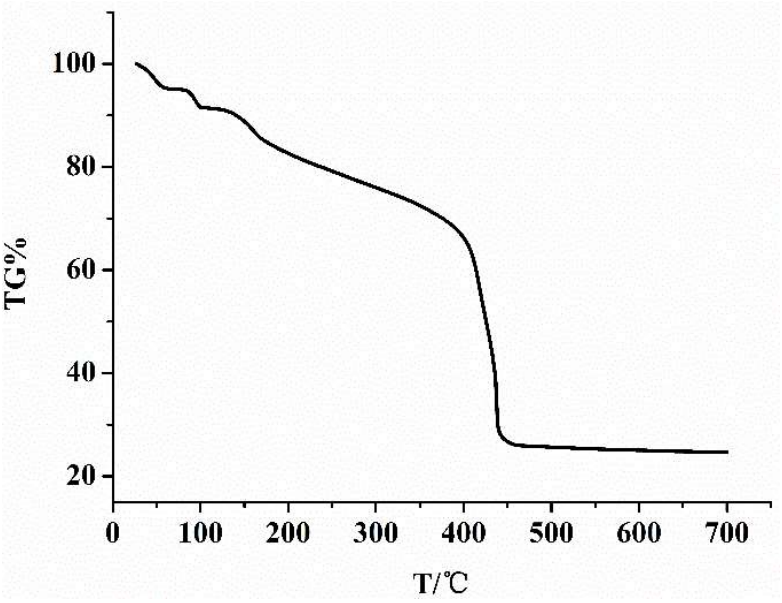


Fig. S7 TGA curve of **NUM-2**.

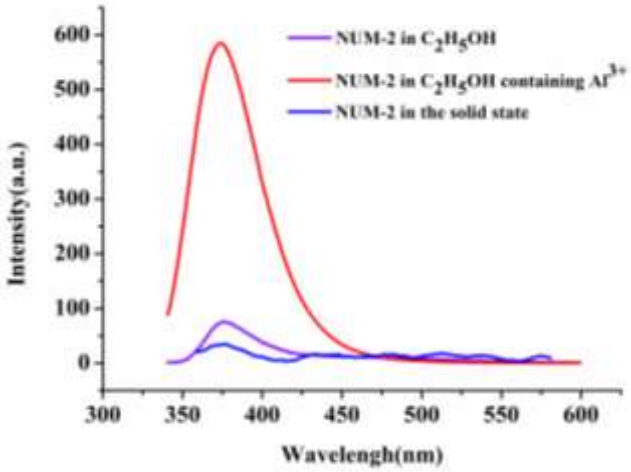


Fig. S8 The luminescent spectra of **NUM-2** in solid state, in C_2H_5OH solution, and in C_2H_5OH solution containing Al^{3+} (1×10^{-3} mol L^{-1}) at room temperature, λ_{ex} = 324 nm.

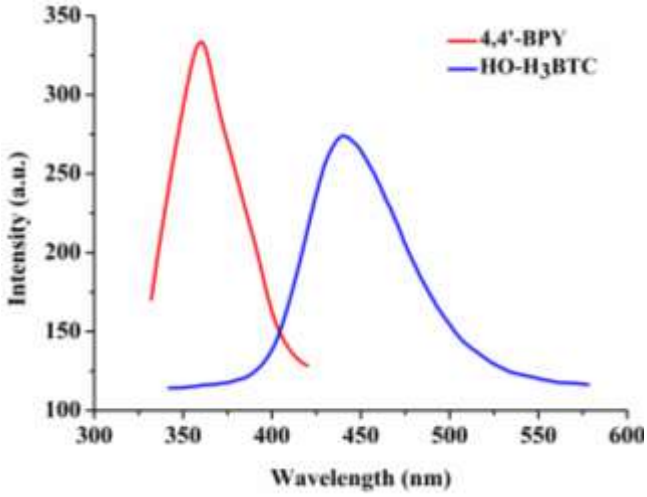


Fig. S9 The luminescent spectra of 4,4'-BPY and HO-H_3BTC in solid state.

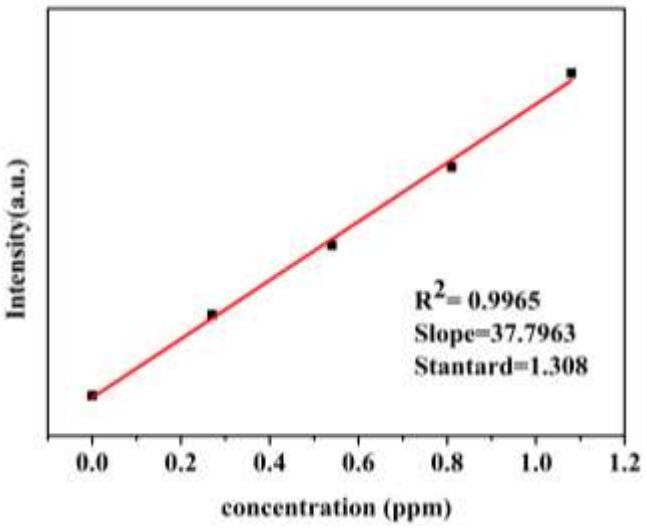


Fig. S10 Fitting plots of the detection limit Al^{3+} in C_2H_5OH solution for **NUM-2**.

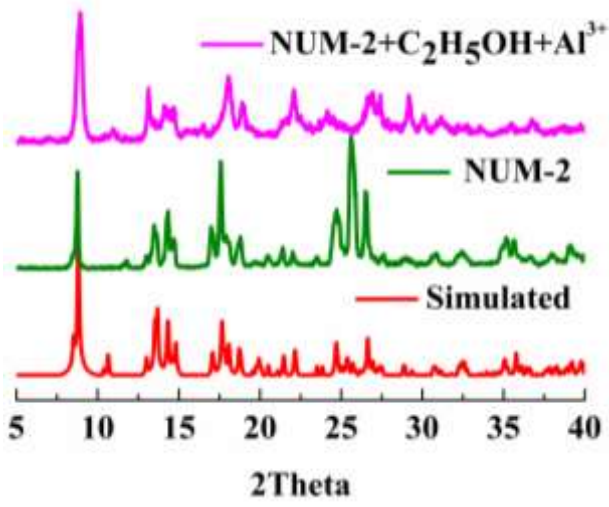


Fig. S11 Comparison of PXRD patterns of the sample at different condition and simulated pattern from single crystal data.

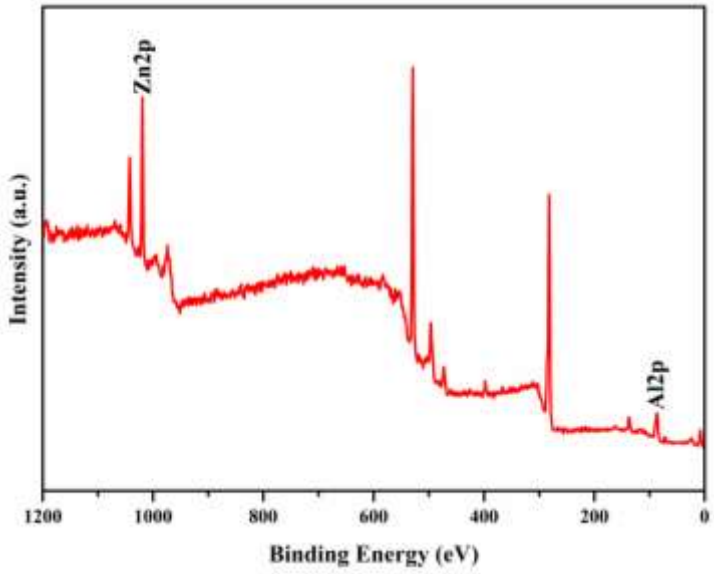


Fig. S12 The XPS pattern of the sample after fluorescent measurement.

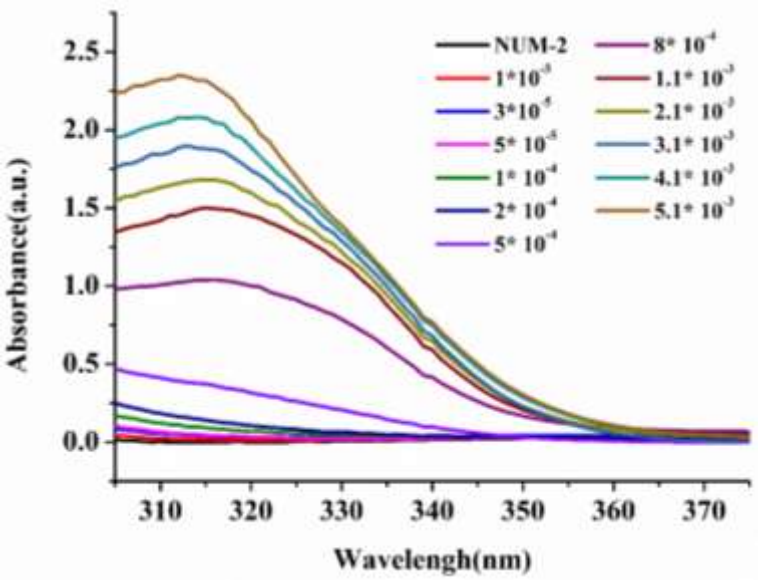


Fig. S13 UV-vis spectra **NUM-2** dispersed in C_2H_5OH treated with gradually increasing Al^{3+} ion concentration (mol L^{-1}).