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Electronic Supporting Information

Highly Selective Luminescent Sensing of Nitrite and Benzaldehyde Based on 3d-4f Heterometallic Metal–Organic Frameworks

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1 Experimental Section

General synthesis procedure

1.1 Synthesis of $\{[Ln_2Zn(abtc)_2(H_2O)_4]\cdot 2H_2O\}_\infty$ (**1**-**2**). $Ln(NO_3)_3\bullet 6H_2O$ [Ln= Sm (**1**), Tb (**2**). 0.1 mmol], $Zn(NO_3)_2$ (0.1 mmol), H_4abtc (0.1 mmol), DMF (6 ml), H_2O (6 ml), and HNO_3 were added to a 25 ml Telfon-lined stainless steel autoclave, and the solution was heated to 160 ℃ for 48 h, then cooled down to room temperature. Orange block crystals of the product were collected by filtration and washed with water several times, and dried in air. The obtained yield based on the H_4abtc were 36% and 41% for **1** and **2**, respectively.

1.2 Characterization

All reagents and solvents for synthesis and analysis were obtained from commercial sources and used without further purification. X-ray powder diffraction (XRPD) intensities were measured on a Rigaku D/max-IIIA diffractometer (Cu Kα, λ =1.54056 Å). Infrared spectra were obtained in the range of 400−4000 cm^{-1} using KBr pellets on a Perkin-Elmer spectrometer. Thermogravimetric analysis (TGA) experiments were performed on a NETZSCH TG 209 instrument in the temperature range of 25-800 °C with a heating rate of 10 °C min^{-1} under nitrogen stream. The photoluminescence was measured with an Edinburgh Instruments FLS920P fluorescence spectrometer.

1.3 Single- Crystal Structure Determination

Single crystal X-ray diffraction analyses were carried out on a Bruker SMART 1000 CCD diffractometer with Mo Ka monochromated radiation (λ=0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares fitting on F^2 using SHELXS-97 and SHELXL-97 programs.[1] Absorption corrections were applied by using multi-scan program SADABS. All the metal atoms were located first, and then the oxygen, nitrogen and carbon atoms were subsequently found in difference Fourier maps. The hydrogen atoms of the ligands were placed geometrically. Crystallographic and refinement details are summarized in Table S1. Selected bond lengths and bond angles are listed in Table S2-S3. Crystallographic information files (CIFs) corresponding to MOFs **1** and **2** have been deposited to Cambridge Crystallographic Data Centre (CCDC numbers 1456716-1456717).

2 Characterization of complexes

2.1 Crystal data and structure refinement

Table S1 Crystal data and structure refinement for **1** and **2**

	1	**2**
Empirical formula	$C_{32}H_{24}N_4O_{22}Sm_2Zn$	$C_{32}H_{24}N_4O_{22}Tb_2Zn$
Formula weight	1182.62	1199.76
Crystal system	orthorhombic	orthorhombic
space group	Iba2	Iba2
a (Å)	13.390(3)	13.368(3)
b(Å)	24.074(5)	23.922(5)
c(Å)	13.179(3)	13.092(3)
α(˚)	90	90
β(˚)	90	90
γ(˚)	90	90
V($Å^3$)	4248.5(15)	4186.8(15)
Z	4	4
D_{cal}（Mg/m^3）	1.849	1.903
Theta range（deg）	3.38 to 50.02	3.4 to 50
R(int)	0.0336	0.0510
Data/res/parameters	3734/7/281	3678/55/276
GOF on F^2	1.011	1.239
R_1,wR_2 [I>2sigma(I]	0.1244, 0.2952	0.0468, 0.1506
R_1, wR_2 (all data)	0.1253, 0.2993	0.0502, 0.1555

Table S2 Bond lengths [Å] and angles [deg] for complex **1**.

O(4)-Sm(1)#1	2.503(12)	O(3)-Sm(1)#1	2.628(15)
O(3)-Zn(1)#2	2.126(13)	Sm(1)-O(6)	2.690(9)
Sm(1)-O(5)	2.371(9)	Sm(1)-O(10)	2.356(13)
Sm(1)-O(9)	2.427(13)	Sm(1)-O(7)#4	2.278(9)
Sm(1)-O(1)	2.491(11)	Sm(1)-O(2)	2.511(12)
Zn(1)-O(8)	1.962(10)	Zn(1)-O(8)#7	1.962(10)
O(2)-Sm(1)-O(4)#3	84.6(4)	O(2)-Sm(1)-O(3)#3	66.1(4)
O(2)-Sm(1)-O(6)	142.1(4)	O(2)-Sm(1)-O(5)	129.3(5)
O(2)-Sm(1)-O(10)	141.4(5)	O(2)-Sm(1)-O(9)	75.0(4)
O(2)-Sm(1)-O(7)#4	76.3(4)	O(3)#3-Sm(1)-O(4)#3	50.1(4)
O(2)-Sm(1)-O(1)	53.6(4)	O(6)-Sm(1)-O(4)#3	130.6(4)
O(6)-Sm(1)-O(3)#3	144.3(4)	O(5)-Sm(1)-O4(3)	90.7(4)
O(5)-Sm(1)-O(3)#3	139.2(5)	O(5)-Sm(1)-O(6)	50.8(3)
O(10)-Sm(1)-O(4)#3	76.9(5)	O(10)-Sm(1)-O(3)#3	76.1(4)

O(10)-Sm(1)-O(6)	70.8(5)	O(10)-Sm(1)-O(5)	85.1(6)
O(9)-Sm(1)-O(4)#3	143.3(5)	O(9)-Sm(1)-O(3)#3	137.4(4)
O(9)-Sm(1)-O(6)	67.8(4)	O(9)-Sm(1)-O(5)	79.7(5)
O(9)-Sm(1)-O(10)	136.2(5)	O(7)#4-Sm(1)-O(4)#3	123.7(4)
O(7)#4-Sm(1)-O(3)#3	73.8(4)	O(7)#4-Sm(1)-O(6)	90.7(3)
O(7)#4-Sm(1)-O(5)	141.2(3)	O(7)#4-Sm(1)-O(10)	86.1(6)
O(7)#4-Sm(1)-O(9)	81.0(5)	O(1)-Sm(1)-O(4)#3	69.9(4)
O(1)-Sm(1)-O(3)#3	95.6(4)	O(1)-Sm(1)-O(6)	118.8(4)
O(1)-Sm(1)-O(5)	77.5(4)	O(1)-Sm(1)-O(10)	142.0(5)
O(1)-Sm(1)-O(9)	73.5(5)	O(1)-Sm(1)-O(7)#4	127.8(4)
O(3)#5-Zn(1)-O(3)#6	108.8(8)	O(8)-Zn(1)-O(3)#6	102.9(5)
O(8)#7-Zn(1)-O(3)#5	102.9(5)	O(8)-Zn(1)-O(8)#7	156.8(7)
O(8)-Zn(1)-O(3)#5	90.6(5)		

Symmetry transformations used to generate equivalent atoms:
#1 +x, 2-y, -1/2+z; #2 1/2+x, 1/2+y, -1/2+z; #3 +x, 2-y, 1/2+z;
#4 1/2+x, 3/2-y, +z; #5 1/2-x, 3/2-y, 1/2+z; #6 -1/2+x, -1/2+y, 1/2+z;
#7 -x, 1-y, +z; #8 -1/2+x, 3/2-y, +z; #9 1-x, 1-y, +z;
#10 -x, 2-y, +z

Table S3 Bond lengths [Å] and angles [deg] for complex **2**.

O(3)-Tb(1)#1	2.453(9)	O(4)-Tb(1)#1	2.461(9)
Zn(1)-O(5)#5	1.950(7)	O(8)-Tb(1)#2	2.324(6)
Zn(1)-O(1)#5	2.136(9)	O(7)-Tb(1)#2	2.668(6)
Zn(1)-O(1)	2.136(9)	Tb(1)-O(6)	2.259(6)
O(5)-Zn(1)	1.950(7)	Tb(1)-O(8)#4	2.324(6)
Tb(1)-O(10)	2.343(11)	Tb(1)-O(9)	2.411(10)
Tb(1)-O(2)	2.423(9)	Tb(1)-O(4)#3	2.461(9)
Tb(1)-O(3)#3	2.453(9)	Tb(1)-O(1)	2.591(10)
Tb(1)-O(7)#4	2.668(6)	O(6)-Tb(1)-O(10)	86.0(4)
O(6)-Tb(1)-O(8)#4	140.3(2)	O(5)#5-Zn(1)-O(5)	160.4(5)
O(8)#4-Tb(1)-O(10)	84.4(5)	O(5)#5-Zn(1)-O(1)#5	100.7(3)
O(6)-Tb(1)-O(9)	80.0(4)	O(5)-Zn(1)-O(1)#5	90.9(3)
O(8)#4-Tb(1)-O(9)	80.9(4)	O(5)#5-Zn(1)-O(1)	90.9(3)
O(10)-Tb(1)-O(9)	136.3(3)	O(5)-Zn(1)-O(1)	100.7(3)
O(6)-Tb(1)-O(2)	126.5(3)	O(1)#5-Zn(1)-O(1)	107.1(6)
O(8)#4-Tb(1)-O(2)	88.1(3)	O(10)-Tb(1)-O(2)	76.3(4)
O(9)-Tb(1)-O(2)	143.2(3)	O(6)-Tb(1)-O(4)#3	128.0(3)
O(8)#4-Tb(1)-O(4)#3	77.9(4)	O(10)-Tb(1)-O(4)#3	142.3(4)
O(9)-Tb(1)-O(4)#3	73.3(3)	O(2)-Tb(1)-O(4)#3	70.1(3)
O(6)-Tb(1)-O(3)#3	76.9(3)	O(8)#4-Tb(1)-O(3)#3	130.0(4)
O(10)-Tb(1)-O(3)#3	141.2(3)	O(9)-Tb(1)-O(3)#3	74.7(3)
O(2)-Tb(1)-O(3)#3	86.4(3)	O(4)#3-Tb(1)-O(3)#3	53.6(3)

O(6)-Tb(1)-O(1)	75.8(3)	O(8)#4-Tb(1)-O(1)	137.7(4)
O(10)-Tb(1)-O(1)	76.0(3)	O(9)-Tb(1)-O(1)	137.6(3)
O(2)-Tb(1)-O(1)	51.2(3)	O(4)#3-Tb(1)-O(1)	95.3(3)
O(3)#3-Tb(1)-O(1)	66.2(3)	O(6)-Tb(1)-O(7)#4	88.6(2)
O(8)#4-Tb(1)-O(7)#4	51.9(2)	O(10)-Tb(1)-O(7)#4	70.8(4)
O(9)-Tb(1)-O(7)#4	67.8(4)	O(2)-Tb(1)-O(7)#4	129.4(3)
O(4)#3-Tb(1)-O(7)#4	119.3(3)	O(3)#3-Tb(1)-O(7)#4	141.6(3)
O(1)-Tb(1)-O(7)#4	144.2(3)		

Symmetry transformations used to generate equivalent atoms:

#1 +x, 1-y, 1/2+z; #2 -1/2+x, 3/2-y, +z; #3 +x, 1-y, -1/2+z;
#4 1/2+x, 3/2-y, +z; #5 2-x, 1-y, +z; #6 3-x, 1-y, +z;
#7 1-x, 1-y, +z

2.2 IR

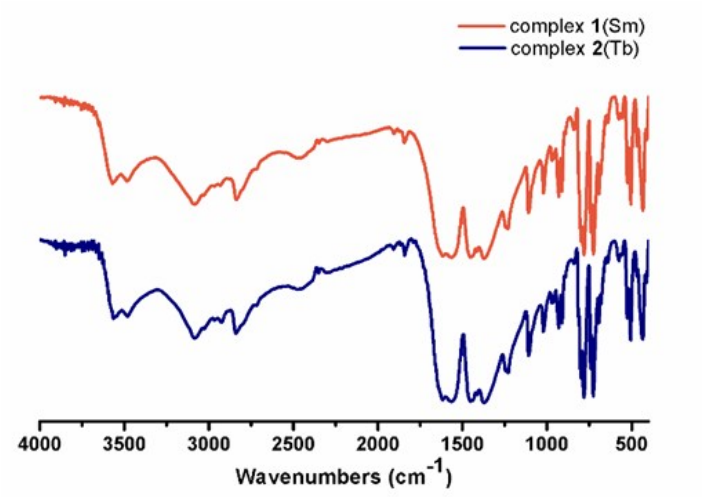

Fig. S1 FTIR spectra of compounds **1** and **2**.

2.3 XRD pattern

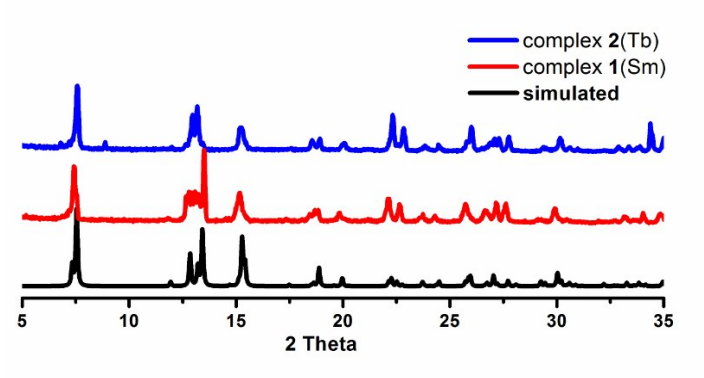

Fig. S2 Comparison of the simulated and experimental PXRD patterns: **1** and **2**.

2.4 TGA

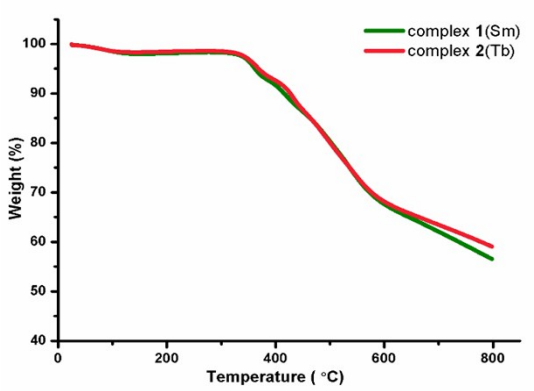

Fig. S3 Thermogravimetric analyses curve of polymers **1**-**2** under the N_2 atmosphere in the range of 25–800 ˚C.

2.5 Solid state luminescent

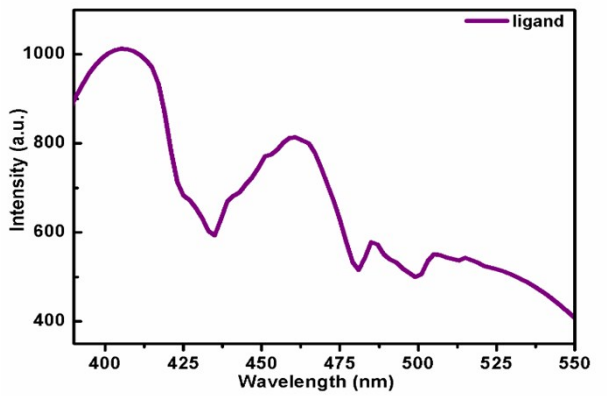

Fig. S4 Emission spectra of the ligand when excited at 362 nm.

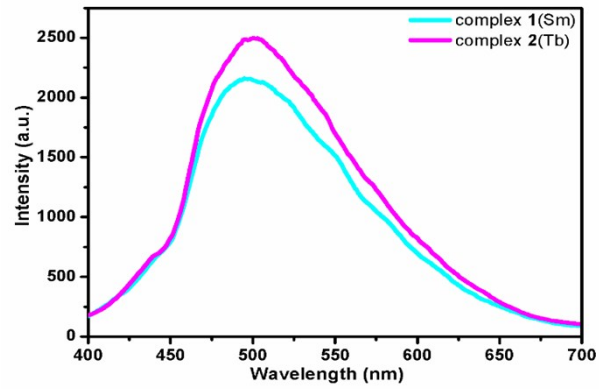

Fig. S5 Emission spectra of complexes **1** and **2** when excited at 362 nm.

2.6 Sensing properties

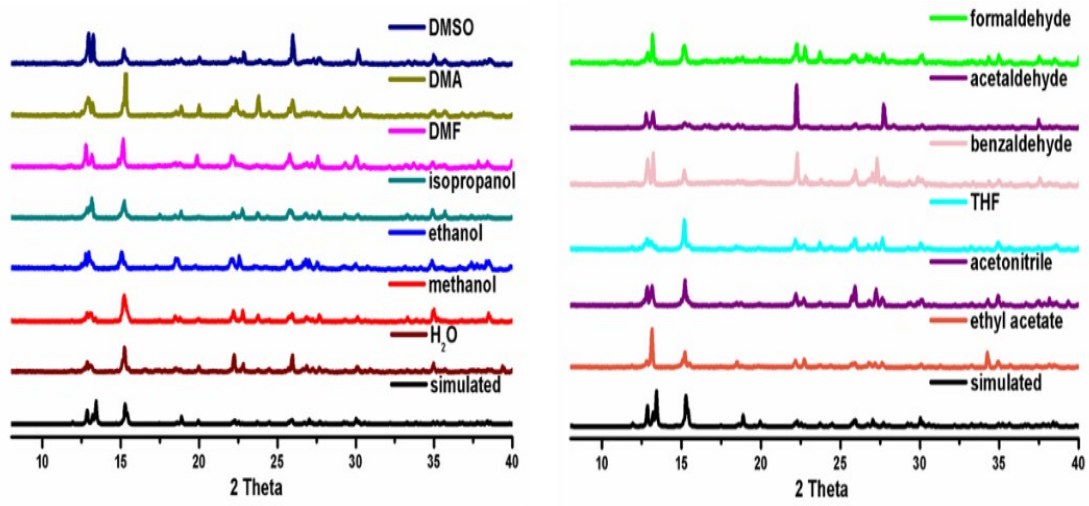

Fig. S6 PXRD patterns of simulated from the X-ray single structure of **1**, and **1** samples soaked in H_2O, methanol, ethanol, isopropanol, N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), acetonitrile, ethyl acetate, formaldehyde, acetaldehyde, and benzaldehyde, respectively.

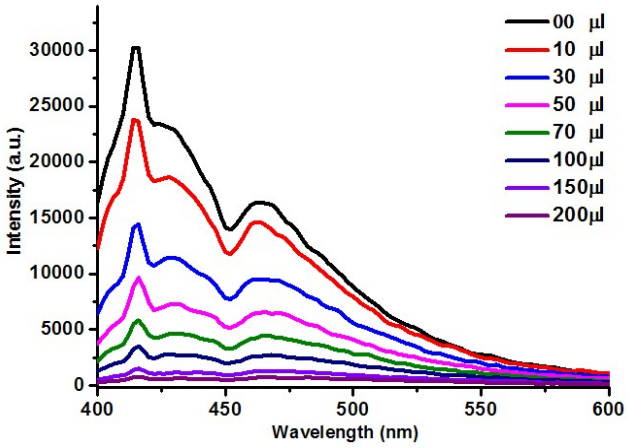

Fig. S7 Quenching of fluorescence intensity of **1** by incremental addition of benzaldehyde solution to a 3.5 ml suspension of **1** in THF.

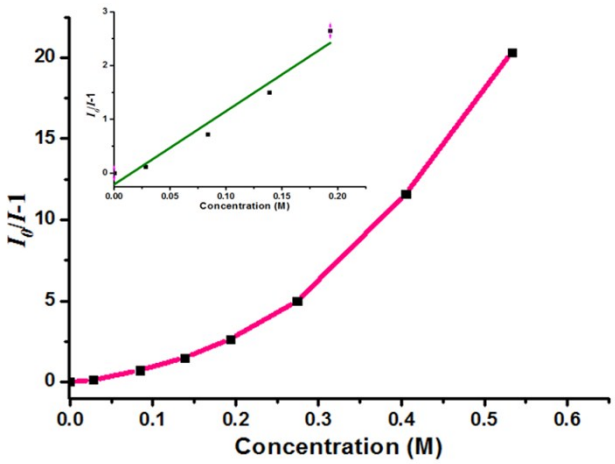

Fig. S8 Stern–Volmer plot of I_0/I versus the benzaldehyde concentration in THF (emission peak around 468 nm).

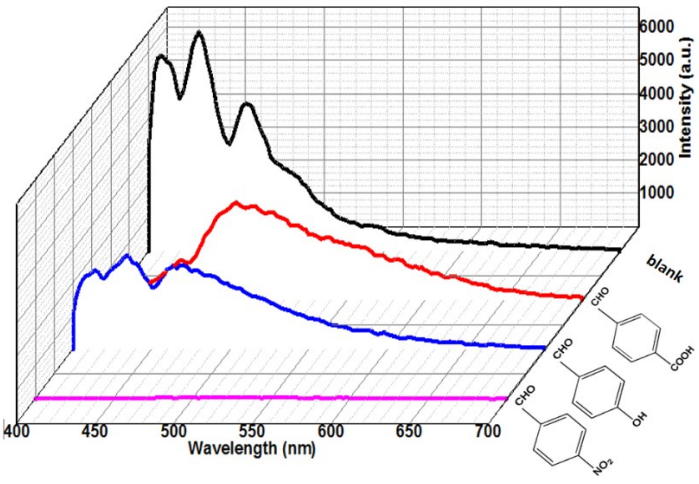

Fig. S9 Emission spectra of compound **1** in three different aromatic aldehydes when excited at 370 nm.

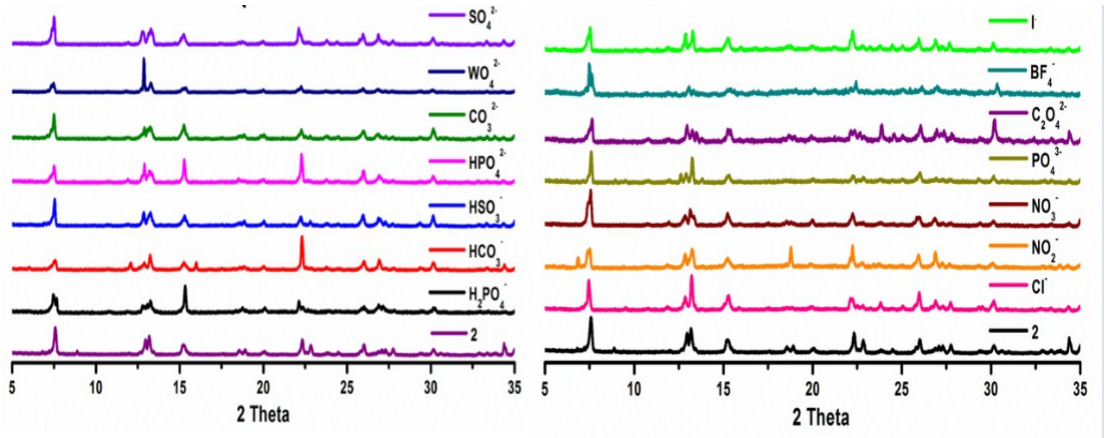

Fig. S10 PXRD patterns of compound **2** after immersing in various anion aqueous solutions.

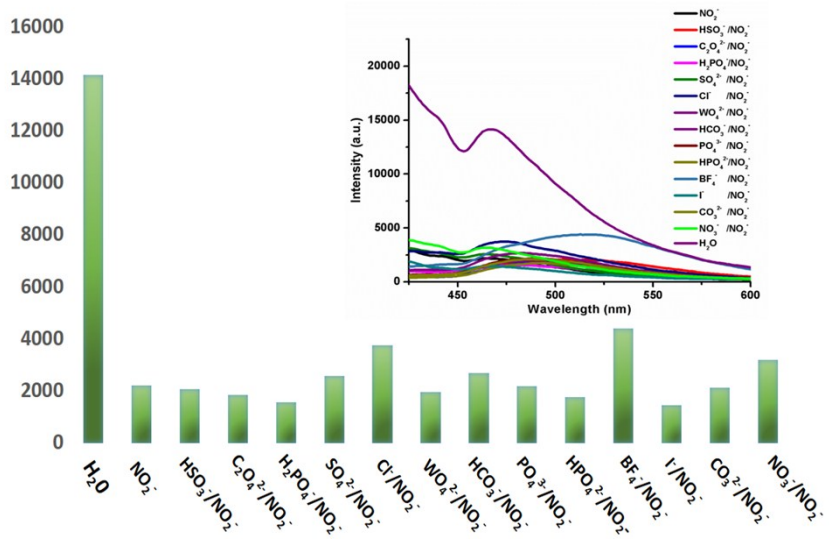

Fig. S11 Comparison of the luminescence intensity of **2** under mixed anions (10^{-2} M).

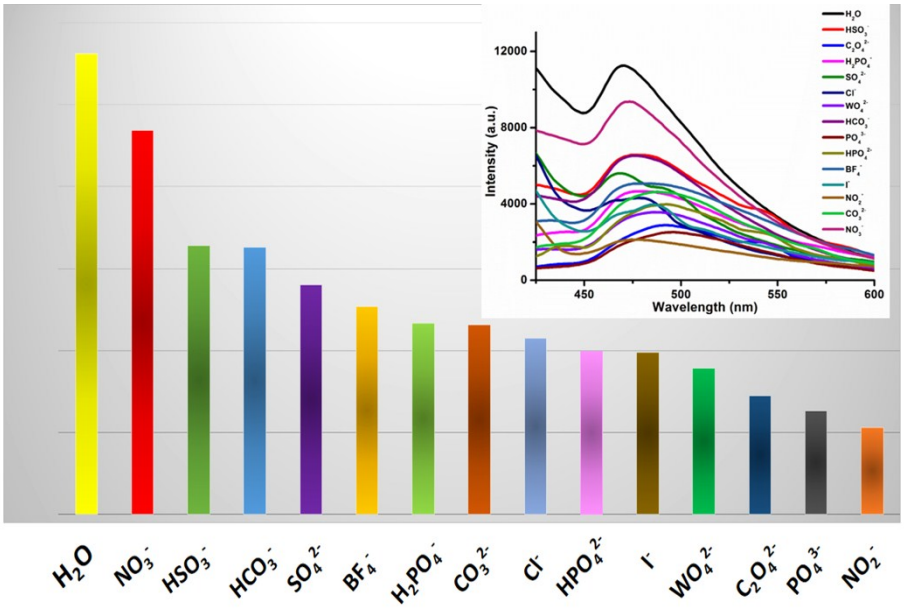

Fig. 12 Fluorescence response of **1** towards different anions when excited at 370 nm.

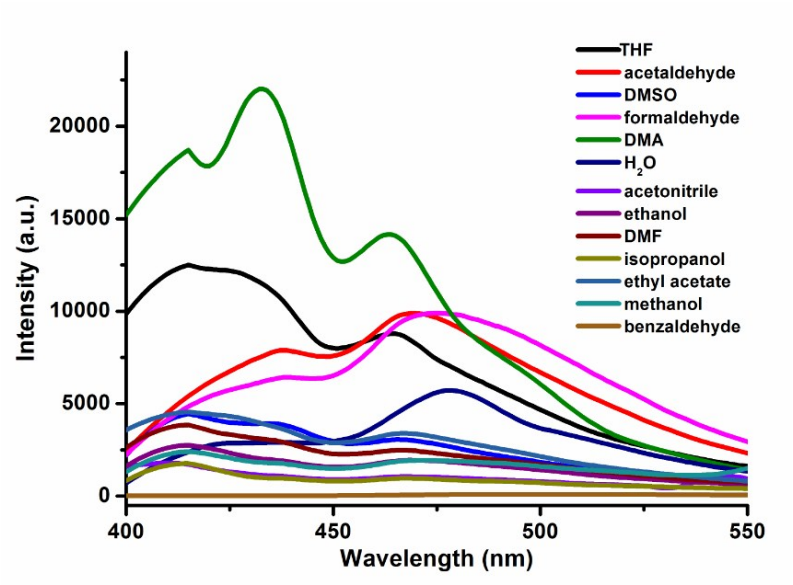

Fig. S13 Emission spectra of compound **2** in different solvents when excited at 370 nm

References

1. G. Sheldrick, *Acta Crystallogr., Sect. A； Fundam. Crystallogr.,* 2008, **64**, 112.