Supporting Information

Two Lanthanide Metal-Organic Frameworks as Remarkably Selective and Sensitive Bifunctional Luminescence Sensor for Metal Ions and Small Organic Molecules

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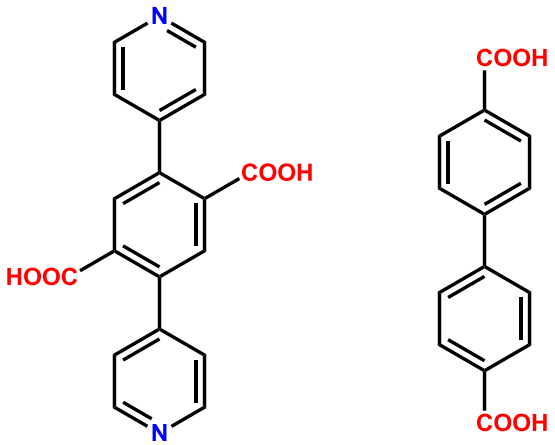
1. Experimental section.

Materials and measurements. Reagents and solvents employed were commercially available. Ligand H_2L was synthesized by palladium-catalyzed cross-coupling reaction and oxidation reaction. IR absorption spectra of the compounds **1** - **2** were recorded in the range of 400–4000 cm^{-1} on a Nicolet (Impact 410) spectrometer with KBr pellets (5 mg of sample in 500 mg of KBr). C, H and N analyses were carried out with a Perkin Elmer 240C elemental analyzer. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Mo-K_α radiation (λ = 0.71073 Å), in which the X-ray tube was operated at 40 kV and 40 mA. The as-synthesized samples were characterized by thermogravimetric analysis (TGA) on a Perkin Elmer thermogravimetric analyzer Pyris 1 TGA up to 1073 K using a heating rate of 10 K min^{-1} under N_2 atmosphere. Fluorescence spectra for the compounds were conducted with a F-4600 FL Spectrophotometer at room temperature.



H_2L **BPDC**

Scheme S1. Pyridine-Carboxylate, and BPDC Ligand.

Synthesis of complex 1. A mixture of H_2O (2 ml) containing the H_2L (9.6 mg, 0.03 mmol), BPDC (3.4mg, 0.015mmol) and $Eu(NO_3)_2$ $6H_2O$ (93.8mg, 0.21 mmol) was mixed in a Teflon vessel within the autoclave. The vessel was heated at 180 ℃ for 96 h and then cooled to room temperature. Large quantities of yellow crystals were obtained and crystals were filtered off, washed with mother liquid, and dried under ambient conditions. The yellow crystals of **1** were collected in 38% yield (based on H_2L ligand). Elemental analysis calcd. for $C_{25}H_{17}EuN_3O_{10}$ (**1**): C, 44.72%; H, 2.53%;

N, 6.26%, Found: C, 44.68%; H, 2.49%, N, 6.28%. The IR spectra of complex **1** is shown in the Figure S6.

Synthesis of complex 2. A mixture of H_2O (2 ml) containing the H_2L (9.6 mg, 0.03 mmol), BPDC (3.4mg, 0.015mmol) and $Tb(NO_3)_2$ $6H_2O$ (68mg, 0.15 mmol) was mixed in a Teflon vessel within the autoclave. The vessel was heated at 180 ℃ for 96 h and then cooled to room temperature. Large quantities of yellow crystals were obtained and crystals were filtered off, washed with mother liquid, and dried under ambient conditions. The yellow crystals of **2** were collected in 47% yield (based on H_2L ligand). Elemental analysis calcd. for $C_{25}H_{17}TbN_3O_{10}$ (**2**): C, 44.27%; H, 2.51%; N, 6.19%, Found: C, 44.24%; H, 2.52%, N, 6.20%. The IR spectra of complex **2** is shown in the Figure S7.

X-ray crystallography. Single crystals of complexes **1-2** were tested on a Bruker SMART APEX CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 296 K. From the data reduction to the structure determination, the follow procedures were used: the International Tables for X-ray Crystallography,[1] SAINT,[2] SADABS,[3] XPREP,[4] SHELXTL-97[5] and SHELXTL-97 program[6] package.

2. Selected bond lengths (Å) and angles (deg) for complexes 1-2.

Table S1. Crystal data and structural refinement parameters of complexes **1-2**.

Complexes	**1**	**2**
Empirical formula	$C_{25}H_{17}EuN_3O_{10}$	$C_{25}H_{17}TbN_3O_{10}$
Formula weight	671.38	678.34
Crystal system	Monoclinic	Monoclinic
Space group	*P*2(1)/*n*	*P*2(1)/*n*
a / Å	10.6381(13)	10.6273(10)
b / Å	18.837(2)	18.7534(17)
c / Å	12.0604(15)	11.9852(11)
α / °	90	90
β/ °	94.139(2)	94.0280(10)

γ/ °	90	90
V / Å^3	2410.5(5)	2382.7(4)
Z	4	4
D_{calcd} / g cm^{-3}	1.850	1.891
/ mm^{-1}	2.669	3.035
F(000)	1324	1332
θ min-max / °	2.01, 25.00	2.17, 27.44
Tot., uniq. data	17555, 4231	20948, 5399
R(int)	0.0433	0.0331
Nref, Npar	4, 360	3, 354
R_1, wR_2 [$I > 2\sigma(I)$]	0.0272, 0.0691	0.0234, 0.0608
GOF on F^2	1.048	1.049
Min. and max resd dens (e·Å^{-3})	-1.096, 1.255	-0.894, 1.299

Table S2. Selected bond lengths (Å) and angles (deg) for complexes **1-2**.

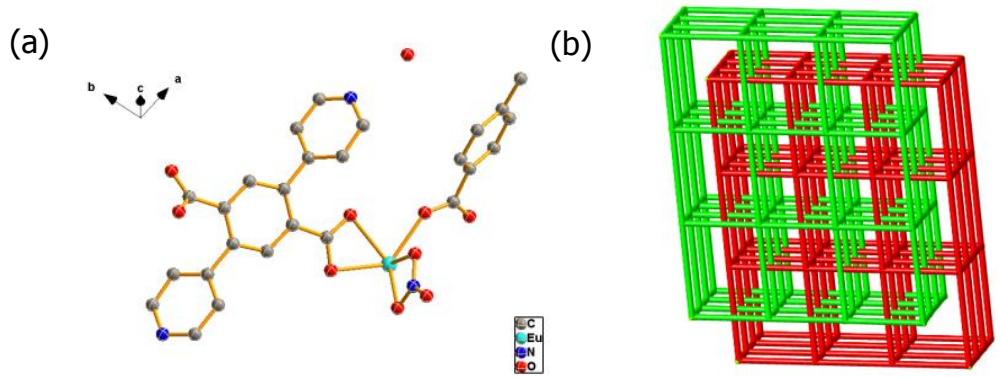
Complex **1**			
Eu(1)-O(3)	2.329(3)	Eu(1)-O(4)#3	2.350(2)
Eu(1)-O(5)#4	2.405(2)	Eu(1)-O(2)	2.422(2)
Eu(1)-O(1)	2.482(3)	Eu(1)-O(7)	2.502(3)
Eu(1)-O(8)	2.504(3)	Eu(1)-O(6)#5	2.511(2)
Eu(1)-O(5)#5	2.610(2)	O(5)-Eu(1)#6	2.405(2)
O(5)-Eu(1)#2	2.610(2)	O(6)-Eu(1)#2	2.511(2)
O(3)-Eu(1)-O(4)#3	137.50(9)	O(3)-Eu(1)-O(5)#4	74.10(8)
O(4)#3-Eu(1)-O(5)#4	75.65(9)	O(3)-Eu(1)-O(2)	128.83(9)
O(4)#3-Eu(1)-O(2)	91.40(8)	O(5)#4-Eu(1)-O(2)	148.99(8)

O(3)-Eu(1)-O(1)	76.27(9)	O(4)#3-Eu(1)-O(1)	138.56(9)
O(5)#4-Eu(1)-O(1)	145.79(9)	O(2)-Eu(1)-O(1)	52.91(8)
O(3)-Eu(1)-O(7)	75.19(13)	O(4)#3-Eu(1)-O(7)	126.28(11)
O(5)#4-Eu(1)-O(7)	78.44(11)	O(2)-Eu(1)-O(7)	87.46(12)
O(1)-Eu(1)-O(7)	77.78(11)	O(3)-Eu(1)-O(8)	122.36(11)
O(4)#3-Eu(1)-O(8)	77.15(11)	O(5)#4-Eu(1)-O(8)	75.96(9)
O(2)-Eu(1)-O(8)	73.71(9)	O(1)-Eu(1)-O(8)	106.74(10)
O(7)-Eu(1)-O(8)	51.11(12)	O(3)-Eu(1)-O(6)#5	97.22(9)
O(4)#3-Eu(1)-O(6)#5	76.79(9)	O(5)#4-Eu(1)-O(6)#5	125.08(8)
O(2)-Eu(1)-O(6)#5	77.19(9)	O(1)-Eu(1)-O(6)#5	75.23(10)
O(7)-Eu(1)-O(6)#5	152.99(11)	O(8)-Eu(1)-O(6)#5	140.03(10)
O(3)-Eu(1)-O(5)#5	69.53(9)	O(4)#3-Eu(1)-O(5)#5	75.10(8)
O(5)#4-Eu(1)-O(5)#5	76.97(8)	O(2)-Eu(1)-O(5)#5	127.38(8)
O(1)-Eu(1)-O(5)#5	108.05(9)	O(7)-Eu(1)-O(5)#5	141.24(12)
O(8)-Eu(1)-O(5)#5	145.09(10)	O(6)#5-Eu(1)-O(5)#5	50.33(7)
Complex **2**			
O(1)-Tb(1)	2.393(2)	O(2)-Tb(1)	2.465(2)
O(3)-Tb(1)#3	2.3733(19)	O(3)-Tb(1)#1	2.585(2)
O(4)-Tb(1)#1	2.480(2)	O(5)-Tb(1)	2.299(2)
O(6)-Tb(1)#4	2.324(2)	O(7)-Tb(1)	2.470(3)
O(8)-Tb(1)	2.482(2)	Tb(1)-O(3)#6	2.585(2)
Tb(1)-O(3)#5	2.3733(19)	Tb(1)-O(4)#6	2.480(2)
O(5)-Tb(1)-O(6)#4	138.05(8)	O(5)-Tb(1)-O(3)#5	74.35(7)
O(6)#4-Tb(1)-O(3)#5	76.09(7)	O(5)-Tb(1)-O(1)	129.07(7)
O(6)#4-Tb(1)-O(1)	90.62(7)	O(3)#5-Tb(1)-O(1)	148.37(7)

O(5)-Tb(1)-O(2)	76.12(7)	O(6)#4-Tb(1)-O(2)	138.18(8)
O(3)#5-Tb(1)-O(2)	145.72(8)	O(1)-Tb(1)-O(2)	53.32(7)
O(5)-Tb(1)-O(7)	75.09(11)	O(6)#4-Tb(1)-O(7)	126.60(10)
O(3)#5-Tb(1)-O(7)	78.57(10)	O(1)-Tb(1)-O(7)	87.21(10)
O(2)-Tb(1)-O(7)	77.35(10)	O(5)-Tb(1)-O(4)#6	97.28(8)
O(6)#4-Tb(1)-O(4)#6	76.79(8)	O(3)#5-Tb(1)-O(4)#6	125.66(7)
O(1)-Tb(1)-O(4)#6	77.06(7)	O(2)-Tb(1)-O(4)#6	75.02(8)
O(7)-Tb(1)-O(4)#6	152.35(9)	O(5)-Tb(1)-O(8)	122.44(9)
O(6)#4-Tb(1)-O(8)	76.95(9)	O(3)#5-Tb(1)-O(8)	75.64(7)
O(1)-Tb(1)-O(8)	73.42(8)	O(2)-Tb(1)-O(8)	106.80(9)
O(7)-Tb(1)-O(8)	51.42(11)	O(4)#6-Tb(1)-O(8)	139.85(8)
O(5)-Tb(1)-O(3)#6	69.56(8)	O(6)#4-Tb(1)-O(3)#6	75.27(7)
O(3)#5-Tb(1)-O(3)#6	76.97(7)	O(1)-Tb(1)-O(3)#6	127.77(7)
O(2)-Tb(1)-O(3)#6	108.34(8)	O(4)#6-Tb(1)-O(3)#6	50.89(6)

Symmetry Codes: for **1:** #1 = - *x* + 2, - *y* , - *z* + 1, #2 = *x* -1/2, - *y* + 1/2, *z* + 1/2, #3 = - *x* + 1, - *y*, - *z*, , #4 = - *x* + 1/2, *y* - 1/2, - *z* + 1/2, #5 = *x* + 1/2, - *y* + 1/2, *z* - 1/2, #6 = - *x* + 1/2, *y* + 1/2, - *z* + 1/2.; for **2**: #1 = *x* - 1/2, - *y* + 1/2, *z* + 1/2, #2 = - *x* + 2, - *y* , - *z* + 2, #3 = - *x* + 1/2, *y* + 1/2, - *z* + 3/2, #4 = - *x* + 1, - *y*, - *z* +1, #5 = - *x* +1/2, *y* -1/2, - *z* +3/2, #6 = *x* + 1/2, -*y* + 1/2, *z* - 1/2.

3. Structural drawing for complexes 1-3.



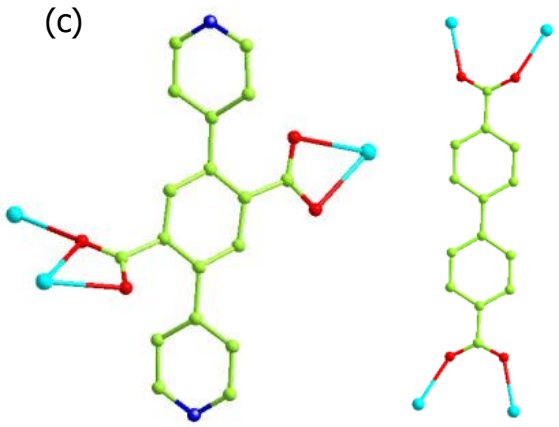


Figure S1 (a) Coordination environment of **1**. Symmetry code: #1 = - *x* + 2, - *y* , - *z* + 1, #2 = *x* -1/2, - *y* + 1/2, *z* + 1/2, #3 = - *x* + 1, - *y*, - *z*, , #4 = - *x* + 1/2, *y* - 1/2, - *z* + 1/2, #5 = *x* + 1/2, - *y* + 1/2, *z* - 1/2, #6 = - *x* + 1/2, *y* + 1/2, - *z* + 1/2. (b) Topological representation of **1**. (c) The coordination modes of L ligand (left) and BPDC ligand (right).

4. Powder X-ray diffraction patterns of complexes 1-2.

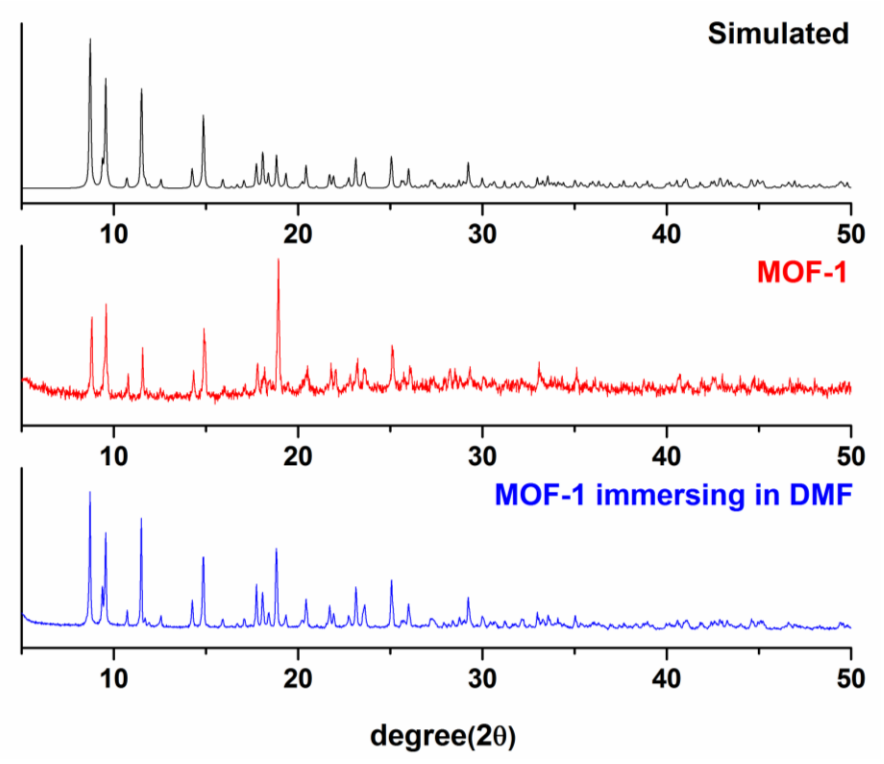


Figure S2 Powder X-ray diffraction patterns of complex **1**.

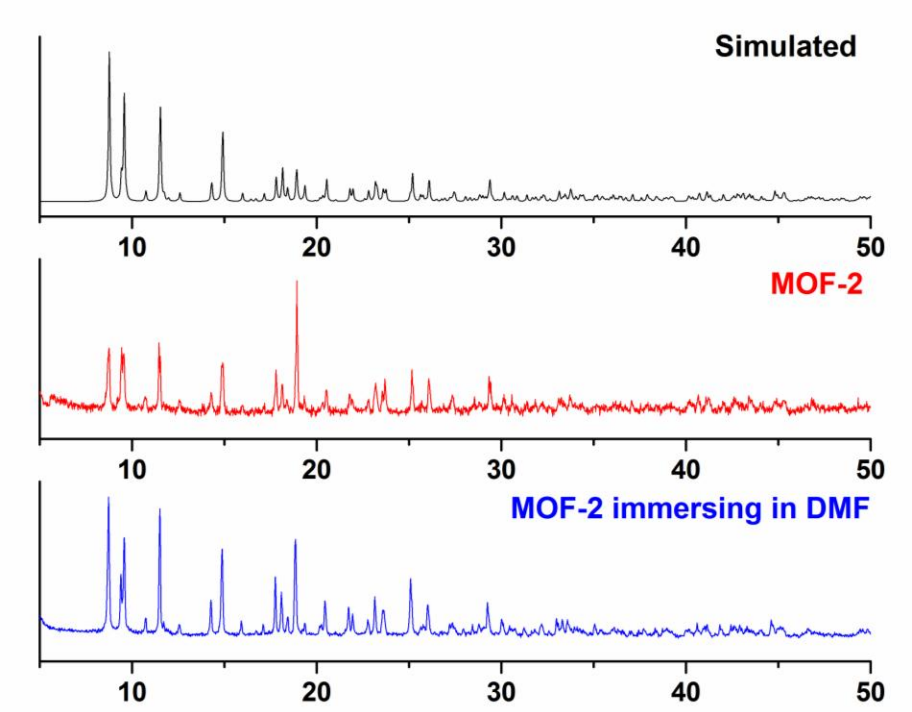


Figure S3 Powder X-ray diffraction patterns of complex **2**.

5. IR spectra of complexes 1-2 and related ligands.

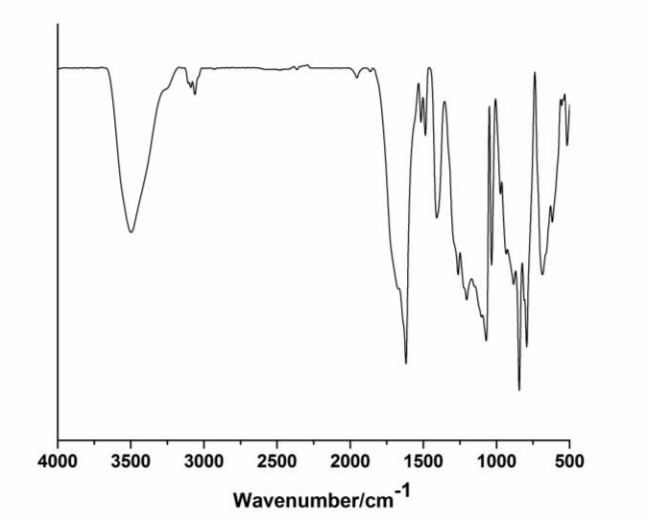


Figure S4 IR spectra of H_2L ligand.

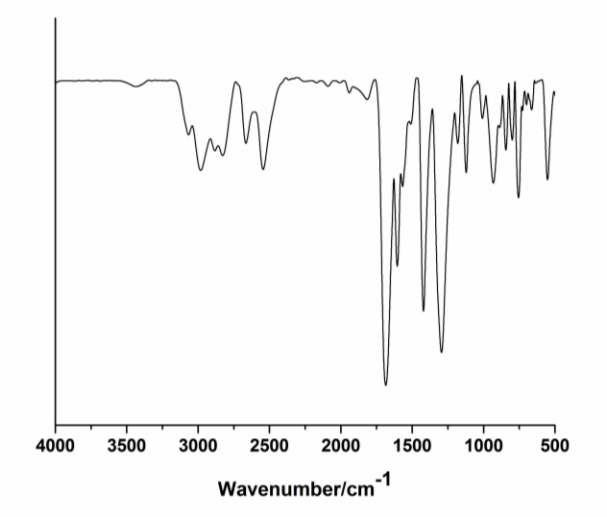


Figure S5 IR spectra of BPDC ligand.

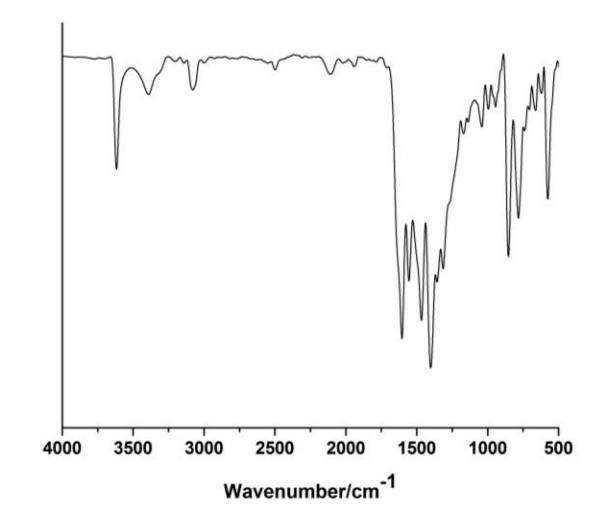


Figure S6 IR spectra of complex **1**.

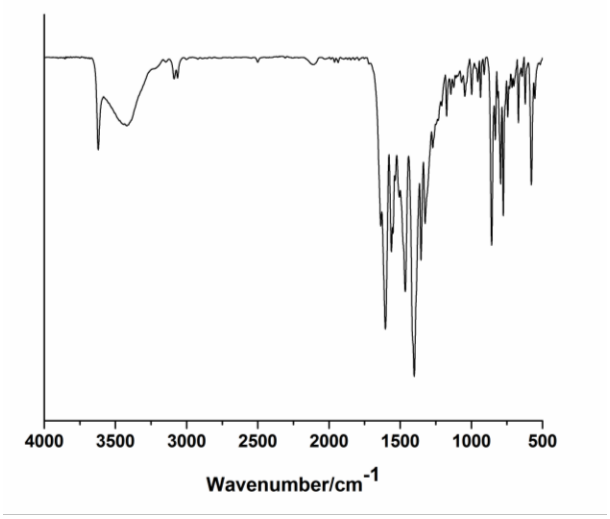


Figure S7 IR spectra of complex **2**.

6. Solid-state photoluminescent spectra of 1 and 2.

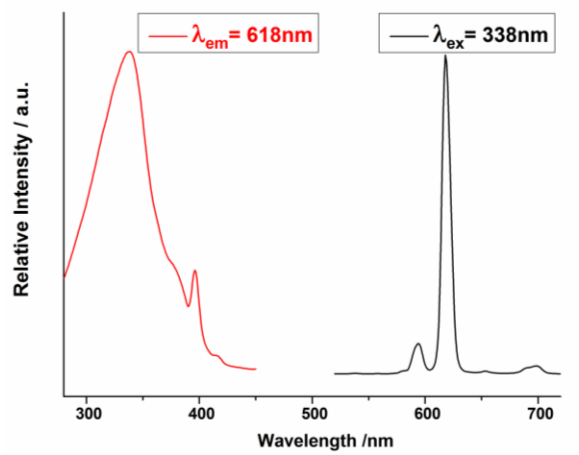


Figure S8 Solid-state photoluminescent spectra of **1**.

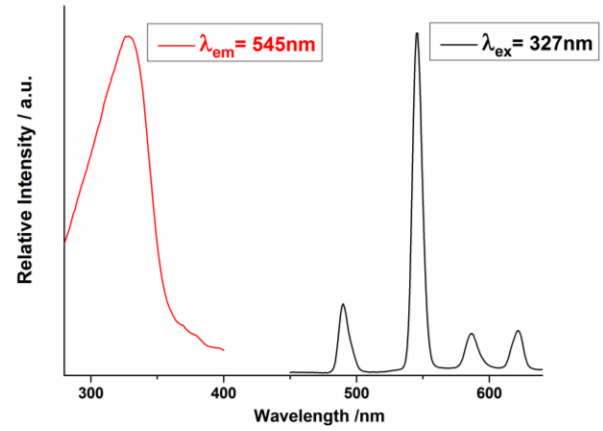


Figure S9 Solid-state photoluminescent spectra of **2**.

7. The TGA diagrams of complexes 1-2.

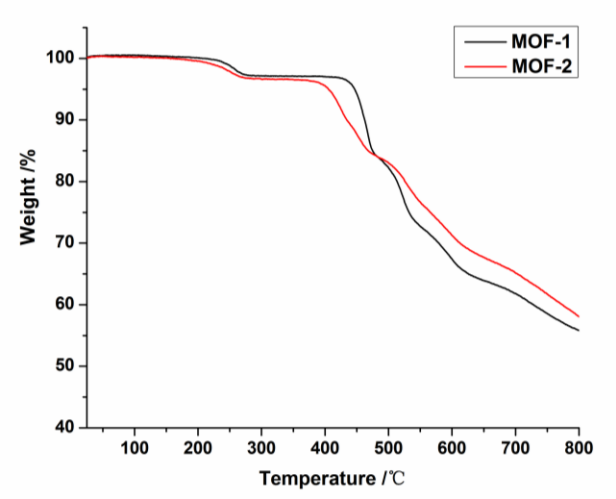


Figure S10 The TGA diagrams of complexes **1-2.**

8. The decay lifetime of compound 1 and 2.

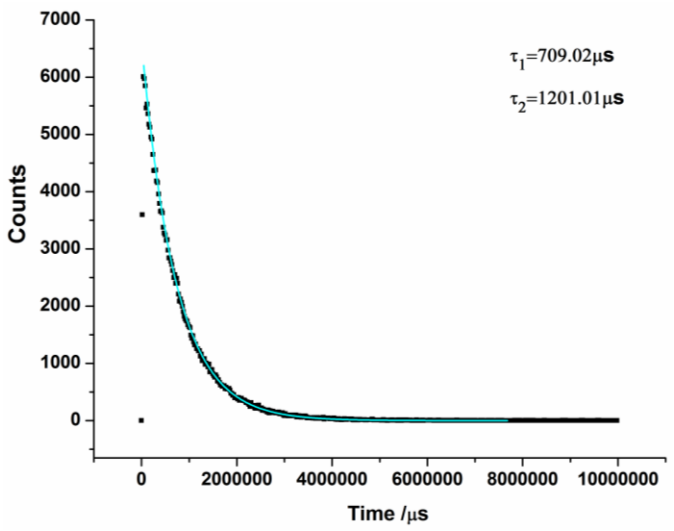


Figure S11 The fitted decay curve for complex **1** in the solid state. The sample was excited at 335 nm. Blank circles: experimental data; Solid line: fitted by Fit = $A+B_1 \times \exp(-t/\tau_1)+B_2 \times \exp(-t/\tau_2)$.

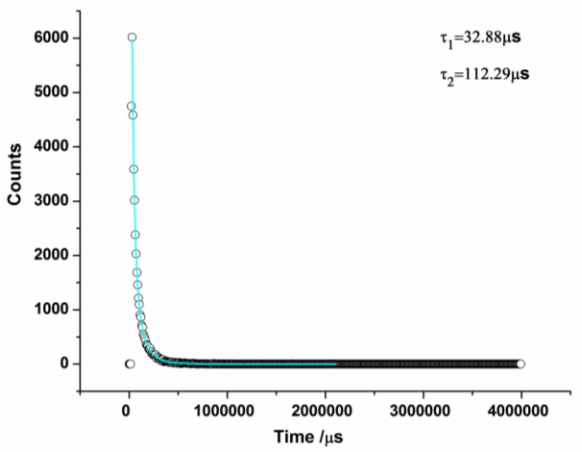


Figure S12 The fitted decay curve for complex **2** in the solid state. The sample was excited at 327 nm. Blank circles: experimental data; Solid line: fitted by Fit = $A+B_1 \times \exp(-t/\tau_1)+B_2 \times \exp(-t/\tau_2)$.

9. The changes of the luminescence intensity upon the addition of analyte.

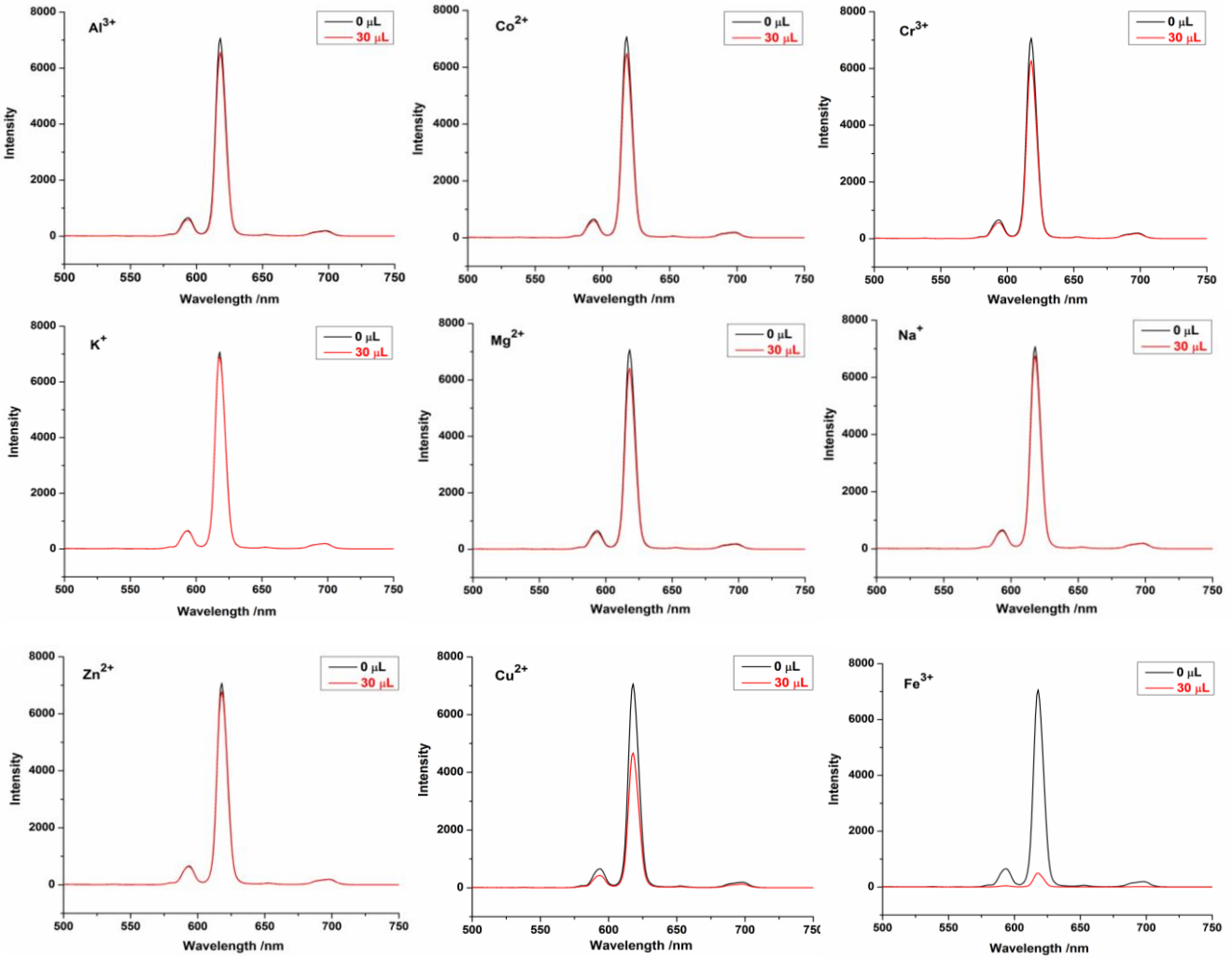


Figure S13 The fluorescence spectra of MOF-1 in DMF solution upon the addition of 10^{-2} mol/L of various metal ions.

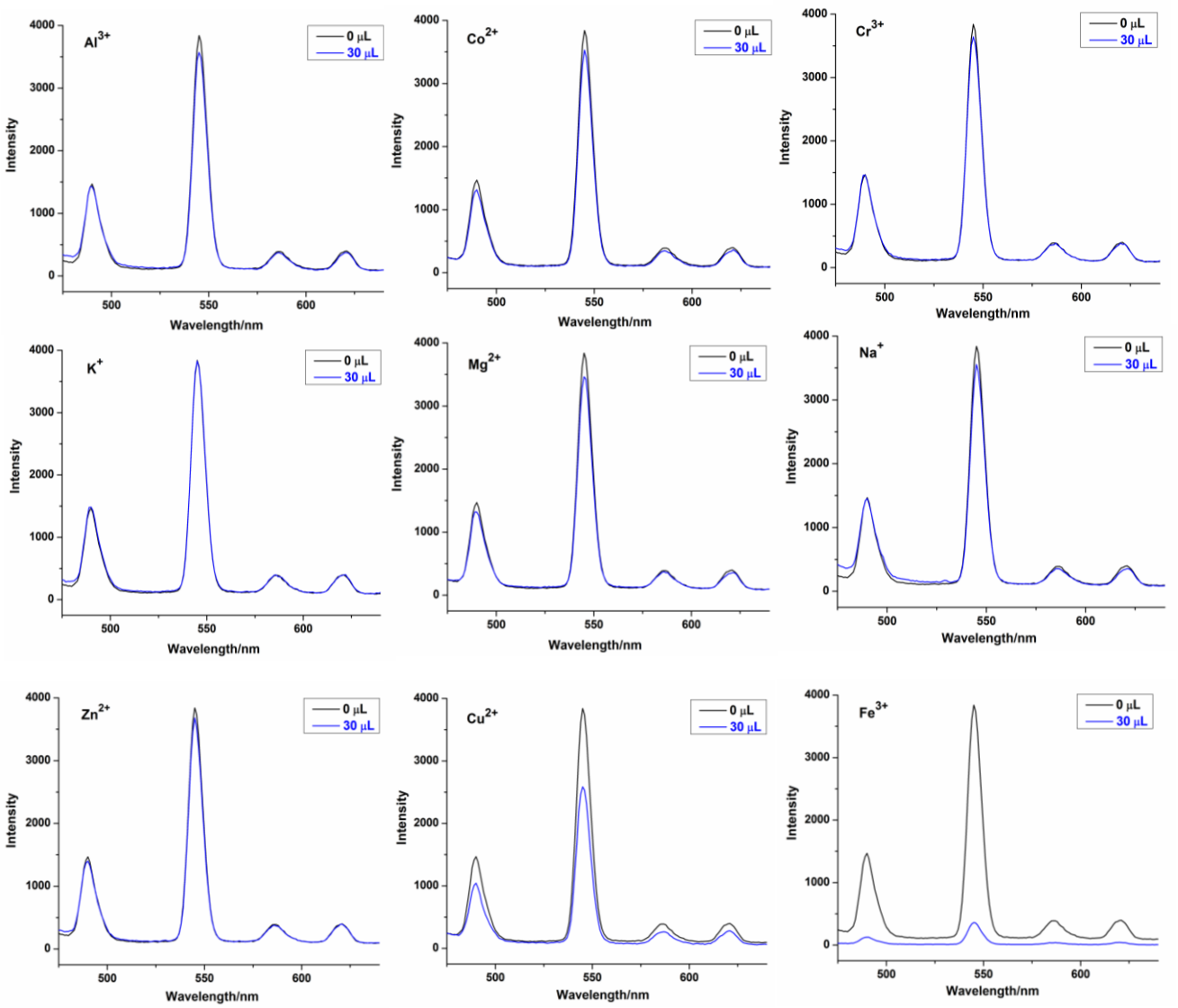


Figure S14 The fluorescence spectra of MOF-2 in DMF solution upon the addition of 10^{-2} mol/L of various metal ions.

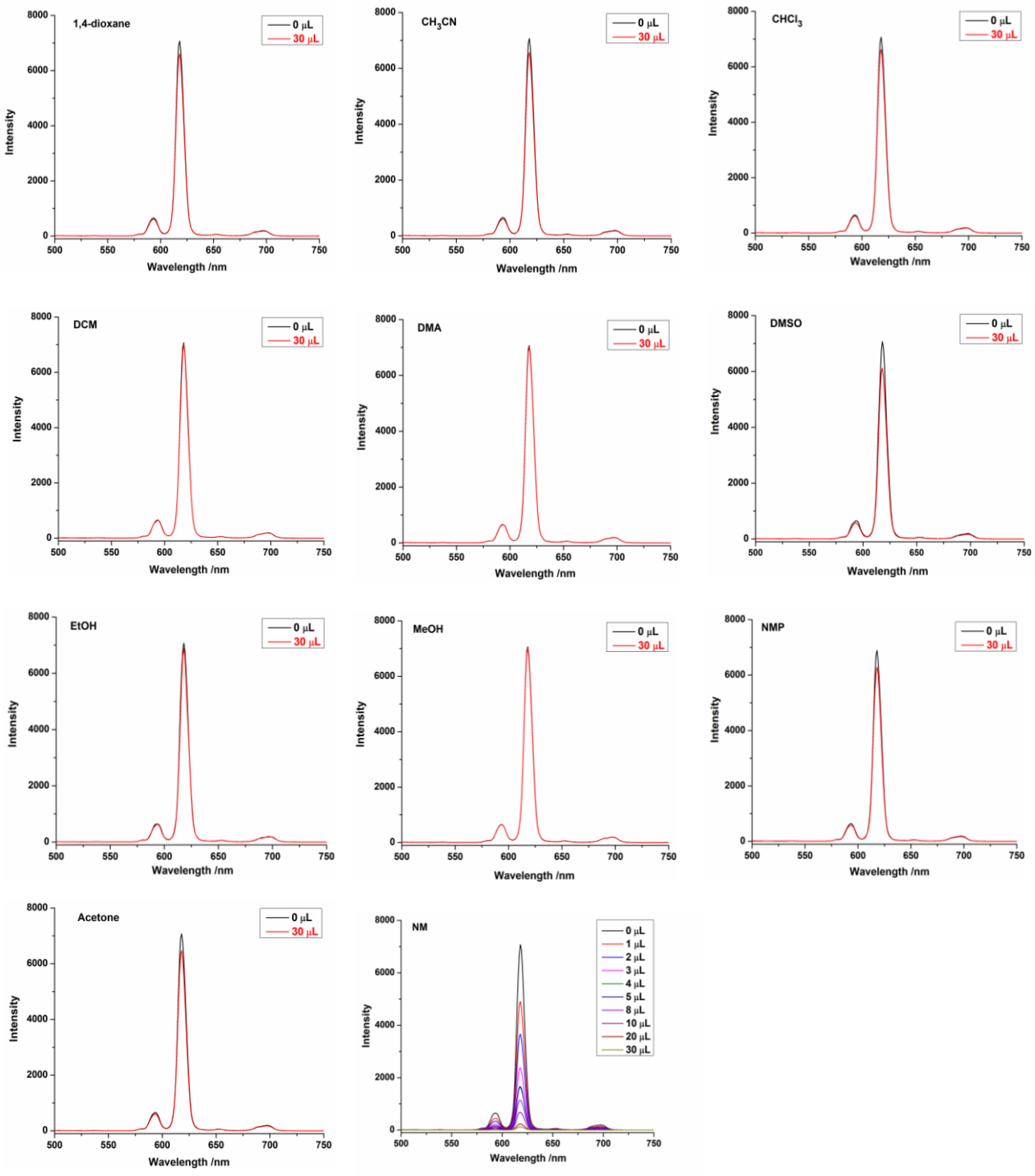


Figure S15 The fluorescence spectra of MOF-1 in DMF solution upon the addition of various solvents.

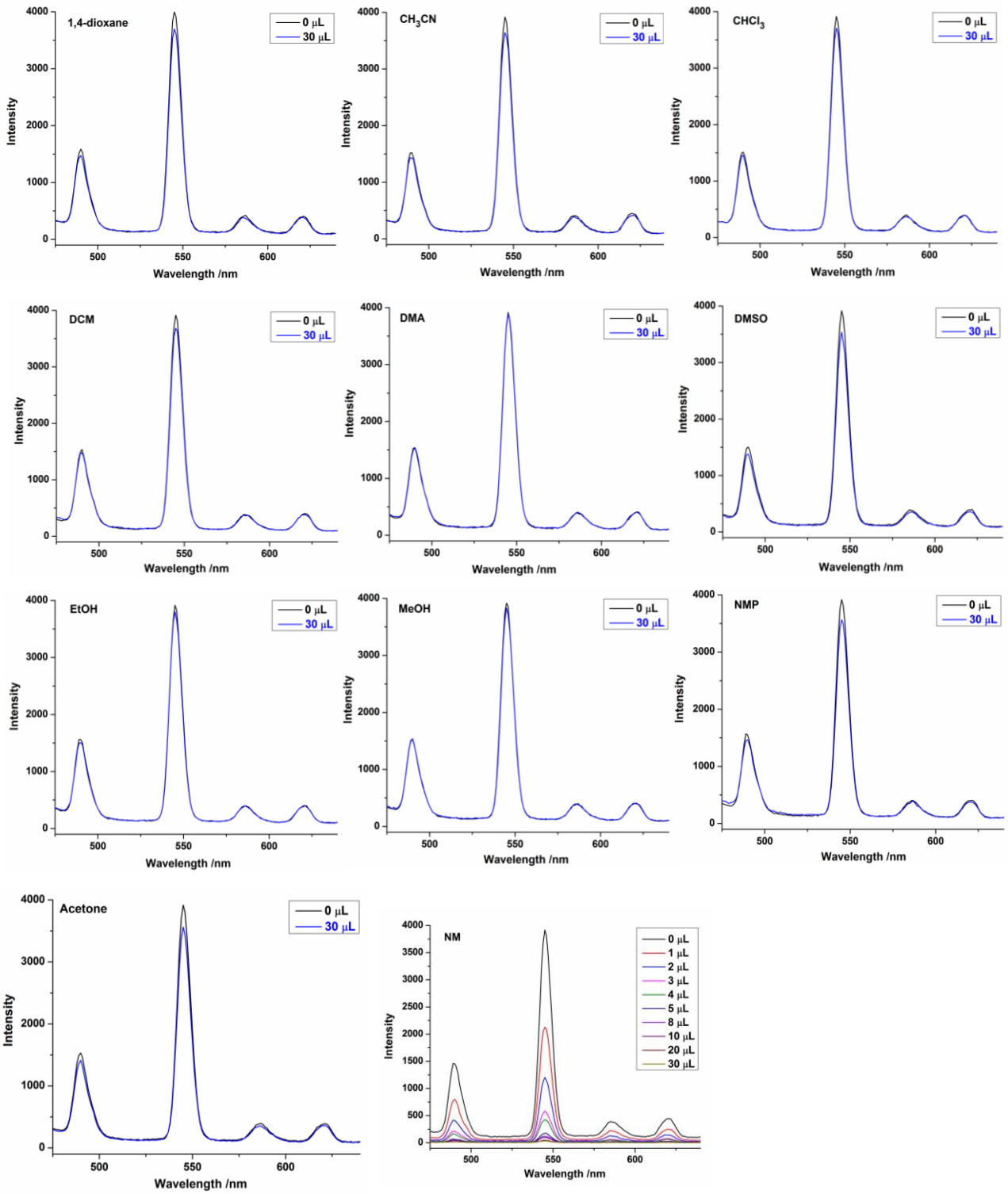


Figure S16 The fluorescence spectra of MOF-2 in DMF solution upon the addition of various solvents.

10. The quenching relationship between nitromethane and MOFs 1 and 2.

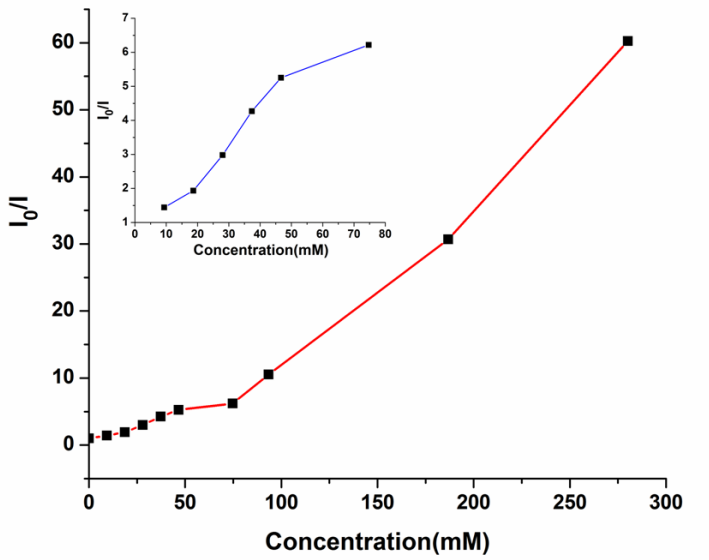


Figure S17. SV curve for **1** by gradual addition of nitromethane. The inset demonstrates the quenching relationship at low concentrations of nitromethane.

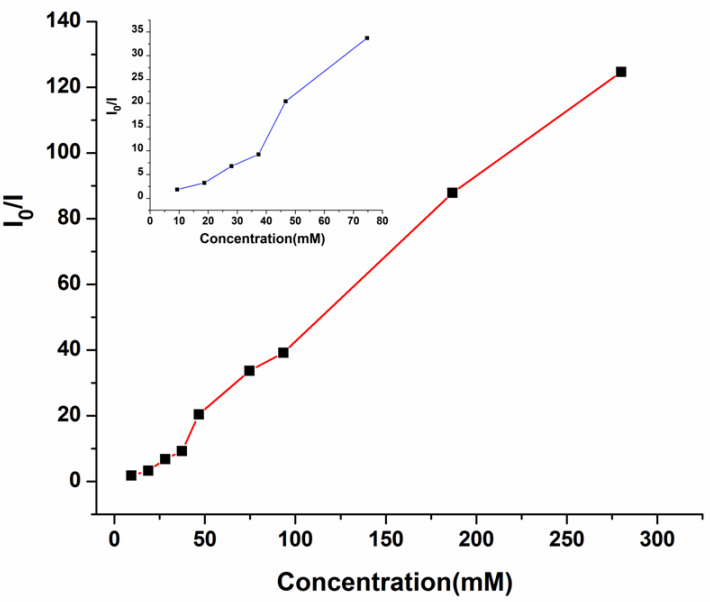


Figure S18. SV curve for **2** by gradual addition of nitromethane. The inset demonstrates the quenching relationship at low concentrations of nitromethane.

11. The N1s XPS results of complexes 1-2 and after addition of Fe^{3+}

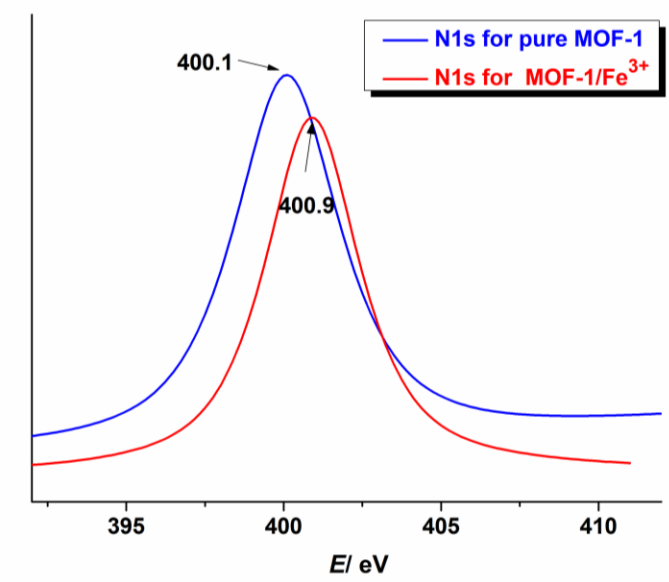


Figure S19. XPS spectra of the **1** (blue) and Fe^{3+}-incorporated **1** (red) activated in 0.01 mol/L DMF solution of $Fe(NO_3)_3$.

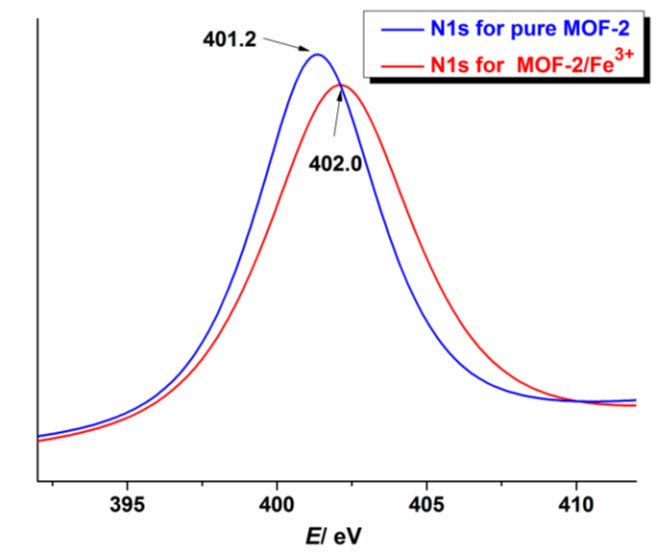


Figure S20. XPS spectra of the **2** (blue) and Fe^{3+}-incorporated **2** (red) activated in 0.01 mol/L DMF solution of $Fe(NO_3)_3$.

12. The UV-Vis spectra of ligands, NM, and complexes 1-2 in DMF solution.

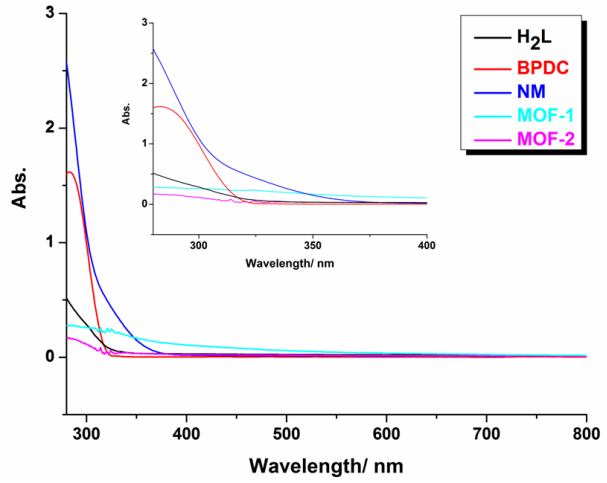


Figure S21. The UV-Vis spectra of ligands, NM, and complexes **1** and **2** in DMF solution. The inset demonstrates the absorption spectra in the range of 280-400 nm.

13. The ICP results of complexes 1-2 after treated with Fe^{3+} for 12 hours.

Table S3

	MOF-1/μM	MOF-2/μM
Initial value/Fe^{3+}	0.75	0.75
After treated with Fe^{3+} for 12 hours/Fe^{3+}	0.34	0.52

14. The detection limit table of selected luminescent Ln-MOFs materials for Fe^{3+}.

Table S4

Ln-MOF luminescent materials	substrates	detection limit/(mol/L)	ref
Tb-DSOA	Fe^{3+}	10^{-6}	26
$[(CH_3)_2NH_2]$ [Tb(bptc)] xsolvents	Fe^{3+}	10^{-5}	27
$[Eu(HL)(H_2O)_2]$ $2H_2O$	Fe^{3+}	10^{-6}	28
EuL	Fe^{3+}	10^{-4}	29
$[Eu(BTPCA)(H_2O)]$ 2DMF $3H_2O$	Fe^{3+}	10^{-5}	30
Our work	Fe^{3+}	5×10^{-7}	

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