Supporting Information

Water-stable Eu-MOFs fluorescent sensors for trivalent metal ions and the nitrobenzene

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Contents

Table S1. Bond lengths [Å] and angles [º] for MOF **1**

MOF 1					
Eu(1)-O(10)	2.309(9)	Eu(1)-O(4)	2.373(10)	Eu(1)-O(8)#1	2.396(10)
Eu(1)-O(11)#2	2.404(9)	Eu(1)-O(1)#3	2.418(8)	Eu(1)-O(5)	2.420(9)
Eu(1)-O(12)#2	2.486(9)	Eu(1)-O(3)	2.499(9)	Eu(1)-Eu(02)#1	3.9960(8)
Eu(2)-O(7)	2.320(10)	Eu(2)-O(9)	2.329(10)	Eu(2)-O(14)	2.414(10)
Eu(2)-O(2)#4	2.463(10)	Eu(2)-O(13)	2.478(13)	Eu(2)-O(15)	2.482(11)
Eu(2)-O(6)#2	2.542(9)	Eu(2)-O(5)#2	2.571(9)	Eu(2)-O(1)#4	2.632(9)
Eu(2)-Eu(01)#2	3.9960(8)	O(1)-Eu(1)#3	2.418(8)	O(1)-Eu(2)#5	2.632(9)
O(2)-Eu(2)#5	2.463(10)	O(5)-Eu(2)#1	2.571(9)	O(6)-Eu(2)#1	2.542(9)
O(8)-Eu(1)#2	2.396(10)	O(11)-Eu(1)#1	2.404(9)	O(12)-Eu(1)#1	2.486(9)

O(10)-Eu(1)-O(4)	134.7(3)	O(10)-Eu(1)-O(8)#1	78.8(4)
O(4)-Eu(1)-O(8)#1	80.1(4)	O(10)-Eu(1)-O(11)#2	81.8(3)
O(4)-Eu(1)-O(11)#2	98.0(4)	O(8)#1-Eu(1)-O(11)#2	149.8(3)
O(10)-Eu(1)-O(1)#3	137.1(3)	O(4)-Eu(1)-O(1)#3	78.2(3)
O(8)#1-Eu(1)-O(1)#3	82.6(3)	O(11)#2-Eu(1)-O(1)#3	126.8(3)
O(10)-Eu(1)-O(5)	75.1(3)	O(4)-Eu(1)-O(5)	147.9(3)
O(8)#1-Eu(1)-O(5)	98.7(3)	O(11)#2-Eu(1)-O(5)	98.4(3)
O(1)#3-Eu(1)-O(5)	69.9(3)	O(10)-Eu(1)-O(12)#2	121.6(3)
O(4)-Eu(1)-O(12)#2	91.0(4)	O(8)#1-Eu(1)-O(12)#2	156.3(3)
O(11)#2-Eu(1)-O(12)#2	52.8(3)	O(1)#3-Eu(1)-O(12)#2	74.0(3)
O(5)-Eu(1)-O(12)#2	77.4(3)	O(10)-Eu(1)-O(3)	82.9(3)
O(4)-Eu(1)-O(3)	53.2(3)	O(8)#1-Eu(1)-O(3)	76.7(3)
O(11)#2-Eu(1)-O(3)	78.2(3)	O(1)#3-Eu(1)-O(3)	129.4(3)
O(5)-Eu(1)-O(3)	158.1(3)	O(12)#2-Eu(1)-O(3)	115.3(3)
O(10)-Eu(1)-Eu(02)#1	97.8(3)	O(4)-Eu(1)-Eu(02)#1	113.8(3)
O(8)#1-Eu(1)-Eu(02)#1	73.4(3)	O(11)#2-Eu(1)-Eu(02)#1	132.4(2)
O(1)#3-Eu(1)-Eu(02)#1	39.6(2)	O(5)-Eu(1)-Eu(02)#1	38.1(2)
O(12)#2-Eu(1)-Eu(02)#1	90.6(2)	O(3)-Eu(1)-Eu(02)#1	149.3(2)
O(7)-Eu(2)-O(9)	84.5(4)	O(7)-Eu(2)-O(14)	79.4(4)
O(9)-Eu(2)-O(14)	75.5(4)	O(7)-Eu(2)-O(2)#4	127.0(3)
O(9)-Eu(2)-O(2)#4	126.5(4)	O(14)-Eu(2)-O(2)#4	143.1(4)
O(7)-Eu(2)-O(13)	77.4(5)	O(9)-Eu(2)-O(13)	70.5(5)
O(14)-Eu(2)-O(13)	140.2(4)	O(2)#4-Eu(2)-O(13)	75.9(5)
O(7)-Eu(2)-O(15)	158.6(4)	O(9)-Eu(2)-O(15)	74.3(4)
O(14)-Eu(2)-O(15)	97.7(4)	O(2)#4-Eu(2)-O(15)	66.7(4)
O(13)-Eu(2)-O(15)	92.6(5)	O(7)-Eu(2)-O(6)#2	125.7(3)
O(9)-Eu(2)-O(6)#2	125.6(4)	O(14)-Eu(2)-O(6)#2	69.0(3)
O(2)#4-Eu(2)-O(6)#2	74.2(4)	O(13)-Eu(2)-O(6)#2	149.7(4)
O(15)-Eu(2)-O(6)#2	71.2(4)	O(7)-Eu(2)-O(5)#2	79.2(3)
O(9)-Eu(2)-O(5)#2	147.9(3)	O(14)-Eu(2)-O(5)#2	74.5(3)
O(2)#4-Eu(2)-O(5)#2	85.0(4)	O(13)-Eu(2)-O(5)#2	130.9(4)
O(15)-Eu(2)-O(5)#2	120.7(4)	O(6)#2-Eu(2)-O(5)#2	50.8(3)

O(7)-Eu(2)-O(1)#4	77.1(3)	O(9)-Eu(2)-O(1)#4	137.8(4)
O(14)-Eu(2)-O(1)#4	135.5(3)	O(2)#4-Eu(2)-O(1)#4	50.7(3)
O(13)-Eu(2)-O(1)#4	68.6(4)	O(15)-Eu(2)-O(1)#4	117.1(3)
O(6)#2-Eu(2)-O(1)#4	95.6(3)	O(5)#2-Eu(2)-O(1)#4	64.4(3)
O(7)-Eu(2)-Eu(01)#2	59.7(3)	O(9)-Eu(2)-Eu(01)#2	143.9(3)
O(14)-Eu(2)-Eu(01)#2	99.7(3)	O(2)#4-Eu(2)-Eu(01)#2	78.6(3)
O(13)-Eu(2)-Eu(01)#2	95.8(4)	O(15)-Eu(2)-Eu(01)#2	141.1(3)
O(6)#2-Eu(2)-Eu(01)#2	83.1(2)	O(5)#2-Eu(2)-Eu(01)#2	35.52(19)
O(1)#4-Eu(2)-Eu(01)#2	35.86(18)	Eu(1)#3-O(1)-Eu(02)#5	104.5(3)
Eu(01)-O(5)-Eu(2)#1	106.4(3)		

Symmetry codes: #1 -x+3/2,y+1/2,-z+3/2 #2 -x+3/2,y-1/2,-z+3/2 #3 -x+1,y,-z+3/2
#4 x+1/2,y-1/2,z #5 x-1/2,y+1/2,z

Table S2. Bond lengths [Å] and angles [º] for MOF **2**

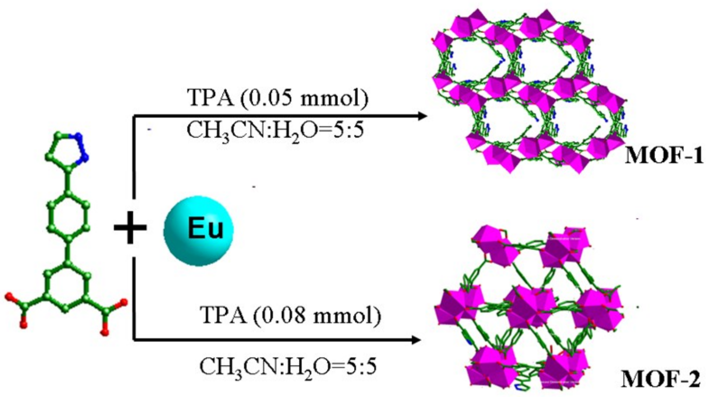
MOF 2					
Eu(1)-O(8)	2.335(3)	Eu(1)-O(17)#1	2.352(3)	Eu(1)-O(10)#2	2.410(3)
Eu(1)-O(7)#3	2.422(3)	Eu(1)-O(25)	2.440(3)	Eu(1)-O(9)#2	2.458(3)
Eu(1)-O(18)#4	2.474(3)	Eu(1)-O(24)	2.501(3)	Eu(1)-O(8)#3	2.869(3)
Eu(1)-Eu(1)#3	3.9996(12)	Eu(2)-O(12)#2	2.379(3)	Eu(2)-O(13)	2.387(3)
Eu(2)-O(15)	2.427(3)	Eu(2)-O(3)	2.441(3)	Eu(2)-O(5)	2.473(3)
Eu(2)-O(14)	2.506(3)	Eu(2)-O(13)#2	2.531(3)	Eu(2)-O(4)	2.594(3)
Eu(2)-O(16)	2.917(4)	Eu(2)-O(6)	3.011(4)	Eu(3)-O(11)	2.342(3)
Eu(3)-O(6)	2.343(3)	Eu(3)-O(13)	2.355(3)	Eu(3)-O(16)#2	2.420(3)
Eu(3)-O(1)#4	2.422(4)	Eu(3)-O(4)	2.437(3)	Eu(3)-O(2)#4	2.513(3)
Eu(3)-N(4)#5	2.606(4)	Eu(3)-O(12)	3.086(3)	O(1)-Eu(3)#6	2.422(4)
O(13)-Eu(2)#2	2.531(3)	O(2)-Eu(3)#6	2.513(3)	O(7)-Eu(1)#3	2.422(3)
O(8)-Eu(1)#3	2.869(3)	O(12)-Eu(2)#2	2.379(3)	O(9)-Eu(1)#2	2.458(3)
O(10)-Eu(1)#2	2.410(3)	O(16)-Eu(3)#2	2.420(3)	O(17)-Eu(1)#1	2.352(3)
O(18)-Eu(1)#6	2.474(3)	N(4)-Eu(3)#5	2.606(4)		

O(8)-Eu(1)-O(17)#1	87.03(10)	O(8)-Eu(1)-O(10)#2	93.45(10)
O(17)#1-Eu(1)-O(10)#2	145.67(10)	O(8)-Eu(1)-O(7)#3	127.66(10)
O(17)#1-Eu(1)-O(7)#3	78.07(10)	O(10)#2-Eu(1)-O(7)#3	125.83(9)
O(8)-Eu(1)-O(25)	145.51(11)	O(17)#1-Eu(1)-O(25)	75.84(10)
O(10)#2-Eu(1)-O(25)	84.98(11)	O(7)#3-Eu(1)-O(25)	78.21(11)
O(8)-Eu(1)-O(9)#2	131.23(9)	O(17)#1-Eu(1)-O(9)#2	141.04(10)
O(10)#2-Eu(1)-O(9)#2	53.65(9)	O(7)#3-Eu(1)-O(9)#2	72.21(9)
O(25)-Eu(1)-O(9)#2	73.92(10)	O(8)-Eu(1)-O(18)#4	71.50(10)
O(17)#1-Eu(1)-O(18)#4	133.45(10)	O(10)#2-Eu(1)-O(18)#4	78.21(10)
O(7)#3-Eu(1)-O(18)#4	83.32(10)	O(25)-Eu(1)-O(18)#4	140.68(10)
O(9)#2-Eu(1)-O(18)#4	67.45(9)	O(8)-Eu(1)-O(24)	73.03(11)
O(17)#1-Eu(1)-O(24)	74.31(11)	O(10)#2-Eu(1)-O(24)	73.06(10)
O(7)#3-Eu(1)-O(24)	144.38(11)	O(25)-Eu(1)-O(24)	73.59(12)

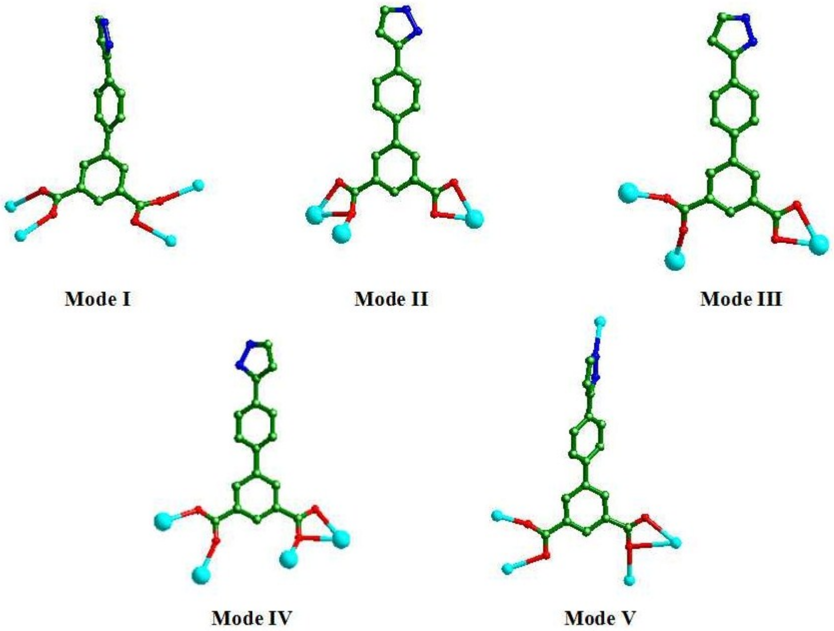
O(9)#2-Eu(1)-O(24)	118.75(11)	O(18)#4-Eu(1)-O(24)	132.23(11)
O(8)-Eu(1)-O(8)#3	80.05(9)	O(17)#1-Eu(1)-O(8)#3	65.47(9)
O(10)#2-Eu(1)-O(8)#3	148.34(9)	O(7)#3-Eu(1)-O(8)#3	48.04(9)
O(25)-Eu(1)-O(8)#3	117.57(10)	O(9)#2-Eu(1)-O(8)#3	108.72(9)
O(18)#4-Eu(1)-O(8)#3	70.31(9)	O(24)-Eu(1)-O(8)#3	132.25(10)
O(8)-Eu(1)-Eu(1)#3	44.96(7)	O(17)#1-Eu(1)-Eu(1)#3	70.85(7)
O(10)#2-Eu(1)-Eu(1)#3	130.22(8)	O(7)#3-Eu(1)-Eu(1)#3	82.93(7)
O(25)-Eu(1)-Eu(1)#3	144.40(7)	O(9)#2-Eu(1)-Eu(1)#3	127.95(7)
O(18)#4-Eu(1)-Eu(1)#3	64.73(7)	O(24)-Eu(1)-Eu(1)#3	108.18(9)
O(8)#3-Eu(1)-Eu(1)#3	35.09(6)	O(12)#2-Eu(2)-O(13)	85.67(10)
O(12)#2-Eu(2)-O(15)	77.61(11)	O(13)-Eu(2)-O(15)	163.24(10)
O(12)#2-Eu(2)-O(3)	135.55(11)	O(13)-Eu(2)-O(3)	108.91(10)
O(15)-Eu(2)-O(3)	82.88(12)	O(12)#2-Eu(2)-O(5)	82.19(11)
O(13)-Eu(2)-O(5)	86.99(11)	O(15)-Eu(2)-O(5)	91.81(12)
O(3)-Eu(2)-O(5)	138.39(11)	O(12)#2-Eu(2)-O(14)	133.46(11)
O(13)-Eu(2)-O(14)	127.11(10)	O(15)-Eu(2)-O(14)	67.47(11)
O(3)-Eu(2)-O(14)	70.29(13)	O(5)-Eu(2)-O(14)	69.61(13)
O(12)#2-Eu(2)-O(13)#2	81.72(9)	O(13)-Eu(2)-O(13)#2	67.36(10)
O(15)-Eu(2)-O(13)#2	108.51(10)	O(3)-Eu(2)-O(13)#2	67.24(10)
O(5)-Eu(2)-O(13)#2	150.56(11)	O(14)-Eu(2)-O(13)#2	137.48(12)
O(12)#2-Eu(2)-O(4)	154.15(9)	O(13)-Eu(2)-O(4)	69.82(9)
O(15)-Eu(2)-O(4)	126.49(11)	O(3)-Eu(2)-O(4)	51.79(10)
O(5)-Eu(2)-O(4)	103.89(10)	O(14)-Eu(2)-O(4)	70.98(11)
O(13)#2-Eu(2)-O(4)	81.32(9)	O(12)#2-Eu(2)-O(16)	63.56(11)
O(13)-Eu(2)-O(16)	123.09(8)	O(15)-Eu(2)-O(16)	47.44(10)
O(3)-Eu(2)-O(16)	73.77(10)	O(5)-Eu(2)-O(16)	129.67(10)
O(14)-Eu(2)-O(16)	107.77(11)	O(13)#2-Eu(2)-O(16)	61.98(8)
O(4)-Eu(2)-O(16)	123.25(9)	O(12)#2-Eu(2)-O(6)	117.52(10)
O(13)-Eu(2)-O(6)	63.64(9)	O(15)-Eu(2)-O(6)	125.65(10)
O(3)-Eu(2)-O(6)	106.36(10)	O(5)-Eu(2)-O(6)	45.93(10)
O(14)-Eu(2)-O(6)	66.25(11)	O(13)#2-Eu(2)-O(6)	124.68(8)
O(4)-Eu(2)-O(6)	59.15(9)	O(16)-Eu(2)-O(6)	173.07(8)
O(11)-Eu(3)-O(6)	142.62(12)	O(11)-Eu(3)-O(13)	116.89(9)
O(6)-Eu(3)-O(13)	76.08(10)	O(11)-Eu(3)-O(16)#2	77.10(11)
O(6)-Eu(3)-O(16)#2	138.54(12)	O(13)-Eu(3)-O(16)#2	72.51(10)
O(11)-Eu(3)-O(1)#4	134.70(12)	O(6)-Eu(3)-O(1)#4	76.63(13)
O(13)-Eu(3)-O(1)#4	88.77(11)	O(16)#2-Eu(3)-O(1)#4	76.33(13)
O(11)-Eu(3)-O(4)	79.10(11)	O(6)-Eu(3)-O(4)	71.40(11)
O(13)-Eu(3)-O(4)	73.14(9)	O(16)#2-Eu(3)-O(4)	122.36(11)
O(1)#4-Eu(3)-O(4)	146.13(11)	O(11)-Eu(3)-O(2)#4	85.97(11)
O(6)-Eu(3)-O(2)#4	109.27(11)	O(13)-Eu(3)-O(2)#4	135.82(10)
O(16)#2-Eu(3)-O(2)#4	77.31(11)	O(1)#4-Eu(3)-O(2)#4	52.72(11)
O(4)-Eu(3)-O(2)#4	150.99(10)	O(11)-Eu(3)-N(4)#5	78.55(11)
O(6)-Eu(3)-N(4)#5	75.77(12)	O(13)-Eu(3)-N(4)#5	147.84(10)

O(16)#2-Eu(3)-N(4)#5	139.61(12)	O(1)#4-Eu(3)-N(4)#	99.52(14)
O(4)-Eu(3)-N(4)#5	83.38(11)	O(2)#4-Eu(3)-N(4)#5	69.26(11)
O(11)-Eu(3)-O(12)	45.94(9)	O(6)-Eu(3)-O(12)	131.27(10)
O(13)-Eu(3)-O(12)	70.96(8)	O(16)#2-Eu(3)-O(12)	60.33(10)
O(1)#4-Eu(3)-O(12)	135.74(12)	O(4)-Eu(3)-O(12)	65.35(9)
O(2)#4-Eu(3)-O(12)	119.41(9)	N(4)#5-Eu(3)-O(12)	118.74(11)
O(11)-Eu(3)-Eu(2)	115.48(8)	O(6)-Eu(3)-Eu(2)	52.60(9)
O(13)-Eu(3)-Eu(2)	37.23(6)	O(16)#2-Eu(3)-Eu(2)	108.12(9)
O(1)#4-Eu(3)-Eu(2)	107.37(9)	O(4)-Eu(3)-Eu(2)	42.71(7)
O(2)#4-Eu(3)-Eu(2)	158.45(7)	N(4)#5-Eu(3)-Eu(2)	111.32(8)
O(12)-Eu(3)-Eu(2)	79.98(6)	Eu(3)-O(13)-Eu(2)	106.12(10)
Eu(3)-O(13)-Eu(2)#2	107.15(10)	Eu(2)-O(13)-Eu(2)#2	112.64(10)
Eu(3)-O(4)-Eu(2)	97.71(10)	Eu(3)-O(6)-Eu(2)	89.21(9)
Eu(1)-O(8)-Eu(1)#3	99.95(9)	Eu(2)#2-O(12)-Eu(3)	91.10(9)
Eu(3)#2-O(16)-Eu(2)	94.49(11)	N(3)-N(4)-Eu(3)#5	117.2(3)

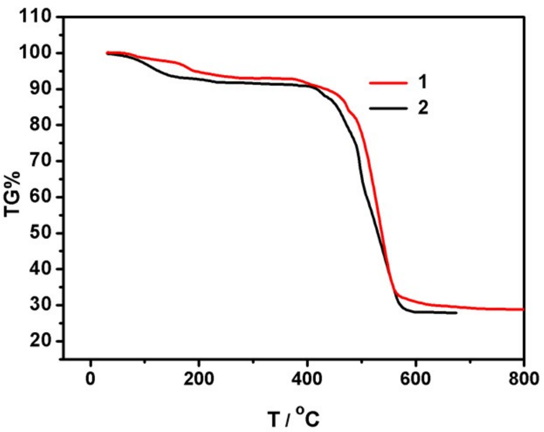
Symmetry codes: #1 -x+1,-y+1,-z #2 -x+1,-y+1,-z+1 #3 -x+2,-y+1,-z
#4 x+1,y,z #5 -x+2,-y,-z+1 #6 x-1,y,z



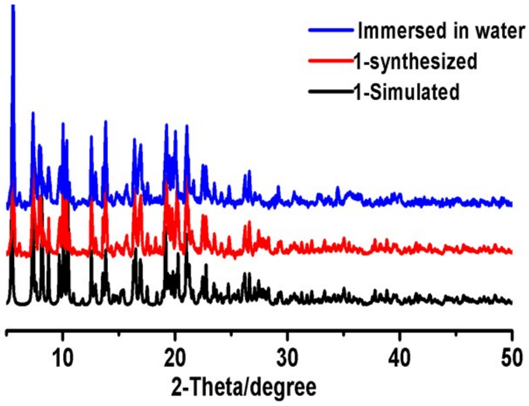
Scheme1. Reaction routes of **1** and **2**.



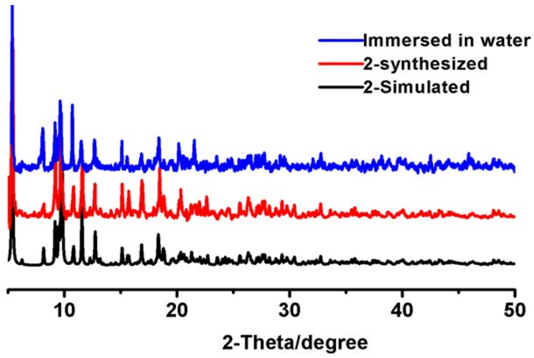
Scheme2. Coordination modes of ligand pdba^{2-} in **1** and **2**.



FigS1. The thermal analyses (TGA) curve of **1** and **2**.

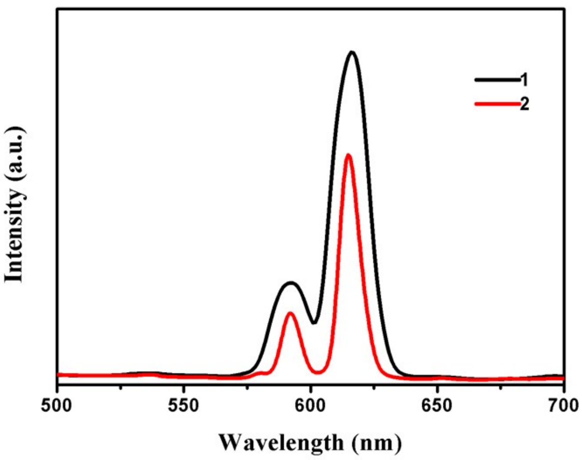


(a)

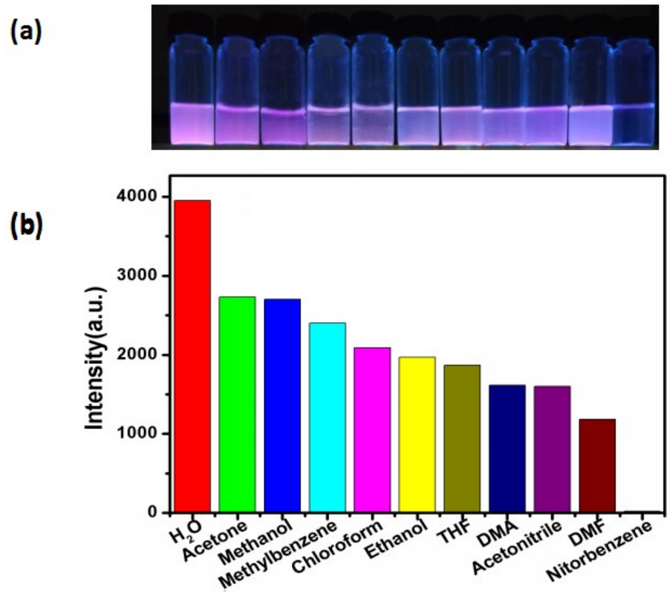


(b)

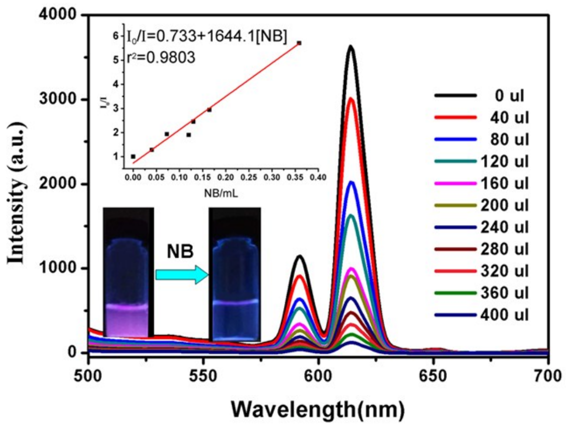
FigS2. The PXRD patterns of **1** and **2** were immersed in water for 24 h, (a) **1**, (b) **2**.



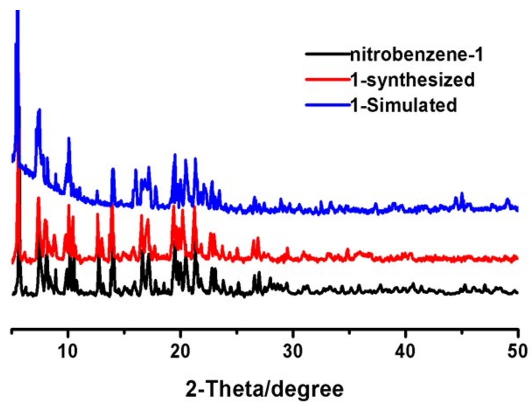
FigS3. The emission spectra of the solid-state MOFs(excitation at 338 nm) **1** and **2**.



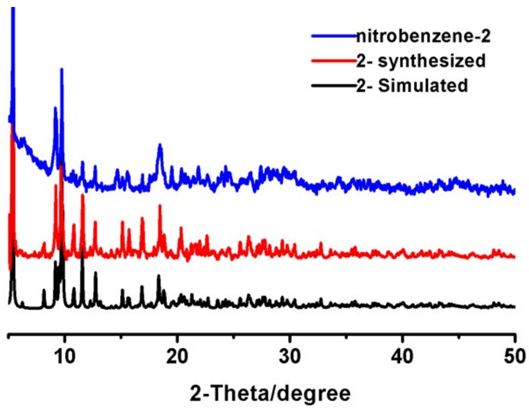
FigS4. (a) The photos were taken under irradiation of UV light (365 nm). (b)Fluorescence response of **2** towards various different solvents, excitation and emission were performed at 338 nm and 617 nm.



FigS5. Fluorescence spectra of **2** with increasing the nitrobenzene(NB) volume (up to down: 0, 40, 80, 120, 160, 200, 240, 280, 320, 360, 400 μL of 0.1 mol L^{-1} nitrobenzene solution).

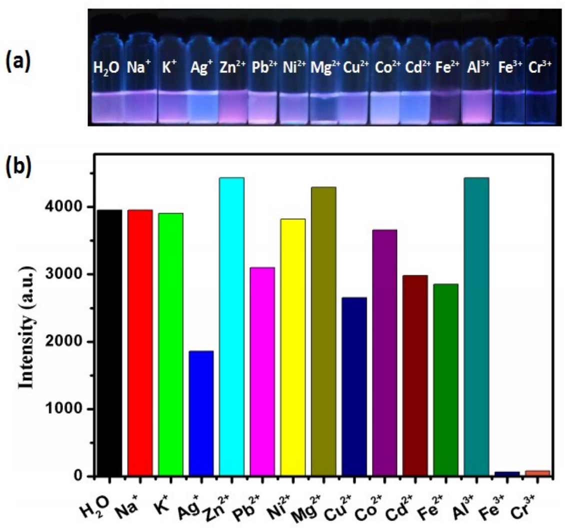


(a)

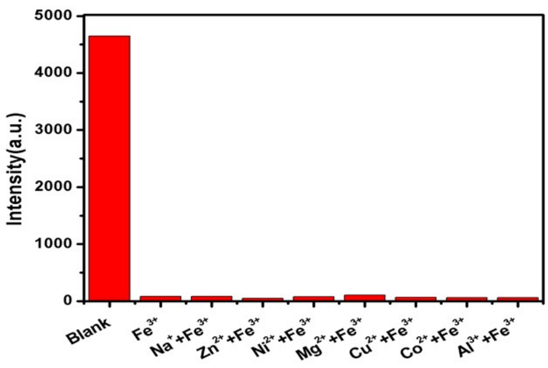


(b)

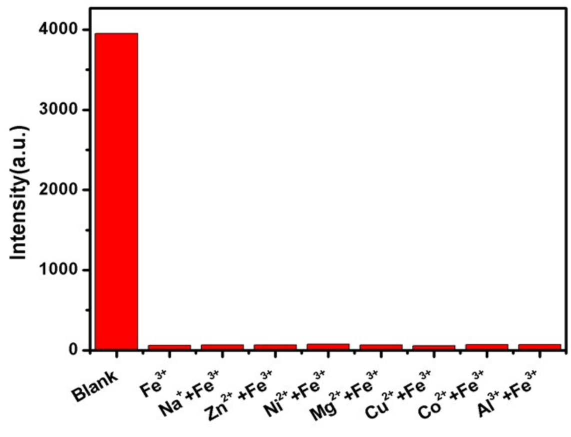
FigS6. The PXRD patterns of **1** and **2** were immersed in 0.1 mol L^{-1} nitrobenzene aqueous solution, (a) **1**, (b) **2**.



FigS7. (a) The photos were taken under irradiation of UV light (365 nm). (b) Fluorescence response of **2** towards 1.0×10^{-2} mol L^{-1} different of various cations, excitation and emission were performed at 338 nm and 617 nm.

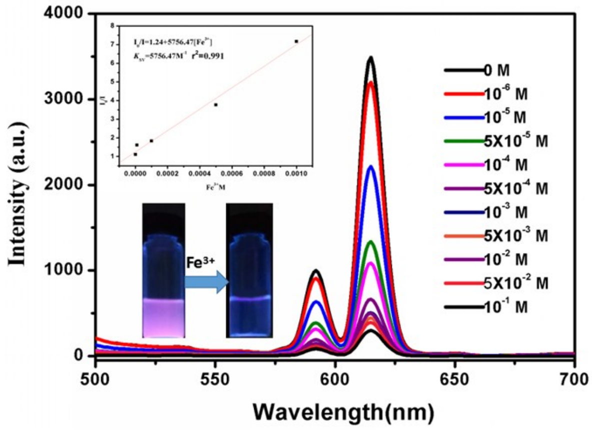


(a)

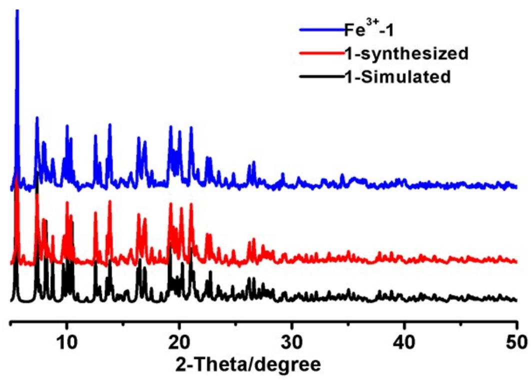


(b)

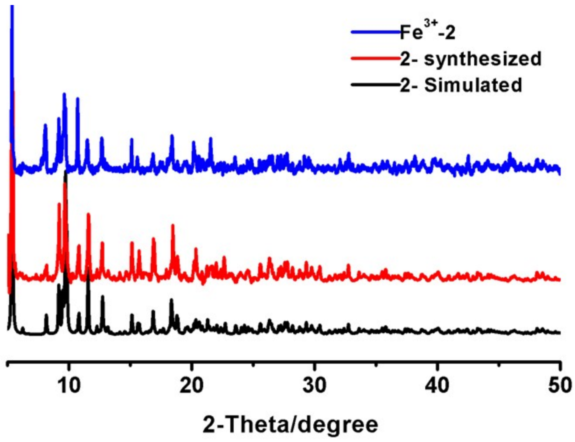
FigS8. Fluorescence response of **1** and **2** towards 1.0×10^{-2} mol L^{-1} Fe^{3+} and different of various cations, excitation and emission were performed at 338 nm and 617 nm. (a) **1**, (b) **2**.



FigS9. The luminescence intensity of **2** upon addition of different concentrations of $Fe(NO_3)_3$ aqueous solutions, (inset) the dose-response graph at 617 nm revealing the Stern-Volmer quenching constant, the K_{SV} was 5756.47 M^{-1} ($r^2 = 0.991$).

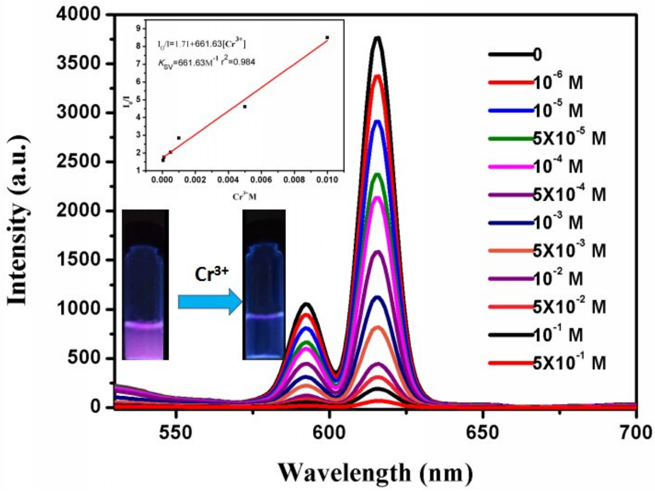


(a)

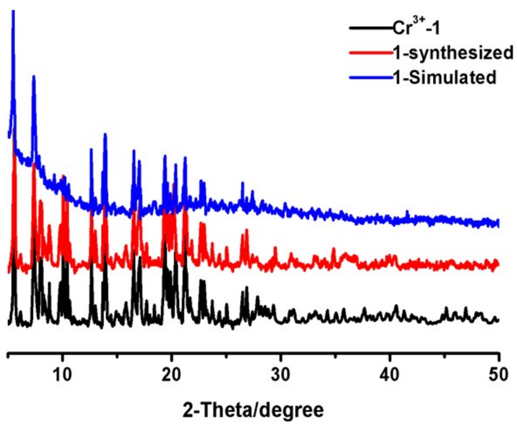


(b)

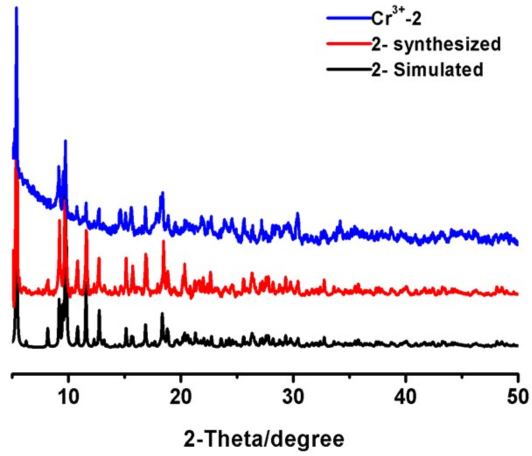
FigS10. The PXRD patterns of **1** and **2** were immersed in 0.1 mol L^{-1} Fe^{3+} aqueous solution, (a) **1**, (b) **2**.



FigS11. The luminescence intensity of **2** upon addition of different concentrations of $Cr(NO_3)_3$ aqueous solutions, (inset) the dose-response graph at 617 nm revealing the luminescence quenching of **2** by Cr^{3+} based on the Stern-Volmer equation.

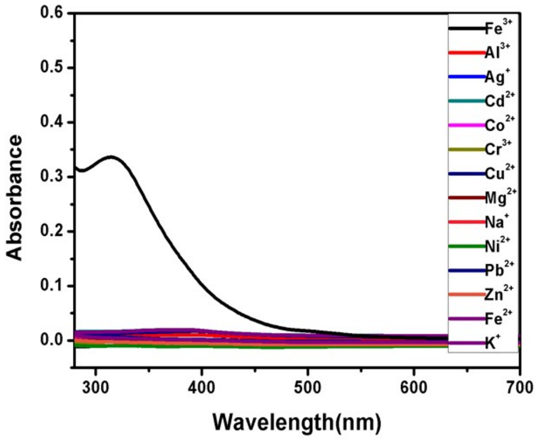


(a)

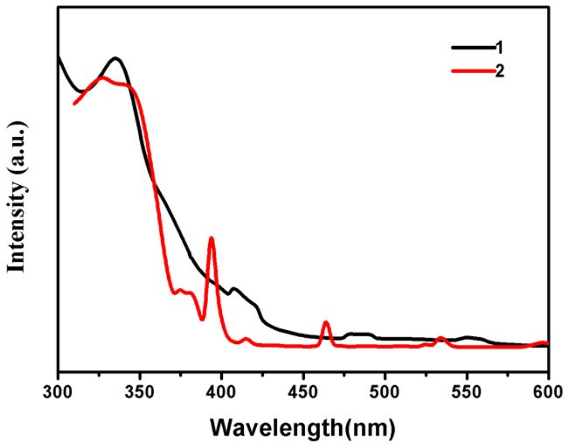


(b)

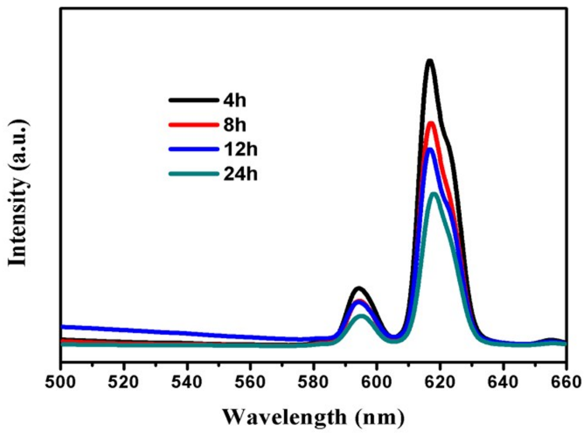
FigS12. The PXRD patterns of **1** and **2** were immersed in 0.1 mol L^{-1} Cr^{3+} aqueous solution, (a) **1**, (b) **2**.



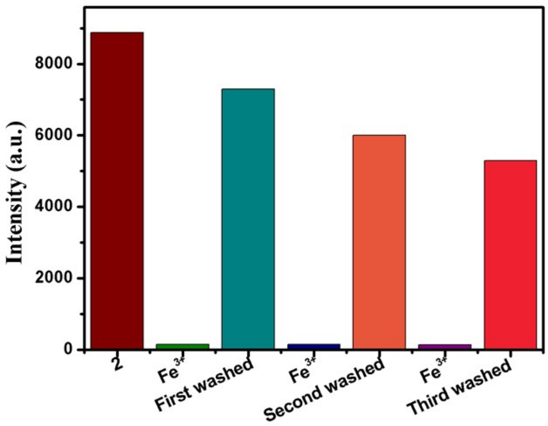
FigS13. UV-Vis spectra of aqueous solutions containing 10^{-4} mol L^{-1} $M(NO_3)_x$ (M = Fe^{3+}, Al^{3+}, Ag^{+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Mg^{2+}, Na^{+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Fe^{2+}, K^{+}).



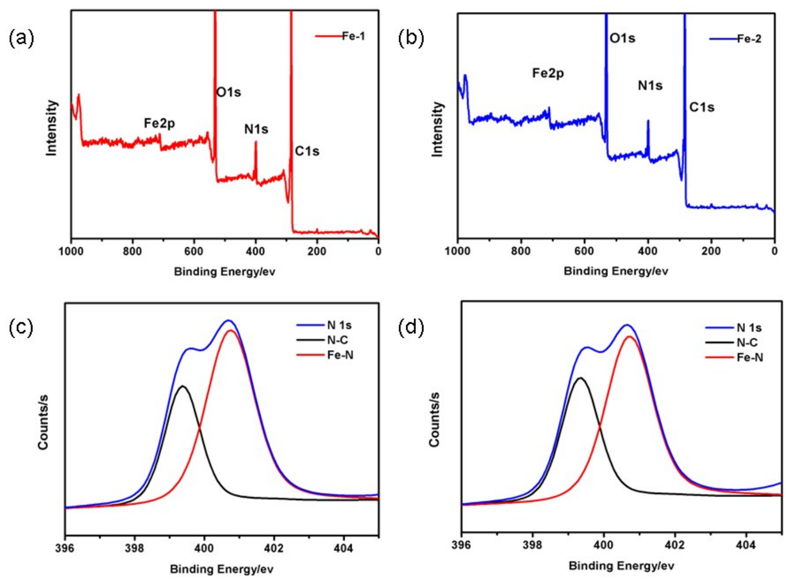
FigS14. The solid state excitation spectrum of **1** and **2** (338 nm).



FigS15. Solid fluorescence intensity of **1** soaked for different time.



FigS16. The luminescence intensity (617 nm) of crystal powder **2** before and after washing.



FigS17. N 1s XPS spectra of Fe-**1** and Fe-**2.**