Multi-responsive Chemosensors for Highly Sensitive and Selective Detection of Fe^{3+}, Cu^{2+}, $Cr_2O_7^{2-}$ and Nitrobenzene based on Luminescent Lanthanide Metal–Organic Frameworks

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Electronic Supplementary Information

Table S1 Selected bond lengths and bond angles for **I-VI**.

Bond lengths (Å)					
I					
La1-O7	2.405(4)	La1-O4	2.468(4)	La1-O9	2.550(5)
La1-O1	2.579(4)	La1-O2a	2.597(4)	La1-O2W	2.601(5)
La1-O2	2.620(4)	La1-O1W	2.633(5)	La1-O8	2.657(4)
II					
Ce1-O9	2.3724(19)	Ce1-O1	2.4358(19)	Ce1-O7	2.512(2)

Ce1-O4	2.5450(19)	Ce1-O1W	2.575(2)	Ce1-O3	2.5760(18)
Ce1-O2W	2.602(2)	Ce1-O3a	2.6043(18)	Ce1-O6	2.6322(19)
III					
Pr1-O8	2.3324(17)	Pr1-O2	2.3986(17)	Pr1-O6	2.4755(18)
Pr1-O5	2.5075(17)	Pr1-O4a	2.5317(17)	Pr1-O2W	2.5314(19)
Pr1-O1W	2.563(2)	Pr1-O4	2.5731(16)	Pr1-O7	2.6024(18)
IV					
Nd1-O5	2.3469(18)	Nd1-O9	2.4041(17)	Nd1-O1	2.4809(18)
Nd1-O6	2.5099(17)	Nd1-O1W	2.5321(19)	Nd1-O7a	2.5427(16)
Nd1-O2W	2.5648(19)	Nd1-O7	2.5888(17)	Nd1-O2	2.6109(17)
V					
Sm1-O5	2.316(2)	Sm1-O8	2.373(2)	Sm1-O1	2.450(2)
Sm1-O7	2.484(2)	Sm1-O2W	2.510(2)	Sm1-O6a	2.515(2)
Sm1-O1W	2.533(3)	Sm1-O6	2.586(2)	Sm1-O2	2.604(2)
VI					
Eu1-O1	2.293(6)	Eu1-O9	2.355(5)	Eu1-O5	2.437(6)
Eu1-O7	2.463(6)	Eu1-O2W	2.487(6)	Eu1-O6a	2.497(5)
Eu1-O1W	2.518(6)	Eu1-O6	2.576(6)	Eu1-O4	2.576(6)
Bond angle (°)					
I					
O7-La1-O4	82.38(15)	O7-La1-O9	129.57(15)	O4-La1-O9	87.98 (15)
O7-La1-O1	82.67 (14)	O4-La1-O1	140.30(15)	O9-La1-O1	129.07(15)
O7-La1-O2a	133.03(14)	O4-La1-O2a	135.95(13)	O9-La1-O2a	85.36(14)
O1-La1-O2a	50.76(13)	O7-La1-O2W	87.26(16)	O4-La1-O2W	75.75(15)
O9-La1-O2W	137.65(15)	O1-La1-O2W	66.98(15)	O2-La1-O2W	80.40(14)
O7-La1-O2	145.64(15)	O4-La1-O2	68.58(13)	O9-La1-O2	69.13(14)
O1-La1-O2	107.90(13)	O2-La1-O2a	68.38(14)	O2W-La1-O2a	68.54(14)
O7-La1-O1W	90.49(16)	O4-La1-O1W	145.50(15)	O9-La1-O1W	70.77(15)
O1-La1-O1W	70.98(15)	O2a-La1-O1W	70.78(14)	O2W-La1-O1W	137.85(15)
O2-La1-O1W	123.85(14)	O7-La1-O8	79.55(14)	O4-La1-O8a	72.90(15)
O9-La1-O8	50.45 (14)	O1-La1-O8	139.07(15)	O2-La1-O8	129.83(14)
O2W-La1-O8	147.26(15)	O2a-La1-O8	107.55(13)	O1W-La1-O8	72.61(14)
II					
O9-Ce1-O1	82.45(7)	O9-Ce1-O7	129.42(7)	O1-Ce1-O7	87.99(7)
O9-Ce1-O4	82.37(6)	O1-Ce1-O4	140.48(7)	O7-Ce1-O4	129.08(7)
O9-Ce1-O1W	86.57(8)	O1-Ce1-O1W	75.78(7)	O7-Ce1-O1W	138.49(7)
O4-Ce1-O1W	67.08(7)	O9-Ce1-O3	145.89(7)	O1-Ce1-O3	68.93(6)
O7-Ce1-O3	69.42(6)	O4-Ce1-O3	107.90(6)	O1W-Ce1-O3	69.10 (7)
O9-Ce1-O2W	90.14(8)	O1-Ce1-O2W	145.68(7)	O7-Ce1-O2W	71.06(7)
O4-Ce1-O2W	70.41(7)	O1W-Ce1-O2W	137.42(7)	O3-Ce1-O2W	70.20(7)
O9-Ce1-O3	132.82(6)	O1-Ce1-O3	136.48(6)	O7-Ce1-O3	85.22(6)
O4-Ce1-O3	50.92(6)	O1W-Ce1-O3	81.36(7)	O3-Ce1-O3a	68.45(7)
O2W-Ce1-O3	123.97(7)	O9-Ce1-O6	79.11(6)	O1-Ce1-O6	72.53(7)
O7-Ce1-O6	50.80(6)	O4-Ce1-O6	138.80(7)	O1W-Ce1-O6	146.58(7)

O3-Ce1-O6	129.92(6)	O2W-Ce1-O6	73.16(7)	O3-Ce1-O6	108.06(6)
III					
O8-Pr1-O2	82.69(6)	O8-Pr1-O6	129.64(6)	O2-Pr1-O6	87.85(6)
O8-Pr1-O5	81.75(6)	O2-Pr1-O5	140.53(6)	O6-Pr1-O5	129.31(7)
O8-Pr1-O4	132.44(6)	O2-Pr1-O4	136.70(5)	O6-Pr1-O4	85.23(6)
O5-Pr1-O4	51.17(5)	O8-Pr1-O2W	86.39(7)	O2-Pr1-O2W	75.91(6)
O6-Pr1-O2W	138.52(6)	O5-Pr1-O2W	67.11(6)	O4-Pr1-O2W	81.49(7)
O8-Pr1-O1W	89.75(7)	O2-Pr1-O1W	145.33(6)	O6-Pr1-O1W	71.19(6)
O5-Pr1-O1W	70.48(6)	O4-Pr1-O1W	70.37(6)	O2W-Pr1-O1W	137.53(6)
O8-Pr1-O4	146.06(6)	O2-Pr1-O4	69.09(6)	O6-Pr1-O4	69.42(6)
O5-Pr1-O4	108.08(5)	O4-Pr1-O4a	68.47(6)	O2W-Pr1-O4	69.14(6)
O1W-Pr1-O4	124.19(6)	O8-Pr1-O7	79.13(6)	O2-Pr1-O7	72.49(6)
O6-Pr1-O7	51.00(6)	O5-Pr1-O7	138.42(6)	O4-Pr1-O7	129.94(5)
O2W-Pr1-O7	146.58(6)	O1W-Pr1-O7	72.86(6)	O4-Pr1-O7a	108.39(5)
IV					
O5-Nd1-O9	82.83(6)	O5-Nd1-O1	129.75(6)	O9-Nd1-O1	87.92(7)
O5-Nd1-O6	81.45(6)	O9-Nd1-O6	140.44(6)	O1-Nd1-O6	129.38(6)
O5-Nd1-O1W	86.20(7)	O9-Nd1-O1W	75.73(6)	O1-Nd1-O1W	138.60(7)
O6-Nd1-O1W	67.20(6)	O5-Nd1-O7	132.54(6)	O9-Nd1-O7	136.58(6)
O1-Nd1-O7	84.91(6)	O6-Nd1-O7	51.59(5)	O1W-Nd1-O7	81.87(6)
O5-Nd1-O2W	89.35(7)	O9-Nd1-O2W	145.13(6)	O1-Nd1-O2W	71.26(7)
O6-Nd1-O2W	70.61(6)	O1W-Nd1-O2W	137.77(6)	O7-Nd1-O2W	70.68(6)
O5-Nd1-O7	146.24(6)	O9-Nd1-O7	69.22(6)	O1-Nd1-O7	69.43(6)
O6-Nd-O7	108.07(5)	O1W-Nd1-O7	69.23(6)	O7-Nd1-O7a	68.17(6)
O2W-Nd1-O7	124.41(6)	O5-Nd1-O2	78.906)	O9-Nd1-O2	72.57(6)
O1-Nd1-O2	51.35(6)	O6-Nd1-O2	138.15(6)	O1W-Nd1-O2	146.32(6)
O7-Nd1-O2	129.91(6)	O2W-Nd1-O2	72.58(6)	O7-Nd1-O2	108.79(5)
V					
O5-Sm1-O8	82.82(8)	O5-Sm1-O1	130.17(8)	O8-Sm1-O1	87.31(8)
O5-Sm1-O7	80.83(8)	O8-Sm1-O7	140.85(8)	O1-Sm1-O7	129.78(8)
O5-Sm1-O2W	85.55(9)	O8-Sm1-O2W	75.72(8)	O1-Sm1-O2W	138.46(9)
O7-Sm1-O2W	67.75(8)	O5-Sm1-O6	132.60(7)	O8-Sm1-O6	136.88(7)
O1-Sm1-O6	84.64(8)	O7-Sm1-O6	52.25(7)	O2W-Sm1-O6	82.78(9)
O5-Sm1-O1W	89.04(9)	O8-Sm1-O1W	144.40(8)	O1-Sm1-O1W	71.77(9)
O7-Sm1-O1W	70.55(8)	O2W-Sm1-O1W	138.29(8)	O6-Sm1-O1W	70.93(9)
O5-Sm1-O6	146.15(8)	O8-Sm1-O6	69.62(7)	O1-Sm1-O6	69.34(8)
O7-Sm1-O6	108.23(7)	O2W-Sm1-O6	69.23(8)	O6-Sm1-O6a	67.90(8)
O1W-Sm1-O6	124.80(8)	O5-Sm1-O2	78.88(8)	O8-Sm1-O2	72.13(8)
O1-Sm1-O2	51.73(8)	O7-Sm1-O2	137.62(9)	O2W-Sm1-O2	145.66(9)
O6-Sm1-O2	129.76(7)	O1W-Sm1-O2	72.30(8)	O6-Sm1-O2	109.35(7)
VI					
O1-Eu1-O9	83.3(2)	O1-Eu1-O5	130.3(2)	O9-Eu1-O5	87.0(2)
O1-Eu1-O7	80.68(19)	O9-Eu1-O7	141.2(2)	O5-Eu1-O7	129.7(2)
O1-Eu1-O2W	85.4(2)	O9-Eu1-O2W	75.9(2)	O5-Eu1-O2W	138.5(3)

O7-Eu1-O2W	67.9(2)	O1-Eu1-O6	146.0(2)	O9-Eu1-O6	69.63(18)
O5-Eu1-O6	69.85(19)	O7-Eu1-O6	107.76(19)	O2W-Eu1-O6	68.79(19)
O1-Eu1-O1W	88.3(2)	O9-Eu1-O1W	143.5(2)	O5-Eu1-O1W	71.8(2)
O7-Eu1-O1W	70.9(2)	O2W-Eu1-O1W	138.8(2)	O6-Eu1-O1W	71.86(19)
O1-Eu1-O6	132.75(19)	O9-Eu1-O6	136.60(18)	O5-Eu1-O6	84.3(2)
O7-Eu1-O6	52.55(18)	O2W-Eu1-O6	83.1(2)	O6-Eu1-O6a	67.4(2)
O1W-Eu1-O6	125.72(19)	O1-Eu1-O4	79.03(19)	O9-Eu1-O4	71.85(19)
O5-Eu1-O4	51.76(19)	O7-Eu1-O4	137.7(2)	O2W-Eu1-O4	145.5(2)
O6-Eu1-O4	129.60(19)	O1W-Eu1-O4	71.69(19)	O6-Eu1-O4	129.60(19)

Table S2 Distances and angles of hydrogen bonds.

D	H	A	d(D-H)	d(H...A)	d(D...A)	∠(D-H...A)
C2	H2	O2	0.93	2.52	3.400(12)	158
C2	H2	O3	0.93	2.58	3.094(12)	115

Table S3 Comparison of the corresponding lengths (Å, (average)) for **I-VI**.

	I	II	III	IV	V	VI
Ln−OW	2.617	2.589	2.547	2.548	2.522	2.503
Ln−$O_{carboxyl}$	2.554	2.525	2.484	2.498	2.475	2.457
Ln···Ln	4.3159(20)	4.2833(5)	4.2204(13)	4.2500(6)	4.2322(5)	4.2202(10)

Remark: OW, oxygen atom of the coordinated water; $O_{carboxyl}$, oxygen atom of the carboxylic group, Ln−$O_{carboxyl}$, average length.

Table S4 The ICP-AES data after 12 h of soaking in Fe^{3+} and Cu^{2+} ions.

Ions	The initial concentration (mg/L)	Residual ion concentration in solution (mg/L)	Adsorption percentage (%)
Fe^{3+}	5.585	2.858	48.83
Cu^{2+}	6.355	6.250	16.52

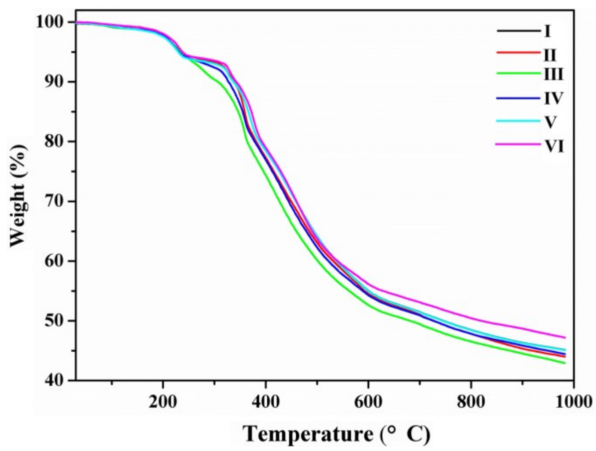


Fig. S1 TGA curve of compound **I-VI**.

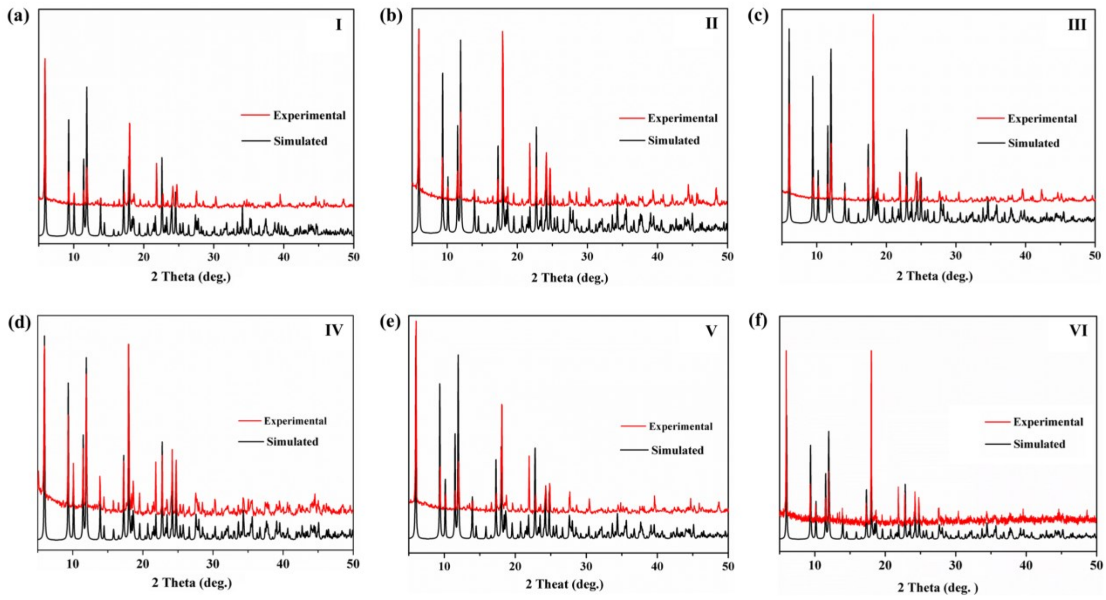


Fig. S2 PXRD patterns of compounds **I-VI**.

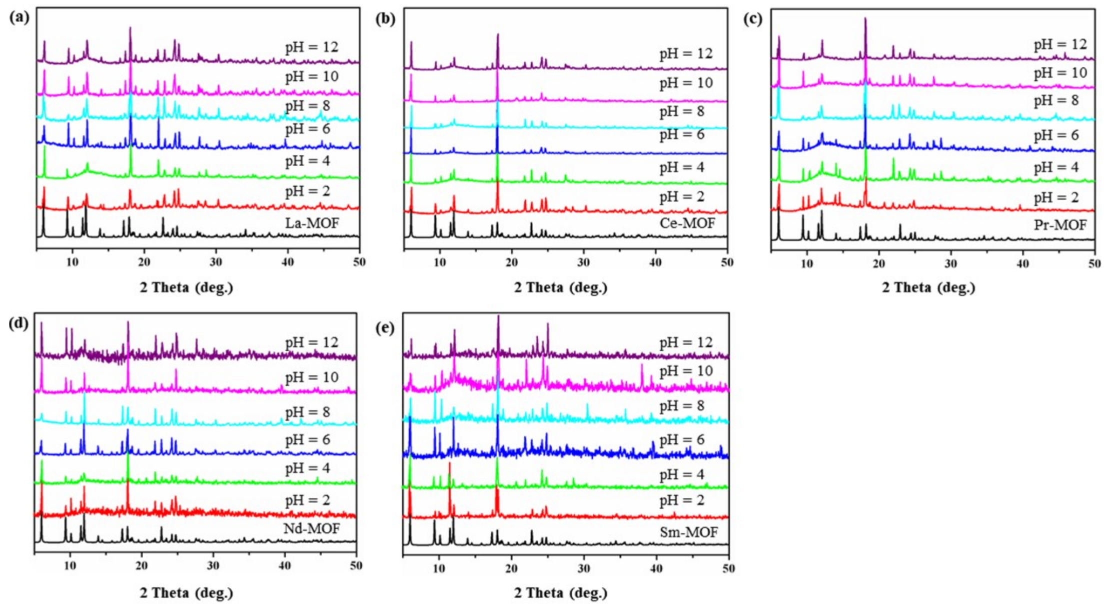


Fig. S3 The PXRD of I-V soaked into aqueous solutions with different pH values.

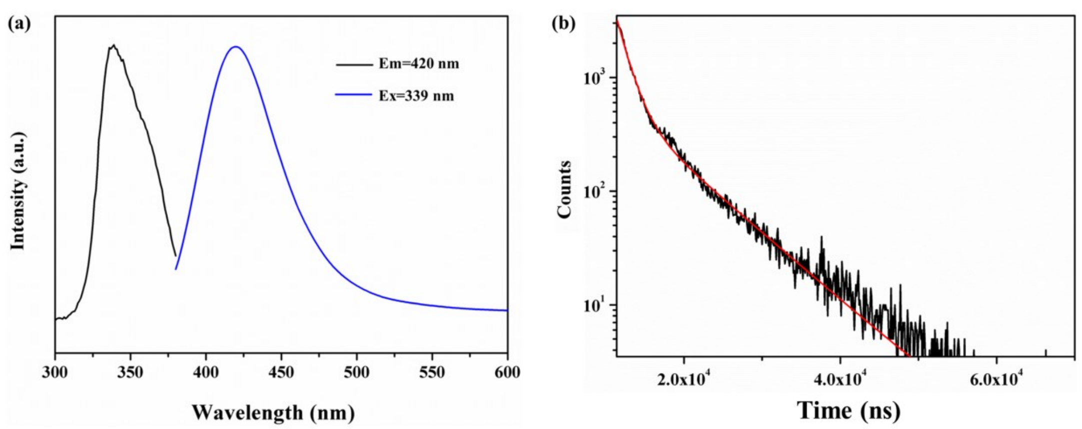
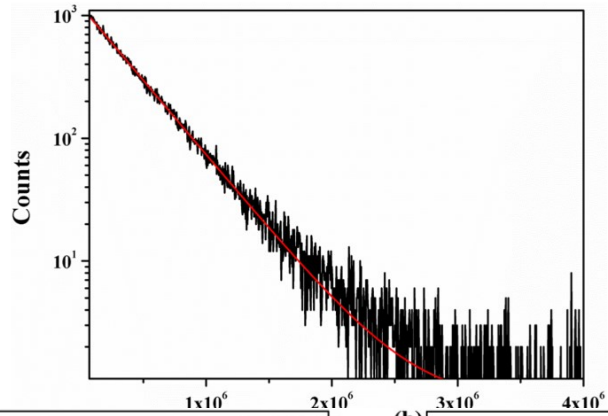


Fig. S4 (a) The excitation spectrum (λ_{em} = 420 nm) (black) and the emission spectra of H_4dpc, (λ_{ex} = 339 nm) (blue) of H_4dpc recorded at 298 K. (b) Luminescence decay of H_4dpc ligand.



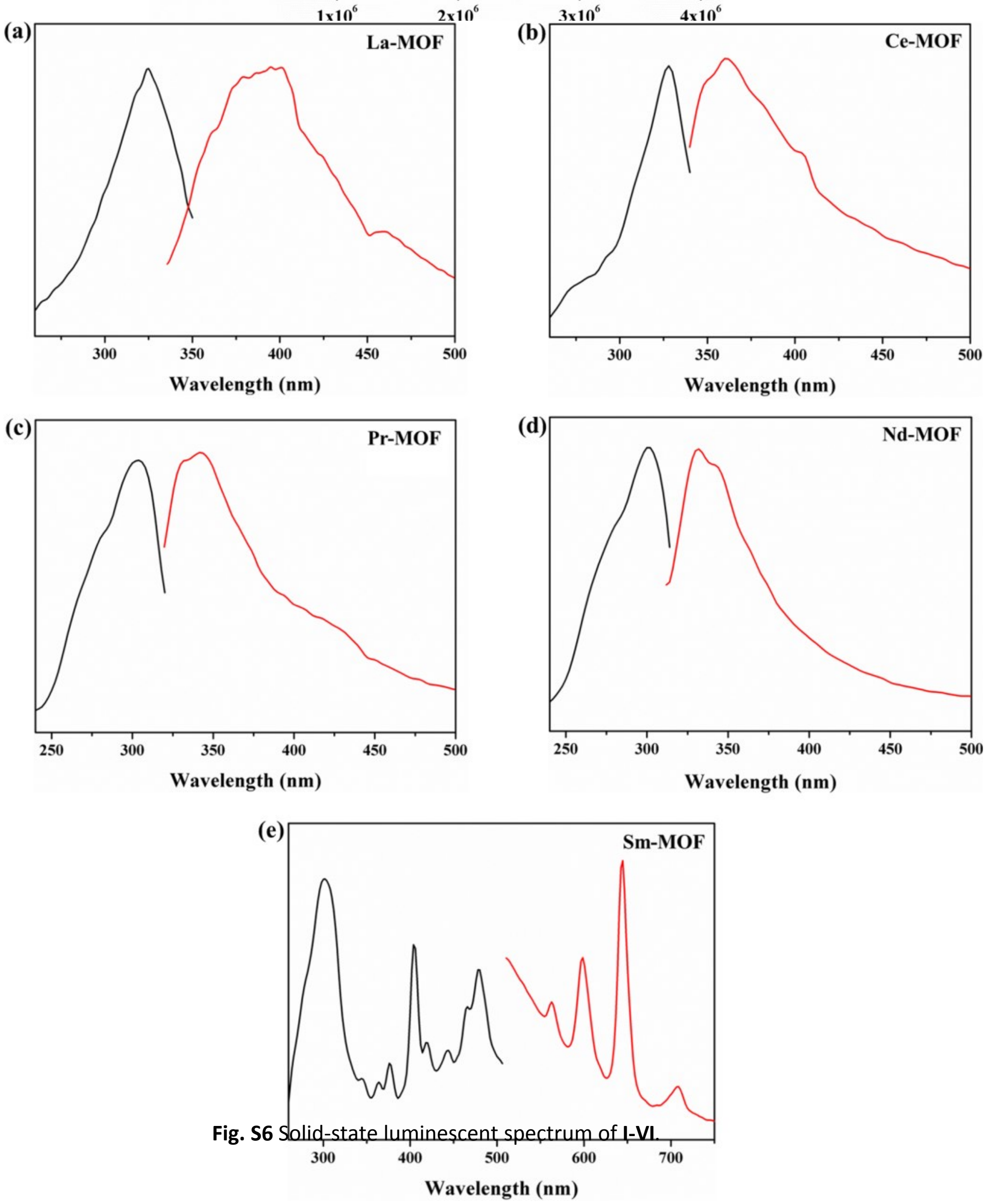


Fig. S6 Solid-state luminescent spectrum of **I-VI**.

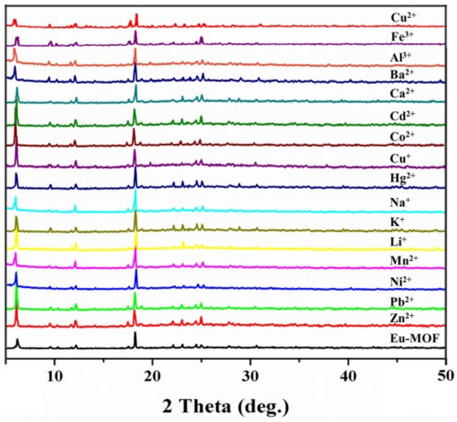


Fig. S7 The PXRD of Eu-MOF: as-synthesized and immersed in differernt cations solution.

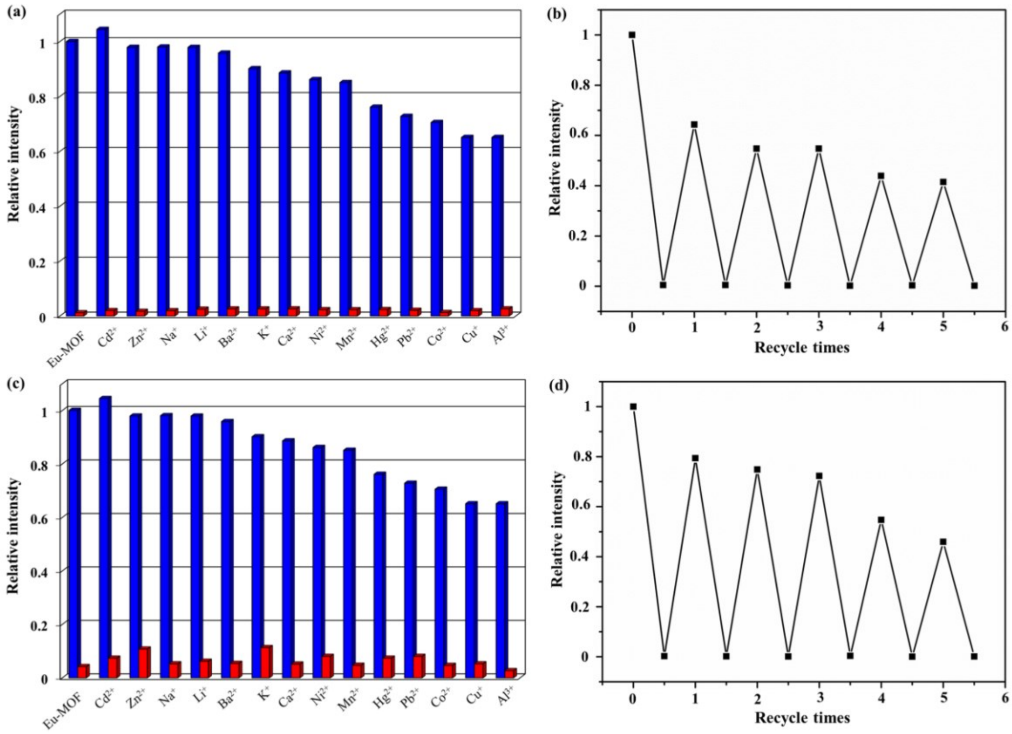


Fig. S8 Comparison of the luminescence intensity ($^5D_0 \rightarrow ^7F_2$) of Eu-MOF in sensing Fe^{3+} (a) and Cu^{2+} (c) with the interference of different cations solvents, red and blue bars represent the before and after the addition of Fe^{3+} (a) and Cu^{2+} (c), respectively. Quenching and recovery tests of Eu-MOF for Fe^{3+} (b) and Cu^{2+} (d) in DMF.

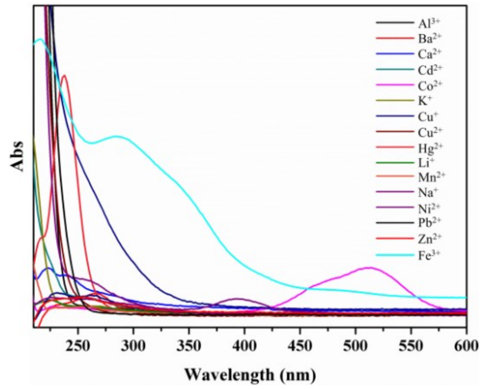


Fig. S9 The UV-vis adsorption spectra of various cations.

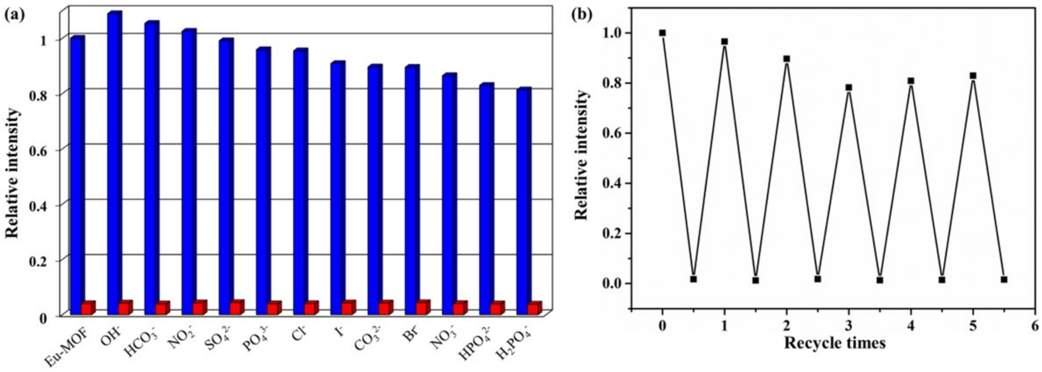


Fig. S10 (a) Comparison of the luminescence intensity ($^5D_0 \rightarrow {}^7F_2$) of Eu-MOF in sensing $Cr_2O_7^{2-}$ with the interference of different anions solvents, red and blue bars represent the before and after the addition of $Cr_2O_7^{2-}$. (b) quenching and recovery tests of Eu-MOF for $Cr_2O_7^{2-}$ in DMF.

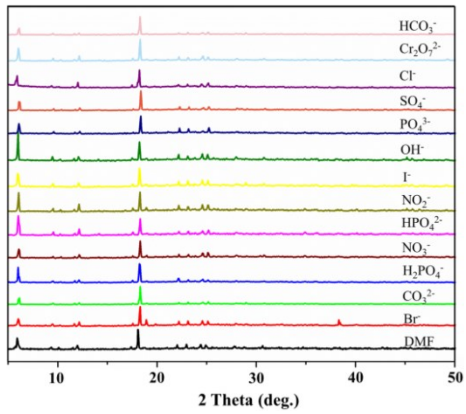


Fig. S11 The PXRD of Eu-MOF: as-synthesized and immersed in differernt anions solution.

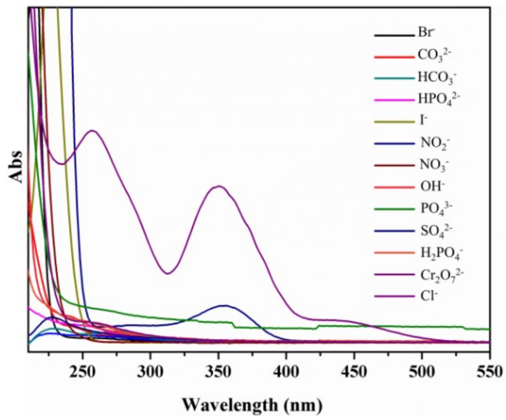


Fig. S12 The UV-vis adsorption spectra of various anions.