Supporting Information

Fluorescent cadmium(II) metal-organic frameworks exhibiting excellent stability and detection ability to Fe^{3+} and MnO_4^- ions

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Table S1. Selected crystallographic data and structure refinement for compounds **NLMOF-1** and **NLMOF-2**

Compound	**NLMOF-1**	**NLMOF-2**
Empirical formula	$C_{162}H_{99}Cd_{4.25}O_{24}$	$C_{108}Cd_2O_{16}KH_{67}$
Formula weight	2879.1499	1884.51
Temperature	190(2)	190(2)
Crystal system	monoclinic	tetragonal
Space group	*C*2/*c*	$P4_32_12$
a (Å)	17.9028(5)	10.0200(5)
b (Å)	38.1443(11)	10.0200(5)
c (Å)	31.7645(9)	88.189(4)
α (°)	90	90
β (°)	98.922(2)	90
γ (°)	90	90
V (Å^3)	21429.2(11)	8854.2(10)
Z	4	4
D(g/cm^3)	0.892	1.414
Mu(mm^{-1})	2.510	3.269
F(0 0 0)	5868.0	3832.0
Unique reflections	17720	7054
Observed reflections	147613	92511
R_{int}	0.1175	0.1873
R_1, wR_2 [$I > 2\sigma(I)$]	R_1 = 0.0878, wR_2 = 0.2326	R_1 = 0.1182, wR_2 = 0.2915
R_1, wR_2 (all data)	R_1 = 0.1537, wR_2 = 0.2632	R_1 = 0.1844, wR_2 = 0.3252
Goodness-of-fit on F^2	1.184	1.168

Table S2. Selected bond lengths (Å) and bond angles (◦) for **NLMOF-1**

NLMOF-1			
Cd3-O(1_2)	1.681(16)	O(2_2)-Cd4-O(4_2)#3	172.5(4)
Cd3-O(3_1)#2	2.295(8)	O(3_2)#2-Cd4-O(4_2)#2	55.1(2)
Cd3-O(3_2)#3	2.448(9)	O(3_2)#3-Cd4-O(4_2)#2	91.9(2)
Cd3-O(7_1)	2.481(9)	O(2_2)#4-Cd4-O(4_2)#2	172.5(4)
Cd4-O(3_2)#2	2.346(5)	O(2_2)-Cd4-O(4_2)#2	86.8(4)
Cd4-O(3_2)#3	2.346(5)	O(4_2)#3-Cd4-O(4_2)#2	85.8(3)
Cd4-O(2_2)#4	2.388(16)	O(3_1)#5-Cd2-O(8_1)#6	97.2(2)
Cd4-O(2_2)	2.388(16)	O(3_1)#5-Cd2-O(2_1)	140.7(2)
Cd4-O(4_2)#3	2.407(6)	O(8_1)#6-Cd2-O(2_1)	93.1(2)
Cd4-O(4_2)#2	2.407(6)	O(3_1)#5-Cd2-O(6_1)#7	94.5(2)
Cd2-O(3_1)#5	2.225(5)	O(8_1)#6-Cd2-O(6_1)#7	147.2(2)
Cd2-O(8_1)#6	2.230(6)	O(2_1)-Cd2-O(6_1)#7	97.0(2)
Cd2-O(2_1)	2.248(6)	O(3_1)#5-Cd2-O(5_1)#7	121.48(19)
Cd2-O(6_1)#7	2.280(5)	O(8_1)#6-Cd2-O(5_1)#7	92.6(2)
Cd2-O(5_1)#7	2.428(6)	O(2_1)#6-Cd2-O(5_1)#7	95.6(2)
Cd2-O(1_1)	2.594(7)	O(6_1)#7-Cd2-O(5_1)#7	55.4(2)
Cd1-O(5_1)#9	2.408(6)	O(3_1)#5-Cd2-O(1_1)	87.1(2)
Cd1-O(5_1)#10	2.408(6)	O(8_1)#6-Cd2-O(1_1)	116.6(2)
Cd1-O(8_1)#11	2.471(7)	O(2_1)-Cd2-O(1_1)	54.7(2)
Cd1-O(8_1)#7	2.471(7)	O(6_1)-Cd2-O(1_1)	94.5(2)
Cd1-O(4_1)#12	2.481(7)	O(5_1)#7-Cd2-O(1_1)	137.1(2)
Cd1-O(4_1)	2.481(7)	O(5_1)#9-Cd1-O(5_1)#10	165.3(4)
O(1_2)-Cd3-O(3_1)#2	152.1(9)	O(5_1)#9-Cd1-O(8_1)#11	103.8(2)
O(1_2)-Cd3-O(3_2)#3	104.5(6)	O(5_1)#10-Cd1-O(8_1)#11	87.4(2)
O(3_1)#2-Cd3-O(3_2)#3	83.0(3)	O(5_1)#9-Cd1-O(8_1)#7	87.4(2)
O(1_2)-Cd3-O(7_1)	105.2(6)	O(5_1)#10-Cd1-O(8_1)#7	103.8(2)
O(3_1)#2-Cd3-O(7_1)	81.7(3)	O(8_1)#11-Cd1-O(8_1)#7	81.3(3)
O(3_2)#3-Cd3-O(7_1)	142.0(6)	O(5_1)#9-Cd1-O(4_1)#12	92.1(2)
O(3_2)#2-Cd4-O(3_2)#3	136.8(3)	O(5_1)#10-Cd1-O(4_1)#12	80.4(2)
O(3_2)#2-Cd4-O(2_2)#4	124.1(5)	O(8_1)#11-Cd1-O(4_1)#12	79.8(2)
O(3_2)#3-Cd4-O(2_2)#4	84.8(4)	O(8_1)#7-Cd1-O(4_1)#12	160.4(3)
O(3_2)#2-Cd4-O(2_2)	84.8(4)	O(5_1)#9-Cd1-O(4_1)	80.4(2)
O(3_2)#2-Cd4-O(2_2)	124.1(5)	O(5_1)#10-Cd1-O(4_1)	92.1(2)
O(2_2)#-Cd4-O(2_2)	100.6(8)	O(8_1)#11-Cd1-O(4_1)	160.4(3)
O(3_2)#2-Cd4-O(4_2)#3	91.9(2)	O(8_1)#7-Cd1-O(4_1)	79.8(2)
O(3_2)#3-Cd4-O(4_2)#3	55.1(2)	O(4_1)#12-Cd1-O(4_1)	119.5(3)
O(2_2)#4-Cd4-O(4_2)#3	86.8(4)		

#2 -1/2+X,-1/2+Y,+Z #3 1/2-X,-1/2+Y,1/2-Z #4 -X,+Y,1/2-Z #5 +X,2-Y,1/2+Z #6 1/2+X,3/2-Y,1/2+Z #7 1/2+X,1/2+Y,+Z #9 1/2+X,3/2-Y,-1/2+Z #10 3/2-X,3/2-Y,1-Z #11 3/2-X,1/2+Y,1/2-Z #12 2-X,+Y,1/2-Z

Table S3. Selected bond lengths(Å) and bond angles(°) for **NLMOF-2**

NLMOF-2			
K(1)-O(1)	2.882(17)	O(1)#3-K(I)-O(5)#7	127.0(4)
K(1)-O(4)	3.23(2)	O(4)-K(I)-O(4)#5	66.5(8)
K(1)-O(4)#3	3.23(2)	O(5)#7-K(I)-O(4)#5	47.2(4)
K(1)-O(5)#4	3.14(2)	O(5)#6-K(I)-O(4)#5	71.0(5)
K(1)-O(5)#5	3.14(2)	O(5)#6-K(I)-O(4)	47.2(4)
K(1)-O(7)#6	2.70(2)	O(5)#7-K(I)-O(4)	71.0(5)
K(1)-O(7)#7	2.70(2)	O(5)#6-K(I)-O(5)#7	106.1(7)
Cd(1_1)#2-O(1)	2.375(16)	O(7)#10-K(I)-O(1)#4	68.3(5)
Cd(1_1)#2-O(2)	2.381(17)	O(7)#11-K(I)-O(1)#3	68.3(5)
Cd(1_1)#5-O(3)	2.21(2)	O(7)#10-K(I)-O(1)#3	87.3(6)
Cd(1_1)-O(6)	2.165(17)	O(7)#11-K(I)-O(1)#4	87.3(6)
Cd(1_1)#10-O(7)	2.325(19)	O(7)#10-K(I)-O(4)	130.2(5)
Cd(1_1)#10-O(8)	2.36(2)	O(7)#10-K(I)-O(4)#5	126.5(6)
O(1)#3-K(I)-O(1)#4	147.4(8)	O(7)#11-K(I)-O(4)	126.5(6)
O(1)#3-K(I)-O(4)	73.6(5)	O(7)#11-K(I)-O(4)#5	130.2(5)
O(1)#4-K(I)-O(4)#5	73.6(5)	O(7)#11-K(I)-O(5)#7	161.8(6)
O(1)#3-K(I)-O(4)#5	138.8(6)	O(7)#11-K(I)-O(5)#6	86.7(5)
O(1)#4-K(I)-O(4)	138.8(6)	O(7)#10-K(I)-O(5)#6	161.8(6)
O(1)#3-K(I)-O(5)#6	74.7(5)	O(7)#10-K(I)-O(5)#7	86.7(5)
O(1)#4-K(I)-O(5)#7	74.7(5)	O(7)#11-K(I)-O(7)#10	84.3(9)
O(1)#4-K(I)-O(5)#6	127.0(4)		
#3 -1+Y,1+X,-Z #4 -1/2-X,1/2+Y,-1/4-Z #5 -1/2+Y,1/2-X,1/4+Z #6 +Y,1+X,-Z; #7 +X,1+Y,+Z			

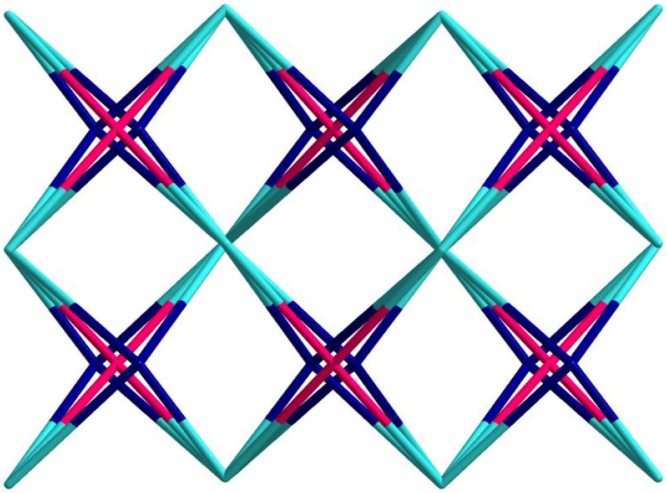

Fig. S1 Topology graph of **NLMOF-1**

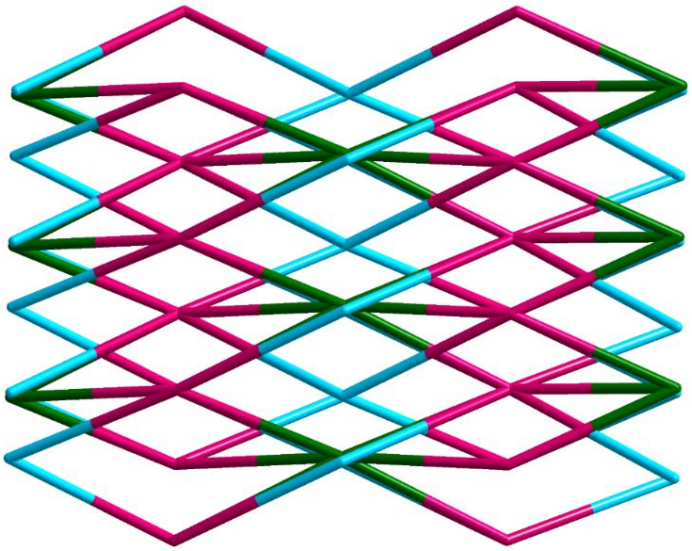

Fig. S2 Topology graph of **NLMOF-2**

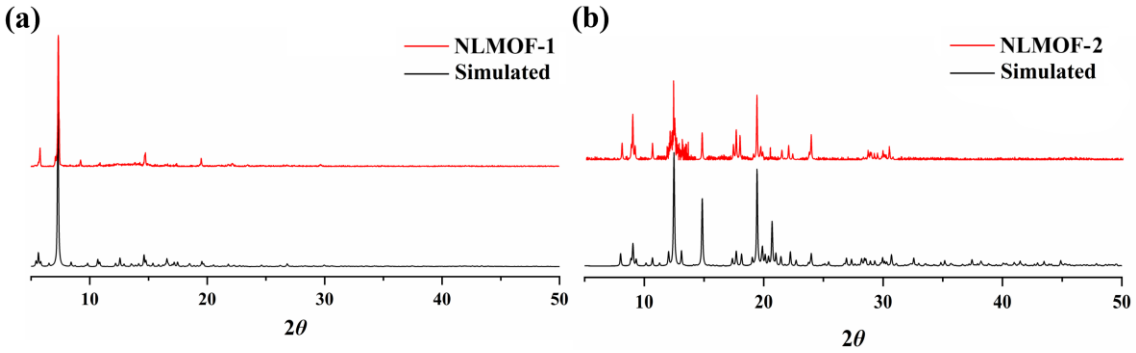

Fig. S3 Powder X-ray diffraction pattern of **NLMOF-1** and **NLMOF-2**

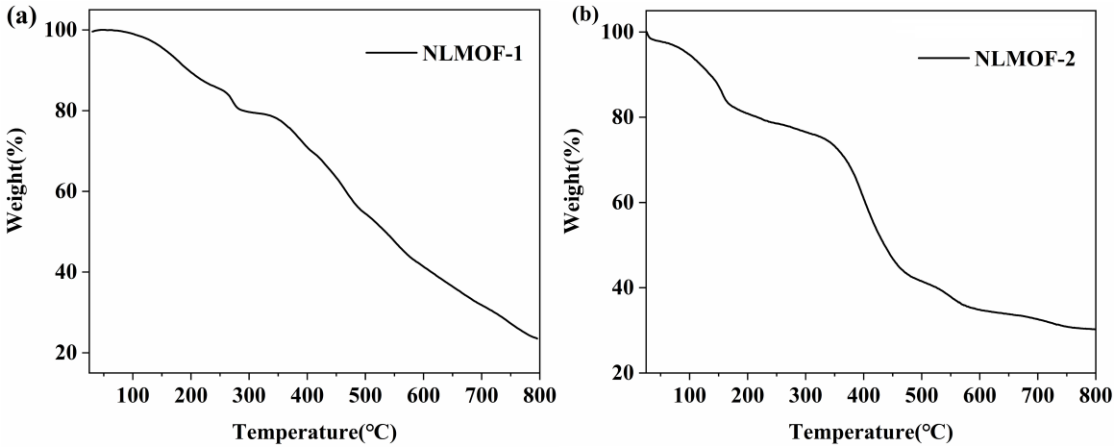

Fig. S4 (a) TG curve of **NLMOF-1**; (b) TG curve of **NLMOF-2**

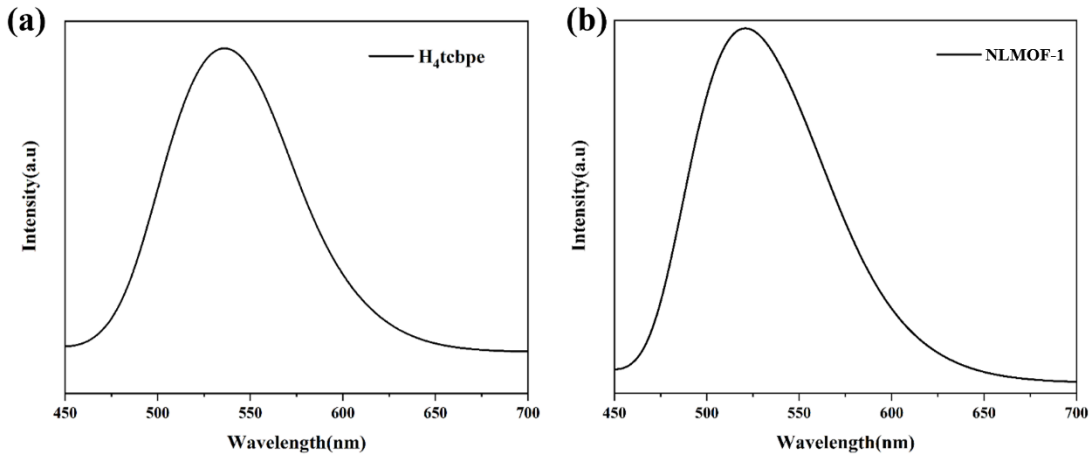

Fig. S5 The solid state flurescence spectrum of H_4tcbpe ligand (a) and **NLMOF-1** (b)

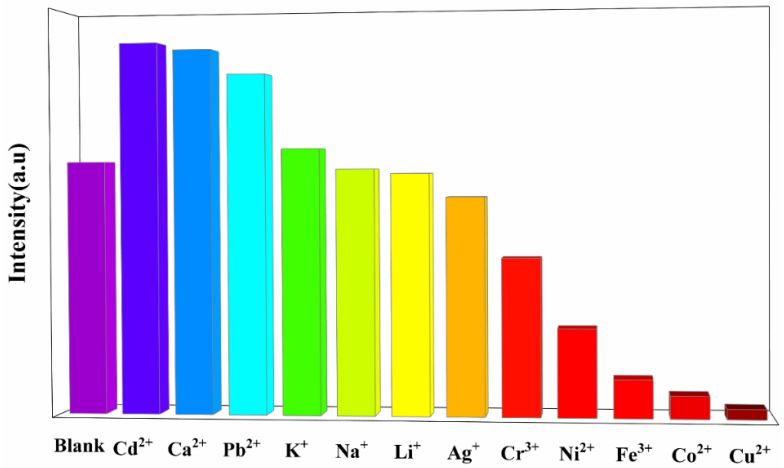

Fig. S6 Emission spectra of **NLMOF-1** in 10mM different cations at 430 nm in H_2O

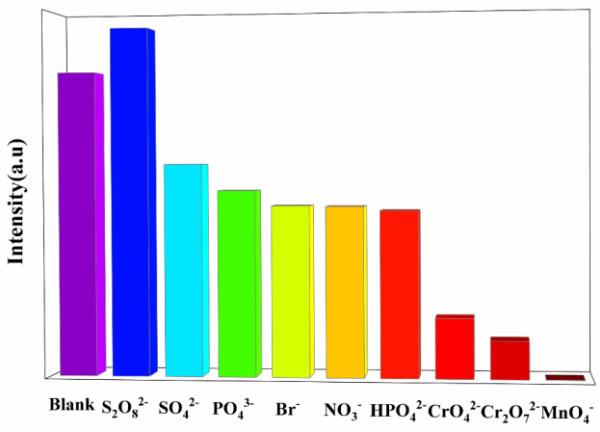

Fig. S7 Emission spectra of **NLMOF-1** in 10mM different anions at 430 nm in H_2O

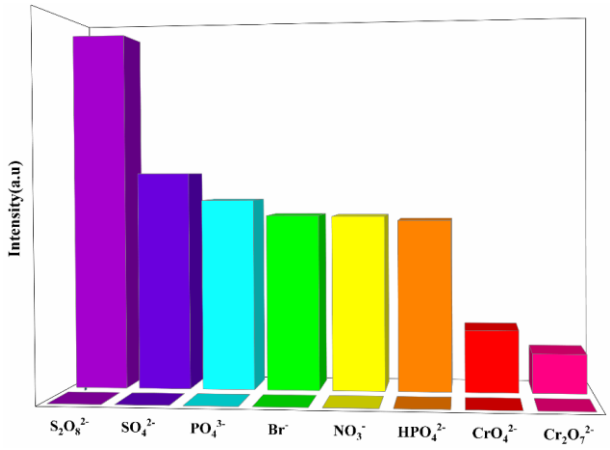

Fig. S8 Fluorescence intensity of **NLMOF-1** when MnO_4^- coexists with other anions in H_2O

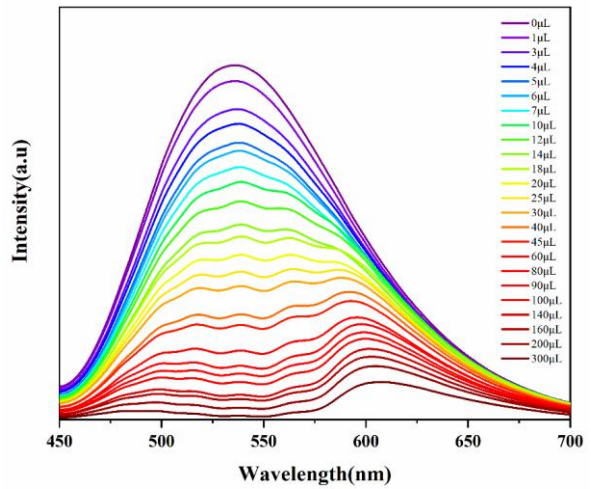

Fig. S9 Emission spectra of **NLMOF-1** dispersed in H_2O with different concentrations of MnO_4^-

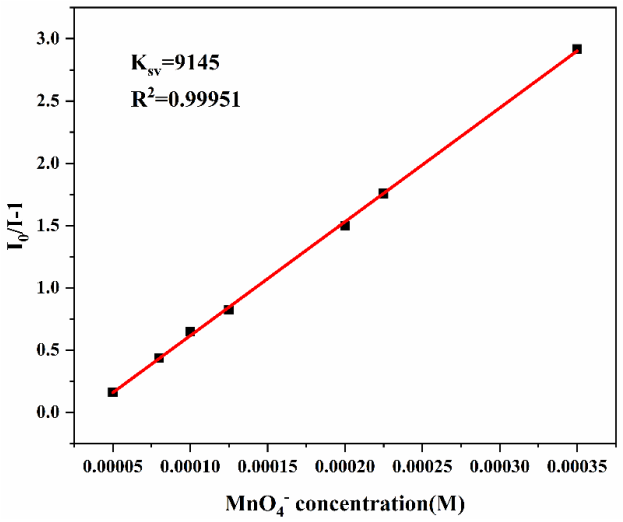

Fig. S10 Stern-Volmer plot of different concentrations of MnO_4^- exist in H_2O of **NLMOF-1**

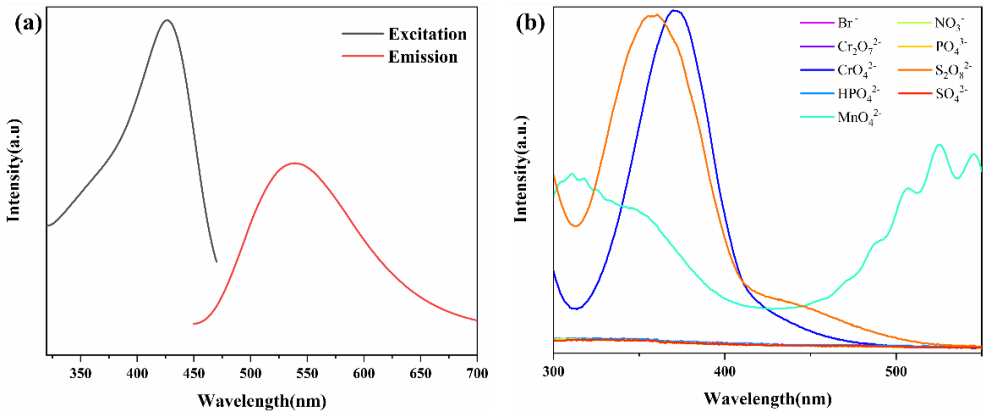

Fig. S11 (a) Excitation spectra of **NLMOF-1** in aqueous solution; (b) UV-vis adsorption spectra of $Na_x(A)$ in aqueous solution

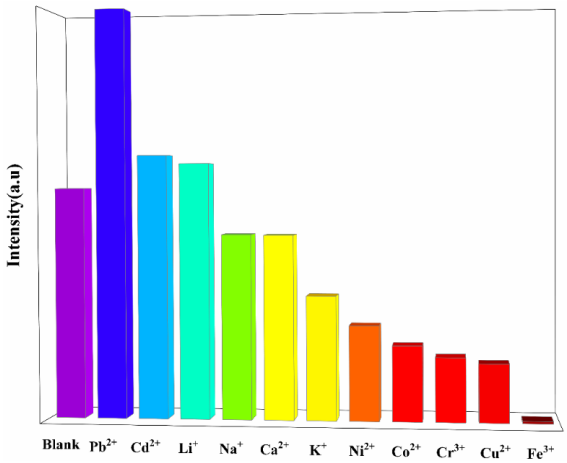

Fig. S12 Emission spectra of **NLMOF-1** in 10mM different cations at 430 nm in DMF

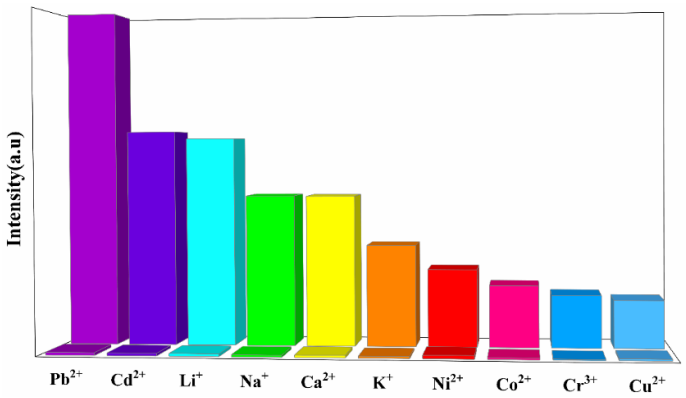

Fig. S13 Fluorescence intensity of **NLMOF-1** when Fe^{3+} coexists with other cations in DMF

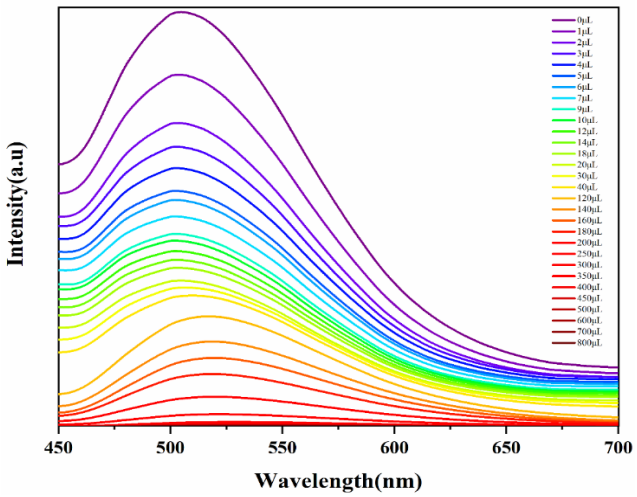

Fig. S14 Emission spectra of **NLMOF-1** dispersed in DMF with different concentrations of Fe^{3+}

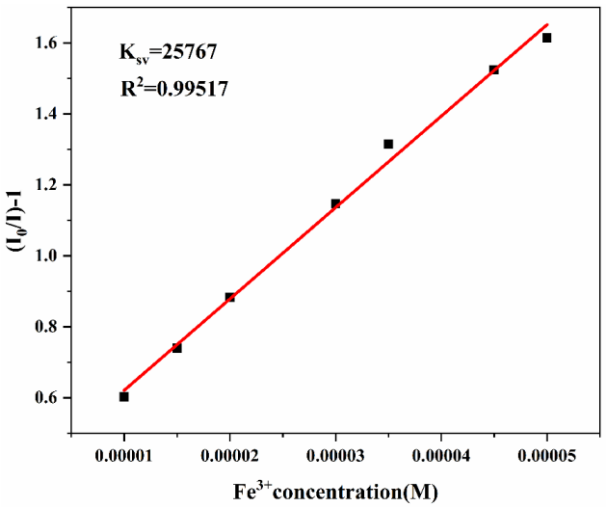

Fig. S15 Stern-Volmer plot of different concentrations of Fe^{3+} exist in **NLMOF-1**

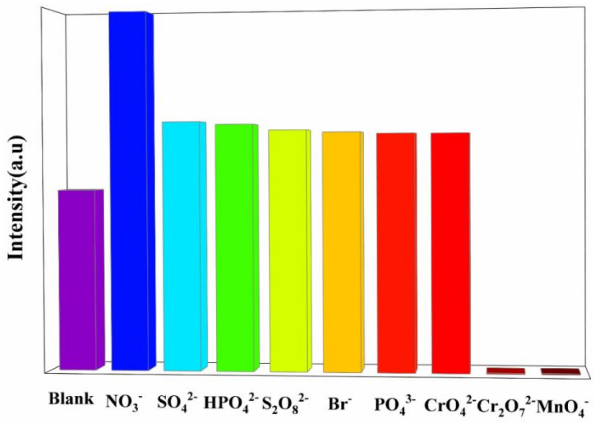

Fig. S16 Emission spectra of **NLMOF-1** in 10mM different anions at 430 nm in DMF

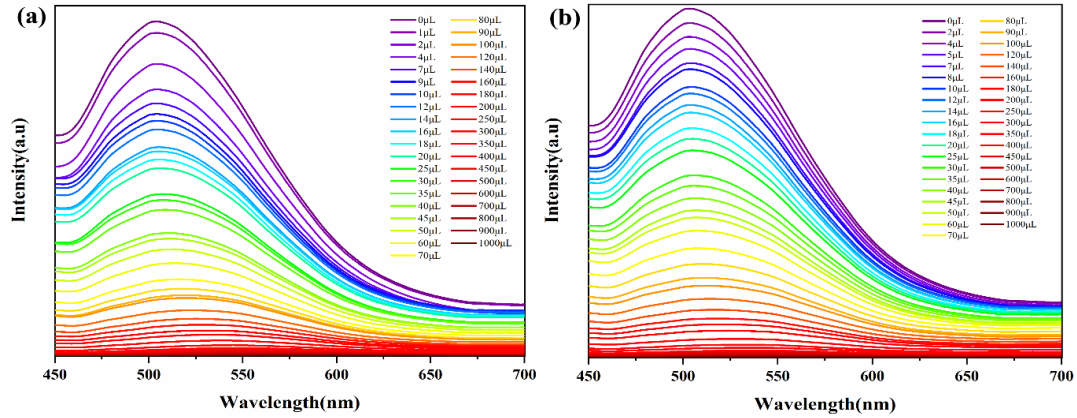

Fig. S17 (a) Emission spectra of **NLMOF-1** dispersed in DMF with different concentrations of $Cr_2O_7^{2-}$; (b) Emission spectra of **NLMOF-1** dispersed in DMF with different concentrations of MnO_4^-

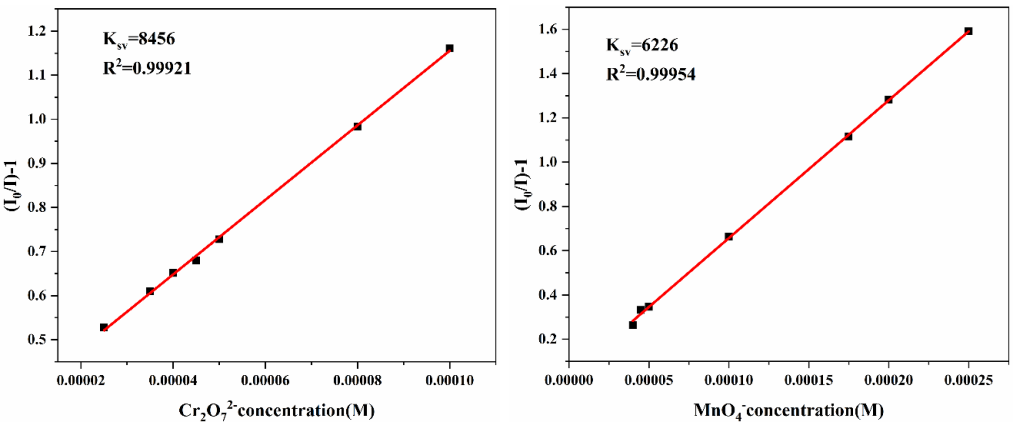

Fig. S18 (a) Stern-Volmer plot of different concentrations of $Cr_2O_7^{2-}$ exist of **NLMOF-1** in DMF; (b) Stern-Volmer plot of different concentrations of MnO_4^- exist of **NLMOF-1** in DMF

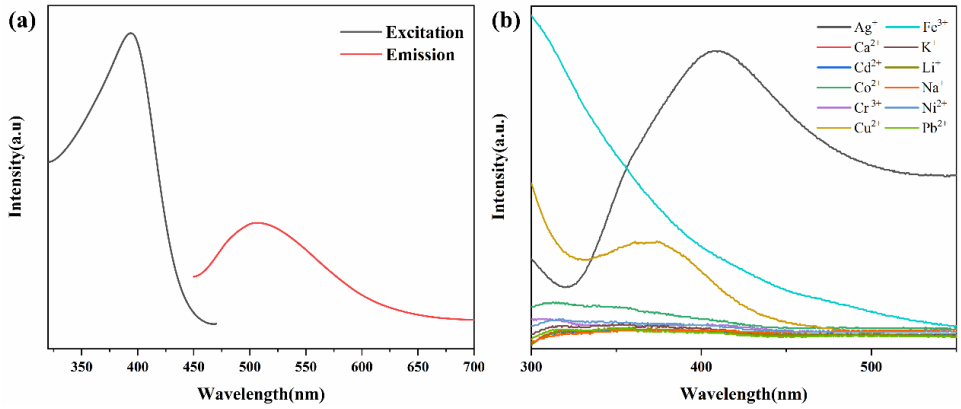

Fig. S19 (a) Excitation spectra of **NLMOF-1** in DMF solution; (b) UV-vis adsorption spectra of $M(NO_3)_x$ in DMF solution

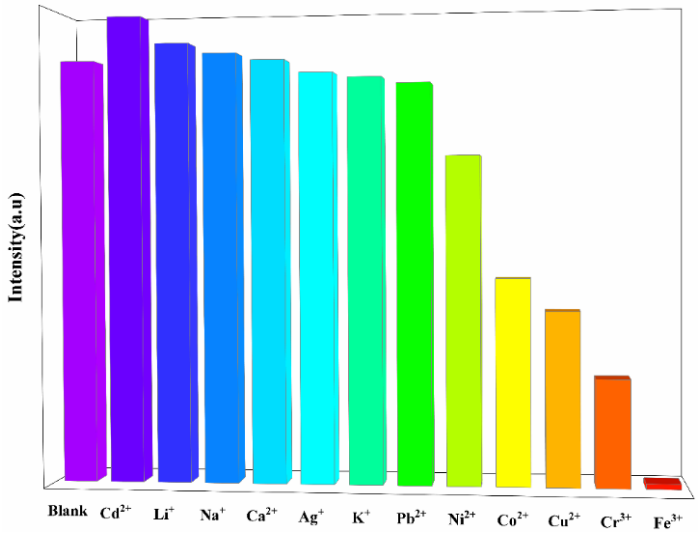

Fig. S20 Emission spectra of **NLMOF-1** in 10mM different cations at 430 nm in acetonitrile

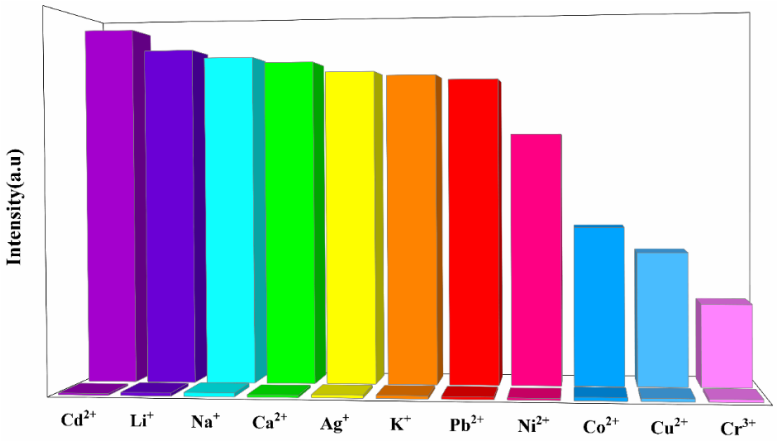

Fig. S21 Fluorescence intensity of **NLMOF-1** when Fe^{3+} coexists with other cations in acetonitrile

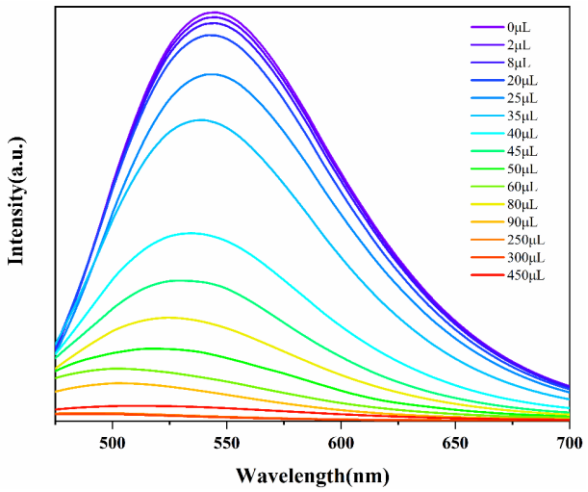

Fig. S22 Emission spectra of **NLMOF-1** dispersed in acetonitrile with different concentrations of Fe^{3+}

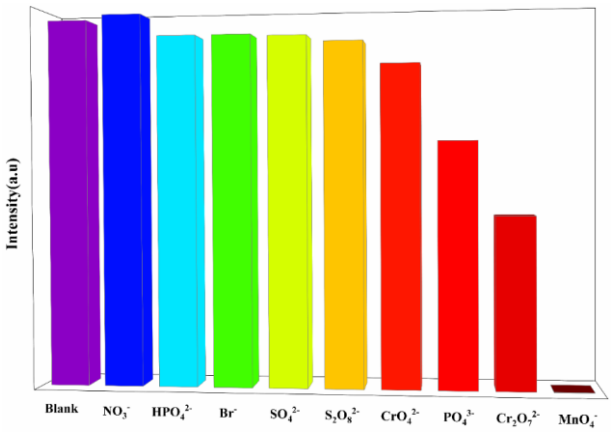

Fig. S23 Emission spectra of **NLMOF-1** in 10mM different anions at 430 nm in acetonitrile

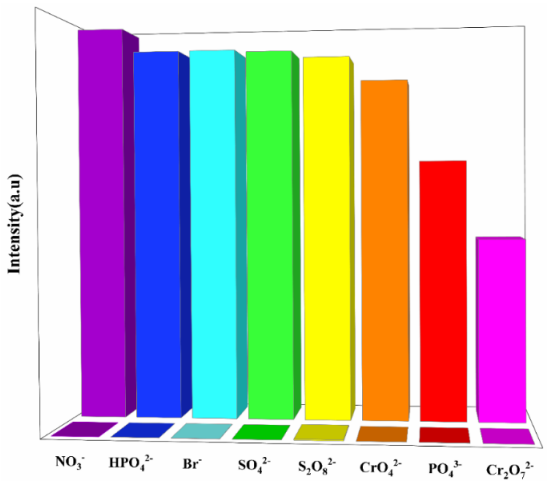

Fig. S24 Fluorescence intensity of **NLMOF-1** when MnO_4^- coexists with other anions in acetonitrile

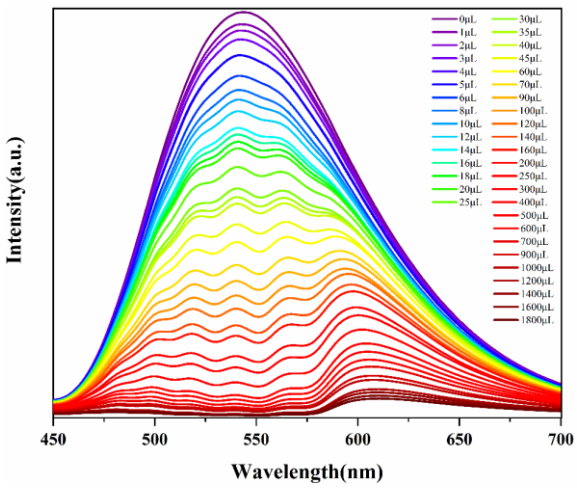

Fig. S25 Emission spectra of **NLMOF-1** dispersed in acetonitrile with different concentrations of MnO_4^-

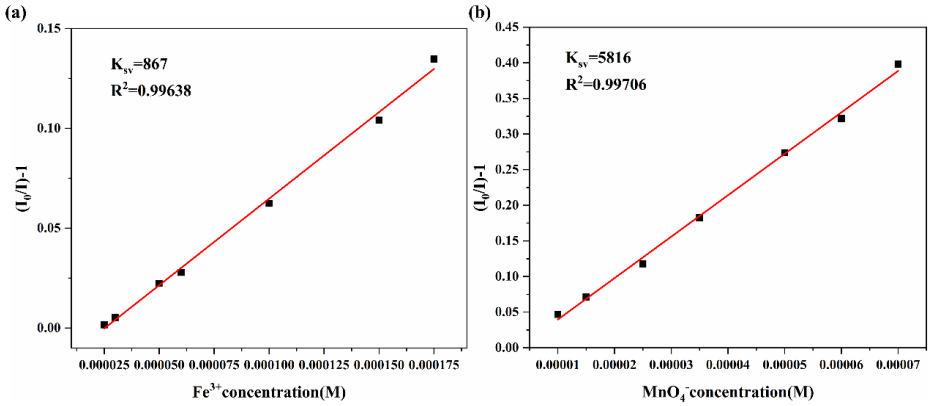

Fig. S26 (a) Stern-Volmer plot of different concentrations of Fe^{3+} exist of **NLMOF-1** in acetonitrile; (b) Stern-Volmer plot of different concentrations of MnO_4^- exist of **NLMOF-1** in acetonitrile

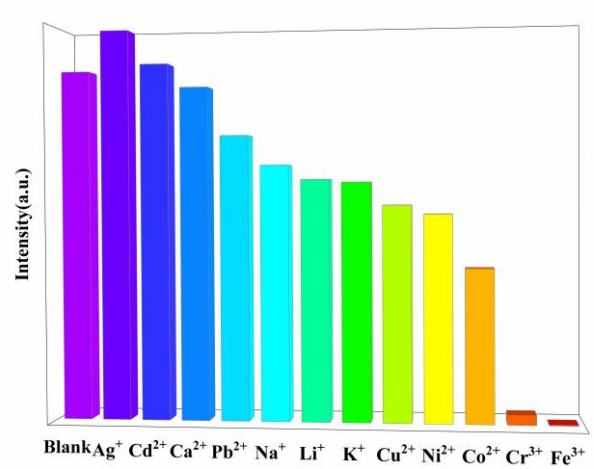

Fig. S27 Emission spectra of **NLMOF-1** in 10mM different cations at 430 nm in methanol

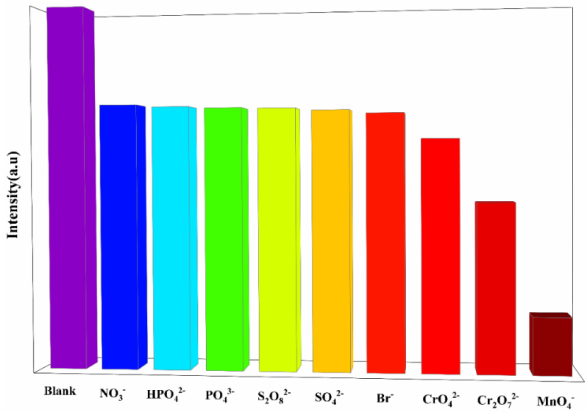

Fig. S28 Emission spectra of **NLMOF-1** in 10mM different anions at 430 nm in methanol

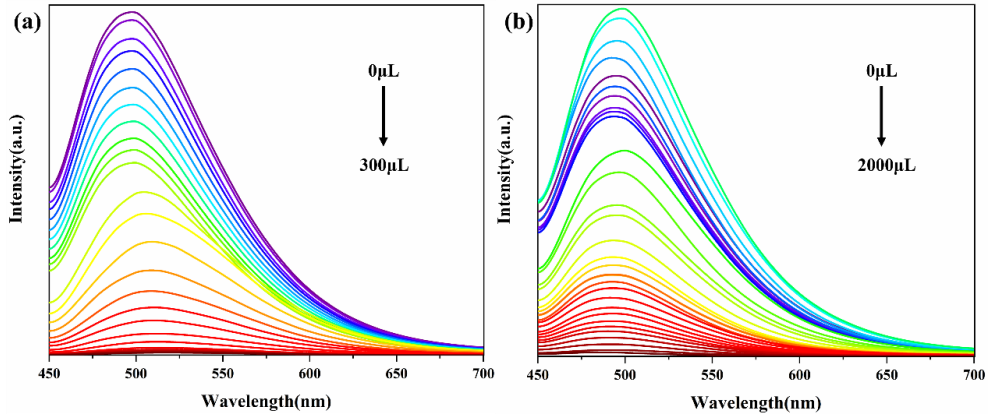

Fig. S29 (a) Emission spectra of **NLMOF-1** dispersed in methanol with different concentrations of Fe^{3+}; (b) Emission spectra of **NLMOF-1** dispersed in methanol with different concentrations of Cr^{3+}

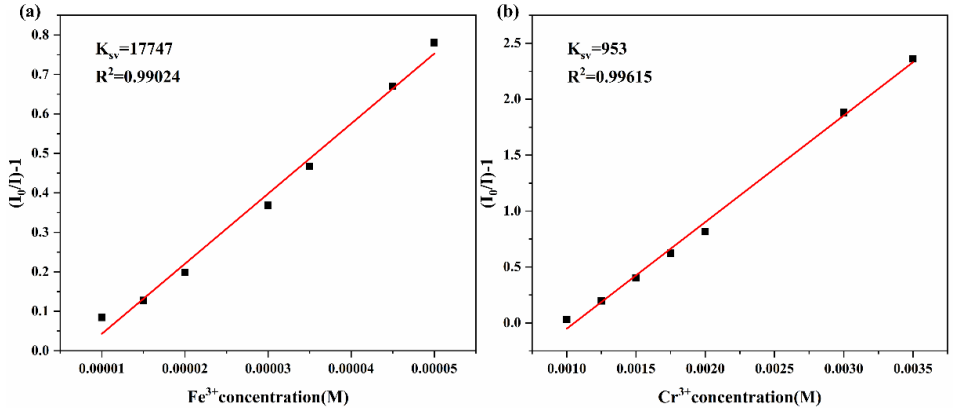

Fig. S30 (a) Stern-Volmer plot of different concentrations of Fe^{3+} exist of **NLMOF-1** in methanol; (b) Stern-Volmer plot of different concentrations of Cr^{3+} exist of **NLMOF-1** in methanol

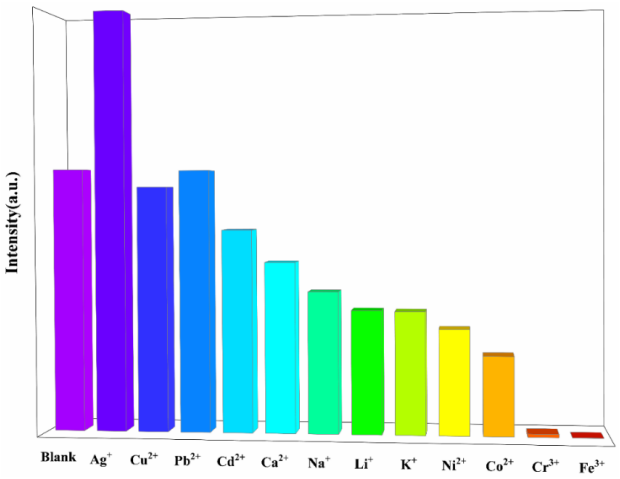

Fig. S31 Emission spectra of **NLMOF-1** in 10mM different cations at 430 nm in ethanol

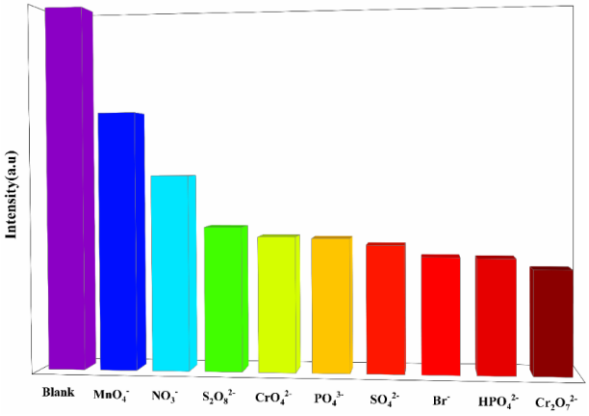

Fig. S32 Emission spectra of **NLMOF-1** in 10mM different anions at 430 nm in ethanol

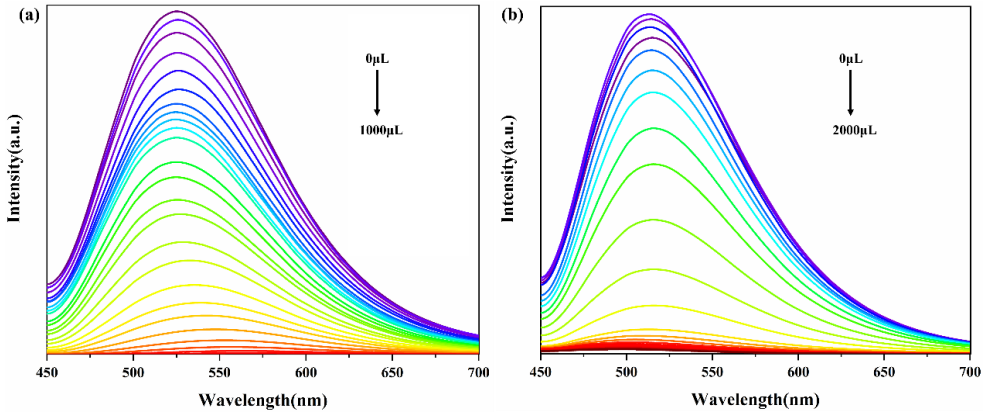

Fig. S33 (a) Emission spectra of **NLMOF-1** dispersed in ethanol with different concentrations of Fe^{3+}; (b) Emission spectra of **NLMOF-1** dispersed in ethanol with different concentrations of Cr^{3+}

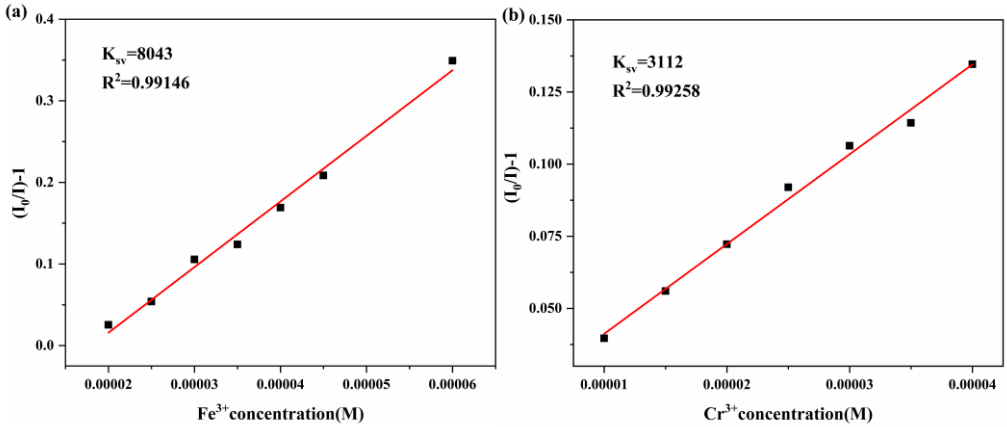

Fig. S34 (a) Stern-Volmer plot of different concentrations of Fe^{3+} exist of **NLMOF-1** in ethanol; (b) Stern-Volmer plot of different concentrations of Cr^{3+} exist of **NLMOF-1** in ethanol

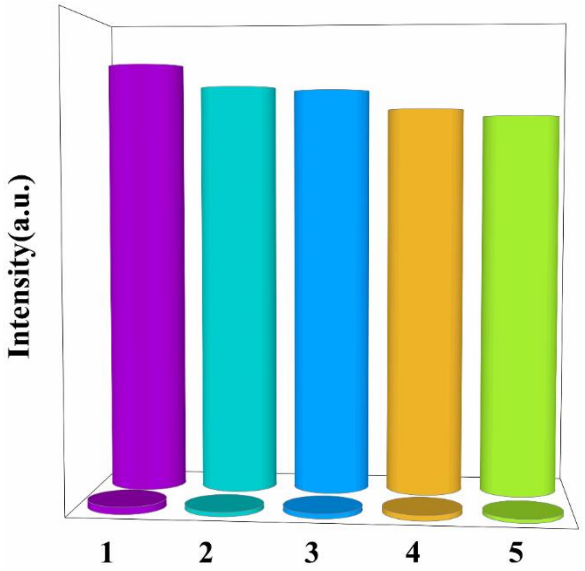

Fig. S35 The recyclability of the quenching ability of **NLMOF-1** immersed in DMA and in the presence of 0.01 M aqueous solution of Fe^{3+} ions

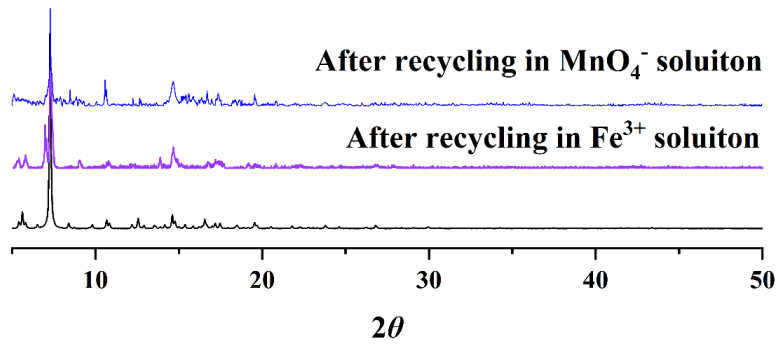

Fig. S36 The PXRD patterns of **NLMOF-1** treated with Fe^{3+} and MnO_4^- solution in DMA

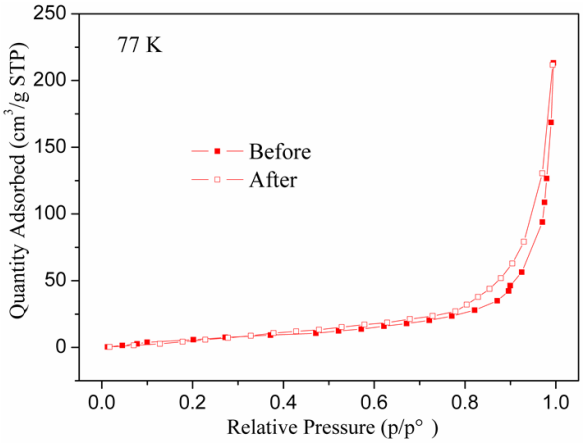

Fig. S37 N_2 adsorption of **NLMOF-1** before and after sensing experiments.

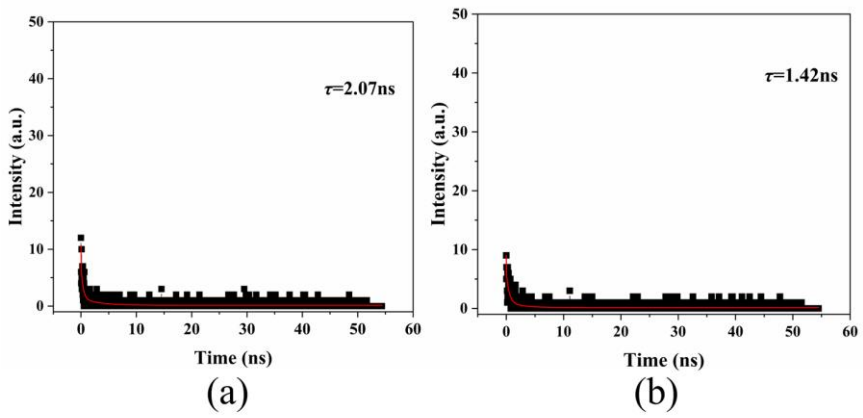

Fig. S38 Fluorescence lifetimes of (a) **NLMOF-1** and (b) **NLMOF-1@**Fe^{3+}(20μL, 0.01mol/L).