Supporting Information

Four new metal-organic frameworks based on diverse secondary building units: sensing properties and magnetic properties

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Table S1 Selected bond lengths (Å) and bond angles (°) for **1-2**

Complex **1**			
Zn(1)-O(1)	2.000(3)	Zn(1)-O(5)	1.933(4)
Zn(1)-O(2)#1	2.122(4)	Zn(2)-O(1)#1	2.094(5)
Zn(1)-O(4)#2	1.959(3)	Zn(2)-O(8)	2.055(5)
Zn(1)-O(7)	2.40(3)	Zn(2)-O(2)	2.165(3)
Zn(2)-O(2)#3	2.165(3)	Zn(2)-O(9)#3	2.075(4)
Zn(2)-O(9)	2.075(4)	O(1)-Zn(1)#4	2.000(3)
O(1)-Zn(2)#1	2.094(5)	O(1)-Zn(1A)	1.998(10)
O(1)-Zn(1A)#4	1.998(10)	O(2)-Zn(1)#1	2.122(4)
O(1)-Zn(1)-O(7)	84.1(6)	O(2)#1-Zn(1)-O(7)	163.8(7)
O(4)#2-Zn(1)-O(1)	111.56(14)	O(4)#2-Zn(1)-O(2)#1	95.94(15)
O(4)#2-Zn(1)-O(7)	82.8(4)	O(5)-Zn(1)-O(1)	131.76(15)
O(5)-Zn(1)-O(2)#1	99.56(18)	O(5)-Zn(1)-O(4)#2	116.23(15)

O(5)-Zn(1)-O(7)	95.4(6)	O(1)#1-Zn(2)-O(2)#3	78.29(13)
O(1)#1-Zn(2)-O(2)	78.29(13)	O(2)#3-Zn(2)-O(2)	90.35(19)
O(9)-Zn(2)-O(2)#3	171.52(16)	O(8)-Zn(2)-O(1)#1	166.4(2)

Symmetrical codes: #1 -x+1, -y+1, -z+1; #2 –x+1/2, y-1/2, z-1/2; #3 x, -y+3/2, z; #4 x, -y+1/2, z; #5 –x+1/2, y+1/2, z+1/2.

Complex **2**

Zn(1)-O(1)	1.934(4)	Zn(2)-O(4)#4	2.037(4)
Zn(1)-O(5)#1	1.927(4)	Zn(2)-O(9)#4	2.035(5)
Zn(1)-O(6)#2	2.038(4)	Zn(2)-O(10)	2.041(4)
Zn(1)-O(7)#3	1.982(4)	Zn(2)-O(11)	1.958(5)
Zn(2)-O(3)	2.042(4)	O(4)-Zn(2)#4	2.037(4)
O(5)-Zn(1)#5	1.927(4)	O(6)-Zn(1)#2	2.038(4)
O(7)-Zn(1)#6	1.982(4)	O(9)-Zn(2)#4	2.035(5)
O(1)-Zn(1)-O(6)#2	99.92(18)	O(1)-Zn(1)-O(7)#3	107.08(19)
O(1)-Zn(1)-C(23)#3	104.6(2)	O(5)#1-Zn(1)-O(1)	123.52(18)
O(5)#1-Zn(1)-O(6)#2	100.06(17)	O(5)#1-Zn(1)-O(7)#3	121.22(18)
O(7)#3-Zn(1)-O(6)#2	98.49(18)	O(4)#4-Zn(2)-O(3)	157.9(2)
O(4)#4-Zn(2)-O(10)	89.29(19)	O(9)#4-Zn(2)-O(3)	87.8(2)
O(9)#4-Zn(2)-O(4)#4	86.8(2)	O(10)-Zn(2)-O(3)	87.8(2)
O(9)#4-Zn(2)-O(10)	158.3(2)	O(11)-Zn(2)-O(3)	100.3(2)
O(11)-Zn(2)-O(4)#4	101.9(2)	O(11)-Zn(2)-O(9)#4	101.0(3)

Symmetrical codes: #1 x+1, y, z; #2 –x+2, -y+2, -z; #3 x+1, y, z-1; #4 –x+2, -y+1, -z+1; #5 x-1, y, z; #6 x-1, y, z+1.

Complex **3**

Co(1A)-O(1)#1	1.928(7)	Co(1A)-O(16)	2.17(4)

Co(1A)-O(1)	1.929(7)	Co(1)-O(16A)#1	2.04(3)
Co(1A)-O(2)	2.086(6)	Co(1)-O(16A)	2.04(3)
Co(1A)-O(2)#1	2.086(6)	Co(4)-O(5)#2	2.044(6)
Co(1)-O(1)	2.254(9)	Co(4)-O(5)	2.044(6)
Co(1)-O(1)#1	2.254(9)	Co(4)-O(6)	2.172(6)
Co(1)-O(2)#1	2.172(7)	Co(4)-O(6)#2	2.172(6)
Co(1)-O(2)	2.173(7)	Co(4)-O(8)#3	2.063(6)
Co(4)-O(8)#4	2.063(6)	Co(3)-O(3)#5	2.036(5)
Co(3)-O(6)#6	2.209(6)	Co(3)-O(7)#3	2.015(6)
Co(3)-O(9)	1.997(6)	Co(3)-O(10)	2.131(8)
Co(3)-O(11)	2.148(10)	Co(2)-O(12)	2.033(6)
Co(2)-O(12)#7	2.033(6)	Co(2)-O(13)#7	2.162(6)
Co(2)-O(13)	2.162(6)	Co(2)-O(14)#7	2.097(7)
Co(2)-O(14)	2.097(7)	O(6)-Co(3)#4	2.209(6)
O(3)-Co(3)#5	2.036(5)	O(7)-Co(3)#3	2.015(6)
O(8)-Co(4)#6	2.063(6)	O(1)#1-Co(1A)-O(1)	167.4(8)
O(1)#1-Co(1A)-O(2)#1	66.0(3)	O(1)-Co(1A)-O(2)#1	116.0(3)
O(1)#1-Co(1A)-O(2)	116.0(3)	O(1)-Co(1A)-O(2)	66.0(3)
O(1)-Co(1A)-O(16)	83.7(4)	O(2)-Co(1A)-O(16)	98.2(4)
O(2)-Co(1A)-O(2)#1	163.6(7)	O(1)#1-Co(1)-O(1)	116.6(6)
O(2)-Co(1)-O(1)	59.3(3)	O(2)#1-Co(1)-O(1)#1	59.3(3)
O(2)-Co(1)-O(1)#1	100.6(4)	O(16A)-Co(1)-O(1)	80.2(8)
O(2)#1-Co(1)-O(2)	143.8(7)	O(16A)-Co(1)-O(1)#1	159.6(7)
O(16A)#1-Co(1)-O(2)	108.2(8)	O(16A)-Co(1)-O(2)#1	108.2(8)

O(16A)#1-Co(1)-O(2)#1	98.1(7)	O(16A)-Co(1)-O(16A)#1	86.4(16)
O(16A)-Co(1)-O(2)	98.1(7)	O(5)-Co(4)-O(6)	85.6(2)
O(5)#2-Co(4)-O(5)	180.0	O(5)#2-Co(4)-O(6)#2	85.6(2)
O(5)-Co(4)-O(6)#2	94.4(2)	O(5)#2-Co(4)-O(6)	94.4(2)

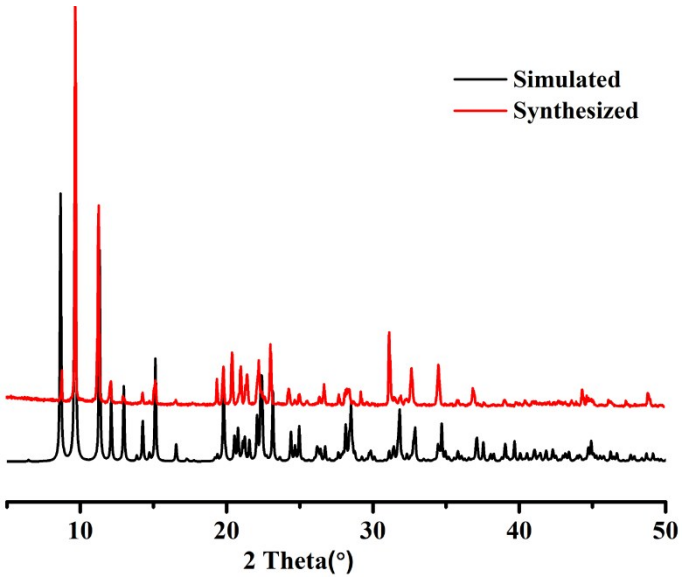
Symmetrical codes: #1 –x+1, y, -z+3/2; #2 –x+3/2, -y+5/2, -z+1; #3 -x+3/2, -y+3/2, -z+1; #4 x, y+1, z; #5 -x+3/2, -y+1/2, -z+1; #5 -x+3/2, -y+1/2, -z+1; #6 x, y-1, z; #7 -x+2, -y+1, -z+2.

Complex **4**

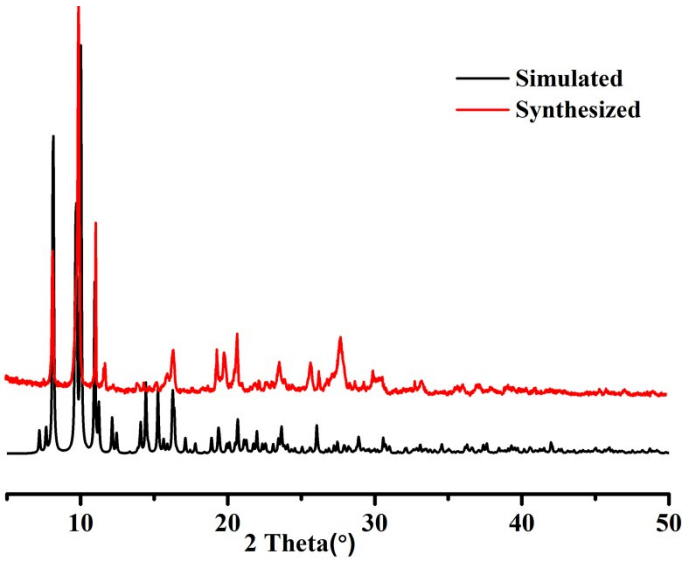
Mn(1)-O(1)#1	2.130(2)	Mn(2)-O(4)	2.090(3)
Mn(1)-O(1)	2.131(2)	Mn(2)-O(7)#3	2.334(3)
Mn(1)-O(3)#2	2.178(3)	Mn(2)-O(11)#4	2.149(3)
Mn(1)-O(3)#3	2.178(3)	Mn(2)-O(12)	2.236(4)
Mn(1)-O(7)#1	2.301(2)	Mn(2)-O(13)	2.201(3)
Mn(1)-O(7)	2.301(2)	Mn(3)-O(5)	2.526(3)
Mn(2)-O(2)#3	2.083(3)	Mn(3)-O(6)	2.183(3)
Mn(3)-O(9)#5	2.335(3)	Mn(3)-O(10)#5	2.306(3)
Mn(3)-O(14)	2.187(3)	Mn(3)-O(15)	2.190(3)
O(2)-Mn(2)#3	2.083(3)	Mn(3)-O(16)	2.186(3)
O(3)-Mn(1)#4	2.178(3)	O(7)-Mn(2)#3	2.334(3)
O(9)-Mn(3)#6	2.335(3)	O(11)-Mn(2)#2	2.149(3)
O(10)-Mn(3)#6	2.306(3)	O(1)-Mn(1)-O(3)#3	94.58(11)
O(1)#1-Mn(1)-O(1)	180.0	O(1)#1-Mn(1)-O(3)#3	85.42(11)
O(1)-Mn(1)-O(3)#2	85.42(11)	O(1)#1-Mn(1)-O(3)#2	94.58(11)
O(1)#1-Mn(1)-O(7)	85.06(9)	O(1)#1-Mn(1)-O(7)#1	94.94(9)
O(1)-Mn(1)-O(7)	94.94(9)	O(1)-Mn(1)-O(7)#1	85.06(9)
O(3)#3-Mn(1)-O(3)#2	180.00(12)	O(3)#3-Mn(1)-O(7)	94.71(10)

O(3)#2-Mn(1)-O(7)	85.29(10)	O(3)#3-Mn(1)-O(7)#1	85.29(10)
O(3)#2-Mn(1)-O(7)#1	94.71(10)	O(2)#3-Mn(2)-O(11)#4	168.09(12)
O(7)-Mn(1)-O(7)#1	180.0	O(2)#3-Mn(2)-O(12)	93.43(16)
O(2)#3-Mn(2)-O(4)	92.39(13)	O(6)-Mn(3)-O(5)	55.25(9)

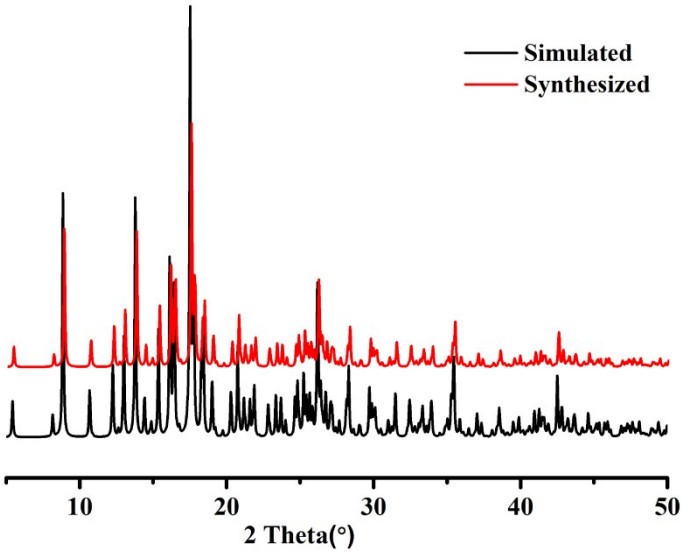
Symmetrical codes: #1 -x+1, -y+1, -z+2; #2 x, y, z+1; #3 -x+1, -y+1, -z+1; #4 x, y, z-1; #5 x-1, y, z; #6 x+1, y, z.



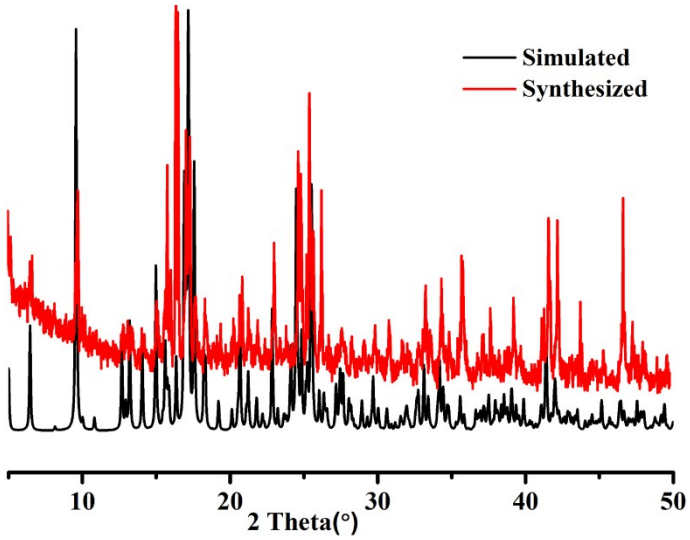
(a)



(b)



(c)



(d)

Fig. S1 PXRD patterns of **1**-**4** in (a-d) simulated from the X-ray single-crystal structure and experimental samples.

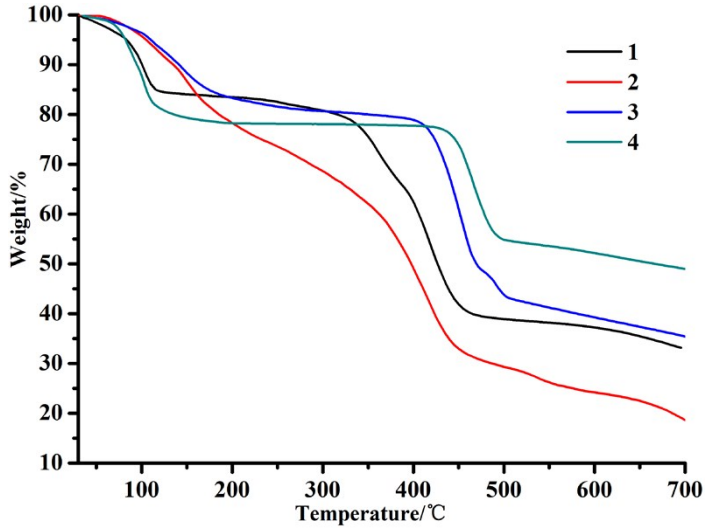


Fig. S2 TGA plots of complexes **1-4**.

Table S2. Standard Deviation (σ) calculation for the detection of CrO_4^{2-} for **1.**

Test	fluorescence intensity (nm)
1	1163.401
2	1165.645
3	1161.315
4	1165.647
5	1162.994
average	1163.800
standard deviation (σ)	1.86

Table S3. Standard Deviation (σ) calculation for the detection of $Cr_2O_7^{2-}$ for **1.**

Test	fluorescence intensity (nm)
1	1263.130
2	1264.456
3	1265.325
4	1265.227
5	1262.294

average	1264.086
standard deviation (σ)	1.33

Table S4. Standard Deviation (σ) calculation for the detection of MnO_4^- for **1.**

Test	fluorescence intensity (nm)
1	1537.481
2	1538.426
3	1535.313
4	1537.237
5	1538.234
average	1537.338
standard deviation (σ)	1.24

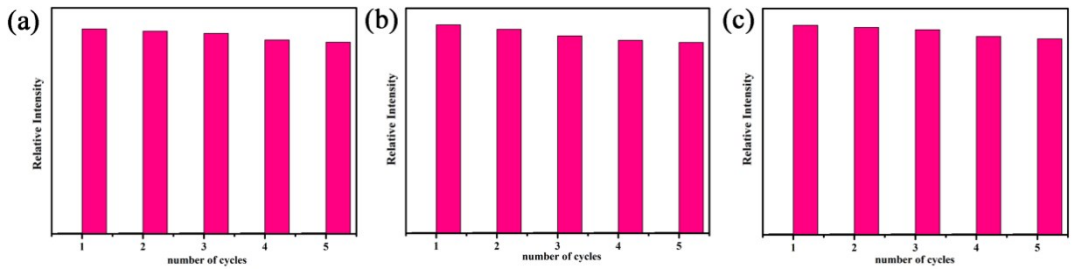


Fig. S3 Multiple cycles for the luminescence quenching of **1** by CrO_4^-, $Cr_2O_7^{2-}$, MnO_4^- and recovery after washing by H_2O for several times.

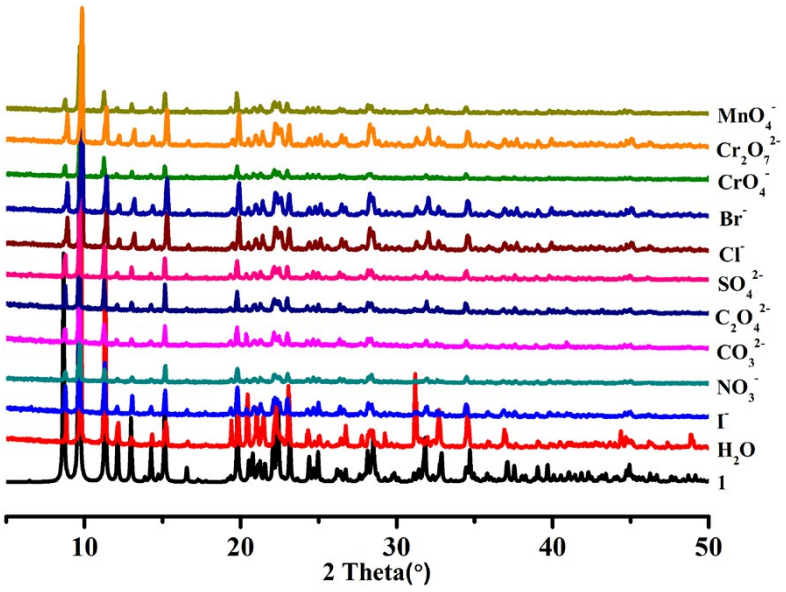


Fig. S4 PXRD patterns of **1** treated by different K_x(anion) aqueous solutions. It indicated that **1** retains its framework after immersed in aqueous solution containing different anions.

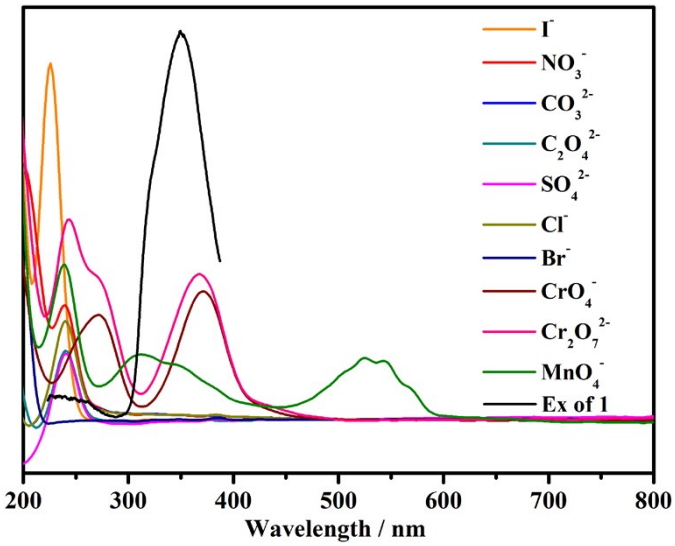


Fig. S5 UV-Vis adsorption spectra of K(anion)$_x$ aqueous solutions and the excitation spectrum of **1**.

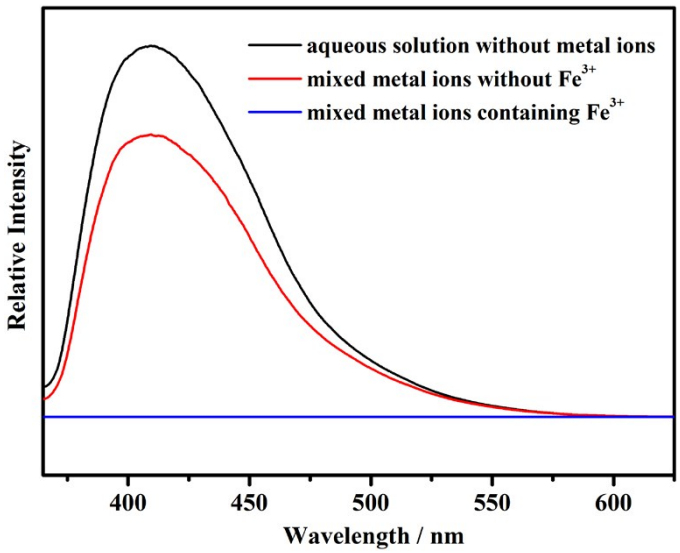


Fig. S6 The emission spectra of **1** with different mixed metal ions.

Table S5. Standard Deviation (σ) calculation for the detection of Fe^{3+} for **1.**

Test	fluorescence intensity (nm)
1	1329.676
2	1328.355
3	1328.386
4	1327.347
5	1326.543
average	1328.061
standard deviation (σ)	1.21

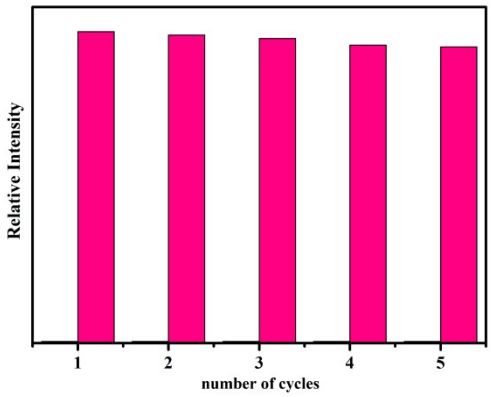


Fig. S7 Multiple cycles for the fluorescence quenching of **1** by Fe^{3+} and recovery after washing by H_2O for several times.

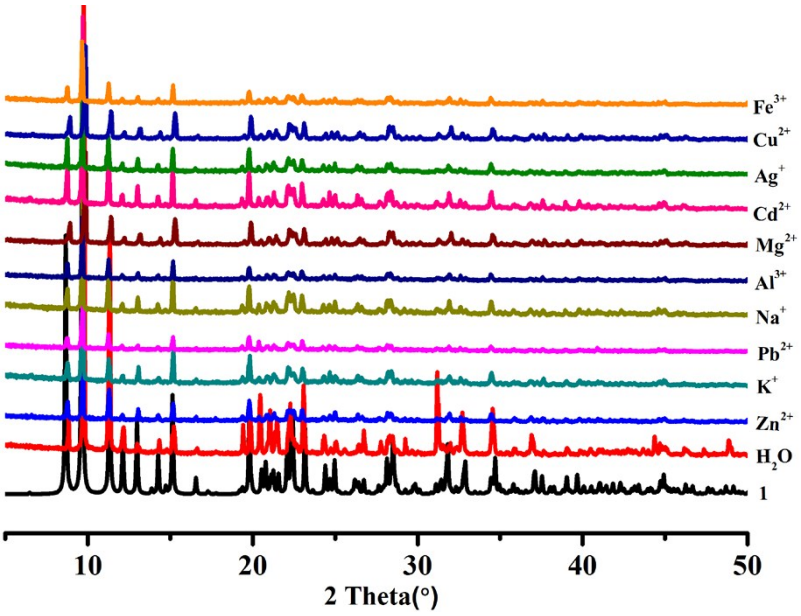


Fig. S8 PXRD patterns of **1** treated by different K(cation)$_x$ aqueous solutions. It indicated that **1** retains its framework after immersed in aqueous solution containing different cations.

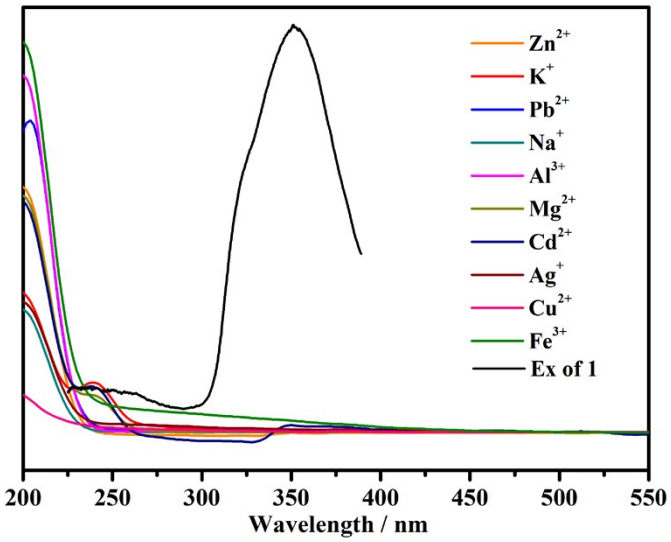


Fig. S9 UV-Vis adsorption spectra of M(NO3)$_x$ aqueous solutions and the excitation spectrum of **1**.

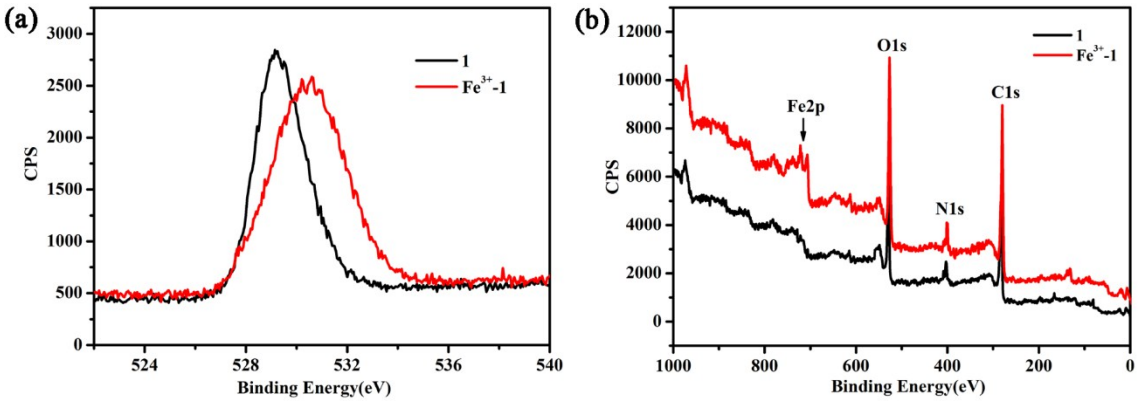


Fig. S10 XPS spectra of O 1s for **1** and Fe^{3+}-**1**.

Table S6. A comparison of various fluorescent materials used for detecting CrO_4^{2-}, $Cr_2O_7^{2-}$ MnO_4^- and Fe^{3+}.

Fluorescent materials	Luminescent substrates	Ksv/M^{-1}	detection limit/M	Ref.
$[Eu(L)(HCOO)(H_2O)]_n$	CrO_4^{2-}	1.53×10^3	1.2×10^{-6}	20a
$[Tb(L)(HCOO)(H2O)]_n$	CrO_4^{2-}	1.30×10^3	1.8×10^{-6}	20a
$[Zn_2(TPOM)(NDC)_2]\cdot 3.5H_2O$	CrO_4^{2-}	7.81×10^3	2.50×10^{-6}	20b
$[Eu_2(tpbpc)_4\cdot CO_3\cdot 4H_2O]\cdot DMF\cdot solvent$	CrO_4^{2-}	4.85×10^3	3.30×10^{-7}	22b
Complex **1**	CrO_4^{2-}	1.3×10^4	4.29×10^{-4}	This work
$[Eu(L)(HCOO)(H_2O)]_n$	$Cr_2O_7^{2-}$	2762.6	1.0×10^{-6}	20a
$[Tb(L)(HCOO)(H_2O)]_n$	$Cr_2O_7^{2-}$	2133.5	2.1×10^{-6}	20a
$[Zn_2(TPOM)(NDC)_2]\cdot 3.5H_2O$	$Cr_2O_7^{2-}$	9.21×10^3	2.35×10^{-6}	20b
$\{[Zn_3(tza)_2(\mu_2\text{-}OH)_2(H_2O)_2]\cdot H_2O\}_n$	$Cr_2O_7^{2-}$	5.02×10^3	-	20d
$\{[Cd(L)(BPDC)]\cdot 2H_2O\}_n$	$Cr_2O_7^{2-}$	6.4×10^3	3.76×10^{-5}	22a
$\{[Cd(L)(SDBA)(H_2O)]\cdot 0.5H_2O\}_n$	$Cr_2O_7^{2-}$	4.97×10^3	4.86×10^{-5}	22a
$[Eu_2(tpbpc)_4\cdot CO_3\cdot 4H_2O]\cdot DMF\cdot solvent$	$Cr_2O_7^{2-}$	1.04×10^4	1.07×10^{-6}	22b
$[Eu_2(H_2O)(DCPA)_3]_n$	$Cr_2O_7^{2-}$	8.7×10^3	1.40×10^{-6}	22d
Complex **1**	$Cr_2O_7^{2-}$	6.6×10^4	6.05×10^{-5}	This work
534-MOF-Tb	MnO_4^-	6.63×10^3	-	20c
[illegible]	MnO_4^-	9.71×10^4		20c

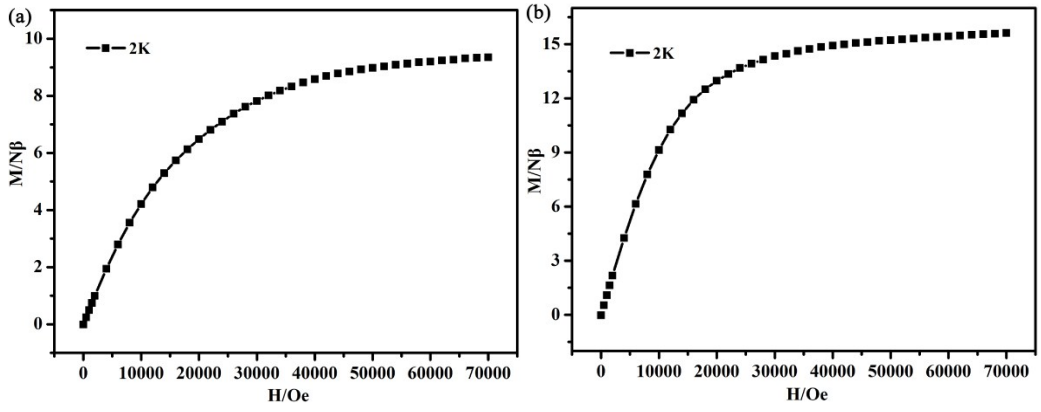
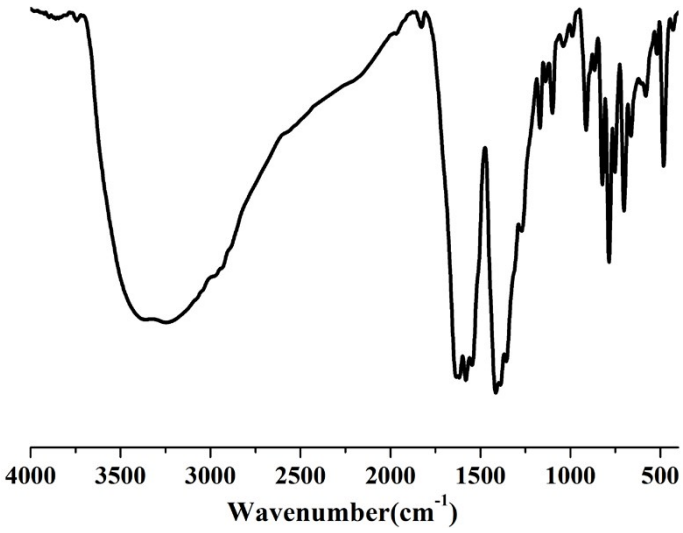
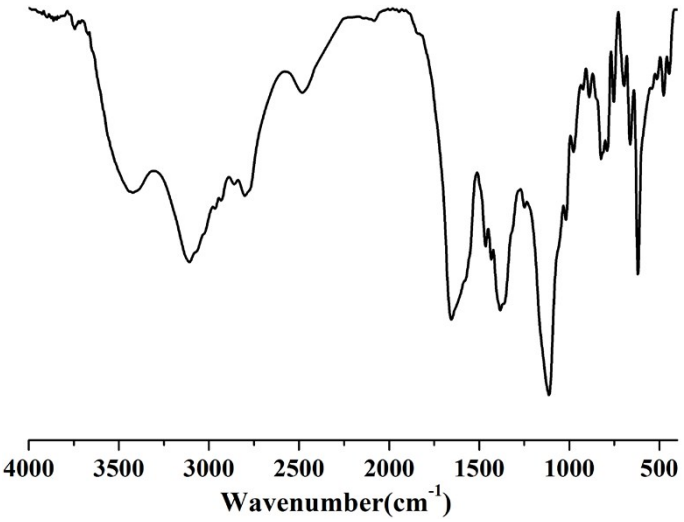


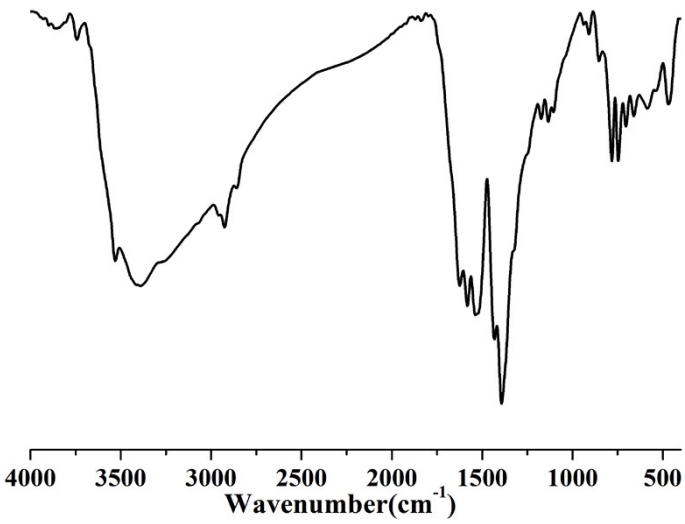
Fig. S11 M versus H plots for **3** and **4**.



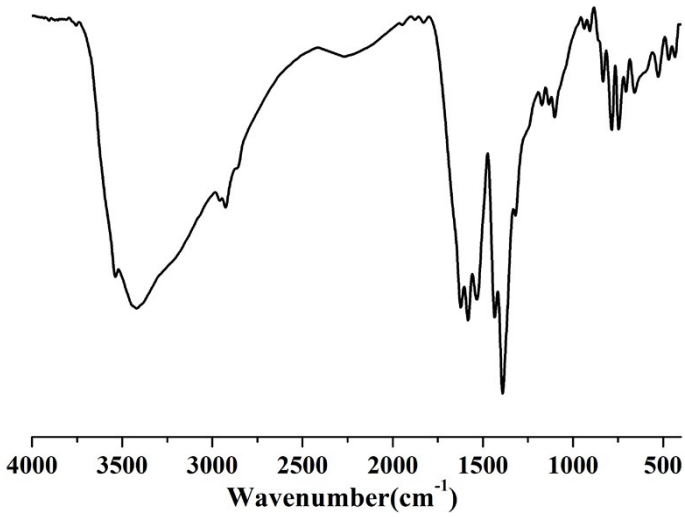
(a)



(b)



(c)



(d)

Fig. S12. IR spectra of the as-synthesized **1-4** in (a-d).