Supporting Information

Seven luminescent metal-organic frameworks constructed by the 5-(triazol-1-yl) nicotinic acid: Luminescent Sensors for Cr^{VI} and MnO_4^- Ions in an Aqueous Medium

Yang-Tian Yan,‡ Feng Cao,‡ Wen-Yan Zhang,* Si-Si Zhang, Fang Zhang, Yao-Yu Wang*

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of the Ministry of Education, Shaanxi Key Laboratory of Physico-Inorganic Chemistry, College of Chemistry & Materials Science, Northwest University, Xi'an 710127, P. R. China

Table S1 Selected bond lengths (Å) and bond angles (°) for **1-7**

Complex **1**			
Cd(1)-O(5)#1	2.46(2)	Cd(2)-O(7)	2.44(2)
Cd(1)-O(5)#2	2.46(2)	Cd(2)-O(2)#5	2.593(6)
Cd(1)-N(4)#3	2.317(4)	Cd(2)-N(1)	2.320(6)
Cd(1)-N(4)	2.317(4)	O(4)-Cd(2)#6	2.624(6)
Cd(1)-N(5)	2.353(4)	O(4)-Cd(2A)#6	2.629(4)
Cd(1)-N(5)#3	2.353(4)	O(8)-Cd(2A)	2.353(5)
Cd(1)-O(6A)#1	2.361(11)	O(3)-Cd(2)#6	2.245(6)
Cd(1)-O(6A)#2	2.361(11)	O(3)-Cd(2A)#6	2.239(4)

Cd(2)-O(4)#4	2.624(6)	O(1)-Cd(2)#7	2.266(6)
Cd(2)-O(8)	2.236(5)	O(1)-Cd(2A)#7	2.289(4)
Cd(2)-O(3)#4	2.245(6)	O(5)-Cd(1)#8	2.46(2)
Cd(2)-O(1)#5	2.266(6)	O(2)-Cd(2)#7	2.593(6)
O(2)-Cd(2A)#7	2.593(4)	Cd(2A)-O(4)#4	2.629(4)
O(7A)-Cd(2A)	2.639(9)	Cd(2A)-O(3)#4	2.239(4)
O(5A)-Cd(2A)	2.397(13)	Cd(2A)-O(1)#5	2.289(4)
O(6A)-Cd(1)#8	2.361(11)	Cd(2A)-O(2)#5	2.593(5)
O(5)#1-Cd(1)-O(5)#2	180.0(8)	N(4)-Cd(1)-O(5)#2	77.4(5)
N(4)#3-Cd(1)-O(5)#2	102.6(5)	N(4)-Cd(1)-O(5)#1	102.6(5)
O(1)#5-Cd(2)-O(2)#5	53.08(15)	O(1)#5-Cd(2)-N(1)	135.7(2)
O(3)#4-Cd(2)-O(1)#5	84.8(2)	O(1)#5-Cd(2)-O(7)	112.3(7)
O(3)#4-Cd(2)-O(4)#4	52.75(15)	O(3)#4-Cd(2)-O(7)	81.2(9)
O(8)-Cd(2)-N(1)	84.95(18)	O(3)#4-Cd(2)-O(2)#5	135.8(2)
O(8)-Cd(2)-O(2)#5	90.7(2)	O(3)#4-Cd(2)-N(1)	138.3(3)
O(8)-Cd(2)-O(7)	154.8(7)	O(1)#5-Cd(2)-O(4)#4	135.5(2)
O(1)#5-Cd(2A)-O(8)	89.09(18)	O(1)#5-Cd(2A)-N(1)	135.53(16)
O(1)#5-Cd(2A)-O(4)#4	133.87(16)	O(1)#5-Cd(2A)-O(2)#5	52.88(12)
O(3)#4-Cd(2A)-O(7A)	80.3(2)	O(3)#4-Cd(2A)-O(5A)	89.7(3)
O(3)#4-Cd(2A)-O(4)#4	52.72(12)	O(3)#4-Cd(2A)-N(1)	140.03(17)
O(8)-Cd(2A)-O(5A)	159.6(3)	O(3)#4-Cd(2A)-O(2)#5	136.14(16)
O(8)-Cd(2A)-O(7A)	147.6(2)	O(3)#4-Cd(2A)-O(1)#5	84.42(15)
O(8)-Cd(2A)-O(2)#5	88.15(18)	O(3)#4-Cd(2A)-O(8)	102.23(18)
O(7)-Cd(2)-O(2)#5	101.0(9)	N(1)-Cd(2)-O(7)	74.6(8)

O(2)#5-Cd(2)-O(4)#4	171.3(2)	N(1)-Cd(2)-O(2)#5	82.71(18)
N(1)-Cd(2)-O(4)#4	88.68(19)	O(4)#4-Cd(2A)-O(7A)	70.76(18)
O(7)-Cd(2)-O(4)#4	77.6(8)	O(8)-Cd(2A)-O(4)#4	84.97(16)
N(1)-Cd(2A)-O(8)	82.80(15)	N(1)-Cd(2A)-O(2)#5	83.11(13)
N(1)-Cd(2A)-O(4)#4	88.99(13)	N(1)-Cd(2A)-O(7A)	75.77(18)
O(2)#5-Cd(2A)-O(7A)	112.7(2)	N(1)-Cd(2A)-O(5A)	98.7(3)
O(2)#5-Cd(2A)-O(4)#4	170.12(17)	O(5A)-Cd(2A)-O(4)#4	115.4(3)
O(1)#5-Cd(2A)-O(5A)	75.5(2)	O(5A)-Cd(2A)-O(2)#5	71.9(3)
O(1)#5-Cd(2A)-O(7A)	123.2(2)	O(5A)-Cd(2A)-O(7A)	50.3(3)

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

Complex **2**			
Cd(1)-O(1)#1	2.2952(15)	N(4)-Cd(1)#4	2.3367(17)
Cd(1)-O(1)	2.2952(15)	Cd(1)-O(3)	2.2885(15)
Cd(1)-N(4)#2	2.3367(17)	Cd(1)-O(3)#1	2.2885(15)
Cd(1)-N(4)#3	2.3367(17)	O(3)#1-Cd(1)-O(1)#1	87.69(6)
O(1)#1-Cd(1)-O(1)	180.0	O(3)#1-Cd(1)-N(4)#3	80.72(6)
O(1)-Cd(1)-N(4)#3	84.30(6)	O(3)-Cd(1)-N(4)#3	99.28(6)
O(1)#1-Cd(1)-N(4)#2	84.30(6)	O(3)-Cd(1)-N(4)#2	80.72(6)
O(1)-Cd(1)-N(4)#2	95.70(6)	O(3)#1-Cd(1)-N(4)#2	99.28(6)
O(1)#1-Cd(1)-N(4)#3	95.70(6)	O(3)#1-Cd(1)-O(3)	180.0
N(4)#2-Cd(1)-N(4)#3	180.00(4)	O(3)-Cd(1)-O(1)#1	92.31(6)
O(3)-Cd(1)-O(1)	87.69(6)	O(3)#1-Cd(1)-O(1)	92.31(6)

z+1 ; #5 x+1, y, z ; #6 x, y-1, z-1 ; #7 x-1, y, z ; #8 x, y+1, z.

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

Complex **3**			
N(4)-Pb(1)#1	2.585(9)	O(2)-Pb(1)-O(7)	154.4(3)
O(2)-Pb(1)	2.740(9)	O(1)-Pb(1)-N(4)#2	74.9(3)
O(1)-Pb(1)	2.388(8)	O(1)-Pb(1)-O(2)	50.1(3)
Pb(1)-N(4)#2	2.585(9)	O(1)-Pb(1)-O(3)	80.6(3)
Pb(1)-O(3)	2.560(9)	O(1)-Pb(1)-O(7)	131.0(3)
Pb(1)-O(7)	2.953(10)	O(3)-Pb(1)-N(4)#2	72.8(3)
N(4)#2-Pb(1)-O(2)	122.6(3)	O(3)-Pb(1)-O(2)	82.6(3)
N(4)#2-Pb(1)-O(7)	73.4(3)	O(3)-Pb(1)-O(7)	122.8(3)
Symmetrical codes: #1 x+1, y, z+1; #2 x-1, y, z-1.			
Complex **4**			
Pb(1)-O(4)	2.504(4)	O(4)-Pb(1)-O(5)	120.22(14)
Pb(1)-O(1)	2.636(4)	O(1)-Pb(1)-N(4)#1	75.68(17)
Pb(1)-O(3)	2.541(4)	O(3)-Pb(1)-O(1)	130.30(15)
Pb(1)-N(4)#1	2.689(5)	O(3)-Pb(1)-N(4)#1	126.53(16)
Pb(1)-O(5)	2.566(4)	O(3)-Pb(1)-O(5)	70.66(14)
O(2)-Pb(1)-O(4)	81.19(15)	O(5)-Pb(1)-O(1)	77.10(16)
O(2)-Pb(1)-O(1)	51.43(14)	O(5)-Pb(1)-N(4)#1	152.54(16)
O(2)-Pb(1)-O(3)	84.61(15)	O(4)-Pb(1)-O(1)	126.13(15)
O(2)-Pb(1)-N(4)#1	83.12(16)	O(4)-Pb(1)-O(3)	52.21(13)
O(2)-Pb(1)-O(5)	77.14(15)	O(4)-Pb(1)-N(4)#1	74.51(15)
Pb(1)-O(2)	2.418(4)		
Symmetrical codes: #1 x, y-1, z; #2 x, y+1, z.			
Complex **5**			

Zn(1)-O(3)	2.1313(16)	O(3)-Zn(1)-O(4)#1	90.18(7)
Zn(1)-O(4)	2.1455(15)	O(4)-Zn(1)-O(4)#1	180.0
Zn(1)-O(4)#1	2.1455(15)	N(1)#1-Zn(1)-O(3)	90.47(7)
Zn(1)-N(1)#1	2.0822(17)	N(1)#1-Zn(1)-O(3)#1	89.53(7)
Zn(1)-N(1)	2.0822(17)	N(1)-Zn(1)-O(3)#1	90.47(7)
O(3)#1-Zn(1)-O(3)	180.0	N(1)-Zn(1)-O(3)	89.53(7)
O(3)#1-Zn(1)-O(4)#1	89.82(7)	N(1)-Zn(1)-O(4)#1	90.43(7)
O(3)#1-Zn(1)-O(4)	90.18(7)	N(1)#1-Zn(1)-O(4)	90.43(7)
N(1)#1-Zn(1)-O(4)#1	89.57(7)	N(1)-Zn(1)-O(4)	89.57(7)
Zn(1)-O(3)#1	2.1313(16)	O(3)-Zn(1)-O(4)	89.82(7)
Symmetrical codes: #1 -x+1, -y+1, -z+1.			
Complex **6**			
Zn(1)-N(1)	2.101(4)	N(1)-Zn(1)-O(3)	92.48(16)
Zn(1)-O(3)	2.297(4)	O(3)#1-Zn(1)-N(1)	121.31(16)
Zn(1)-O(3)#1	1.989(4)	O(3)#1-Zn(1)-O(3)	76.14(16)
Zn(1)-O(8)#2	1.990(4)	O(3)#1-Zn(1)-O(8)#2	139.66(16)
Zn(1)-O(10)	2.028(5)	O(3)#1-Zn(1)-O(10)	94.4(2)
Zn(2)-O(2)	1.952(4)	O(8)#2-Zn(1)-N(1)	97.05(16)
Zn(2)-N(4)#3	2.022(5)	O(8)#2-Zn(1)-O(3)	91.38(16)
Zn(2)-O(6)#4	1.943(4)	O(8)#2-Zn(1)-O(10)	92.2(2)
Zn(2)-O(9)	1.986(5)	O(10)-Zn(1)-N(1)	97.6(2)
O(3)-Zn(1)#1	1.989(4)	O(10)-Zn(1)-O(3)	168.9(2)
O(6)-Zn(2)#4	1.943(4)	O(2)-Zn(2)-N(4)#3	108.37(19)
N(4)-Zn(2)#5	2.021(5)	O(2)-Zn(2)-O(9)	108.5(2)

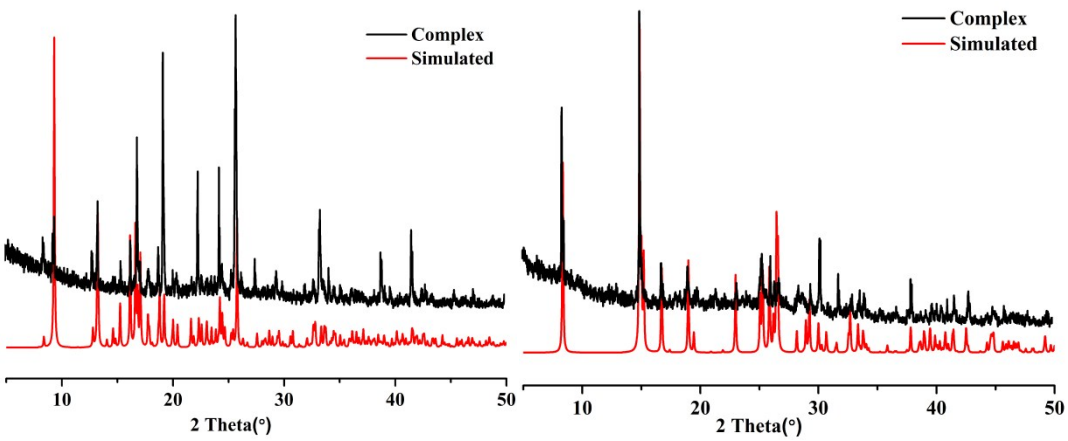
O(8)-Zn(1)#2	1.990(4)	O(6)#4-Zn(2)-O(2)	97.98(17)
O(6)#4-Zn(2)-O(9)	115.7(2)	O(6)#4-Zn(2)-N(4)#3	126.1(2)
O(9)-Zn(2)-N(4)#3	99.4(2)		

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

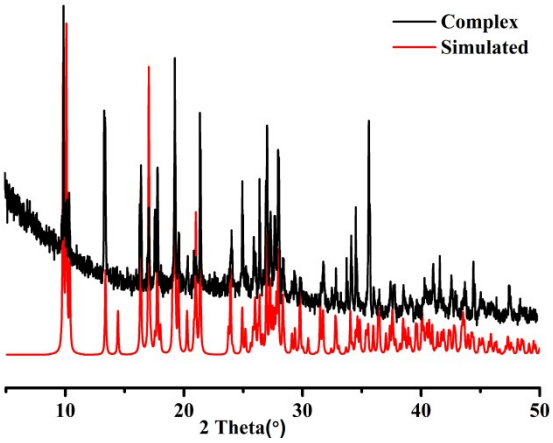
Complex **7**

N(4)-Zn(1)#1	2.051(2)	O(3)#2-Zn(1)-O(4)	178.50(7)
O(3)-Zn(1)#2	2.125(2)	O(6)-Zn(1)-N(4)#1	96.89(8)
Zn(1)-N(4)#1	2.051(2)	O(6)-Zn(1)-O(4)	82.22(8)
Zn(1)-O(4)	2.253(2)	O(6)-Zn(1)-O(3)#2	97.02(8)
Zn(1)-O(3)#2	2.125(2)	O(6)-Zn(1)-O(2)	122.46(9)
Zn(1)-O(6)	2.0067(19)	O(2)-Zn(1)-N(4)#1	139.80(9)
Zn(1)-O(2)	2.023(2)	O(2)-Zn(1)-O(4)	89.31(9)
N(4)#1-Zn(1)-O(4)	88.17(9)	O(2)-Zn(1)-O(3)#2	90.02(8)
N(4)#1-Zn(1)-O(3)#2	93.20(8)		

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

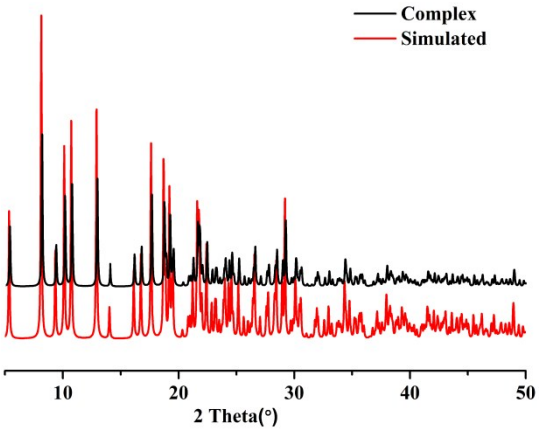


(a)

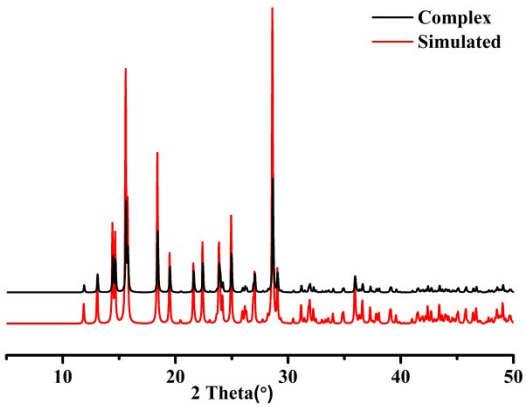

Complex
Simulated
10
20
30
40
50
2 Theta(°)

(b)

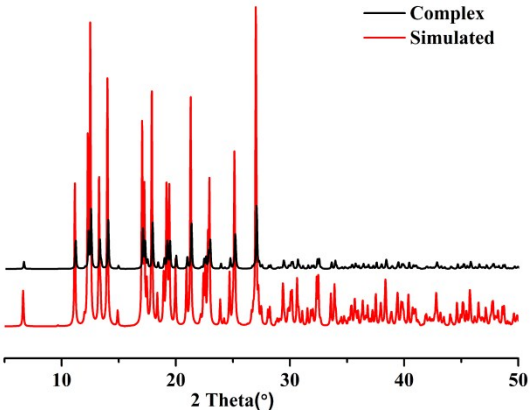
(b)


Complex
Simulated
10
20
30
40
50
2 Theta(°)

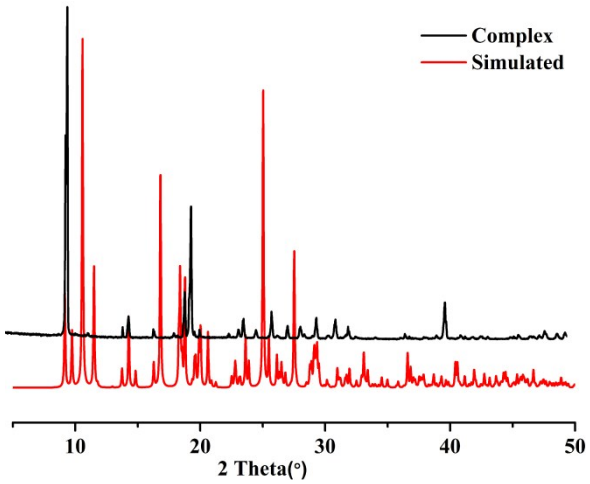
(d)


Complex
Simulated
10
20
30
40
50
2 Theta(°)

(e)


Complex
Simulated
10
20
30
40
50
2 Theta(°)

(f)


Complex
Simulated
10
20
30
40
50
2 Theta(°)

(g)

Fig. S1 PXRD patterns of **1-7** in (a-g) simulated from the X-ray single-crystal structure and experimental samples.

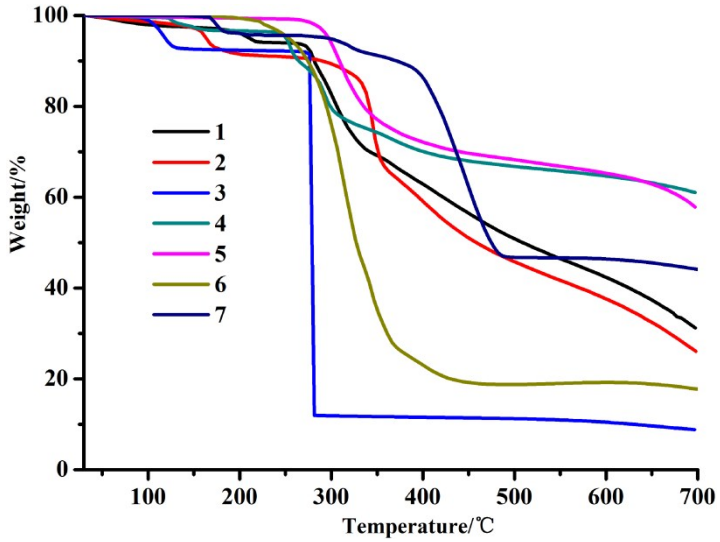


Fig. S2 TGA plots of complexes **1-7**.

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

Test	fluorescence intensity (nm)
1	1214.153
2	1213.355
3	1212.986
4	1214.346
5	1213.003
average	1213.5686
standard deviation (σ)	0.64

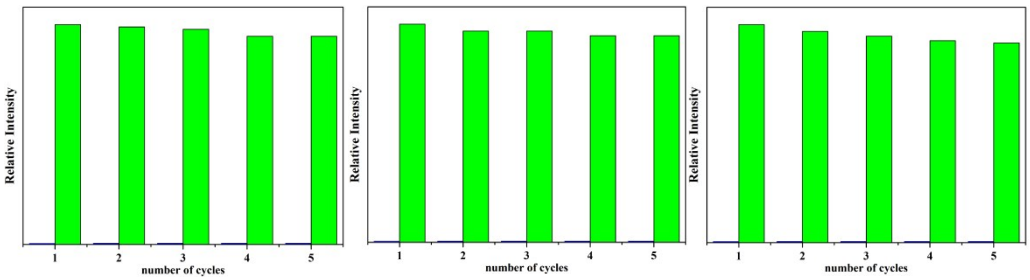
Table S3. Standard Deviation (σ) calculation for the detection of $Cr_2O_7^{2-}$ for **2.**

Test	fluorescence intensity (nm)
1	1319.053

2	1318.855
3	1320.186
4	1319.146
5	1318.703
average	1319.188
standard deviation (σ)	0.58

Table S4.
Standard Deviation (σ) calculation for the detection of MnO_4^- for **2.**

Test	fluorescence intensity (nm)
1	1539.994
2	1537.355
3	1538.186
4	1537.347
5	1539.143
average	1538.405
standard deviation (σ)	1.27



(a) **(b)** **(c)**

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

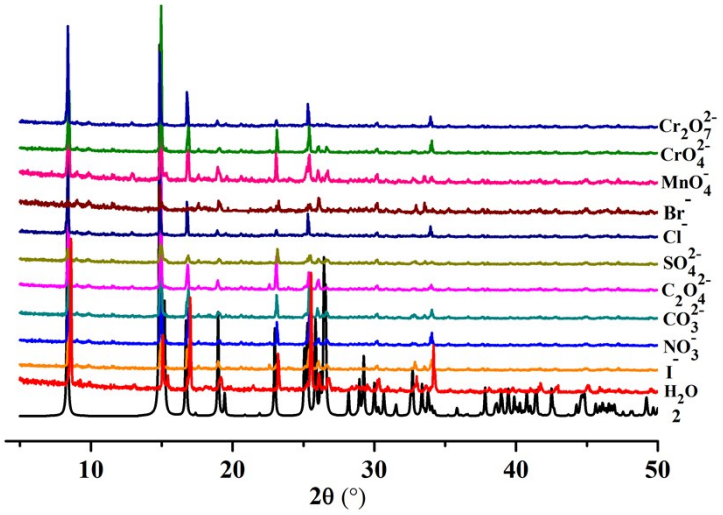


Fig. S4 PXRD patterns of **2** treated by different K_x(anion) aqueous solutions. It indicated that **2** retains its framework after immersed in aqueous solution containing different anions.

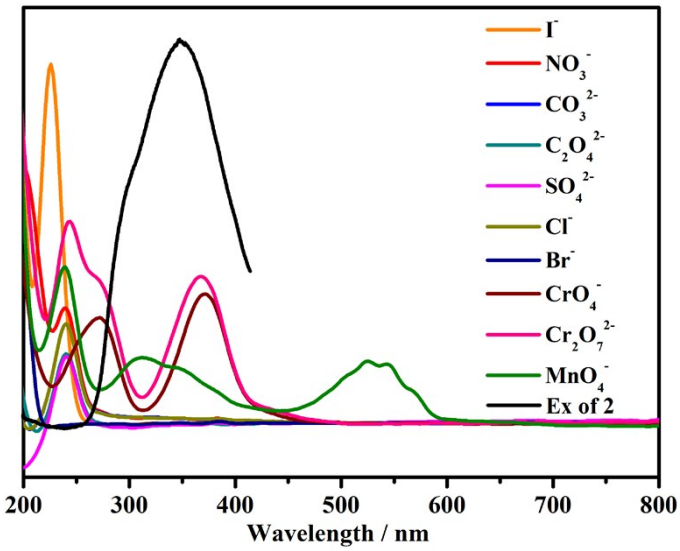
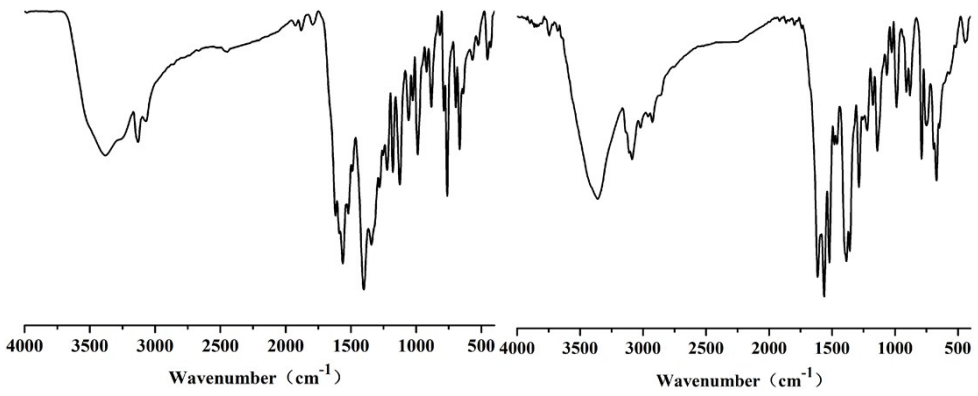


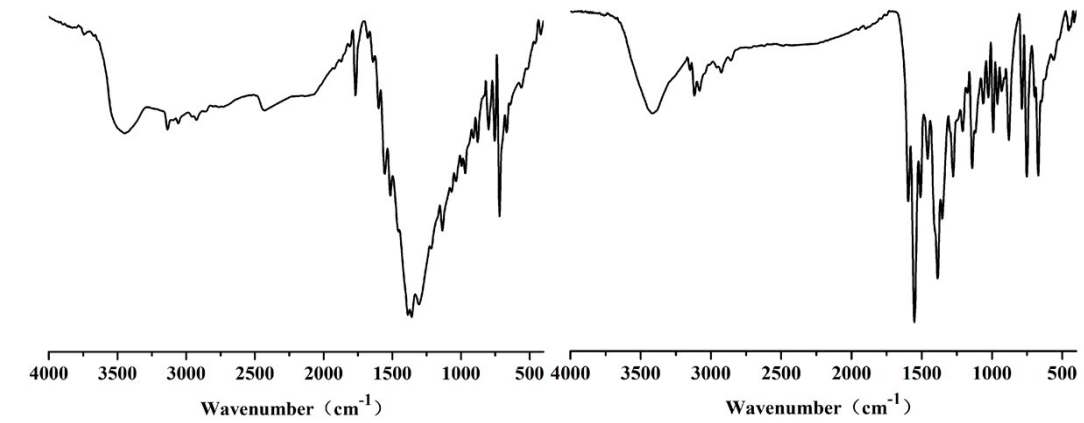
Fig. S5 UV-Vis adsorption spectra of K(anion)$_x$ aqueous solutions and the excitation spectrum of **2**.

Table S5. A comparison of various fluorescent materials used for detecting CrO_4^{2-}, $Cr_2O_7^{2-}$ and MnO_4^-.

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}	17a
$[Tb(L)(HCOO)(H2O)]_n$	CrO_4^{2-}	1.30×10^3	1.8×10^{-6}	17a
$[Zn_2(TPOM)(NDC)_2]\cdot 3.5H_2O$	CrO_4^{2-}	7.81×10^3	2.50×10^{-6}	17b
$[Eu_2(tpbpc)_4\cdot CO_3\cdot 4H_2O]\cdot DMF\cdot solvent$	CrO_4^{2-}	4.85×10^3	3.30×10^{-7}	19b
Complex **2**	CrO_4^{2-}	1.1×10^4	1.75×10^{-4}	This work
$[Eu(L)(HCOO)(H_2O)]_n$	$Cr_2O_7^{2-}$	2762.6	1.0×10^{-6}	17a
$[Tb(L)(HCOO)(H_2O)]_n$	$Cr_2O_7^{2-}$	2133.5	2.1×10^{-6}	17a
$[Zn_2(TPOM)(NDC)_2]\cdot 3.5H_2O$	$Cr_2O_7^{2-}$	9.21×10^3	2.35×10^{-6}	17b
$\{[Zn_3(tza)_2(\mu_2\text{-}OH)_2(H_2O)_2]\cdot H_2O\}_n$	$Cr_2O_7^{2-}$	5.02×10^3	-	17d
$\{[Cd(L)(BPDC)]\cdot 2H_2O\}_n$	$Cr_2O_7^{2-}$	6.4×10^3	3.76×10^{-5}	19a
$\{[Cd(L)(SDBA)(H_2O)]\cdot 0.5H_2O\}_n$	$Cr_2O_7^{2-}$	4.97×10^3	4.86×10^{-5}	19a

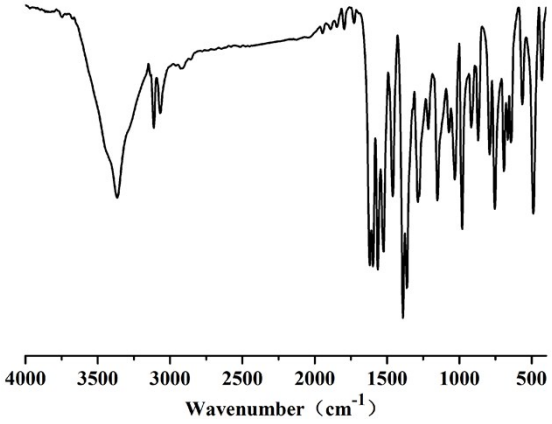


(a) **(b)**

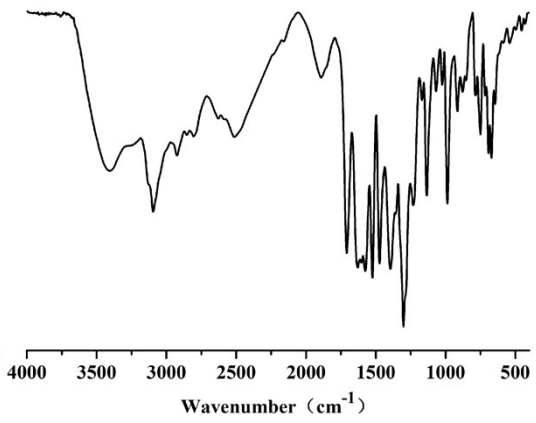


(b)

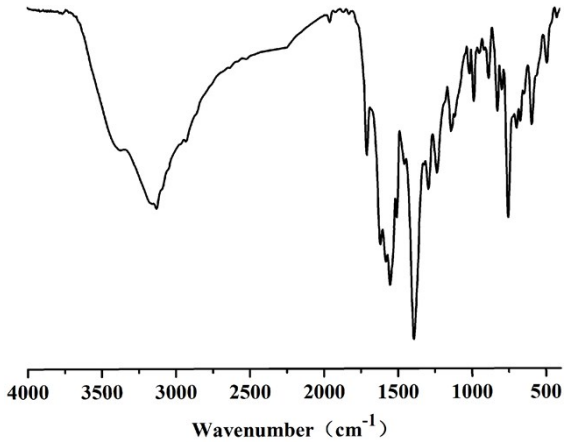
(d)



(e)



(f)



(g)

Fig. S6 IR spectra of the as-synthesized **1**-**7** in (a-g).