Supporting information

Three Zn(Ⅱ)-based MOFs for luminescence sensing of Fe^{3+} and $Cr_2O_7^{2-}$ ions

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Experimental section.

Materials and Methods: Reagents and solvents employed were commercially available. IR spectra of the complexes were recorded on a Nicolet (Impact 410) spectrometer with KBr pellets (5 mg of the sample in 300 mg of KBr) in the range of 400-4000 cm^{-1}. C, H and N elemental analyses were carried out with a Perkin Elmer 240C elemental analyzer. The as-synthesized complexes were characterized by thermo gravimetric analysis (TGA) on a Perkin Elmer thermo gravimetric analyzer Pyris 1 TGA up to 923 K using a heating rate of 10 K min^{-1} under a N_2 atmosphere. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu-K α radiation (λ=0.71073 Å), and the X-ray tube was operated at 40 kV and 40 mA.

X-ray crystallography. Single crystals of compound 1, 2 and 3 were collected on a Bruker SMART APEX CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 296 K. The crystal and refined data are collected in Table S1. Selective bond distances and angles are given in Table S2.

Table S1. Crystal data and structure refinement for Compound **1-3**

Compound	**1**	**2**	**3**
Empirical formula	$C_{40}H_{50}N_2O_6Zn$	$C_{33}H_{37}N_2O_8Zn$	$C_{30}H_{28}NO_7SZn$
Formula weight	720.19	655.01	611.96
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	P2(1)/c	C2/c
a / Å	6.1957(6)	9.2019(4)	15.8925(14)
b / Å	15.4084(14)	13.4743(6)	20.4648(19)
c / Å	19.6221(19)	25.3334(10)	21.081(2)
α / °	98.194(2)	90	90
β/ °	91.550(2)	90.4121(11)	106.8200(10)
γ/ °	100.009(2)	90	90
V / Å^3	1823.3(3)	3141.0(2)	6563.1(11)
Z	2	4	8
D_{calcd} / g cm^{-3}	1.312	1.385	1.239
μ / mm^{-1}	0.722	0.836	0.853
F(000)	764	1372	2536
θ min-max / °	2.761 to 27.831	2.207 to 27.733	1.668 to 25.027
Tot., uniq. Data	15316 / 8481	27618 / 7221	18403 / 5588
R(int)	0.0387	0.0411	0.0615
Nref, Npar	8481, 445	7221, 419	5588, 379
R1 , wR2 [I > 2σ(I)]	0.0588, 0.1537	0.0352, 0.0883	0.0475, 0.1173
GOF on F2	1.088	1.028	1.025
Largest diff. peak and hole (e·Å-3)	1.935 and -0.798	0.316 and -0.628	0.291 and -0.459

$R_1 = \Sigma||Fo|-|Fc||/\Sigma|Fo|$; $wR_2 = [\Sigma w(Fo^2-Fc^2)^2 / \Sigma wFo^4]^{1/2}$

Table S2. Selected bond lengths (Å) and angles (°) for Compound **1**

	1
N(1)-Zn(1)	2.041(3)
N(3)-Zn(1)	2.037(3)
O(5)-Zn(1)	1.950(3)
O(6)-Zn(1)	1.926(3)
O(6)-Zn(1)-O(5)	101.67(13)
O(6)-Zn(1)-N(3)	117.87(13)
O(5)-Zn(1)-N(3)	105.13(12)
O(6)-Zn(1)-N(1)	106.48(12)
O(5)-Zn(1)-N(1)	120.41(13)
N(3)-Zn(1)-N(1)	106.06(12)

Symmetry codes: for 1: #1 = -*x*+2, -*y*+1, -*z*+1; #2 = -*x*-1, -*y*, -*z*; #3 = -*x*, -*y*+2, -*z*+1; #4 = -*x*+2, -*y*+1, -*z*.

	2
N(3)-Zn(1)	2.0099(15)
O(5)-Zn(1)#2	2.0499(15)
O(6)-Zn(1)#3	2.0593(13)
O(9)-Zn(1)#4	2.0414(14)
O(21)-Zn(1)	2.0276(13)
Zn(1)-Zn(1)#3	2.9008(4)
N(3)-Zn(1)-O(21)	103.17(6)
N(3)-Zn(1)-O(9)#5	99.22(6)
O(21)-Zn(1)-O(9)#5	87.54(6)
N(3)-Zn(1)-O(5)#6	99.89(6)
O(21)-Zn(1)-O(5)#6	89.40(6)
O(9)#5-Zn(1)-O(5)#6	160.85(5)
N(3)-Zn(1)-O(6)#3	95.88(6)
O(21)-Zn(1)-O(6)#3	160.77(6)
O(9)#5-Zn(1)-O(6)#3	86.84(6)
O(5)#6-Zn(1)-O(6)#3	89.90(6)

Symmetry codes: for 1: #1 = -*x*, -*y*+1, -*z*+1 ; #2 = *x*, -*y*+1/2, *z*+1/2; #3 = -*x*+2, -*y*, -*z*+1; #4 = -*x*+2, *y*+1/2, -*z*+3/2; #5 = -*x*+2, *y*-1/2, -*z*+3/2; #6 = *x*, -*y*+1/2, *z*-1/2.

	3
O(5)-Zn(1)#1	2.042(3)
O(4)-Zn(1)#2	2.037(3)
O(1)-Zn(1)	2.041(3)
Zn(1)-N(1)	2.021(3)
Zn(1)-N(1)	2.024(3)
Zn(1)-O(7)#3	2.084(3)
Zn(1)-Zn(1)#3	2.9912(8)
N(1)-Zn(1)-O(4)#2	101.15(12)
N(1)-Zn(1)-O(1)	107.30(12)
O(4)#2-Zn(1)-O(1)	88.82(12)
N(1)-Zn(1)-O(5)#5	100.12(12)
O(4)#2-Zn(1)-O(5)#5	158.28(10)
O(1)-Zn(1)-O(5)#5	89.03(12)
N(1)-Zn(1)-O(7)#3	94.25(12)
O(4)#2-Zn(1)-O(7)#3	88.60(12)
O(1)-Zn(1)-O(7)#3	158.39(12)
O(5)#5-Zn(1)-O(7)#3	85.48(12)

Symmetry codes: for 1: #1 = *x*+1/2, *y*+1/2, *z*; #2 = -*x*+1, -*y*+1, -*z*+1; #3 = -*x*+1/2, -*y*+1/2, -*z*+1; #4 = -*x*+1, -*y*, -*z*+2; #5 = *x*-1/2, *y*-1/2, *z*.

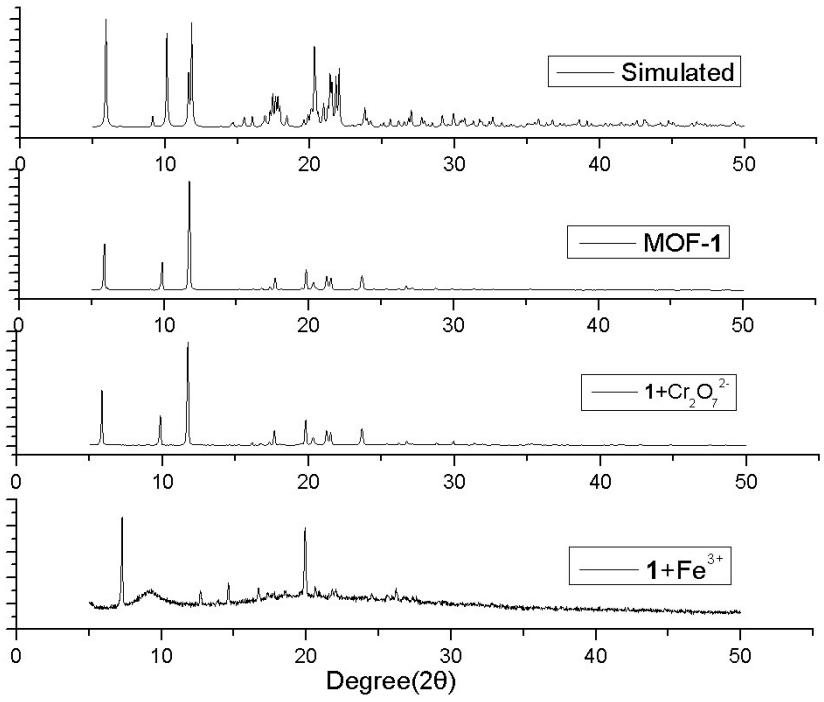

Figure S1 PXRD of **1** before and after immersed in $Cr_2O_7^{2-}$ / Fe^{3+} for 10 hours.

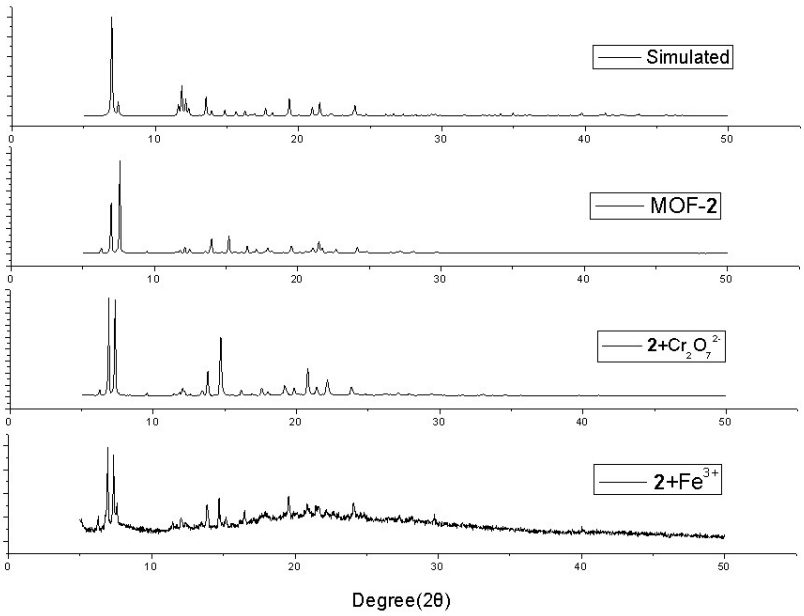

Figure S2 PXRD of **2 b**efore and after immersed in $Cr_2O_7^{2-}$ / Fe^{3+} for 10 hours.

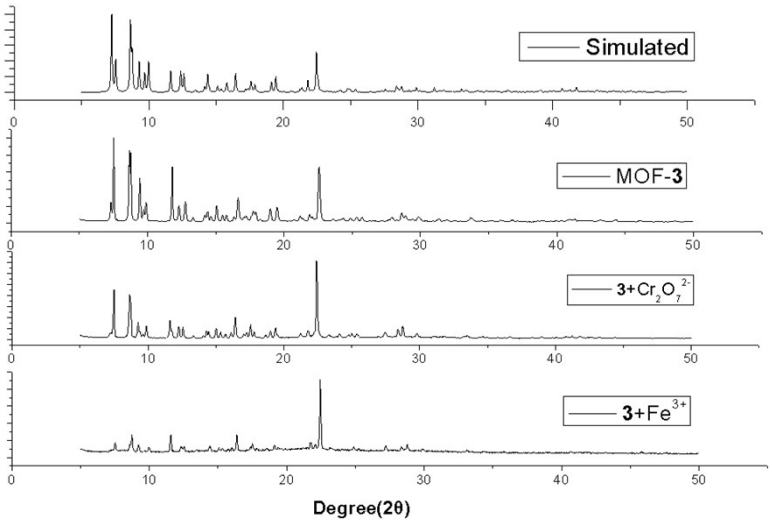

Figure S3 PXRD of **3** before and after immersed in $Cr_2O_7^{2-}$ / Fe^{3+} for 10 hours.

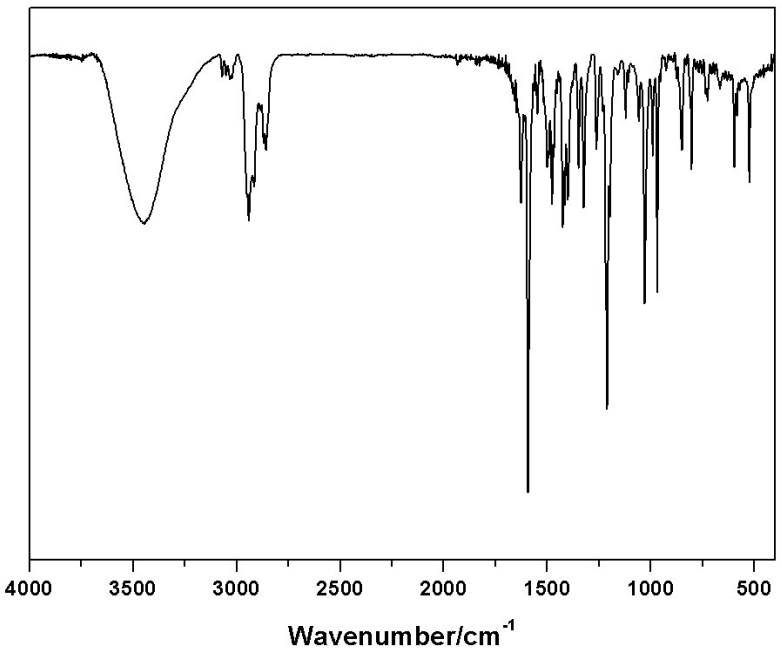

Figure S4 IR spectra of H_2L ligand.

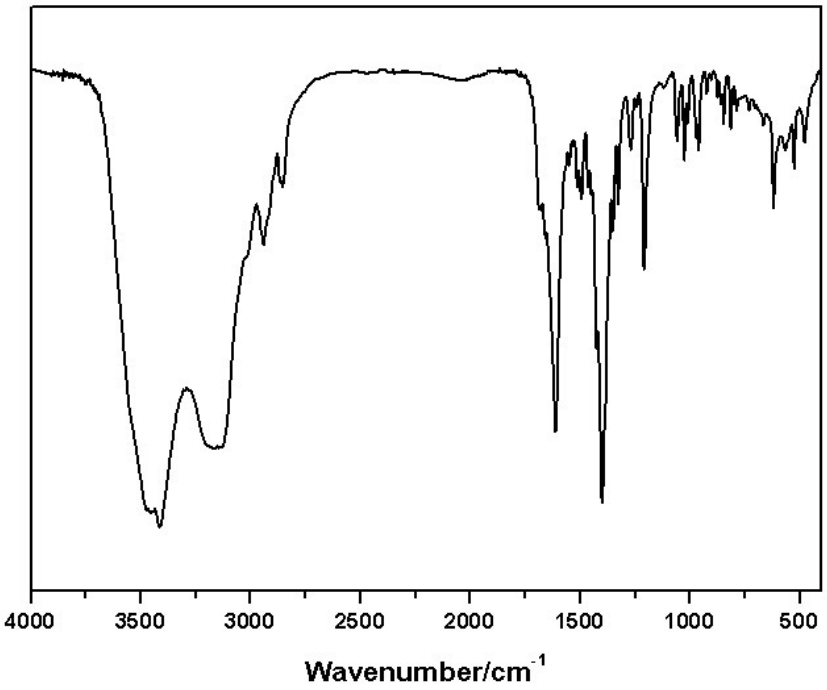

Figure S5 IR spectra of compound **1**.

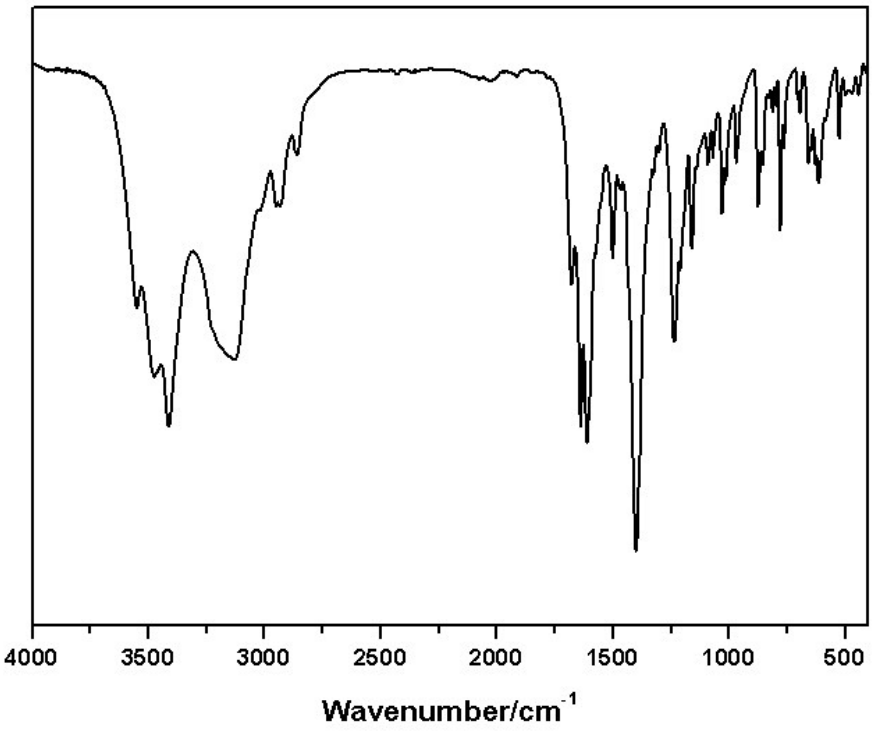

Figure S6 IR spectra of compound **2**.

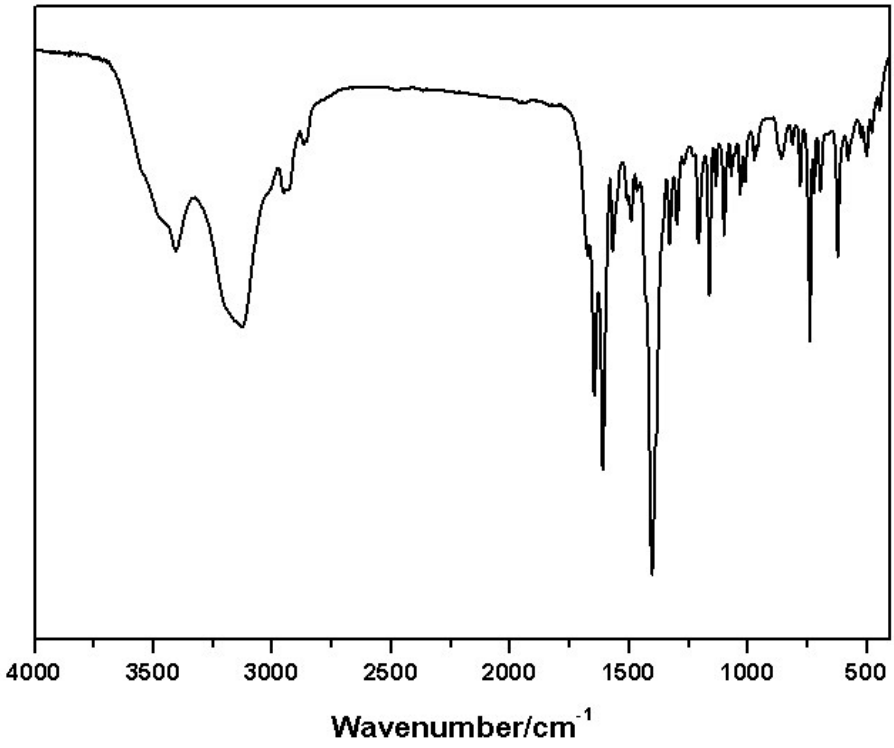

Figure S7 IR spectra of compound **3**.

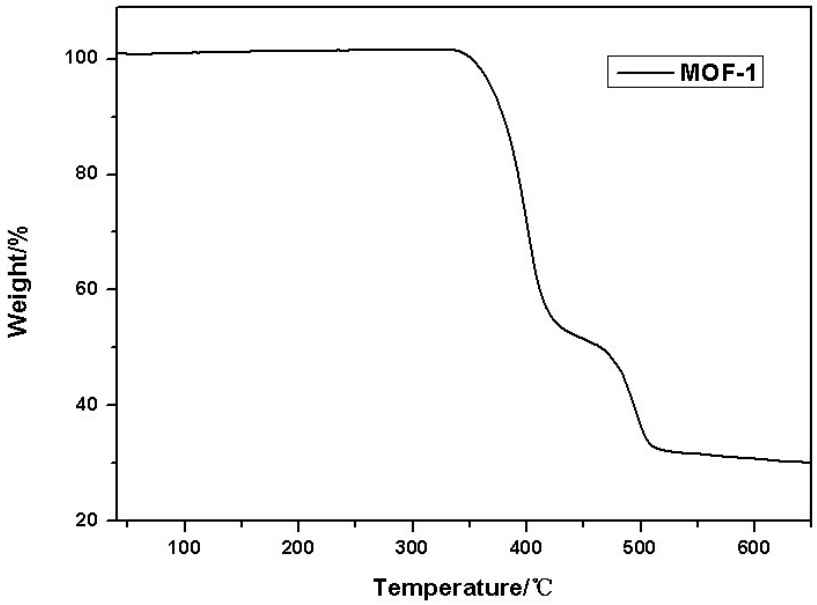

Figure S8 The TGA diagrams of compound **1.**

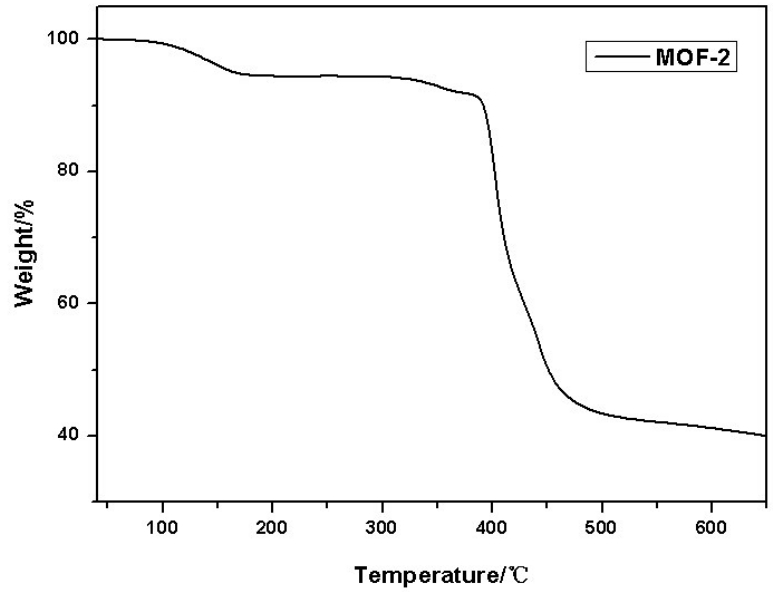

Figure S9 The TGA diagrams of compound **2.**

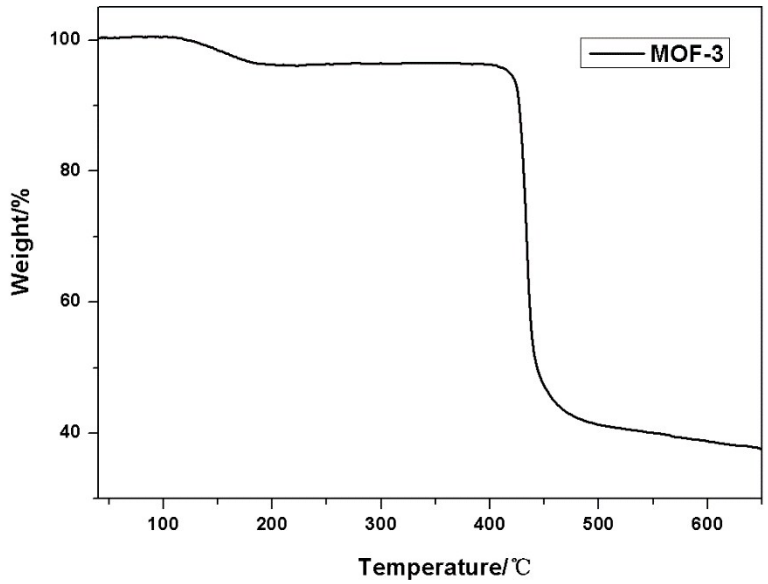

Figure S10 The TGA diagrams of compound **3.**

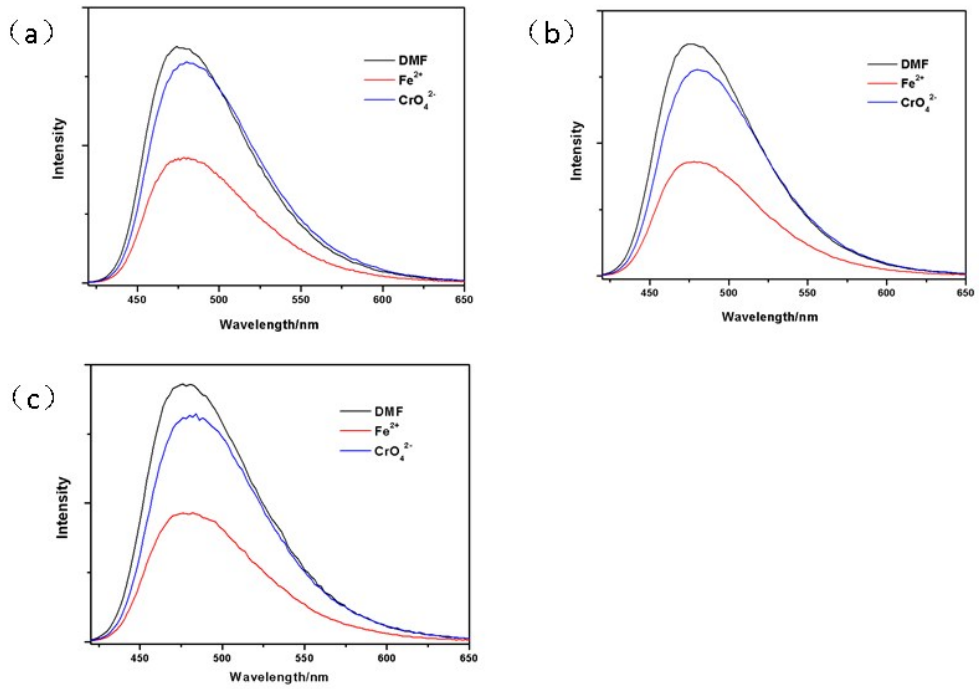

Figure S11 (a) - (c) Fluorescence spectra of MOFs **1**–**3** (DMF suspension, 2.0 mL) added $FeSO_4$ (5×10^{-2} M, 50 μL) and Na_2CrO_4 (5×10^{-3} M, 100 μL).

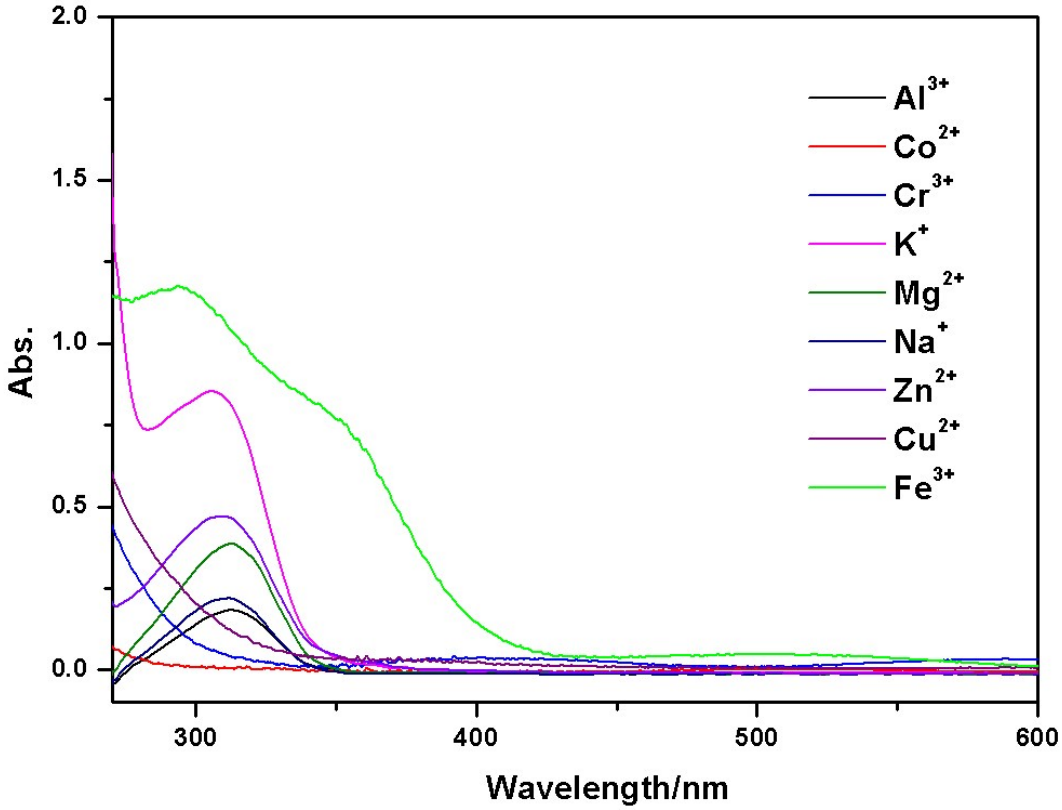

Figure S12 Liquid UV-vis spectra of different metal cations in DMF.

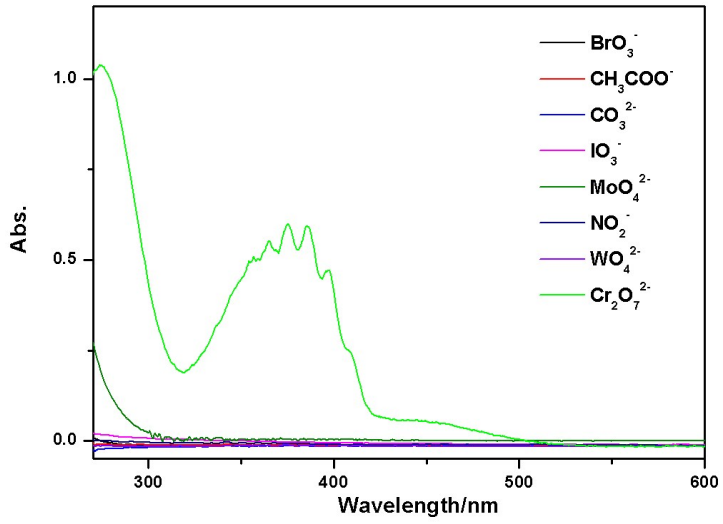

Figure S13 Liquid UV-vis spectra of different inorganic anions in DMF.

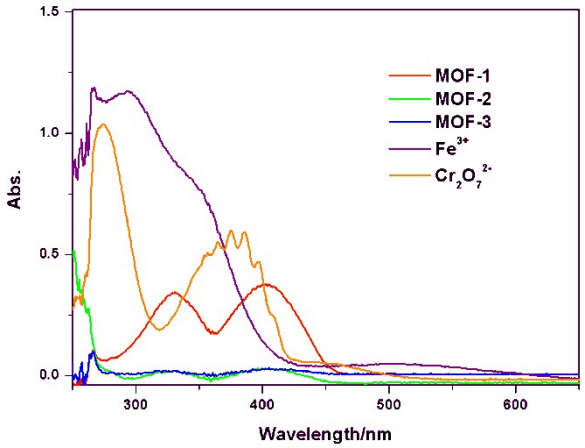

Figure S14 Liquid UV-vis spectra of MOFs **1-3**, Fe^{3+} and $Cr_2O_7^{2-}$ in DMF.