Electronic Supplementary Information

Three new luminescent Cd(II)-MOFs by regulation of tetracarboxylates and auxiliary co-ligands, displaying high sensitivity for Fe^{3+} in aqueous solution†

Yunlong Wu, Guo-Ping Yang*, Xiang Zhou, Jiang Li, Yan Ning, and Yao-Yu Wang*

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, Shaanxi Key Laboratory of Physico-Inorganic Chemistry, College of Chemistry and Materials Science, Northwest University, Xi'an 710069, P.R. China. E-mail: ygp@nwu.edu.cn, wyaoyu@nwu.edu.cn.

Table S1. Selected bond lengths [Å] and angles [º] for three MOFs.

Complex **1**

Cd(1)-O(4)#1	2.249(3)	O(3)#2-Cd(1)-N(2)#3	84.48(12)
Cd(1)-N(1)	2.289(3)	O(4)#1-Cd(1)-O(1)	93.39(11)
Cd(1)-O(3)#2	2.325(3)	N(1)-Cd(1)-O(1)	97.87(12)
Cd(1)-N(2)#3	2.325(3)	O(3)#2-Cd(1)-O(1)	152.64(12)
Cd(1)-O(1)	2.408(3)	N(2)#3-Cd(1)-O(1)	86.41(12)
Cd(1)-O(2)	2.420(3)	O(4)#1-Cd(1)-O(2)	146.76(11)
O(4)#1-Cd(1)-N(1)	103.67(12)	N(1)-Cd(1)-O(2)	89.51(12)
O(4)#1-Cd(1)-O(3)#2	111.39(13)	O(3)#2-Cd(1)-O(2)	99.35(12)
N(1)-Cd(1)-O(3)#2	87.66(12)	N(2)#3-Cd(1)-O(2)	85.65(12)
O(4)#1-Cd(1)-N(2)#3	85.03(12)	O(1)-Cd(1)-O(2)	54.19(10)
N(1)-Cd(1)-N(2)#3	169.98(13)		

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

Complex **2**

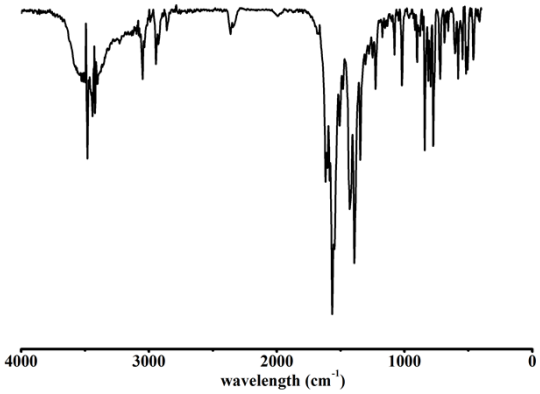
Cd(1)-O(1)	2.291(2)	O(3)#1-Cd(1)-O(4)#1	55.71(8)
Cd(1)-N(2)	2.300(3)	N(1)-Cd(1)-O(4)#1	111.45(10)
Cd(1)-O(3)#1	2.315(3)	O(1)-Cd(1)-O(2)	55.89(7)
Cd(1)-N(1)	2.330(3)	N(2)-Cd(1)-O(2)	94.45(10)
Cd(1)-O(4)#1	2.386(2)	O(3)#1-Cd(1)-O(2)	118.95(9)
Cd(1)-O(2)	2.397(2)	N(1)-Cd(1)-O(2)	143.54(8)
O(1)-Cd(1)-N(2)	101.88(11)	O(4)#1-Cd(1)-O(2)	102.90(8)
O(1)-Cd(1)-O(3)#1	117.23(9)	O(1)-Cd(1)-C(11)#1	140.91(10)
N(2)-Cd(1)-O(3)#1	138.16(10)	N(2)-Cd(1)-C(11)#1	117.10(10)
O(1)-Cd(1)-N(1)	93.35(9)	O(3)#1-Cd(1)-C(11)#1	27.94(9)
N(2)-Cd(1)-N(1)	71.35(10)	N(1)-Cd(1)-C(11)#1	101.34(9)
O(3)#1-Cd(1)-N(1)	91.17(10)	O(4)#1-Cd(1)-C(11)#1	27.84(8)
O(1)-Cd(1)-O(4)#1	153.57(9)	O(2)-Cd(1)-C(11)#1	114.89(8)
N(2)-Cd(1)-O(4)#1	94.86(10)		

Symmetry code: #1: x, -y+1/2, z+1/2.

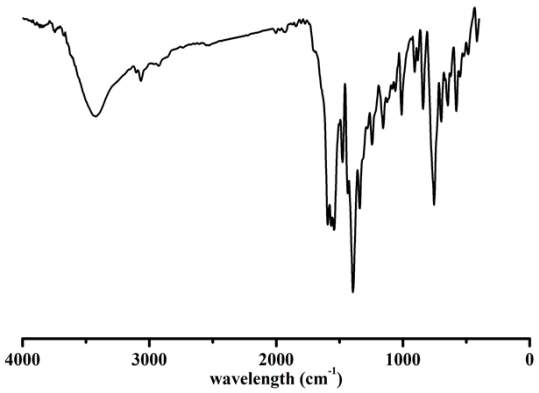
Complex **3**

Cd(1)-O(1)	2.454(3)	N(1)-Cd(1)-O(1)	105.96(13)
Cd(1)-O(2)	2.283(3)	O(2)-Cd(1)-N(2)	121.70(13)
Cd(1)-O(4)#4	2.280(3)	O(4)#5-Cd(1)-N(2)	97.76(12)
Cd(1)-N(1)	2.339(4)	O(4)#4-Cd(1)-N(1)	166.82(12)
Cd(1)-N(2)	2.292(3)	O(2)-Cd(1)-N(1)	98.21(13)
Cd(1)-O(4)#5	2.289(3)	O(4)#5-Cd(1)-N(1)	102.43(12)
O(4)-Cd(1)#2	2.289(3)	N(2)-Cd(1)-N(1)	71.30(13)
O(4)-Cd(1)#1	2.280(3)	O(4)#4-Cd(1)-O(1)	87.16(11)
O(4)#4-Cd(1)-O(2)	90.43(11)	O(2)-Cd(1)-O(1)	54.43(11)
O(4)#4-Cd(1)-O(4)#5	76.63(11)	O(4)#5-Cd(1)-O(1)	86.50(11)
O(4)#4-Cd(1)-N(2)	95.70(12)	N(2)-Cd(1)-O(1)	175.32(13)
O(2)-Cd(1)-O(4)#5	139.67(11)		

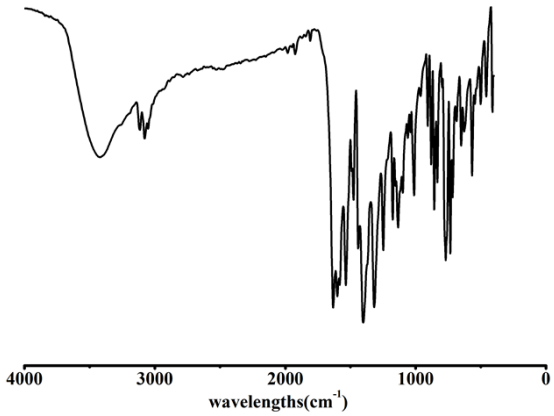
Symmetry codes: #1 : x, -y, z+1/2 ; #2 : -x+3/2, y-1/2, -z+3/2 ; #4 : x, -y, z-1/2 ; #5 : -x+3/2, y+1/2, -z+3/2.



(a)



(b)



(c)

Fig. S1 The FT-IR spectra of complexes **1** (a), **2** (b), and **3** (c).

Table S2. The FT-IR vibrational modes of the functional groups in three MOFs

1	$\upsilon_{O\text{-}Cd}$ ~ 3488 cm^{-1}	$\upsilon^{as}_{(COO^-)}$ ~ 1577 cm^{-1}, $\upsilon^{s}_{(COO^-)}$ ~ 1390 cm^{-1}	$\omega_{C\text{-}H}$ ~ 848 cm^{-1}
2	$\upsilon_{O\text{-}Cd}$ ~ 3415 cm^{-1}	$\upsilon^{as}_{(COO^-)}$ ~ 1580 cm^{-1}, $\upsilon^{s}_{(COO^-)}$ ~ 1382 cm^{-1}	$\omega_{C\text{-}H}$ ~ 760 cm^{-1}
3	$\upsilon_{O\text{-}Cd}$ ~ 3423 cm^{-1}	$\upsilon_{c=o}$ ~ 1645 cm^{-1}; $\upsilon^{as}_{(COO^-)}$ ~ 1405 cm^{-1}, $\upsilon^{s}_{(COO^-)}$~ 1325 cm^{-1}	$\omega_{C\text{-}H}$ ~ 759 cm^{-1}

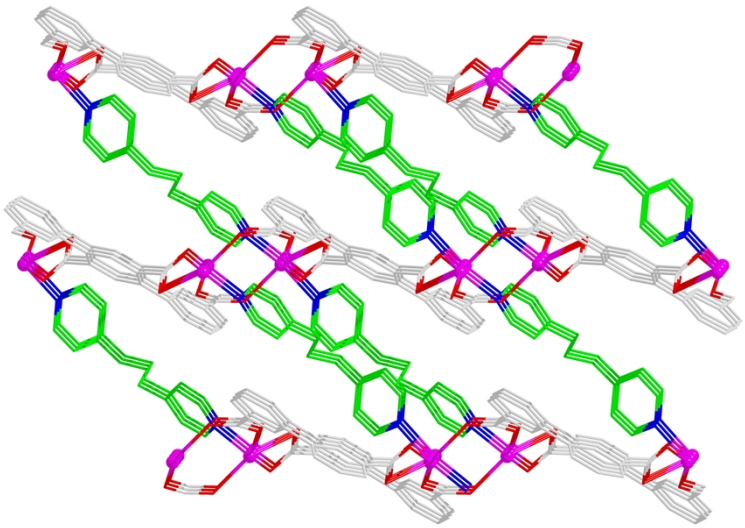


Fig. S2 The 3D framework of **1** viewed along *b* axis.

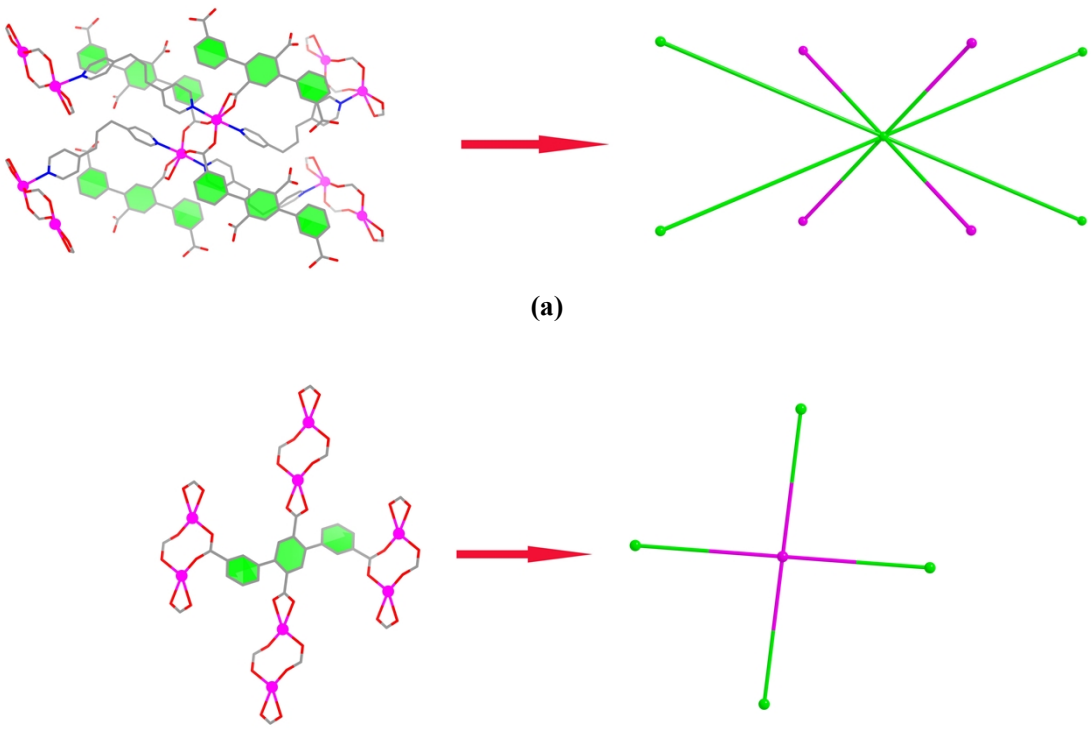


Fig. S3 The dimeric $[Cd_2(COO)_4]$ SBU unit is simplified as eight-connected node (a), and L_1^{4-} ligand is acted as four-connected nodes (b).

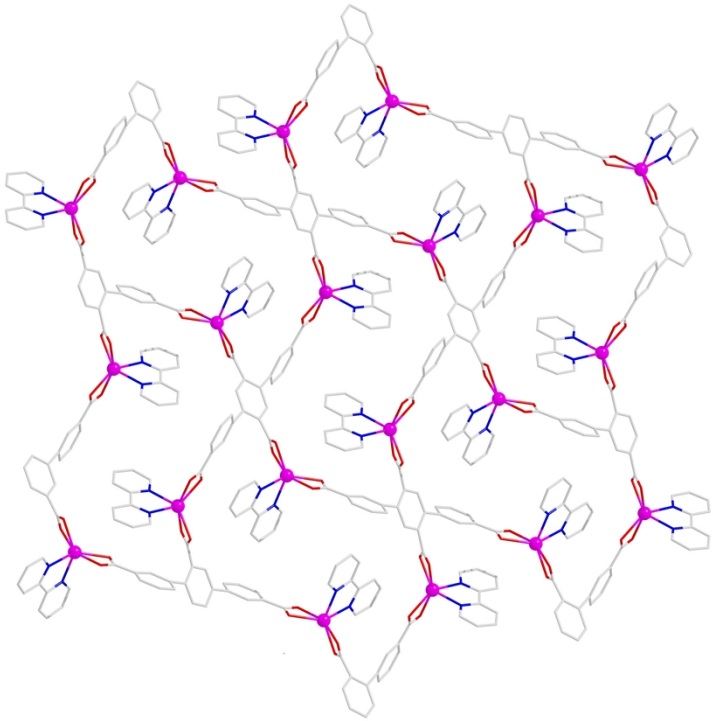
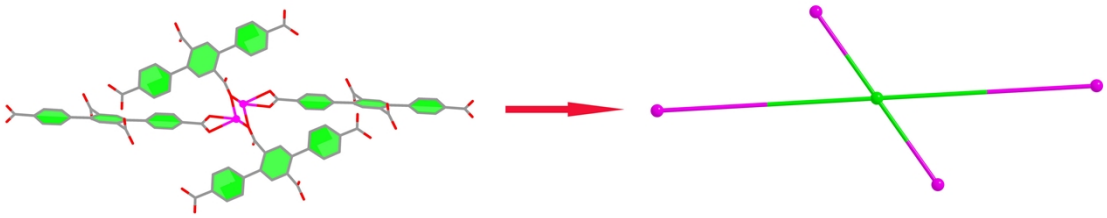
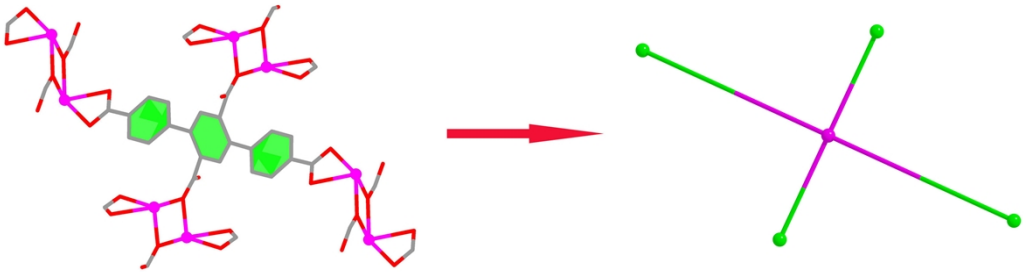


Fig. S4 The 2D grid-like layer of **2**.

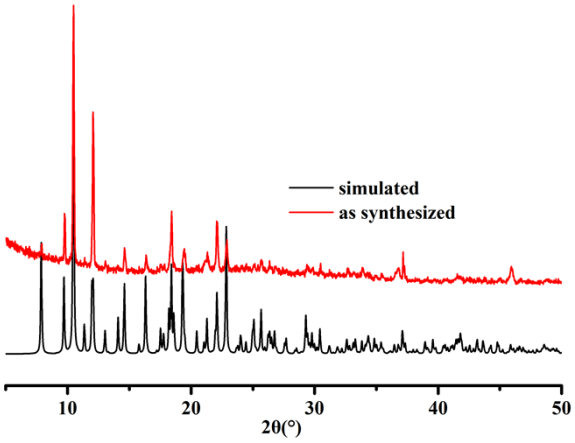


(a)

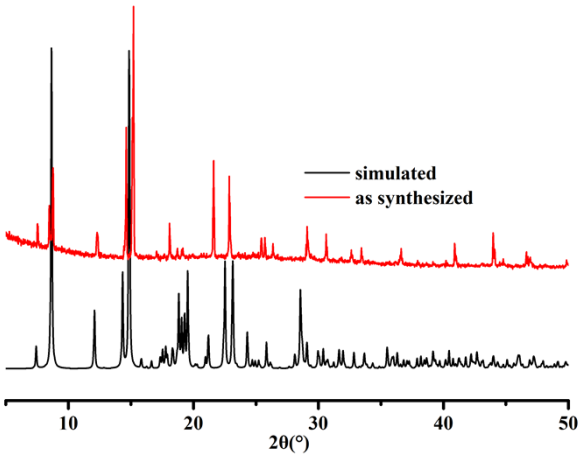


(b)

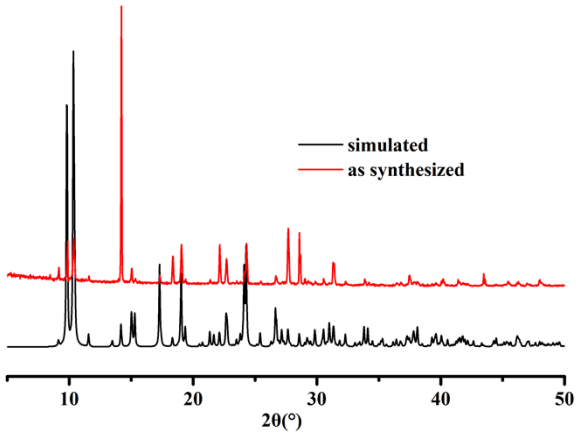
Fig. S5 The dimeric $[Cd_2(COO)_4]$ motif is considered as four-connected node (a), and L_2^{4-} ligand is acted as four-connected nodes (b).



(a)



(b)



(c)

Fig. S6 PXRD patterns of complexes **1** (a), **2** (b), and **3** (c) simulated from the X-ray single crystal structures and as-synthesized products.

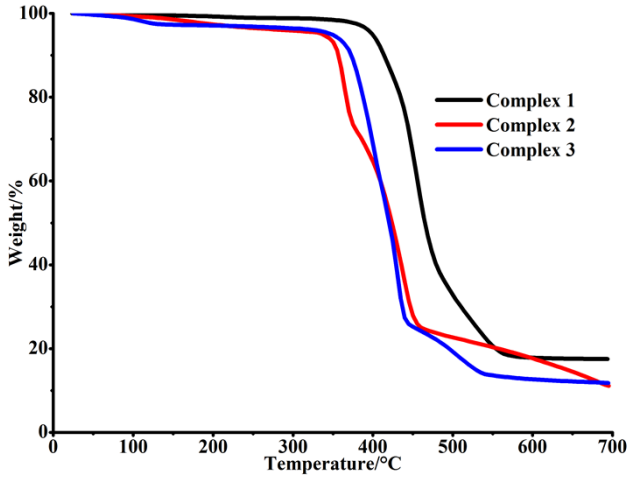
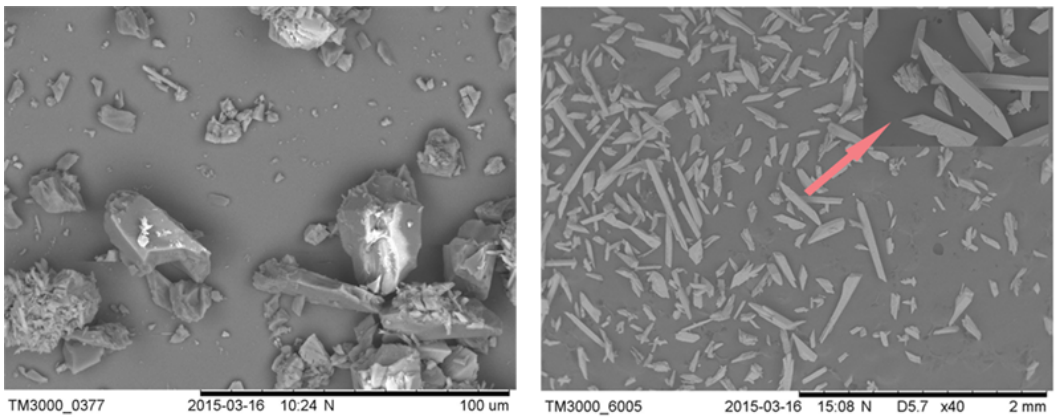


Fig. S7 TGA curves for three complexes.



(a) **(b)**

Fig. S8 The SEM images of grinded sample of **3** (a) and the original shape of **3** (b).

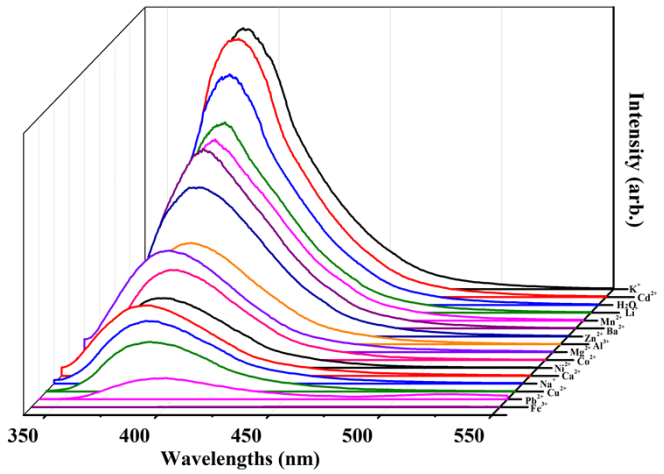


Fig. S9 Emission spectra of **3** with different metal ions.

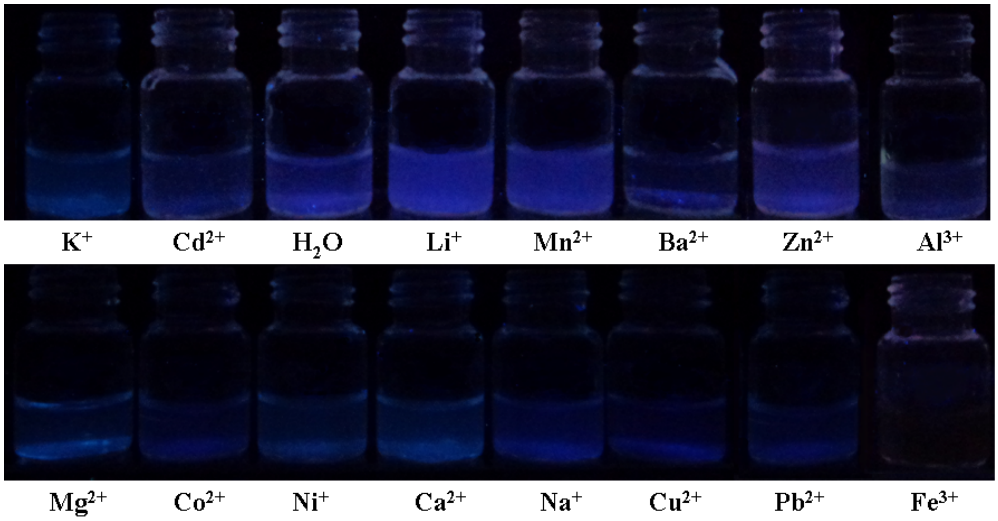
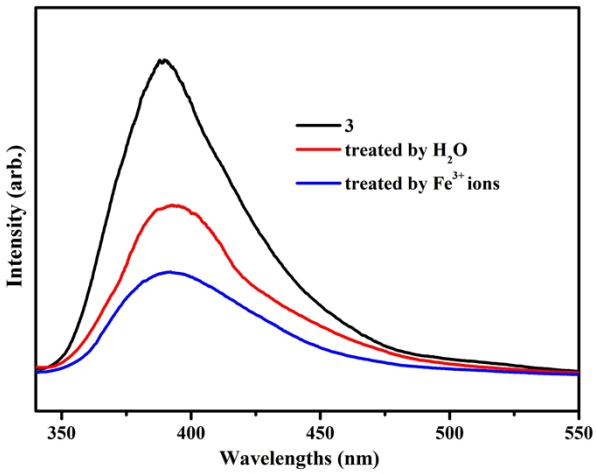
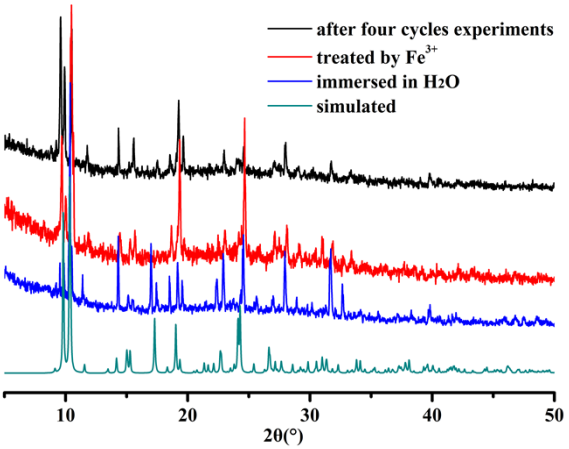


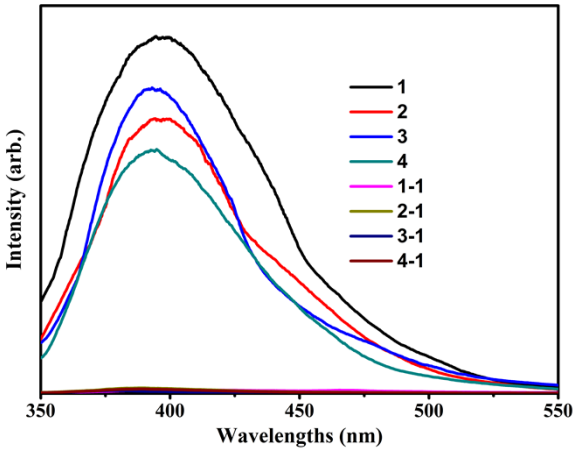
Fig. 10 Color change in aqueous solution containing different metal ions.



(a)



(b)



(c)

Fig. S11 The first cyclic emission spectra (a), PXRD patterns (b), and last four cyclic emission spectra of the sensing experiments of **3** (c).