Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Highly selective luminescence sensing in the detection of nitrobenzene and Fe^{3+} via new Cd(II)-based MOFs

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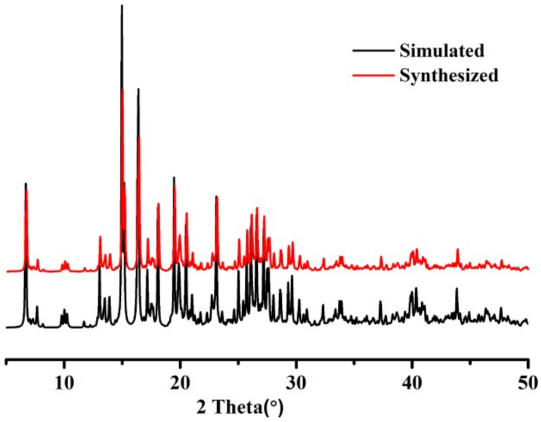
Table S1 Selected bond lengths (Å) and bond angles (º) for **1-3**

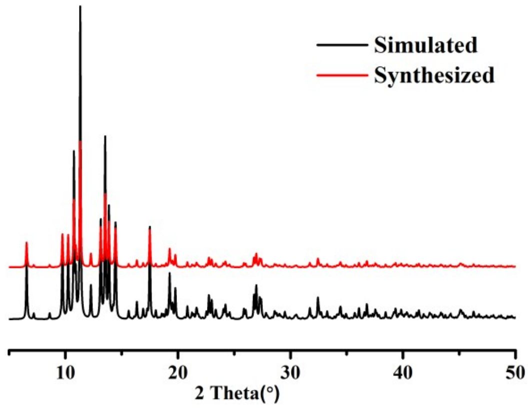
Complex **1**			
Cd(1)-O(1)	2.395(2)	Cd(1)-O(28)	2.230(3)
Cd(1)-O(51)	2.367(3)	Cd(1)-O(52)	2.198(4)
Cd(1)-O(2)	2.360(3)	Cd(1)-O(52A)	2.366(15)
Cd(2)-O(7)	2.349(2)	Cd(2)-O(8)	2.468(3)
Cd(1)-O(50)	2.315(3)	Cd(1)-O(27)	2.604(3)
Cd(2)-O(21)	2.389(2)	Cd(2)-O(22)	2.278(3)
Cd(2)-O(23)	2.418(3)	Cd(2)-O(24)	2.279(3)
Cd(2)-O(20)	2.377(2)	Cd(3)-O(13)	2.343(3)
Cd(3)-O(14)	2.413(2)	Cd(3)-O(15)	2.258(3)
Cd(3)-O(16)	2.257(3)	Cd(3)-O(17)	2.391(4)
Cd(3)-O(37)#1	2.665(3)	Cd(3)-O(38)#1	2.258(2)
Cd(4)-O(31)	2.441(3)	Cd(4)-O(32)	2.336(2)
Cd(4)-O(43)	2.237(3)	Cd(4)-O(44)	2.331(3)
Cd(4)-O(45)	2.363(3)	O(1)-Cd(1)-O(27)	169.27(9)
O(2)-Cd(1)-O(52A)	147.8(5)	O(2)-Cd(1)-O(51)	85.17(11)
O(2)-Cd(1)-O(27)	121.16(9)	O(2)-Cd(1)-O(1)	54.44(8)
O(28)-Cd(1)-O(51)	103.83(11)	O(28)-Cd(1)-O(52A)	130.5(6)
O(50)-Cd(1)-O(52A)	89.7(4)	O(50)-Cd(1)-O(2)	105.50(10)
O(50)-Cd(1)-O(51)	168.93(11)	O(50)-Cd(1)-O(1)	88.92(9)
O(50)-Cd(1)-O(27)	101.81(9)	O(51)-Cd(1)-O(52A)	79.5(4)
O(51)-Cd(1)-O(27)	74.33(9)	O(51)-Cd(1)-O(1)	95.15(9)
O(52)-Cd(1)-O(51)	89.52(18)	O(52)-Cd(1)-O(50)	81.29(16)
O(52)-Cd(1)-O(28)	147.21(16)	O(52)-Cd(1)-O(27)	103.88(19)
O(52)-Cd(1)-O(2)	130.93(17)	O(52)-Cd(1)-O(1)	77.68(18)
O(52A)-Cd(1)-O(27)	81.7(6)	O(52A)-Cd(1)-O(1)	98.7(6)

O(7)-Cd(2)-O(21)	99.20(8)	O(7)-Cd(2)-O(23)	99.07(9)
O(20)-Cd(2)-O(8)	117.32(9)	O(20)-Cd(2)-O(21)	54.67(8)
O(20)-Cd(2)-O(23)	102.63(9)	O(21)-Cd(2)-O(8)	79.01(9)
O(15)-Cd(3)-O(37)#1	136.67(10)	O(15)-Cd(3)-O(38)#1	93.07(11)
O(33)-Cd(4)-O(31)	76.88(9)	O(33)-Cd(4)-O(32)	117.81(8)
O(33)-Cd(4)-O(34)	54.61(8)	O(33)-Cd(4)-O(44)	107.13(11)
Symmetrical codes: #1 x-1,y, z-2; #2 x+1, y, z+2.			
Complex **2**			
O(4)-Cd(1)#1	2.285(7)	Cd(1)-O(8)#3	2.435(7)
Cd(1)-O(4)#2	2.285(7)	Cd(1)-O(7)#3	2.359(7)
Cd(1)-O(1)	2.421(7)	Cd(1)-O(6)#4	2.199(7)
Cd(1)-O(2)	2.409(7)	O(4)#2-Cd(1)-O(1) O(4)#2-	132.7(3)
O(4)#2-Cd(1)-O(2)	79.2(3)	Cd(1)-O(7)#3	96.3(3)
O(4)#2-Cd(1)-O(8)#3	125.8(2)	O(1)-Cd(1)-O(8)#3	91.9(3)
O(2)-Cd(1)-O(1)	53.5(2)	O(2)-Cd(1)-O(8)#3	132.8(3)
O(7)#3-Cd(1)-O(1)	83.6(3)	O(7)#3-Cd(1)-O(2) O(6)#4-	87.6(3)
O(7)#3-Cd(1)-O(8)#3	53.8(2)	Cd(1)-O(4)#2 O(6)#4-	109.4(3)
O(6)#4-Cd(1)-O(1) O(6)#4-	98.6(3)	Cd(1)-O(2) O(6)#4-	124.9(3)
Cd(1)-O(8)#3	87.2(3)	Cd(1)-O(7)#3	141.1(3)
Symmetrical codes: #1 x,y-1,z; #2 x,y+1,z; #3 -x+1/2,y+1/2,-z+1/2; #4 -x,-y+2,-z+1; #5 -x+1/2,y-1/2,-z+1/2.			
Complex **3**			
O(8)-Cd(1)#1	2.272(5)	Cd(1)-O(8)#2	2.272(5)
Cd(1)-O(4)#3	2.323(4)	Cd(1)-O(5)#3	2.392(5)
Cd(1)-O(16)#4	2.229(5)	Cd(1)-O(2)	2.554(5)
Cd(1)-O(1)	2.291(4)	Cd(2)-O(7)#5	2.305(5)
Cd(2)-O(3)#6	2.240(5)	Cd(2)-O(6)#5	2.336(5)
Cd(2)-O(9)	2.331(5)	Cd(2)-O(1)#1	2.250(5)
Cd(2)-O(10) O(7)-	2.275(8)	O(4)-Cd(1)#7 O(16)-	2.323(4)
Cd(2)#5	2.305(5)	Cd(1)#4 O(3)-Cd(2)#6	2.229(5)
O(5)-Cd(1)#7 O(6)-	2.392(5)	O(8)#2-Cd(1)-O(2) O(8)#2-	2.240(5)
Cd(2)#5 O(8)#2-Cd(1)-	2.336(5)	Cd(1)-O(1) O(4)#3-	162.12(18)
O(4)#3 O(8)#2-Cd(1)-O(5)#3	100.51(18)	Cd(1)-O(2) O(16)#4-Cd(1)-	112.32(17)
O(4)#3-Cd(1)-O(5)#3	86.75(19)	O(8)#2 O(16)#4-Cd(1)-	92.85(17)
O(5)#3-Cd(1)-O(2)	55.81(17)	O(5)#3 O(16)#4-Cd(1)-	91.7(2)
O(16)#4-Cd(1)-O(4)#3	91.05(18)	O(2) O(1)-Cd(1)-O(4)#3	146.58(18)
O(16)#4-Cd(1)-O(1)	91.89(19)	O(1)-Cd(1)-O(2)	99.7(2)
O(1)-Cd(1)-O(5)#3 O(7)#5-	95.8(2)	O(7)#5-Cd(2)-O(9)	145.94(18)
Cd(2)-O(6)#5 O(3)#6-	115.59(19)	O(3)#6-Cd(2)-O(6)#5	53.17(15)
Cd(2)-O(7)#5 O(3)#6-	56.39(17)	O(3)#6-Cd(2)-O(1)#1	92.80(19)
Cd(2)-O(9) O(3)#6-Cd(2)-	102.77(18)	O(1)#1-Cd(2)-O(7)#5	157.96(19)
O(10) O(1)#1-Cd(2)-O(6)#5	86.45(18)	O(1)#1-Cd(2)-O(9)	98.55(18)
	84.0(2)		156.0(2)
	103.35(18)		77.51(18)

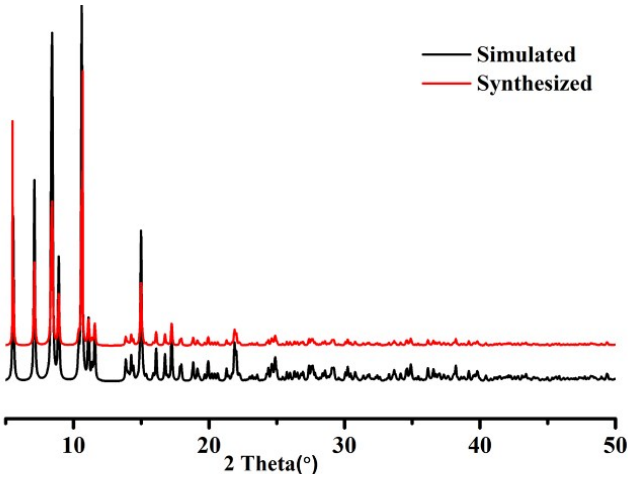
Symmetrical codes: #1 x,y+1,z; #2 x,y-1,z; #3 -x+1/2,y-1/2,-z+1/2; #4 -x+1/2,-y-1/2,-z+1; #5 -x,-y+1,-z+1;#6 -x+1/2,-y+1/2,-z+1; #7 -x+1/2,y+1/2,-z+1/2.



(a)



(b)



(c)

Fig. S1 PXRD patterns of **1**-**3** in (a-c) simulated from the X-ray single-crystal structure and experimental samples.

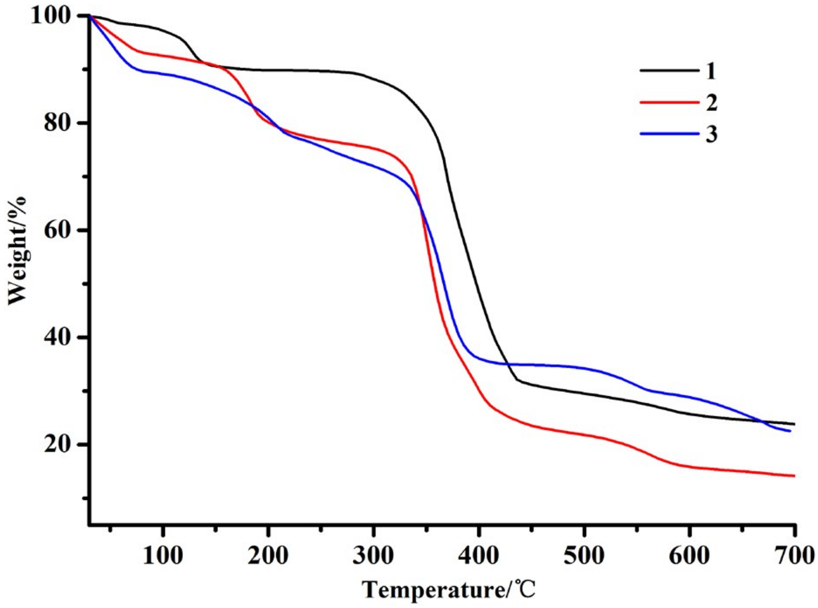
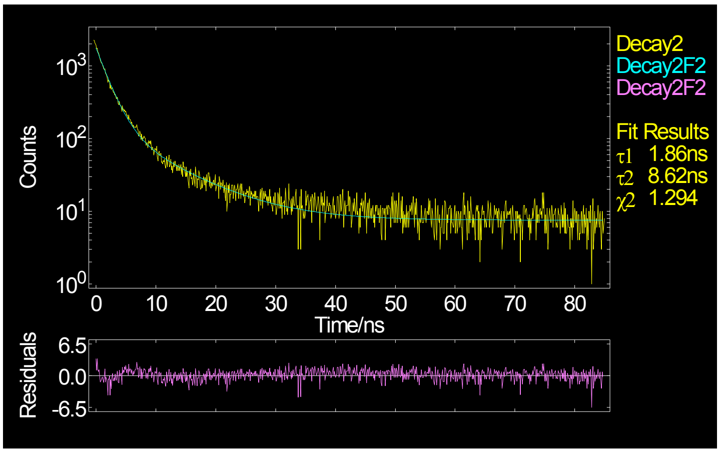
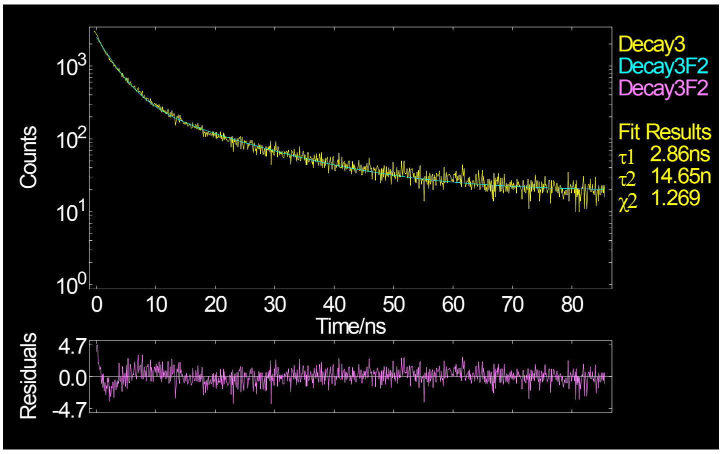


Fig. S2 TGA plots of complexes **1-3**.



(a)



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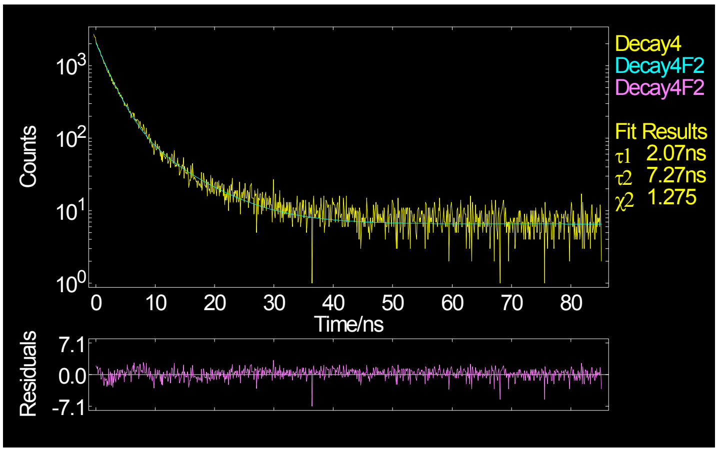
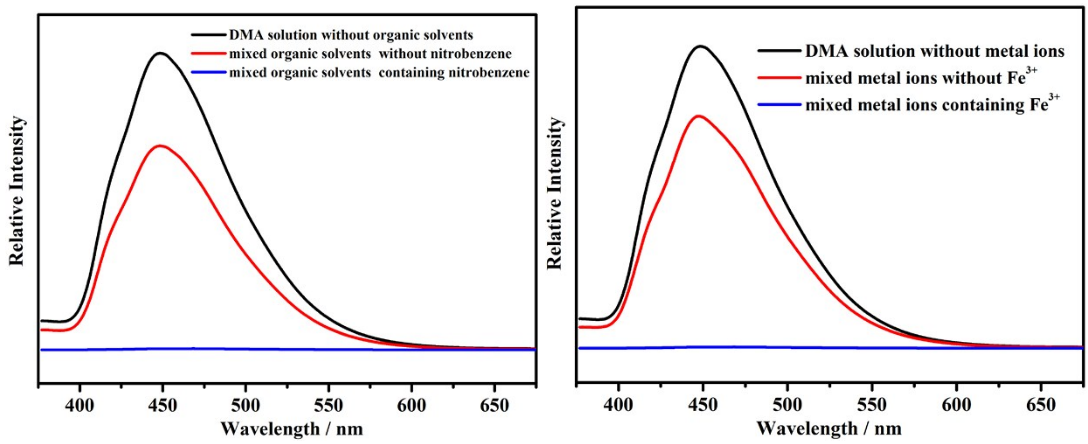


(c)

Fig. S3 Luminescence decay curves of compounds **1** (a), **2** (b), and **3** (c).



(a) (b)

Fig. S4 The emission spectra of **3** with different mixed organic solvents (a) and metal ions (b).

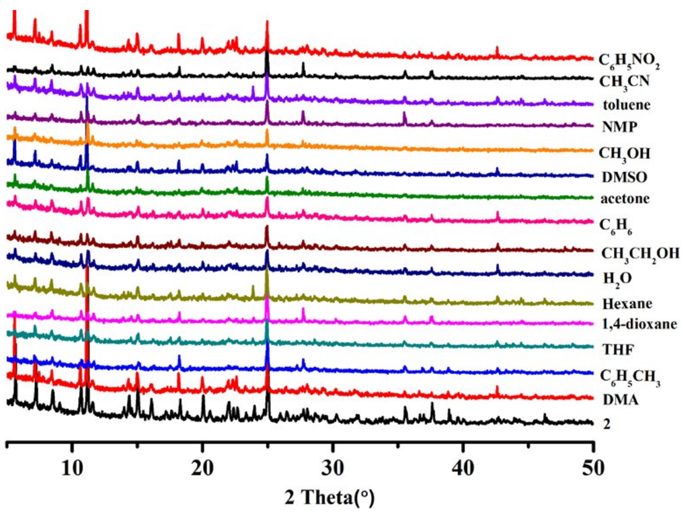
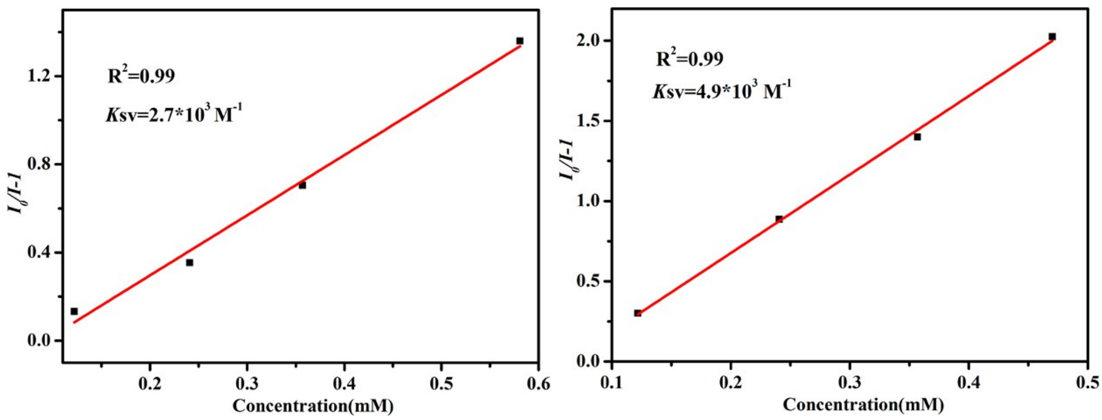


Fig. S5 PXRD patterns of **3** treated by different organic molecular DMA solutions. It indicated that complex **3** retains its framework after immersed in DMA solution containing different organic molecules.



(a) (b)

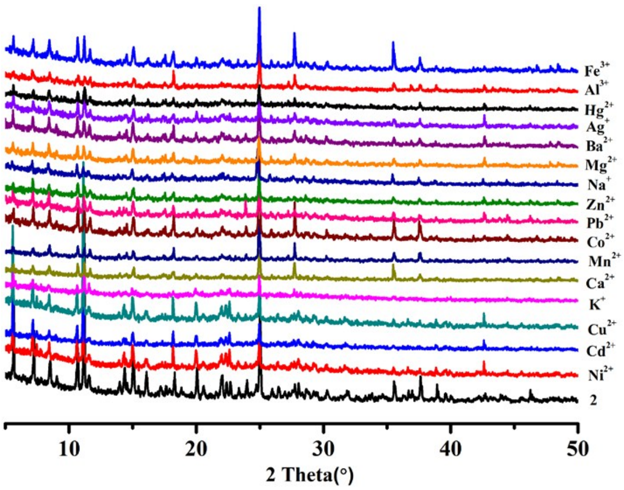
Fig. S6 Stern–Volmer plot of **3** for nitrobenzene (a) and Fe^{3+}(b).

Table S2. Standard Deviation (σ) calculation for the detection of nitrobenzene for **3.**

Test	fluorescence intensity (nm)
1	1854.318
2	1851.261
3	1857.315
4	1852.677
5	1855.394
average	1854.193
standard deviation (σ)	2.29

Table S3. Standard Deviation (σ) calculation for the detection of Fe^{3+} for **3.**

Test	fluorescence intensity (nm)
1	1770.589
2	1772.645
3	1775.876
4	1771.879
5	1773.443
average	1772.8864
standard deviation (σ)	1.97



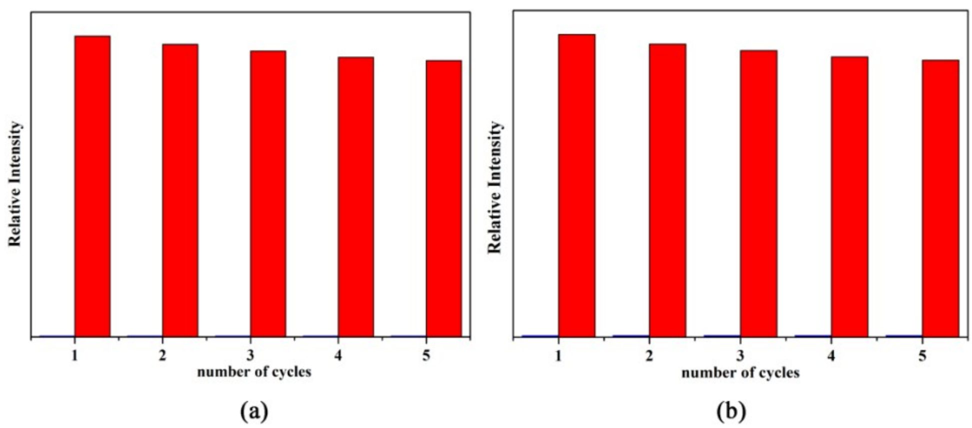


Fig. S7 PXRD patterns of **3** treated by different K(cation)$_x$ DMA solutions. It indicated that **3** retains its framework after immersed in DMA solution containing different anions. Multiple cycles for the fluorescence quenching of **3** by nitrobenzene (a) and Fe^{3+} (b), and recovery after washing by DMA for several times.

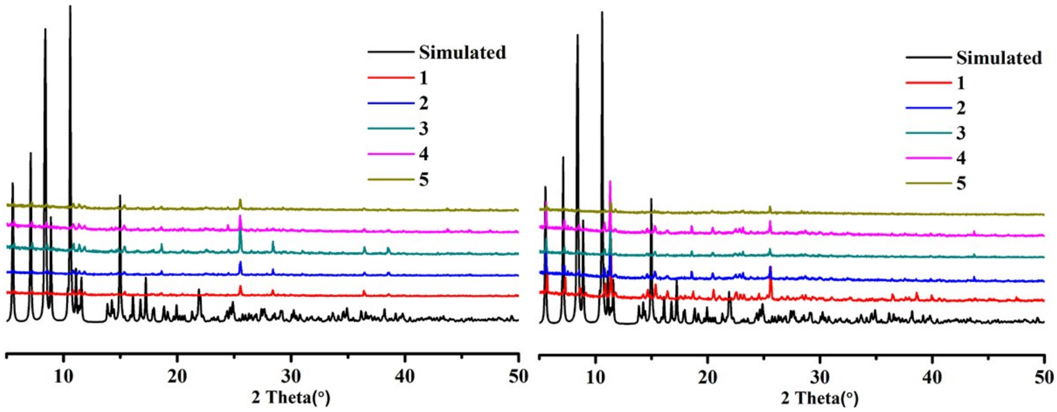


Fig. S8 PXRD patterns of **3** treated by multiple cycles for the fluorescence quenching by nitrobenzene (a) and Fe^{3+} (b).

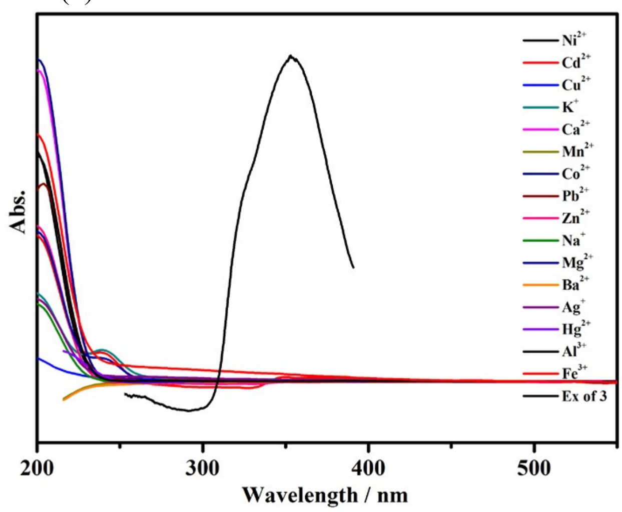
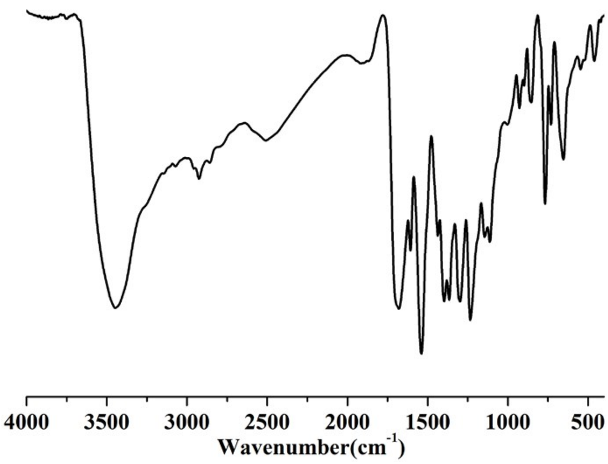
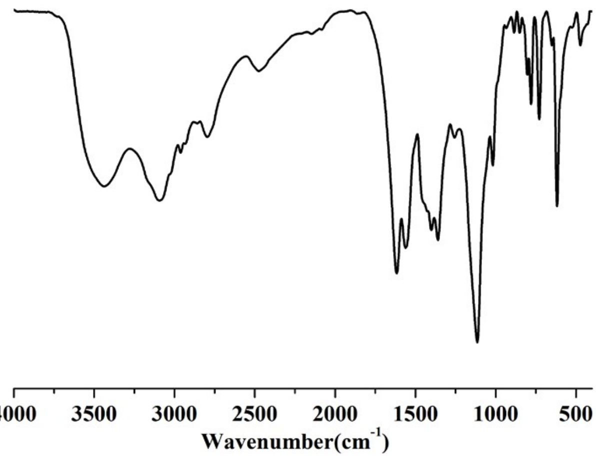


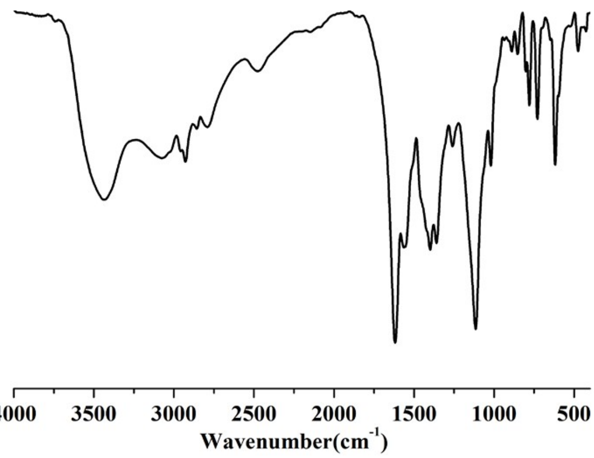
Fig. S9 UV-Vis adsorption spectra of $M(NO3)_X$ aqueous solutions and the excitation spectrum of **3**.



(a)



(b)



(c)

Fig. S10 IR spectra of the as-synthesized **1-3** in (a-c).