

Two Luminescent Transition-Metal–Organic Frameworks with Predesigned Ligand as Highly Sensitive and Selective Iron(III) Sensors

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Supporting Information

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Table S1. Selected bond distances (Å) and angles (°) for **1**

Cd(1)-N(1)	2.275(2)	Cd(1)-N(3)#1	2.306(2)
Cd(1)-N(2)	2.329(3)	Cd(1)-O(1)	2.343(2)
Cd(1)-O(2)#2	2.387(2)	Cd(1)-O(4)#1	2.411(2)
N(1)-Cd(1)-N(2)	94.34(9)	O(2)#2-Cd(1)-O(4)#1	78.66(8)
N(3)#1-Cd(1)-N(2)	96.28(9)	O(1)-Cd(1)-O(4)#1	88.46(8)
N(1)-Cd(1)-O(1)	73.46(8)	N(2)-Cd(1)-O(4)#1	162.83(8)
N(3)#1-Cd(1)-O(1)	86.86(8)	N(3)#1-Cd(1)-O(4)#1	71.51(8)
N(2)-Cd(1)-O(1)	103.22(9)	N(1)-Cd(1)-O(4)#1	101.11(8)
N(1)-Cd(1)-O(2)#2	109.27(8)	O(1)-Cd(1)-O(2)#2	167.11(8)
N(3)#1-Cd(1)-O(2)#2	88.58(8)	N(2)-Cd(1)-O(2)#2	89.25(9)

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

Table S2. Selected bond distances (Å) and angles (°) for **2**.

Zn(1)-O(1)#1	2.141(3)	Zn(1)-O(1)	2.140(3)
Zn(1)-N(2)#2	2.160(5)	Zn(1)-N(3)#1	2.163(3)
Zn(1)-N(3)	2.163(3)	Zn(1)-N(1)	2.185(5)
O(1)-Zn(1)-O(1)#1	179.00(17)	O(1)#1-Zn(1)-N(2)#2	90.50(9)
O(1)-Zn(1)-N(2)#2	90.50(9)	O(1)-Zn(1)-N(3)#1	100.23(14)
O(1)#1-Zn(1)-N(3)#1	79.71(14)	N(2)#2-Zn(1)-N(3)#1	93.64(9)
O(1)-Zn(1)-N(3)	79.71(14)	O(1)#1-Zn(1)-N(3)	100.23(14)
N(2)#2-Zn(1)-N(3)	93.64(9)	N(3)#1-Zn(1)-N(3)	172.71(19)
O(1)-Zn(1)-N(1)	89.50(9)	O(1)#1-Zn(1)-N(1)	89.50(9)
N(2)#2-Zn(1)-N(1)	180.0	N(3)#1-Zn(1)-N(1)	86.36(9)
N(3)-Zn(1)-N(1)	86.36(9)		

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

Table S3. The quenching efficiency of sensors for Fe³⁺

Compounds	Quenching Efficiency	Reference
An azaindole based schiff base AzIm	75%	1
micrometer-sized phase of [Tb(TAIP)(DMF) ₂]	87%	2
copillar[5]arene PF5	88.4%	3
Tyloxapol (one kind of water soluble oligomer)	89%	4
[Zn ₅ (hfipbb) ₄ (trz) ₂ (H ₂ O) ₂]	96.60%	5
Fluorescent conjugated polymer PFCA	99%	6
[(CH ₃) ₂ NH ₂] ₂ ·[Tb(bptc)]·xsolvents	99.06%	7
[Cd(<i>p</i> -CNPhHIDC)(4,4'-bipy) _{0.5}] _n (1)	92.6	This work
[Zn(<i>p</i> -CNPhHIDC)(4,4'-bipy)] _n (2)	88.5	This work

Table S4. Comparison of K_{sv} values of **1** and **2** towards Fe^{3+} ion with other compounds

Compounds	solvents	$K_{sv}(M^{-1})$	Ref.
Rhodamine	CH_3CN	9.75×10^2	8
$Gd_6(L)_3(HL)_2(H_2O)_{10}$	water	7.89×10^2	9
$Eu_2(MFDA)_2(HCOO)_2(H_2O)_6$	DMF	1.58×10^3	10
BUT-14	water	2.17×10^3	11
Tb-DSOA	water	3.54×10^3	12
EuL_3	water	4.10×10^3	13
Bis(rhodamine)-2	CH_3CN	5.10×10^3	14
Eu^{3+} @MIL-53-COOH (Al)	water	5.12×10^3	15
Bis(rhodamine)-1	CH_3CN	7.50×10^3	16
$Eu(atpt)_{1.5}(phen)(H_2O)$	ethanol	7.60×10^3	17
Eu-BPDA	water	1.25×10^4	18
$La(TPT)(DMSO)_2$	ethanol	1.36×10^4	19
BUT-15	water	1.66×10^4	11
Eu-HODA	water	2.09×10^4	20
$\{[Eu_2K_2(dcppa)_2(H_2O)_6] \cdot mH_2O\}_n$	water	4.3×10^4	21
Benzimidazole-based sensor	water	8.51×10^4	22
$[Cd(p-CNPhHIDC)(4,4'-bipy)_{0.5}]_n$ (1)	water	1.99×10^3	This work
$[Zn(p-CNPhHIDC)(4,4'-bipy)]_n$ (2)	water	1.37×10^3	This work

Table S5 The ICP results of complexes **1** and **2** after treated with Fe³⁺ for 12 h

Complex	1	2
Initial value / Fe ³⁺	5.0 × 10 ⁻³ mol/L	5.0 × 10 ⁻³ mol/L
After treated with Fe ³⁺ for 12 h	3.23 × 10 ⁻³ mol/L	3.75 × 10 ⁻³ mol/L

Table S6 The EA results of complexes **1** and **2** after treated with Fe³⁺ for 12 h

Complex	1			2		
	C%	H%	N%	C%	H%	N%
Original samples	45.68	2.01	12.31	55.42	2.63	14.68
After treated with Fe ³⁺ for 12 h	C%	H%	N%	C%	H%	N%
	43.12	2.28	11.72	50.29	2.75	13.36

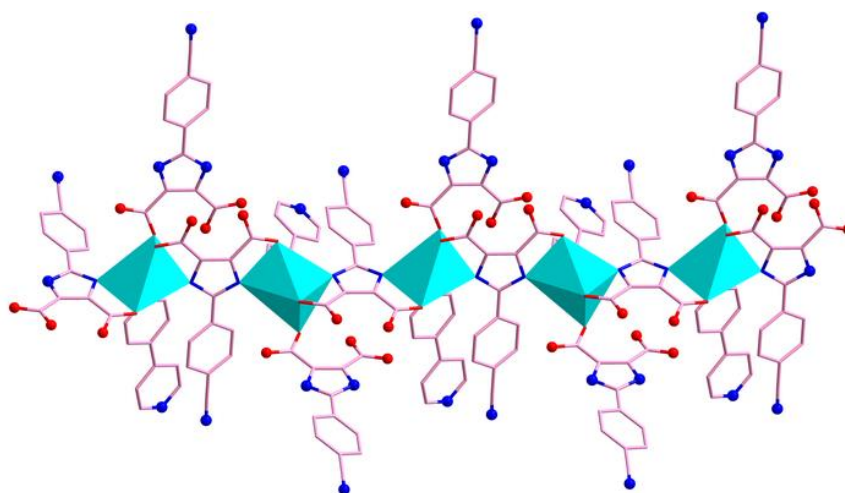
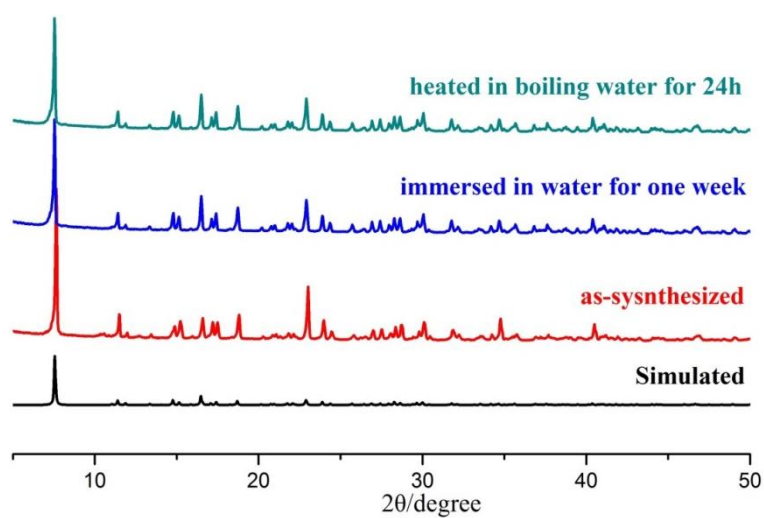


Fig. S1 1D chain of **1** supported by imidazole dicarboxylate ligands



(a)

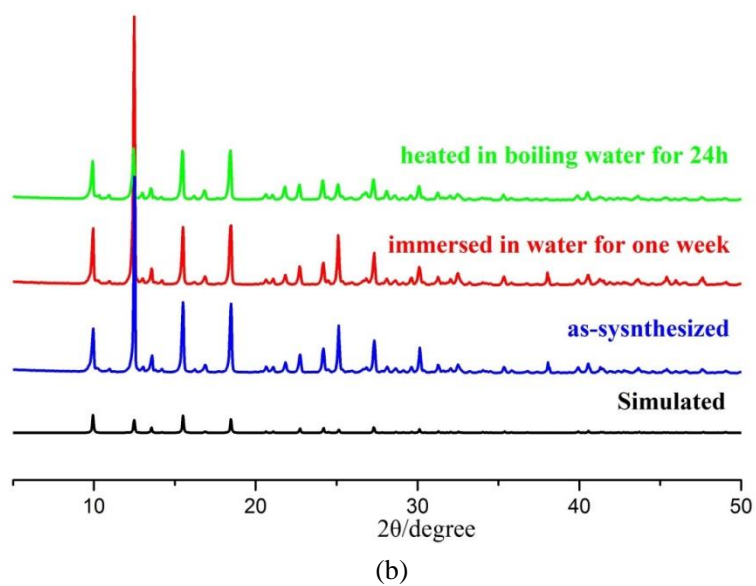


Fig. S2. PXRD patterns of **1** (a) and **2** (b) for the simulated, as-synthesized and after water treated samples.

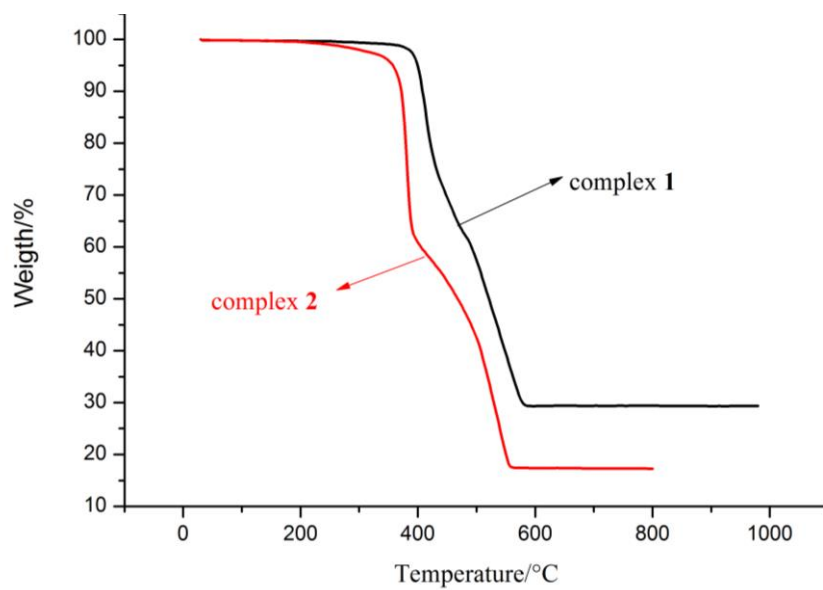
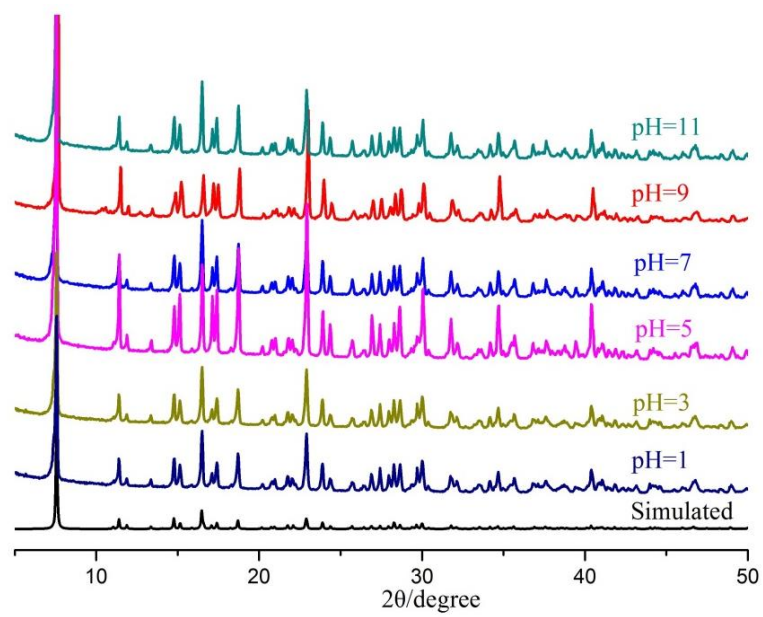


Fig. S3 Thermal gravimetric analyses of complexes **1** and **2**.



(a)

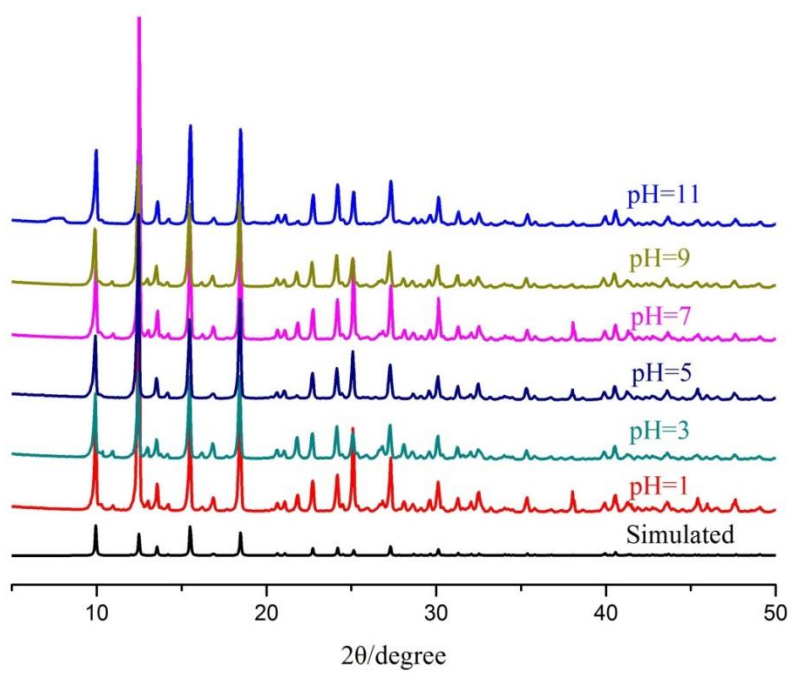
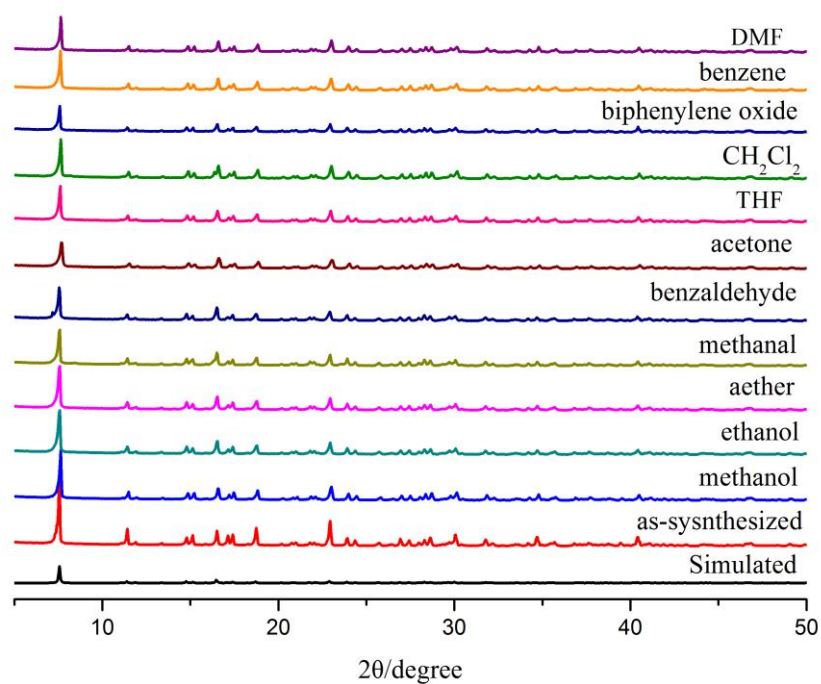


Fig. S4. PXRD patterns of 1 (a) and 2 (b) immersed in different pH solutions



(a)

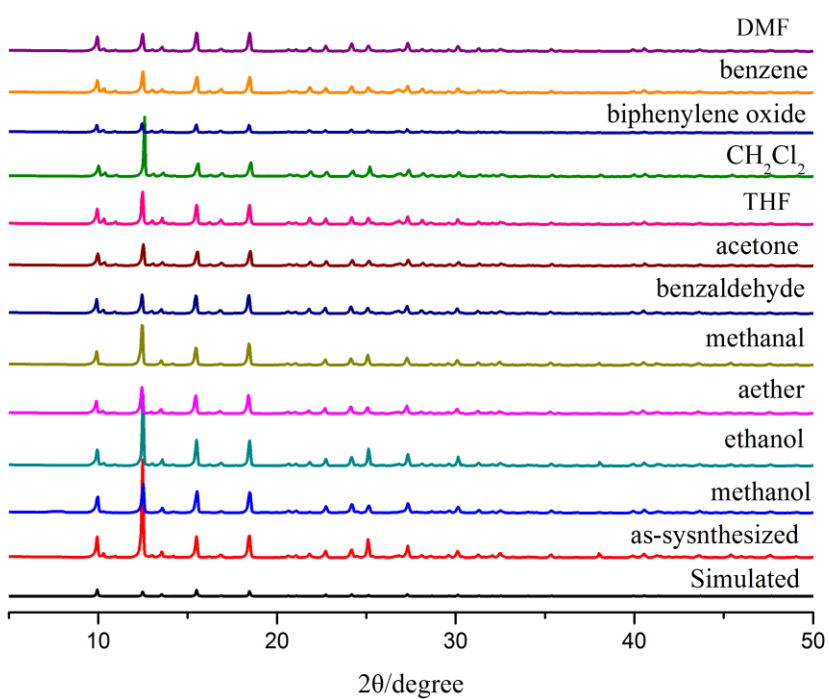


Fig. S5. PXRD patterns of **1** (a) and **2** (b) immersed in different solvents at room temperature.

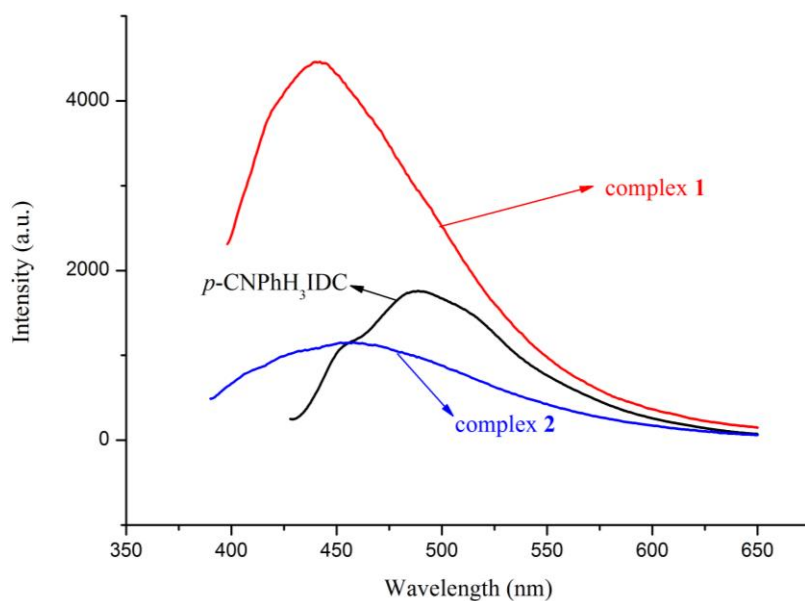
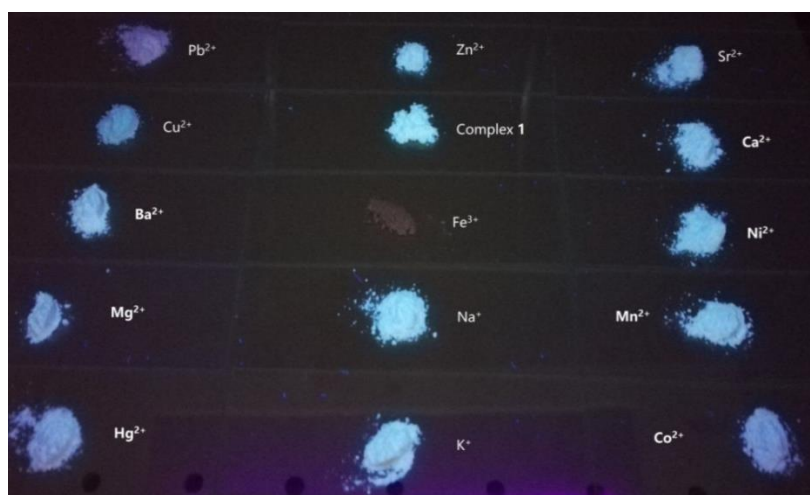
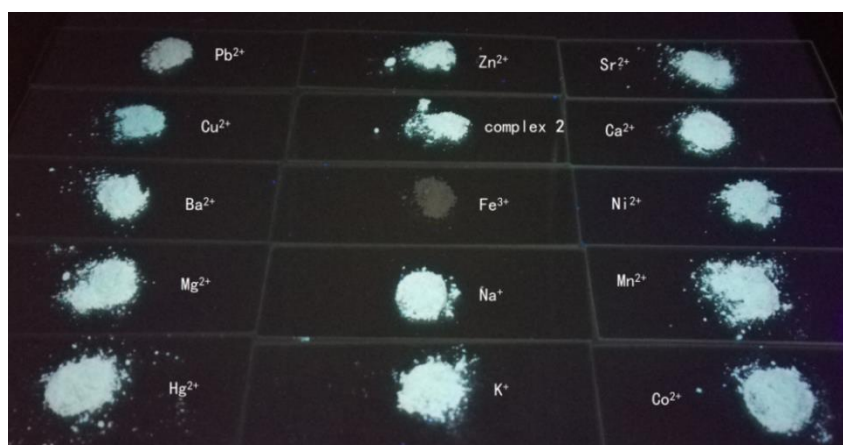


Fig. S6 Solid-state luminescence spectra of free *p*-CNPhH₃IDC ligand and complexes **1** and **2** at room temperature.

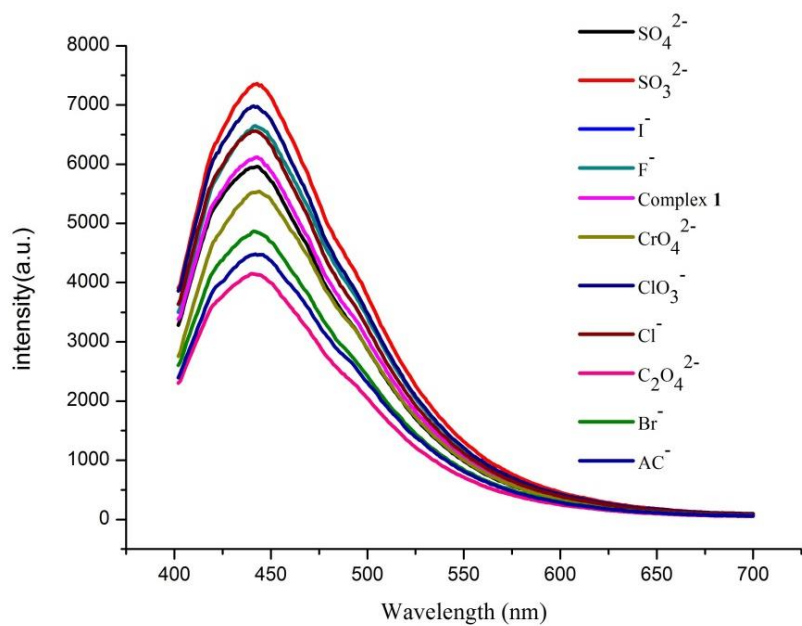


(a)

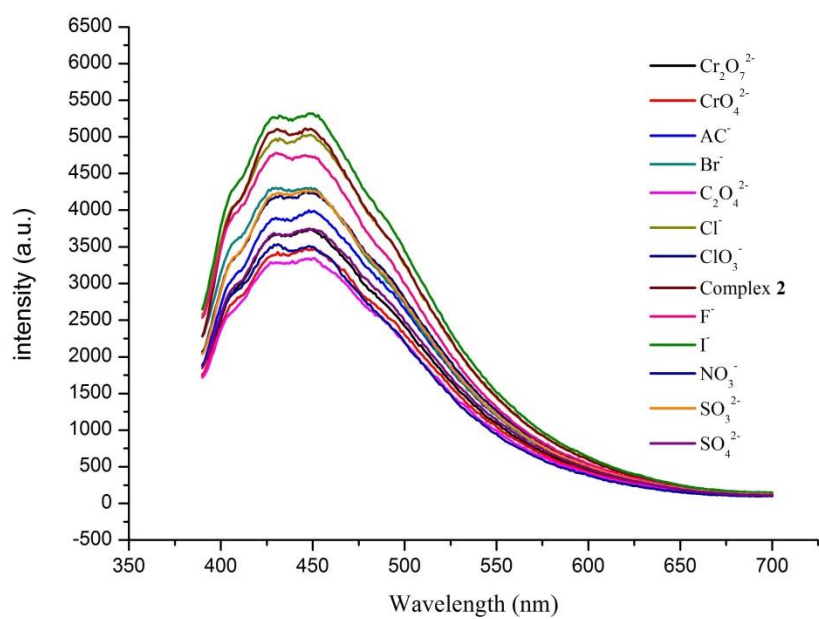


(b)

Fig. S7 The colors of M^{n+} -**1** (a) or -**2** (b) samples at room temperature under the excitation of 365 nm.



(a)



(b)

Fig. S8 Photoluminescence intensity of complex 1 (a) (or 2 (b)) treated by different anions (0.01 M) in aqueous solutions.

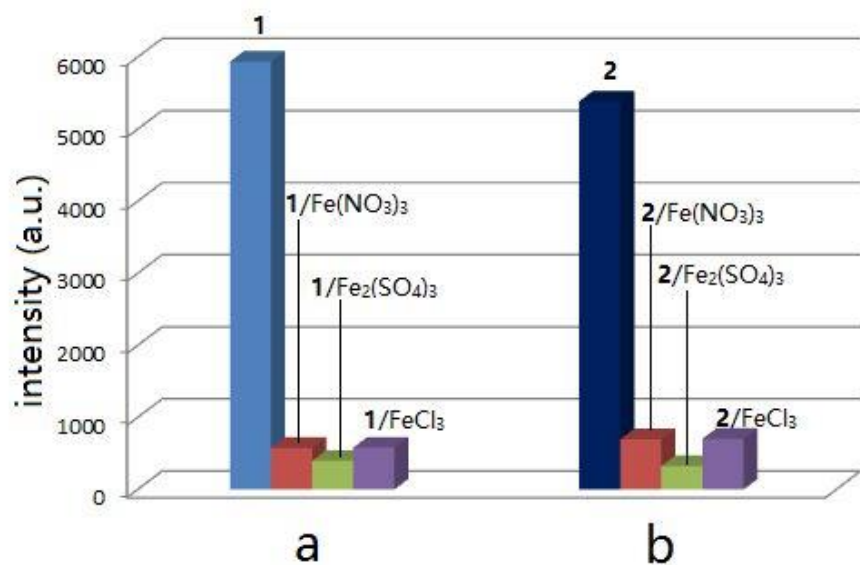
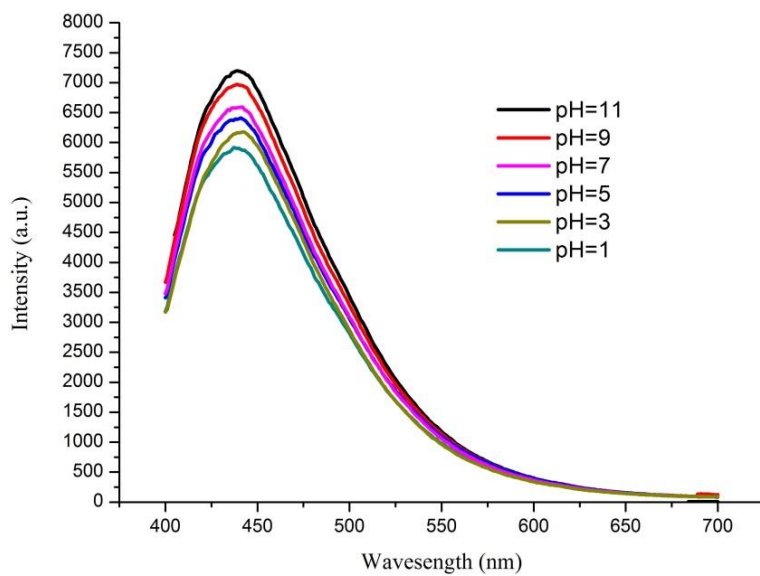
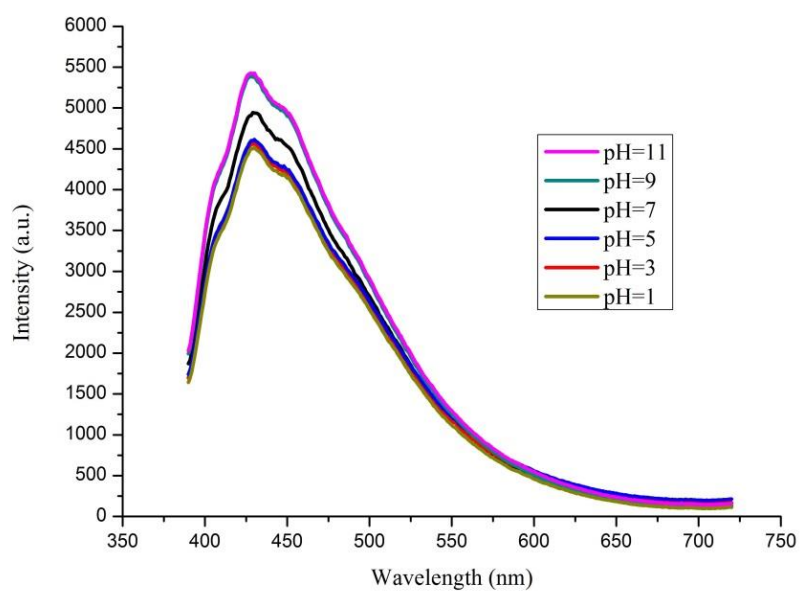


Fig. S9 Photoluminescence intensity of complex **1** (a) (or **2** (b)) treated by different Fe(III) salts (0.01 M) in aqueous solutions.

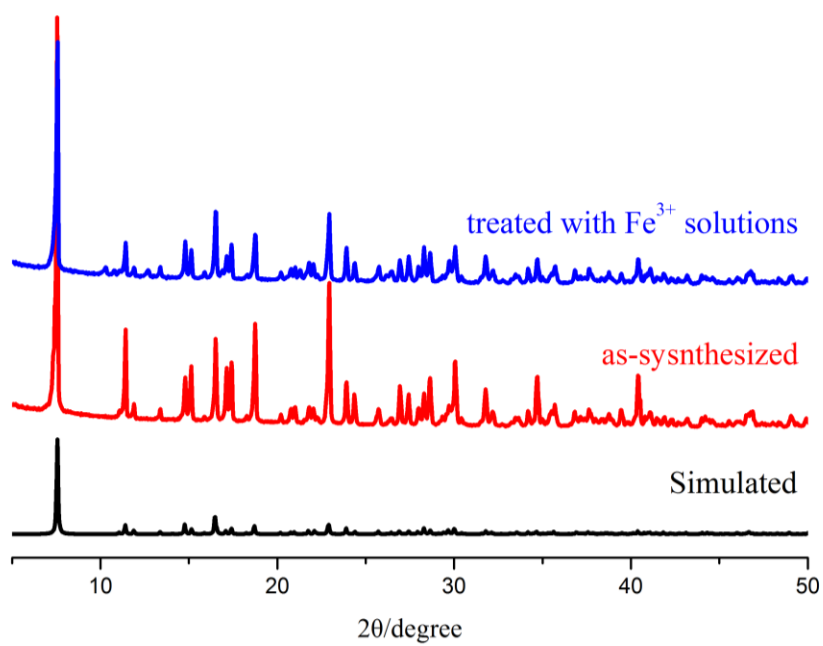


(a)

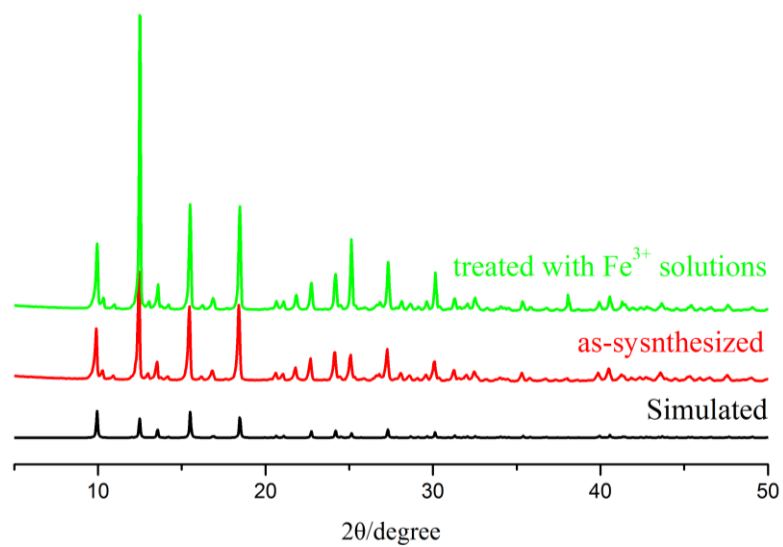


(b)

Fig. S10 Solid-state luminescence spectra of 1 (a) and 2 (b) treated with different pH aqueous solutions

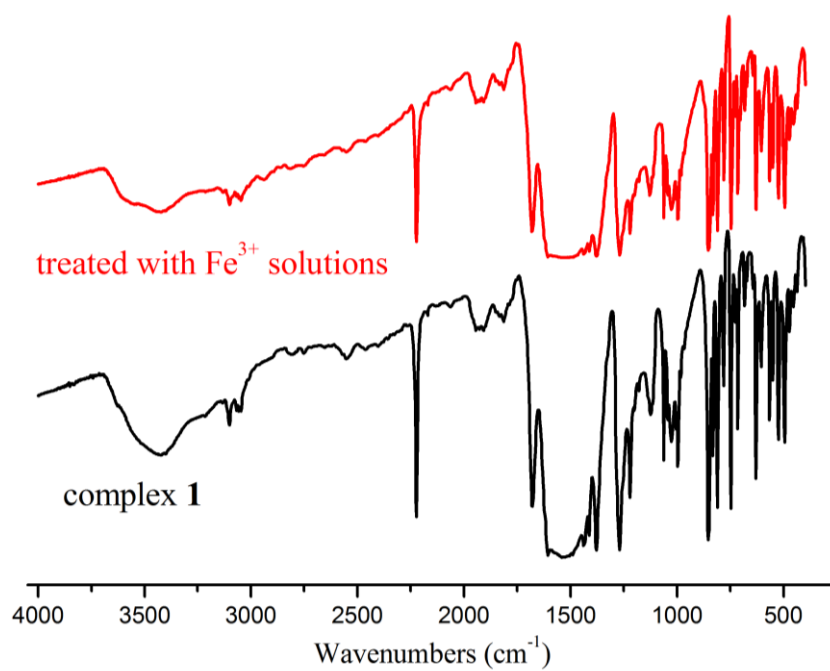


(a)

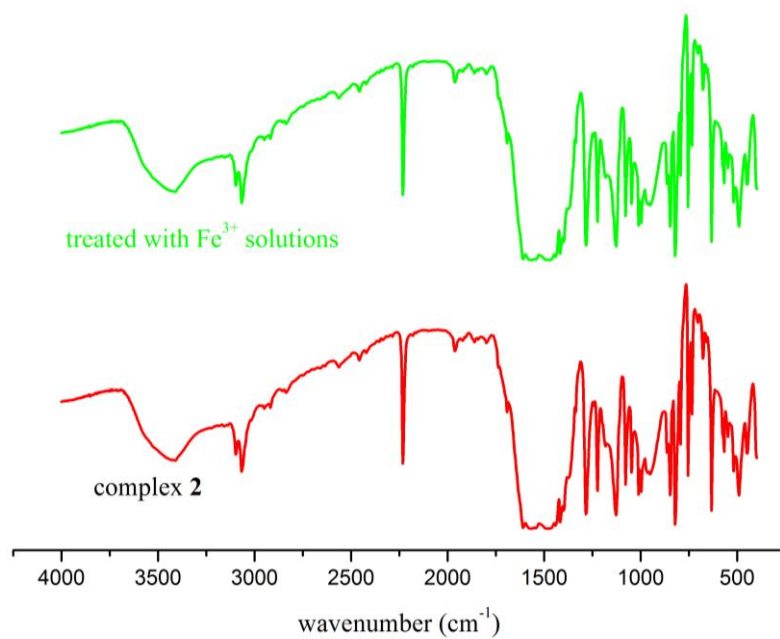


(b)

Fig. S11 PXR D patterns of simulated, as-synthesized, **1** (a) or **2** (b) immersed in aqueous solution of Fe(NO₃)₃.

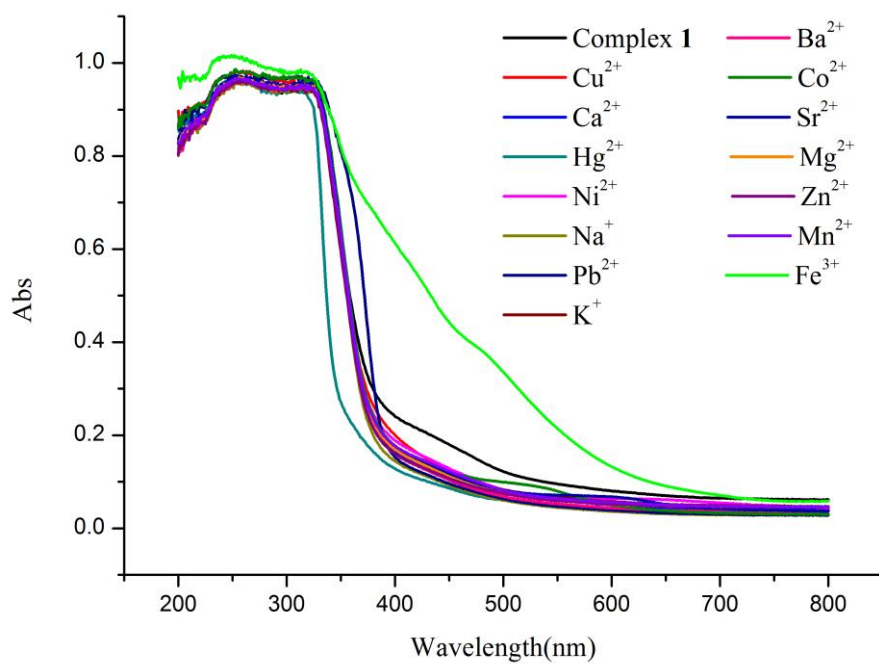


(a)

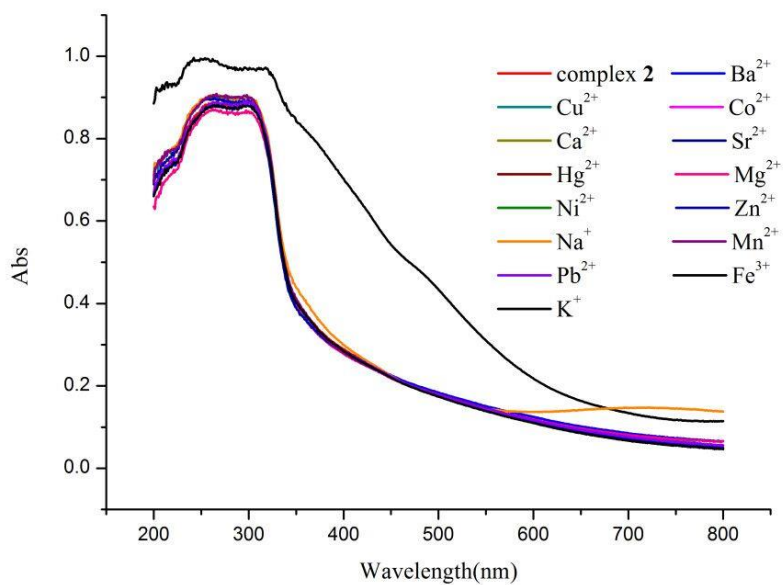


(b)

Fig. S12 IR spectra of **1** (a) or **2** (b) before and after immersed in aqueous solution of Fe(NO₃)₃.

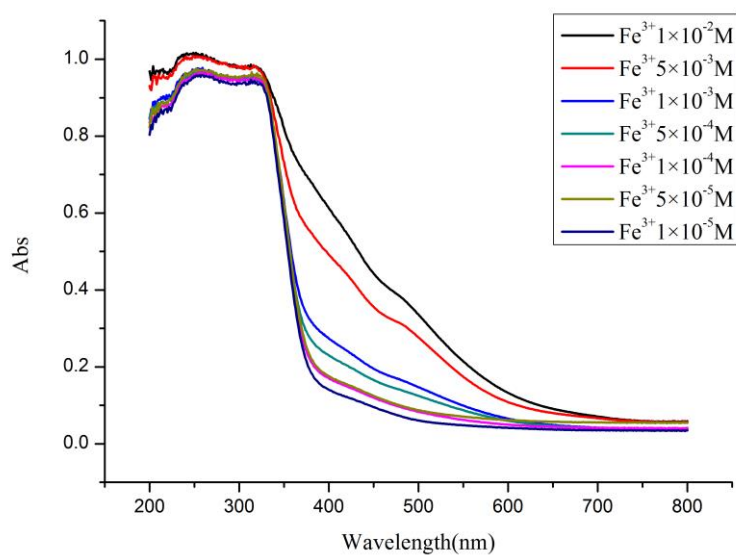


(a)

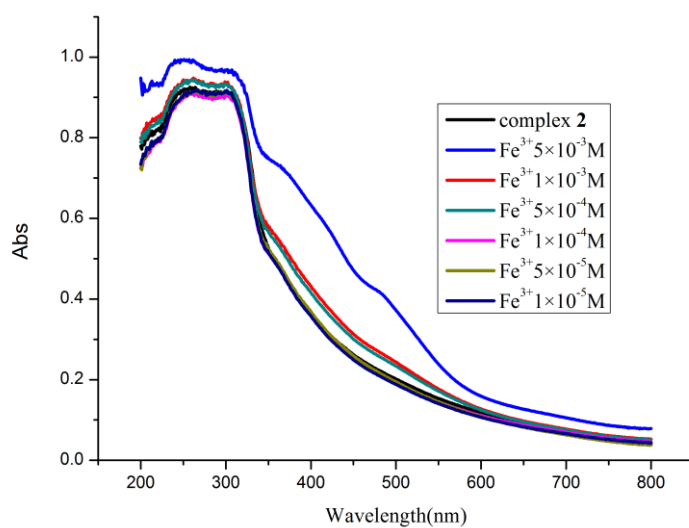


(b)

Fig. S13 UV-vis spectra of **1** (a) or **2** (b) of the MOFs and incorporated-cation samples.



(a)



(b)

Fig. S14. UV-vis spectra of **1** (a) or **2** (b) upon different concentrations of $\text{Fe}(\text{NO}_3)_3$

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