Novel luminescent metal-organic frameworks based on rigid carboxylate ligands for highly selective sensing of Fe^{3+} ions

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Table S1. Selected bond lengths (Å) and angles (deg) for compounds **1–4**

Compound **1**			
Zn(1)-O(7)	1.960(2)	Zn(1)-O(5)	1.961(2)
Zn(1)-O(9)	1.982(2)	Zn(1)-O(1)	1.994(2)
Zn(2)-O(6)	1.998(3)	Zn(2)-O(2)	2.016(2)
Zn(2)-O(8)	2.025(3)	Zn(2)-O(4)	2.148(3)
Zn(2)-O(11)	2.181(4)	Zn(2)-O(3)	2.224(3)
O(7)-Zn(1)-O(5)	134.39(11)	O(7)-Zn(1)-O(9)	111.14(11)
O(5)-Zn(1)-O(9)	102.09(11)	O(7)-Zn(1)-O(1)	97.52(11)
O(5)-Zn(1)-O(1)	107.11(12)	O(9)-Zn(1)-O(1)	99.38(10)
O(6)-Zn(2)-O(2)	116.91(12)	O(6)-Zn(2)-O(8)	91.26(15)
O(2)-Zn(2)-O(8)	90.95(13)	O(6)-Zn(2)-O(4)	147.13(12)
O(2)-Zn(2)-O(4)	94.35(10)	O(8)-Zn(2)-O(4)	98.52(12)
O(6)-Zn(2)-O(11)	82.23(16)	O(2)-Zn(2)-O(11)	86.46(15)
O(8)-Zn(2)-O(11)	170.96(13)	O(4)-Zn(2)-O(11)	90.32(14)
O(6)-Zn(2)-O(3)	88.88(12)	O(2)-Zn(2)-O(3)	153.69(11)
O(8)-Zn(2)-O(3)	93.72(11)	O(4)-Zn(2)-O(3)	59.36(10)
O(11)-Zn(2)-O(3)	92.42(14)		
Compound **2**			
Cd(1)-O(7)	2.271(6)	Cd(1)-O(1)	2.322(5)
Cd(1)-O(9)	2.318(6)	Cd(1)-O(4)	2.324(6)
Cd(1)-O(11)	2.309(12)	Cd(1)-O(3)	2.404(5)
Cd(1)-O(2)	2.491(5)	Cd(2)-O(8)	2.160(6)
Cd(2)-O(10)	2.184(6)	Cd(2)-O(5)	2.301(6)
Cd(2)-O(6)	2.362(6)	Cd(2)-O(1)	2.386(7)

Cd(2)-O(12)	2.376(10)		
O(7)-Cd(1)-O(1)	82.8(2)	O(7)-Cd(1)-O(9)	93.5(3)
O(1)-Cd(1)-O(9)	91.0(2)	O(7)-Cd(1)-O(4)	85.1(2)
O(1)-Cd(1)-O(4)	165.6(2)	O(9)-Cd(1)-O(4)	82.2(2)
O(7)-Cd(1)-O(11)	90.8(4)	O(1)-Cd(1)-O(11)	92.3(3)
O(9)-Cd(1)-O(11)	175.0(4)	O(4)-Cd(1)-O(11)	95.5(3)
O(7)-Cd(1)-O(3)	140.0(2)	O(1)-Cd(1)-O(3)	136.4(2)
O(9)-Cd(1)-O(3)	80.4(2)	O(4)-Cd(1)-O(3)	54.97(19)
O(11)-Cd(1)-O(3)	94.6(4)	O(7)-Cd(1)-O(2)	136.3(2)
O(1)-Cd(1)-O(2)	53.75(19)	O(9)-Cd(1)-O(2)	91.5(2)
O(4)-Cd(1)-O(2)	138.57(19)	O(11)-Cd(1)-O(2)	87.3(3)
O(3)-Cd(1)-O(2)	83.61(19)	O(8)-Cd(2)-O(10)	99.4(3)
O(8)-Cd(2)-O(5)	160.2(3)	O(10)-Cd(2)-O(5)	98.5(2)
O(8)-Cd(2)-O(6)	112.4(2)	O(10)-Cd(2)-O(6)	140.8(3)
O(5)-Cd(2)-O(6)	55.68(19)	O(8)-Cd(2)-O(1)	82.3(2)
O(10)-Cd(2)-O(1)	111.9(2)	O(5)-Cd(2)-O(1)	83.2(2)
O(6)-Cd(2)-O(1)	95.0(2)	O(8)-Cd(2)-O(12)	87.0(4)
O(10)-Cd(2)-O(12)	80.1(4)	O(5)-Cd(2)-O(12)	104.5(4)
O(6)-Cd(2)-O(12)	79.4(4)	O(1)-Cd(2)-O(12)	165.0(4)
Compound **3**			
Zn(1)-O(1)#1	1.9599(16)	Zn(1)-O(1)	1.9599(16)
Zn(1)-O(1)#2	1.9599(16)	Zn(1)-O(1)#3	1.9599(16)
Zn(2)-O(5)#4	2.0052(18)	Zn(2)-O(5)	2.0052(18)
Zn(2)-O(3)	2.0322(18)	Zn(2)-O(3)#4	2.0322(18)
Zn(2)-O(4)#4	2.401(2)	Zn(2)-O(4)	2.401(2)
O(1)#1-Zn(1)-O(1)	129.48(11)	O(1)#1-Zn(1)-O(1)#2	100.49(4)
O(1)-Zn(1)-O(1)#2	100.49(4)	O(1)#1-Zn(1)-O(1)#3	100.49(4)
O(1)-Zn(1)-O(1)#3	100.49(4)	O(1)#2-Zn(1)-O(1)#3	129.48(11)
O(5)#4-Zn(2)-O(5)	106.58(10)	O(5)#4-Zn(2)-O(3)	94.70(7)
O(5)-Zn(2)-O(3)	110.11(8)	O(5)#4-Zn(2)-O(3)#4	110.11(8)
O(5)-Zn(2)-O(3)#4	94.70(7)	O(3)-Zn(2)-O(3)#4	138.27(10)
O(5)#4-Zn(2)-O(4)#4	89.87(8)	O(5)-Zn(2)-O(4)#4	152.10(7)
O(3)-Zn(2)-O(4)#4	90.26(7)	O(3)#4-Zn(2)-O(4)#4	58.01(7)

O(5)#4-Zn(2)-O(4)	152.10(7)	O(5)-Zn(2)-O(4)	89.87(8)
O(3)-Zn(2)-O(4)	58.01(7)	O(3)#4-Zn(2)-O(4)	90.26(7)
O(4)#4-Zn(2)-O(4)	84.99(12)		
Compound **4**			
Cd(1)-O(1)#1	2.171(8)	Cd(1)-O(1)#2	2.171(8)
Cd(1)-O(1)	2.171(8)	Cd(1)-O(1)#3	2.171(8)
Cd(2)-O(5)#4	2.133(19)	Cd(2)-O(5)#5	2.133(19)
Cd(2)-O(3)#6	2.310(7)	Cd(2)-O(3)	2.310(7)
Cd(2)-O(6')#4	2.42(2)	Cd(2)-O(6')#5	2.42(2)
Cd(2)-O(5')#4	2.42(2)	Cd(2)-O(5')#5	2.42(2)
Cd(2)-O(4)#6	2.513(8)	Cd(2)-O(4)	2.513(8)
O(1)#1-Cd(1)-O(1)#2	99.3(2)	O(1)#1-Cd(1)-O(1)	99.3(2)
O(1)#2-Cd(1)-O(1)	132.5(6)	O(1)#1-Cd(1)-O(1)#3	132.5(6)
O(1)#2-Cd(1)-O(1)#3	99.3(2)	O(1)-Cd(1)-O(1)#3	99.3(2)
O(5)#4-Cd(2)-O(5)#5	132.4(12)	O(5)#4-Cd(2)-O(3)#6	123.3(9)
O(5)#5-Cd(2)-O(3)#6	78.2(6)	O(5)#4-Cd(2)-O(3)	78.2(6)
O(5)#5-Cd(2)-O(3)	123.3(9)	O(3)#6-Cd(2)-O(3)	123.3(9)
O(5)#4-Cd(2)-O(4)	130.2(5)	O(5)#5-Cd(2)-O(4)	88.4(8)
O(3)#6-Cd(2)-O(4)	87.0(3)	O(3)-Cd(2)-O(4)	53.1(3)
O(5)#4-Cd(2)-O(4)#6	88.4(8)	O(5)#5-Cd(2)-O(4)#6	130.2(5)
O(3)#6-Cd(2)-O(4)#6	53.1(3)	O(3)-Cd(2)-O(4)#6	87.0(3)
O(4)-Cd(2)-O(4)#6	80.2(5)		

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,z; #2 y-1/2,-x+1/2,-z+3/2; #3 -y+1/2,x+1/2,-z+3/2; #4 x+0,-y+1/2,-z+1/4 for **3**; #1 y+1/2,-x+1/2,-z+3/2; #2 -x+1,-y,z; #3 -y+1/2,x-1/2,-z+3/2; #4 -y+1/2,x-1/2,-z+1/2; #5 -y+1/2,-x+1,z-1/4; #6 x+0,-y+1/2,-z+1/4 for **4**.

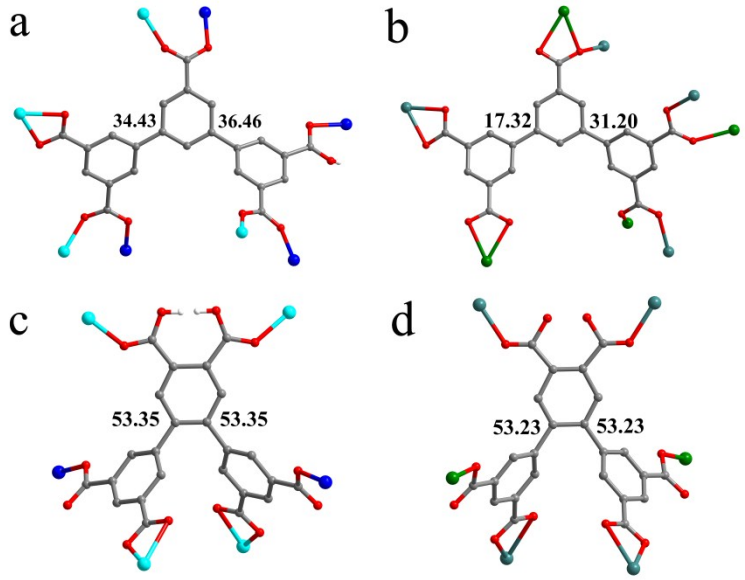

Fig. S1. The types of 5-connected H_5L_1 ligands and 6-connected H_5L_2 ligands with different dihedral angles in (a) **1**, (b) **2**, (c) **3**, (d) **4.** (Zn^{II}(1), blue; Zn^{II}(2), turquoise; Cd^{II}(1), green; Cd^{II}(2) teal; C, gray; O, red; H, white).

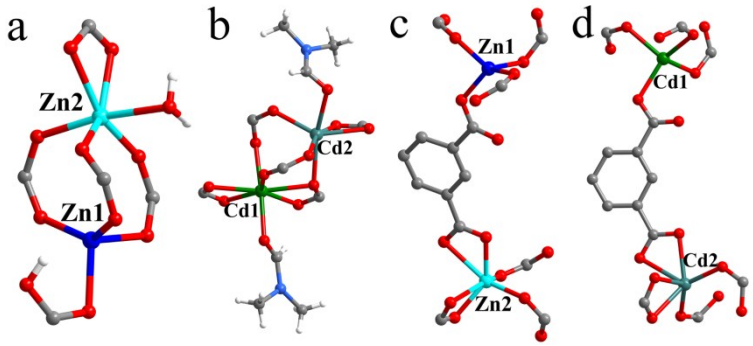

Fig. S2. Zn-O bonds in compound **1** (a), Cd-O bonds in compound **2** (b), Zn-O bonds in compound **3** (c), Cd-O bonds in compound **4** (d). (Zn^{II}(1), blue; Zn^{II}(2), turquoise; Cd^{II}(1), green; Cd^{II}(2) teal; C, gray; O, red; N, light blue; H, white).

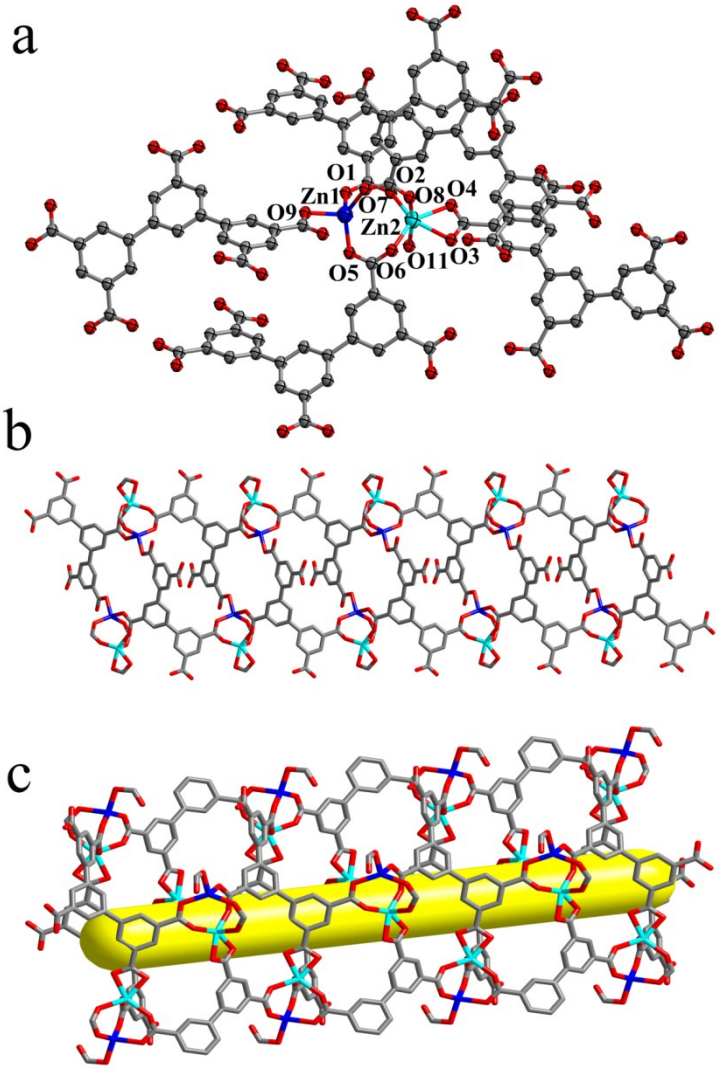

Fig. S3. (a) Local coordination environments of the Zn^{II} ions in **1**. (b) 1D chain with distorted MOS in **1** along the *c* axis. (c) 1D tube in **1**. (four coordinated Zn^{II}(1) ions are marked as blue; six coordinated Zn^{II}(2) ions are marked as turquoise ; C, gray; O, red. All hydrogen atoms and coordinated H_2O are omitted for clarity).

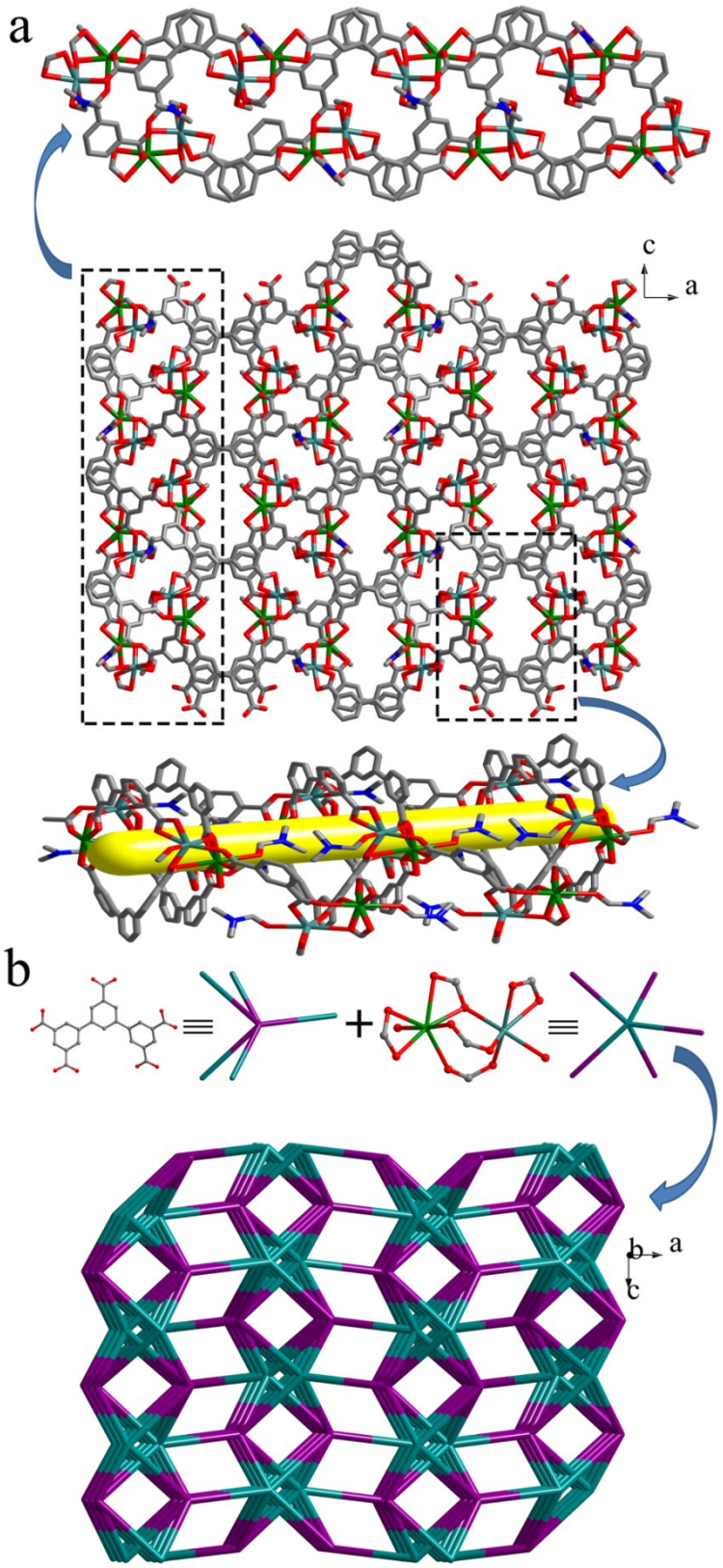
a
c
a
b
b
a
c

Fig. S4. (a) 1D chain in **2** along the *c* axis, 3D framework structure and 1D tube in **2**. (b) Illustration of topology of **2**: simplification of the inorganic clusters (5-connected node, teal), and the organic H_5L_1 linker (5-connected nodes, violet), leading to the (5,5)-connected binodal $\{4^7 \cdot 6^3\}$ topology. (seven coordinated $Cd^{II}(1)$ ions are marked as green; six coordinated $Cd^{II}(2)$ ions are marked as teal ; C, gray; O, red. All hydrogen atoms are omitted for clarity).

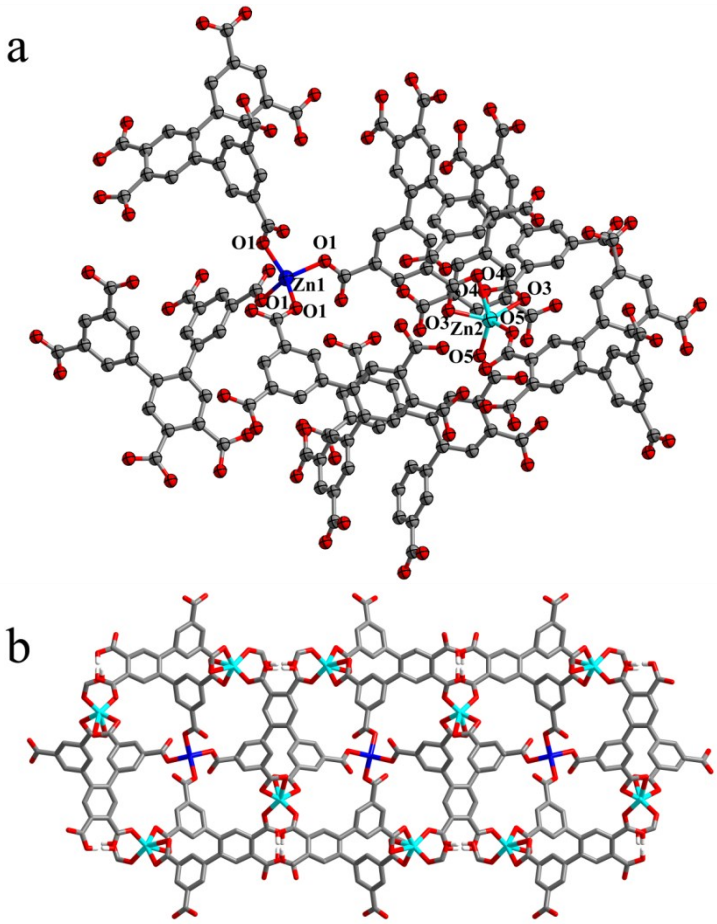

Fig. S5. (a) Local coordination environments of the Zn^{II} ions in **3**. (b) 1D chain with SBUs in **3** along the *c* axis. (four coordinated $Zn^{II}(1)$ ions are marked as blue; six coordinated $Zn^{II}(2)$ ions are marked as turquoise; C, gray; O, red. All hydrogen atoms and $(CH_3)_2NH_2^+$ are omitted for clarity).

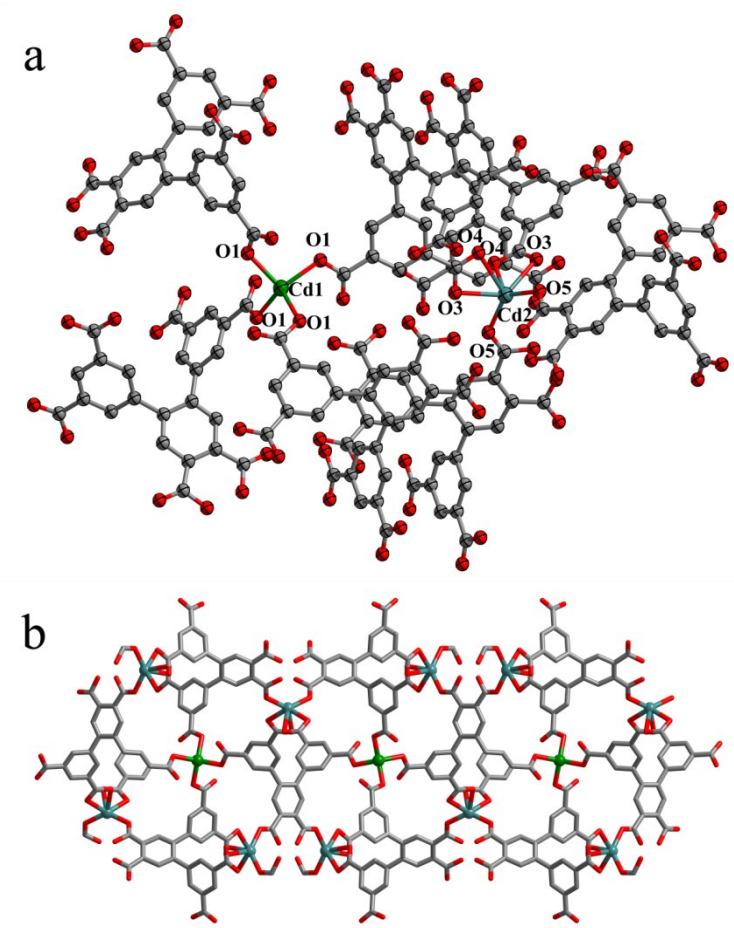

Fig. S6. (a) Local coordination environments of the Cd^{II} ions in **4**. (b) 1D chain with distorted MOS in **4** along the *c* axis. (four coordinated $Cd^{II}(1)$ ions are marked as green; six coordinated $Cd^{II}(2)$ ions are marked as teal; C, gray; O, red. All hydrogen atoms and $(CH_3)_2NH_2^+$ are omitted for clarity).

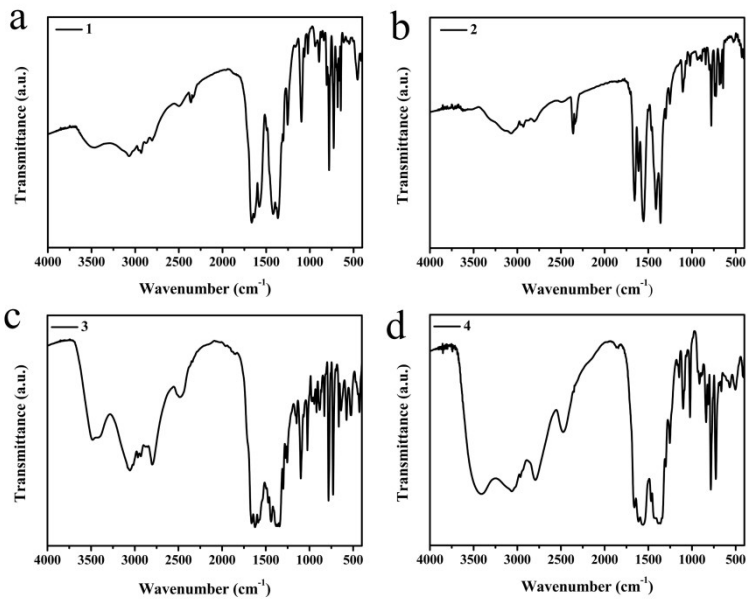

Fig. S7. Infrared spectra for (a) **1**, (b) **2**, (c) **3**, (d) **4.** (KBr, cm^{-1})

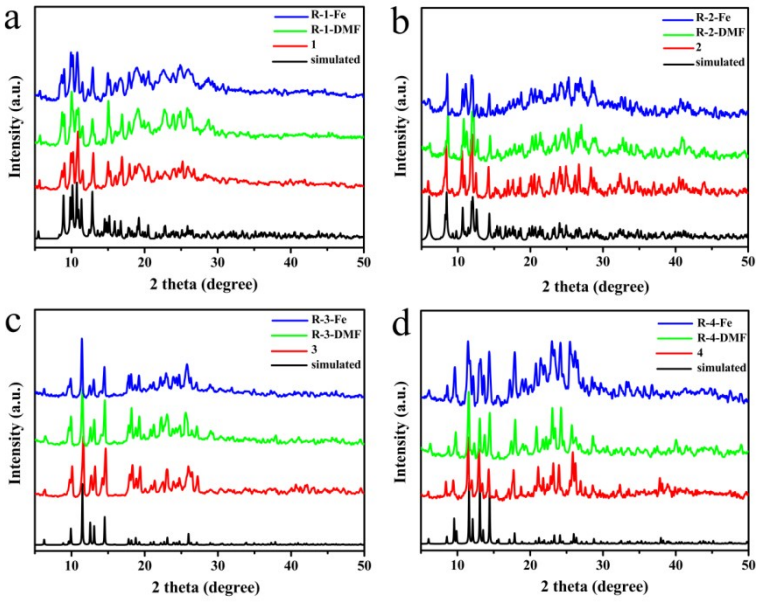

Fig. S8. Simulated (black), experimental (red), after recovery through centrifugation and washing with DMF (green) and after immersed in Fe^{3+} ions solution with 1.1 mM concentration (blue) powder X-ray diffraction (PXRD) patterns for (a) **1**, (b) **2**, (c) **3**, (d) **4**.

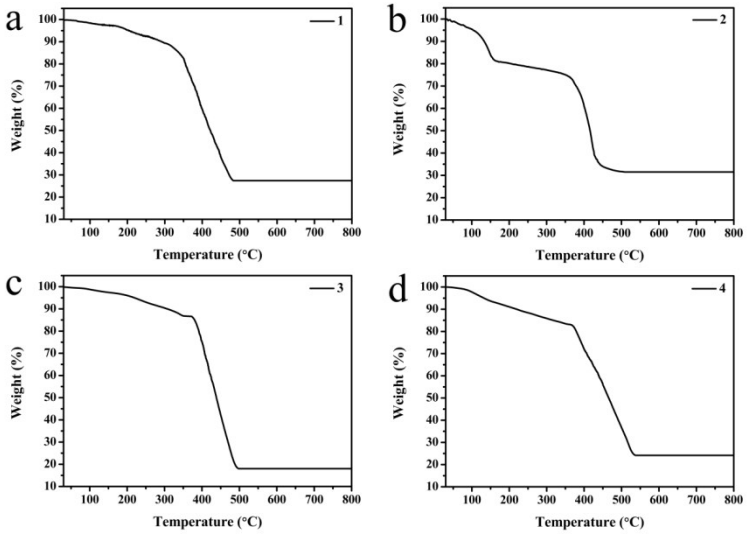

Fig. S9. Thermogravimetric analysis curves for (a) **1**, (b) **2**, (c) **3**, (d) **4**.

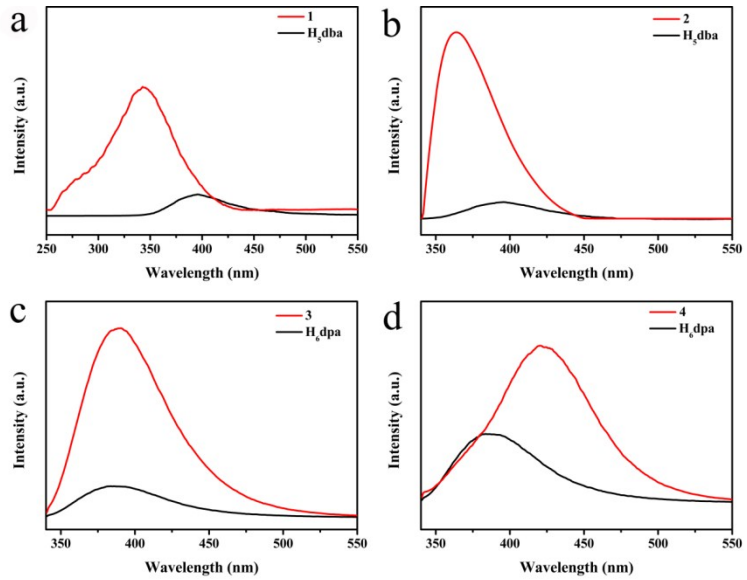

Fig. S10. Fluorescent emission spectra of (a) ligand H_5L_1 (black), **1** (red); (b) ligand H_5L_1 (black), **2** (red); (c) ligand H_5L_2 (black), **3** (red); (d) ligand H_5L_2 (black), **4** (red) in solid state at room temperature.

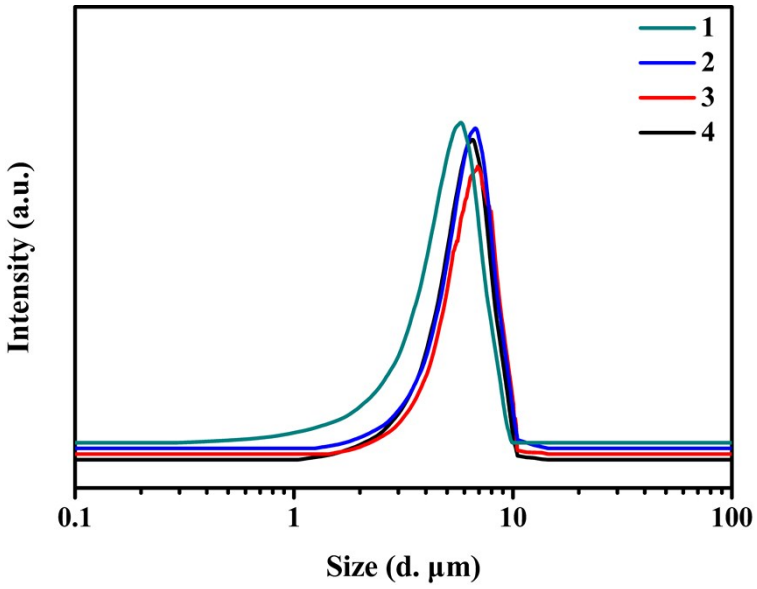

Fig. S11. Particle size distribution of compounds **1–4** by DLS measurement. (the average size of compounds **1–4** after dispersing in DMF solvent are 6.1, 6.7, 6.5 and 6.3 μm in diameter, respectively)

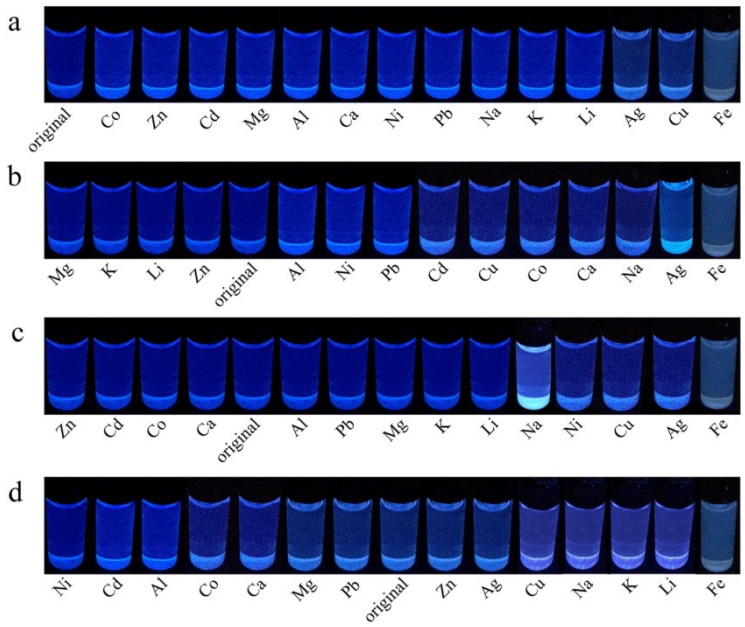

Fig. S12. The color change of the luminescent responses for sensing the different metal ions (M = Na^{+}, K^{+}, Li^{+}, Ag^{+}, Mg^{2+}, Ca^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Al^{3+}, Fe^{3+}) in DMF solution for (a) **1**, (b) **2**, (c) **3**, (d) **4** by the ultraviolet light.

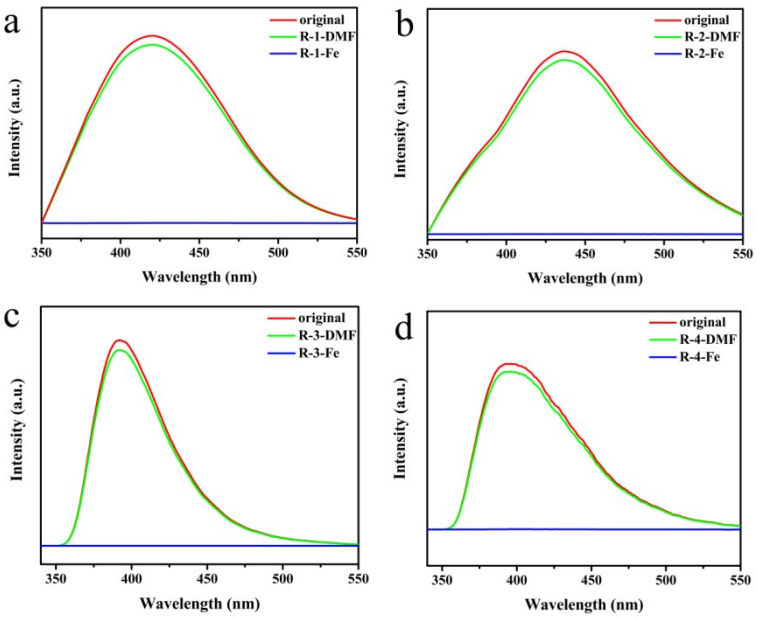

Fig. S13. Fluorescent emission spectra of original (red), after recovery through centrifugation and washing with DMF (green) and after immersed in Fe^{3+} ions solution with 1.1 mM concentration (blue) for (a) **1**, (b) **2**, (c) **3**, (d) **4**.