Supporting Information for

From 2D→3D interpenetration to packing: N-coligands-driven structural assembly and tuning of luminescent sensing activities towards Fe^{3+} and $Cr_2O_7^{2-}$ ions

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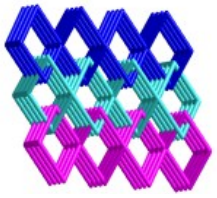
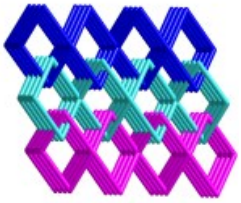
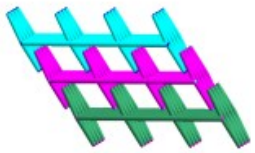
Table. S1 Selected bonds (Å) and angles (deg) of complexes **1**-**3**.

Complex **1**			
Cd1-O1	2.347(4)	O2-Cd1-O4	139.27(12)
Cd1-O2	2.440(3)	O2-Cd1-N1	93.65(16)
Cd1-O3	2.344(3)	O2-Cd1-N2	91.25(16)
Cd1-O4	2.536(3)	O2-Cd1-O4	144.82(13)
Cd1-N1	2.313(5)	O3 -Cd1-O4	53.02(11)
Cd1-N2	2.313(5)	O3-Cd1-N1	91.45(18)
Cd1-O4	2.377(3)	O3-Cd1-N2	91.21(18)
O1-Cd1-O2	54.30(13)	O3-Cd1-O4	128.92(11)
O1-Cd1-O3	140.27(12)	O4-Cd1-N1	88.11(16)
O1-Cd1-O4	165.97(12)	O4-Cd1-N2	89.70(16)
O1-Cd1-N1	87.10(18)	O4-Cd1-N1	86.93(16)
O1-Cd1-N2	93.88(18)	N1-Cd1-N2	174.57(18)
O1-Cd1-O4	90.67(12)	O4-Cd1-O4	75.91(11)
O2-Cd1-O3	86.17(11)		
Complex **2**			
Cd1-O1	2.325(8)	O2-Cd1-N2	92.3(3)
Cd1-O2	2.512(6)	O3-Cd1-O4	55.8(2)
Cd1-O3	2.315(6)	O3-Cd1-O8	130.0(2)
Cd1-O4	2.592(7)	O3-Cd1-N1	89.8(2)
Cd1-O8	2.396(6)	O3-Cd1-N2	91.8(3)
Cd1-N1	2.315(6)	O4-Cd1-O8	74.3(2)
Cd1-N2	2.332(7)	O4-Cd1-N1	90.1(2)
Cd2-O4	2.324(7)	O4-Cd1-N2	87.7(3)
Cd2-O5	2.349(8)	O8-Cd1-N1	87.2(2)
Cd2-O6	2.494(6)	O8-Cd1-N2	88.9(3)
Cd2-O7	2.323(6)	N1-Cd1-N2	175.9(3)
Cd2-O8	2.545(6)	O4-Cd2-O5	87.5(2)
Cd2-N3	2.312(7)	O4-Cd2-O6	141.0(3)
Cd2-N4	2.357(8)	O4-Cd2-O7	130.7(2)
O1-Cd1-O2	53.1(2)	O4-Cd2-O8	76.5(2)
O1-Cd1-O3	140.5(3)	O4-Cd2-N3	86.8(2)
O1-Cd1-O4	162.8(3)	O4-Cd2-N4	90.4(3)
O1-Cd1-O8	89.4(3)	O5-Cd2-O6	53.7(3)
O1-Cd1-N1	94.9(3)	O5-Cd2-O7	141.8(2)
O1-Cd1-N2	86.3(3)	O5-Cd2-O8	163.3(2)
O2-Cd1-O3	87.6(2)	O5-Cd2-N3	93.3(3)
O2-Cd1-O4	143.4(2)	O5-Cd2 -N4	88.7(3)
O2-Cd1 -O8	142.3(2)	O6-Cd2-O7	88.2(2)
O2-Cd1-N1	91.5(2)	O6-Cd2-O8	142.5(2)

O6-Cd2-N3	91.7(2)	N3 -Cd2-N4	176.5(3)
O6-Cd2-N4	91.8(3)	O7-Cd2-N4	89.7(3)
O7-Cd2-O8	54.4(2)	O8-Cd2-N3	90.4(2)
O7-Cd2-N3	90.6(3)	O8-Cd2-N4	87.0(3)
Complex **3**			
Cd1-O1	2.547(5)	O2-Cd1-O4	162.46(15)
Cd1-O2	2.311(4)	O2-Cd1-N1	85.06(16)
Cd1-O3	2.307(4)	O2-Cd1-N4	96.93(16)
Cd1-O4	2.708(5)	O2-Cd1-O4	86.55(15)
Cd1-N1	2.304(4)	O3-Cd1-O4	50.96(14)
Cd1-N4	2.303(5)	O3-Cd1-N1	93.72(14)
Cd1-O4	2.378(4)	O3-Cd1-N4	85.80(16)
O1-Cd1-O2	52.85(15)	O3-Cd1-O4	128.47(15)
O1-Cd1-O3	92.20(14)	O4-Cd1-N1	86.11(14)
O1-Cd1-O4	142.81(13)	O4-Cd1-N4	91.45(15)
O1-Cd1-N1	92.43(15)	O4-Cd1-O4	77.66(14)
O1-Cd1-N4	90.36(17)	N1-Cd1-N4	177.18(16)
O1-Cd1-O4	139.33(15)	O4-Cd1-N1	85.39(15)
O2-Cd1-O3	144.83(15)	O4-Cd1-N4	92.73(18)

Table S2. Comparison of structural characteristics of complexes **1-3**.

		Complex **1**	Complex **2**	Complex **3**
Structural characteristics of the complexes		2D→3D	2D→3D	packing
				
Cd_2O_2 dinuclear unit	Cd···Cd distance (Å)	3.8746(10)	3.9023(10)	3.9673(6)
	Cd-O-Cd angle /deg	103.80	104.73	102.41
Conform-ation of L	Binding model	bi(chelating)	bi(chelating)	bi(chelating)
	Dihedral angle of different benzene rings /deg	80.286 80.969 23.484	83.185 80.646 23.378	72.040 70.064 19.813
	Cd···Cd distance /Å	12.9919	12.6611	11.8359
	-O-C-O Angle /deg	121.626 123.809	123.630 124.281	122.088 122.503
N ligands	Dihedral angle of aromatic rings/deg	28.451 17.406	24.885 8.501	3.020
	Cd···Cd distance /Å	11.6951	14.0069	17.7982

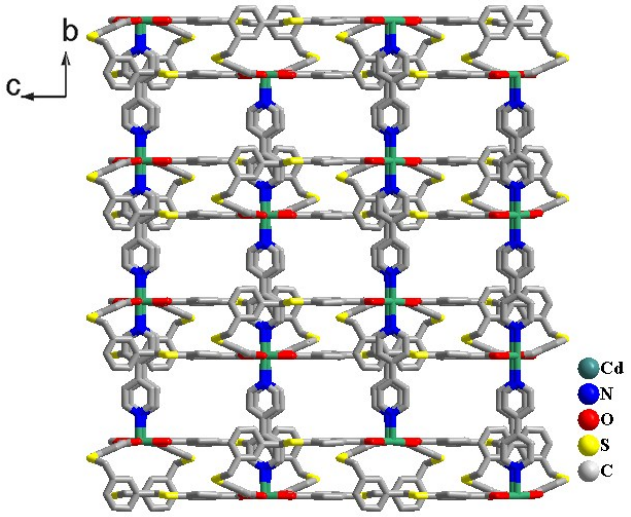


Fig. S1 Perspective view of the channels along bc plane in complex **1**. The disordered solvent molecules are omitted for clarity.

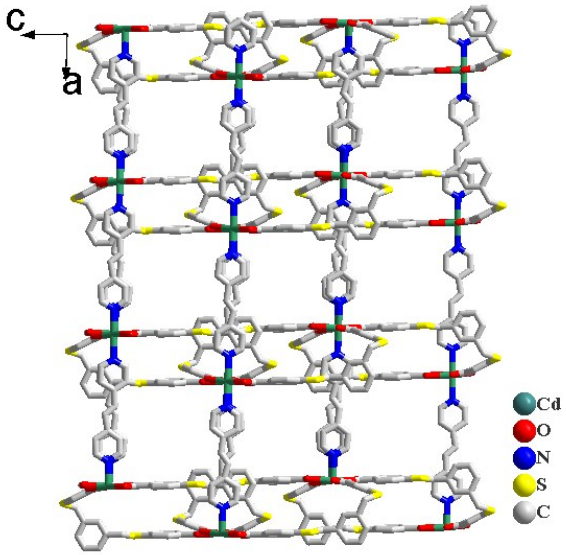


Fig. S2 Perspective view of the channels along ac plane in complex **2**. The disordered solvent molecules are omitted for clarity.

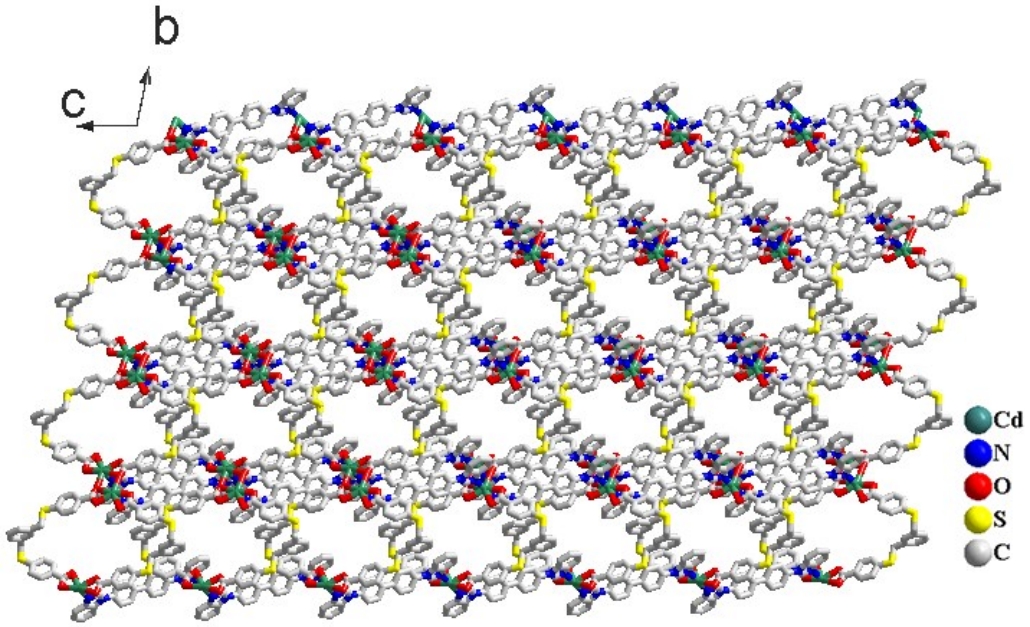


Fig. S3 Perspective view of the channels along bc plane in complex **3**. The disordered solvent molecules are omitted for clarity.

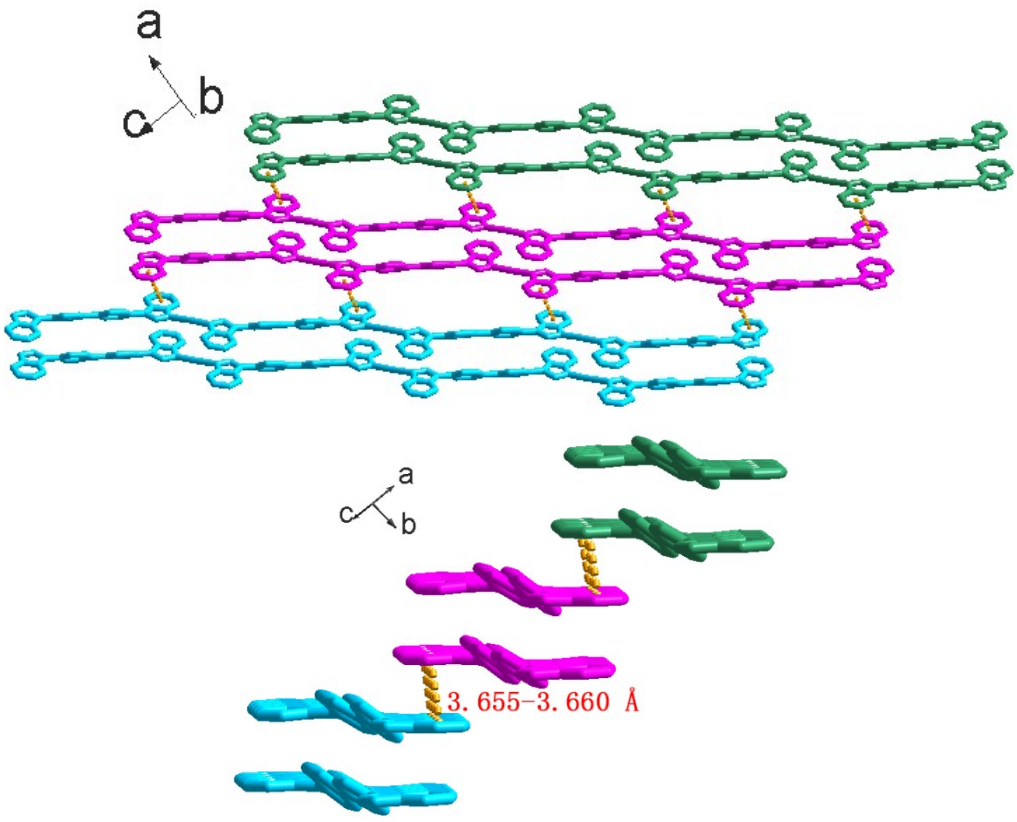
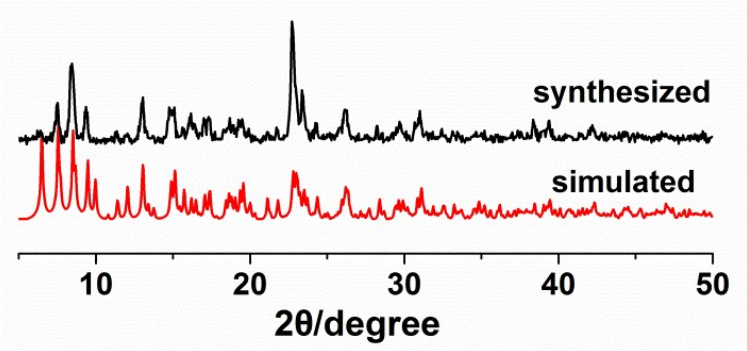
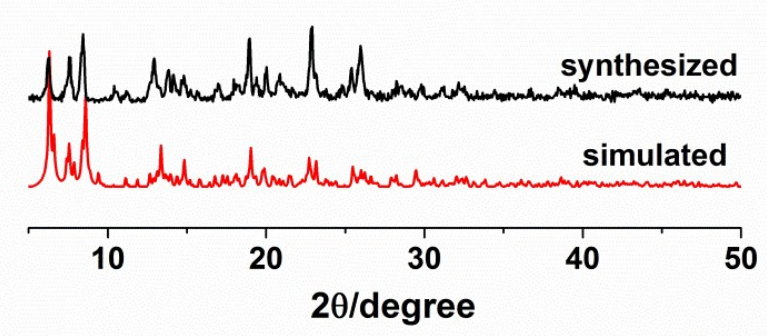


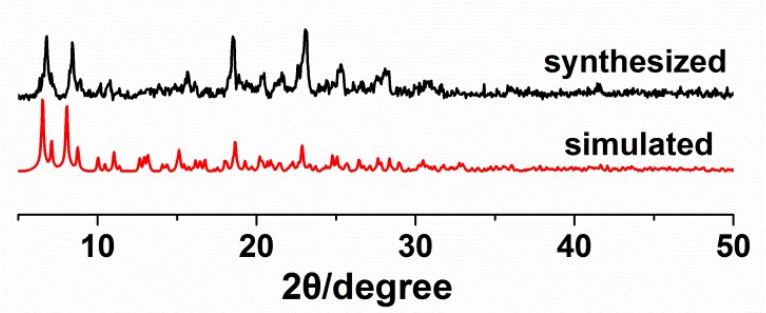
Fig. S4 Stacking of the adjacent layers in complex **3**, showing the π···π stacking interactions and distance between the aromatic rings of bibp ligands from different layers. The disordered solvent molecules and L ligands are omitted for clarity.



(a)



(b)



(c)

Fig. S5 (a)-(c) Powder XRD patterns of complexes **1**-**3**.

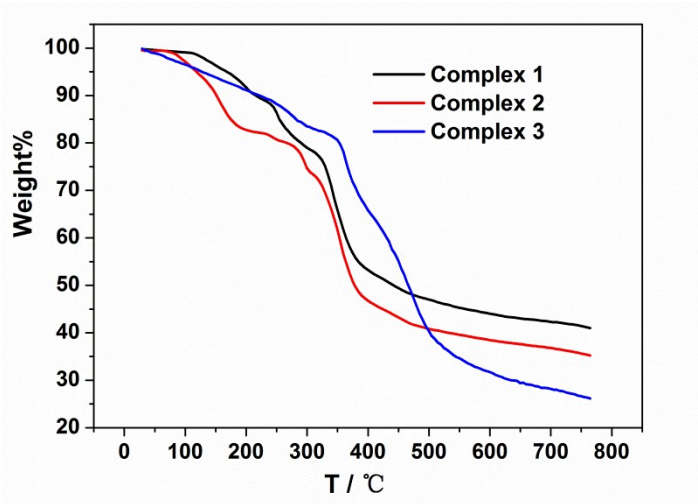


Fig. S6 TG curves of complexes **1**-**3**.

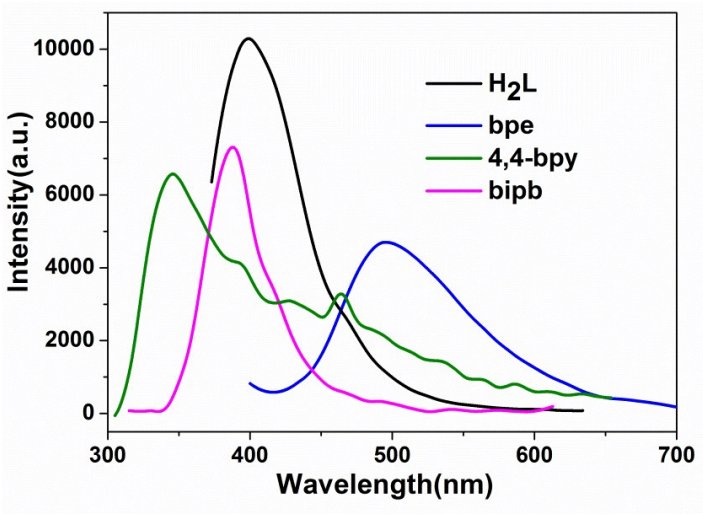


Fig.S7 Solid-state emission spectra of free ligands at room temperature.

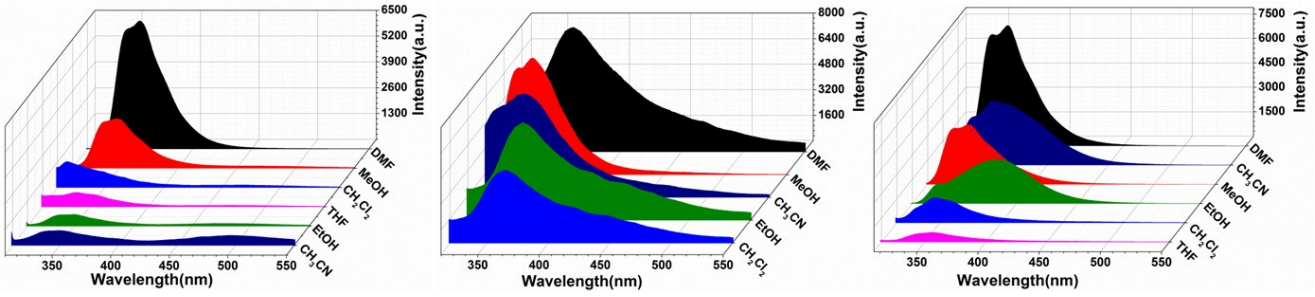


Fig. S8 Fluorescence spectrums of three complexes in different solvents. ((a) for complex **1**, (b) for complex **2**, (c) for complex **3**.

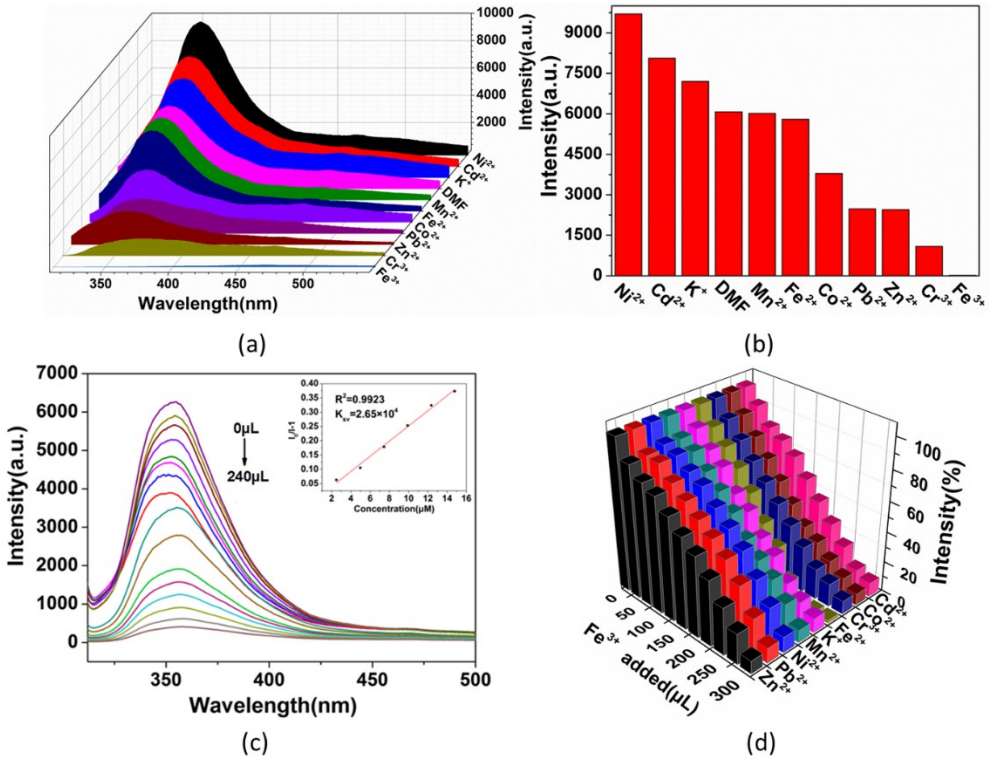


Fig. S9 Luminescence responses of complex **1** dispersed in DMF. (a) luminescence spectra of complex **1** immersed in DMF with various metal ions; (b) luminescence intensities of complex **1** immersed in DMF with various metal ions; (c) luminescence spectra of complex **1** in DMF in the presence of different amounts of Fe^{3+} ions; (d) Fluorescence quenching of complex **1** in DMF solution with the addition of $Fe^{3+}$and other anions.

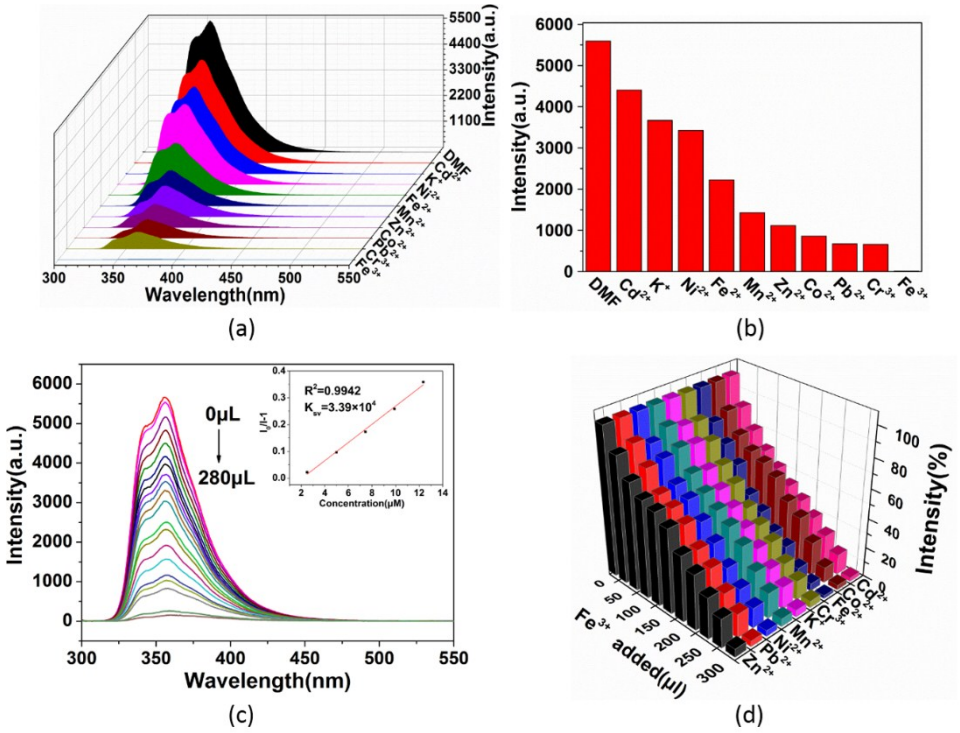


Fig. S10 Luminescence responses of complex **3** dispersed in DMF. (a) luminescence spectra of complex **3** immersed in DMF with various metal ions; (b) luminescence intensities of complex **3** immersed in DMF with various metal ions; (c) luminescence spectra of complex **3** in DMF in the presence of different amounts of Fe^{3+} ions; (d) Fluorescence quenching of complex **3** in DMF and other anions with the addition of Fe^{3+}.

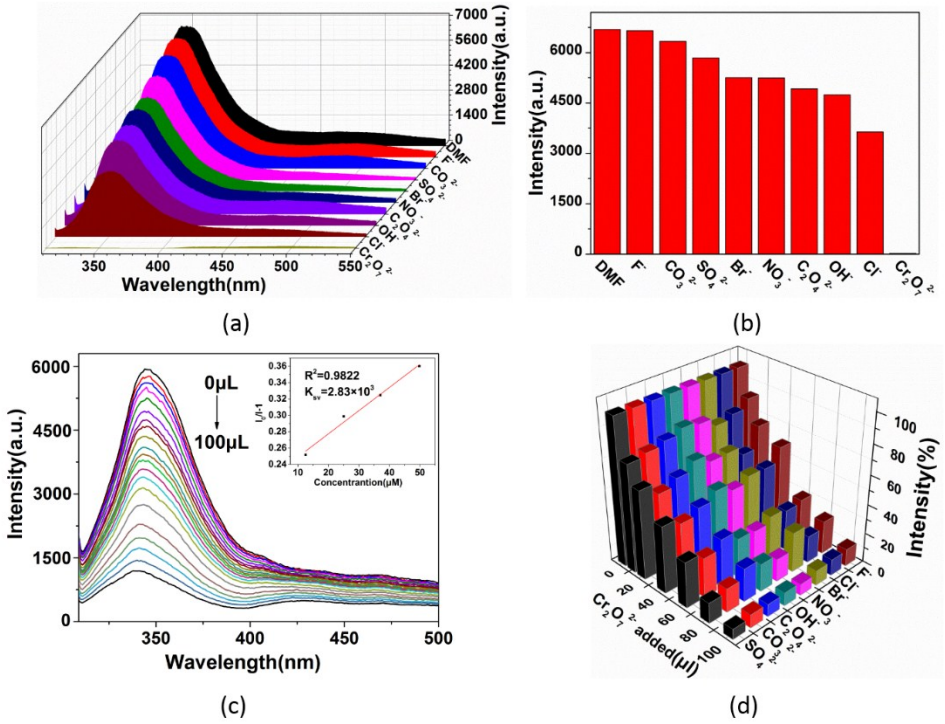


Fig. S11 Luminescence responses of complex **1** dispersed in DMF; (a) luminescence spectra of complex **1** immersed in DMF with various anions; (b) luminescence intensities of complex **1** immersed in DMF with various anions; (c) luminescence spectra of complex **1** in DMF in the presence of different amounts of $Cr_2O_7^{2-}$ ion;(d) Fluorescence quenching of complex **1** in DMF with the addition of $Cr_2O_7^{2-}$ and other anions.

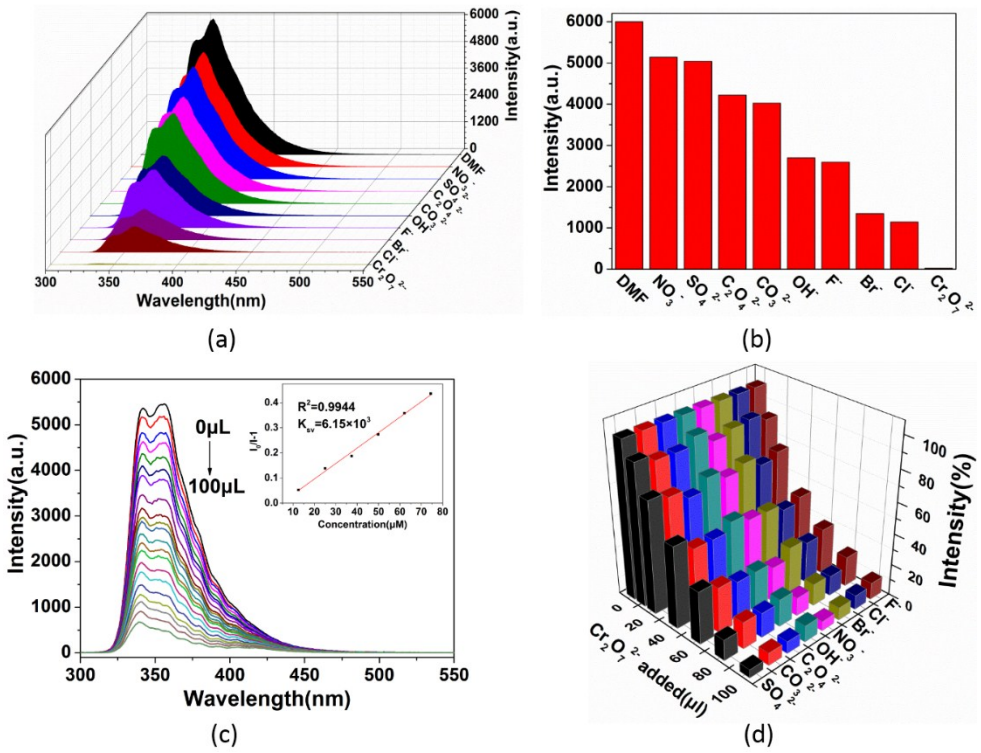
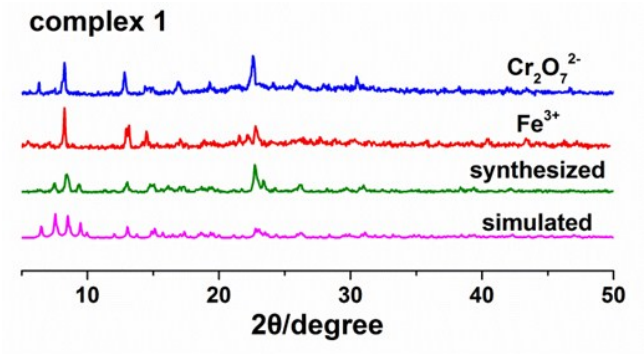
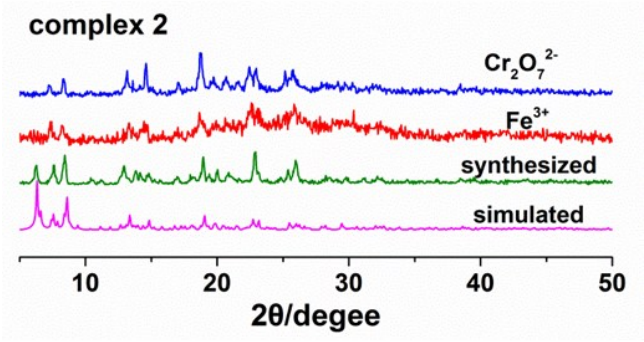


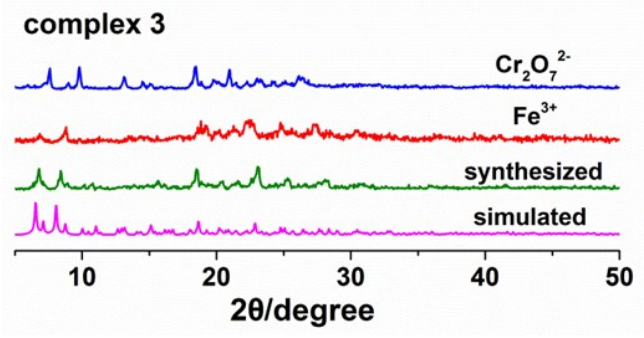
Fig. S12 Luminescence responses of complex **3** dispersed in DMF; (a) luminescence spectra of complex **3** immersed in DMF with various anions; (b) luminescence intensities of complex **3** immersed in DMF with various metal ions; (c) luminescence spectra of complex **3** in DMF in the presence of different amounts of $Cr_2O_7^{2-}$ ions; (d) Fluorescence quenching of complex **3** in DMF with the addition of $Cr_2O_7^{2-}$ and other anions.



(a)



(b)



(c)

Fig. S13 (a)-(c) PXRD of complexes **1-3** after treatment with Fe^{3+} and $Cr_2O_7^{2-}$ in DMF.

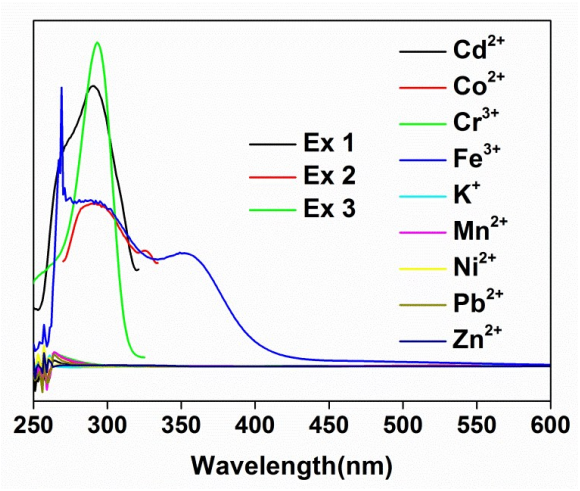
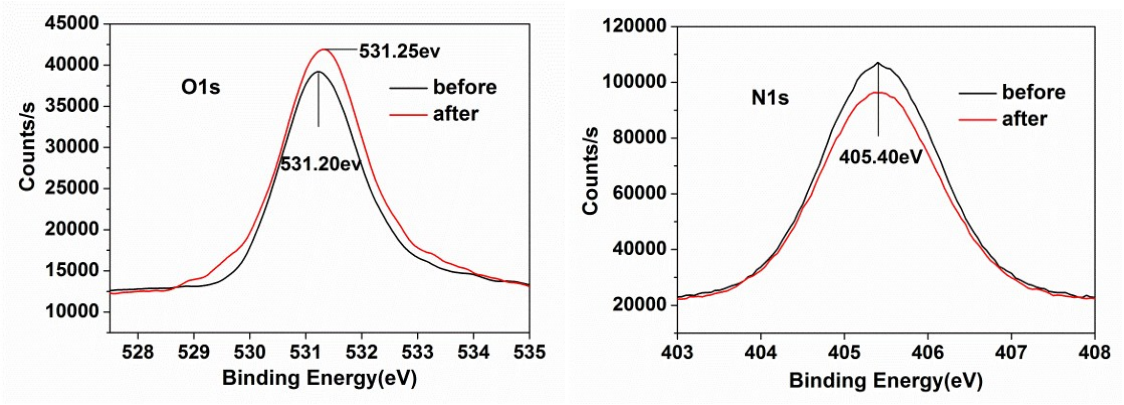
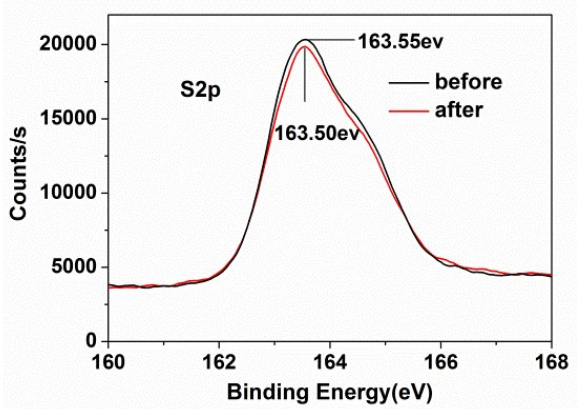


Fig. S14 UV-Vis adsorption spectra of different metal ions in DMF and the excitation spectrum of complexes.



(a) (b)



(c)

Fig. S15 the peak shifts of O1s (a), N1s (b) and S2p (c) of complex **2** before and after treated with Fe^{3+}.

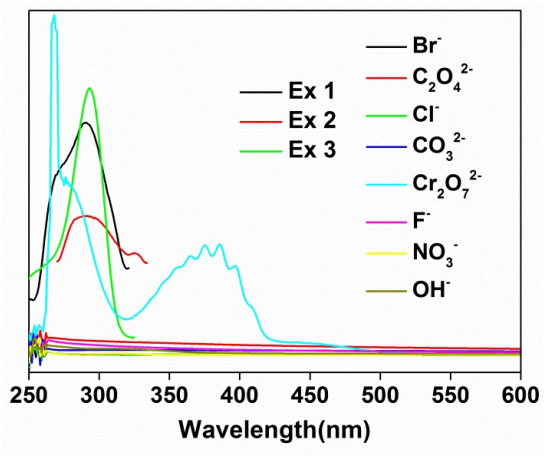
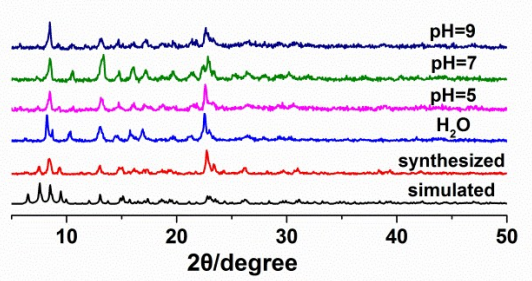
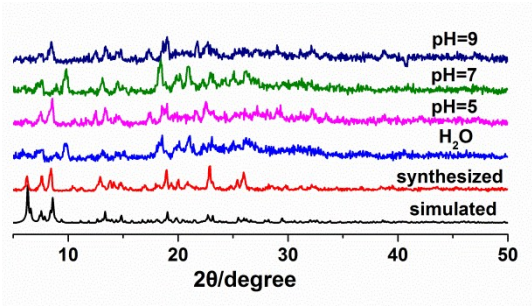


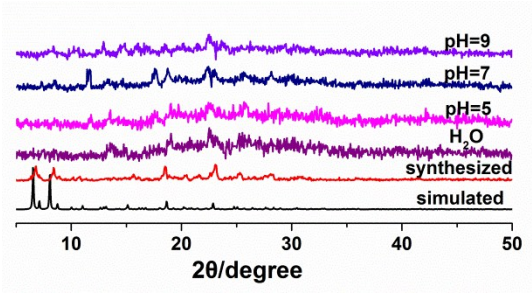
Fig. S16 UV-Vis adsorption spectra of different anions in DMF and the excitation spectrum of three complexes.



Complex **1**

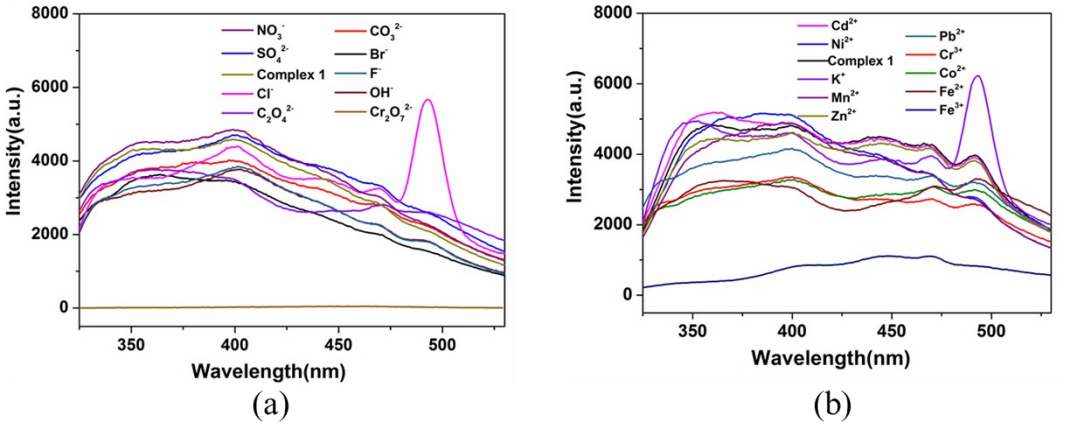


Complex **2**



Complex **3**

Fig. S17 PXRD of complexes **1-3** after immersed in water and aqueous with pH=5-9.



(a) (b)

Fig. S18 Luminescence responses of complex **1** in aqueous solutions of various metal ions (a) and anions (b).