Electronic Supplementary Material (ESI) for RSC Advances.

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Electronic Supporting Information (ESI)

A novel fluorescent phenomenon caused by amine induced ion-exchange between Cd^{2+} and Fe^{3+} ions

Lei Jia,[a,b] Zhe Xue,[a,b] Rong-Rong Zhu,[a,b] Yu-Na Wang,[a,b] Suo-Shu Zhang,[a,b] Xiao Geng,[a,b] Lin Du* [a,b] and Qi-Hua Zhao* [a,b]

[a]Key Laboratory of Medicinal Chemistry for Natural Resource Education Ministry, Yunnan University, Kunming 650091, People's Republic of China

[b]School of Chemical Science and Engineering, School of Pharmacy, Yunnan University, Kunming 650091, People's Republic of China

E-mail: lindu@ynu.edu.cn, qhzhao@ynu.edu.cn

The complex **2** belonging to *C*2/*c* space group crystallizes in the monoclinic crystal system. The asymmetric unit of **2** is made up of one Cd^{2+} ion, one 5-Brp^{2-} ligand, one bpp ligand and one coordinated water molecule. Cd1 is connected to two N donors from two pyridine rings of different dpa ligands, three O atoms from two carboxylate groups of 5-Brp^{2-} ligands and one water O atom. The Cd^{2+} ion assumes a coordination configuration of tetragonal bipyramidal. The two ligands respectively connect adjacent metal centers to form a 1D chain each. Two kinds of 1D chains are combined by metal centers to obtain a two-fold interpenetrating structure. The topological analysis structure shows that the complex **2** has a double-interpolated diamond-like topology with a dot symbol of $\{6^6\}$.

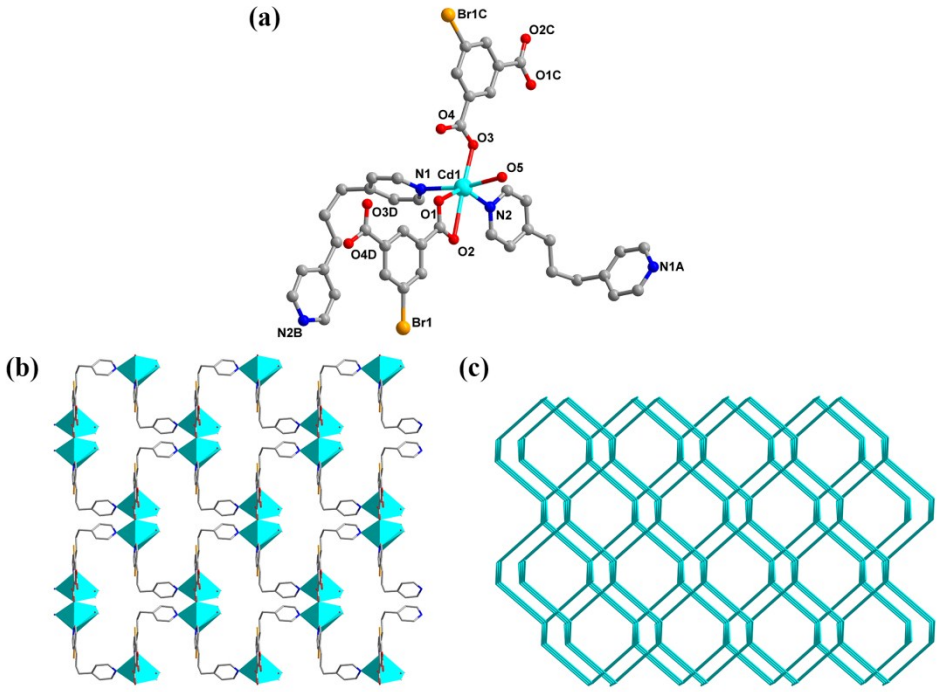

Fig. S1 (a) Coordination environment of Cd(II) in **2** (symmetry code: A: 0.5 + *x*, 0.5 - *y*, 0.5 + *z*; B: -0.5 + *x*, 0.5 - *y*, -0.5 + *z*; C: x, -*y*, 0.5 + *z*; D: *x*, -*y*, -0.5 + *z*) (b) Polyhedral illustration of the linkage through two kinds of ligands in **2** (c) Two-fold interpenetrating 4-connected diamond network with the point symbol being $\{6^6\}$ in **2**. H atoms are omitted for clarity.

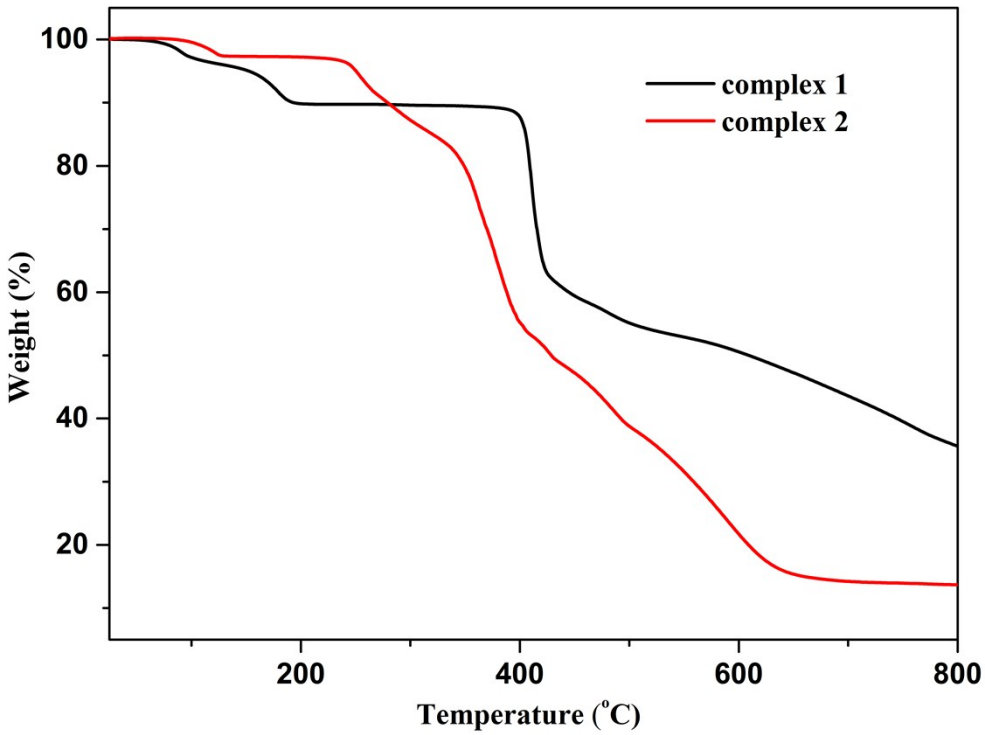

Fig. S2 TGA curves of **1** and **2**.

TGA analysis: For complex **1**, there was a 10.2% weight loss from 25 to 200 °C, meaning one H_2O and 0.5 DMF molecule released. The framework was stable until 400 °C. For complex **2**, there was a 2.7% weight loss from 25 to 140 °C, meaning one coordinated water released. The framework was stable until 220 °C.

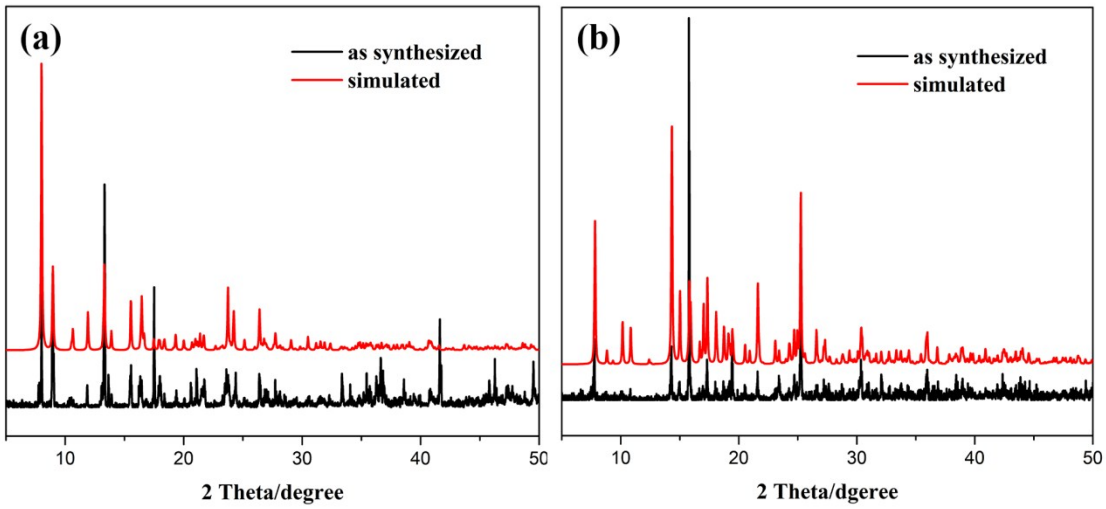

Fig. S3 PXRD patterns of (a) **1** and (b) **2**.

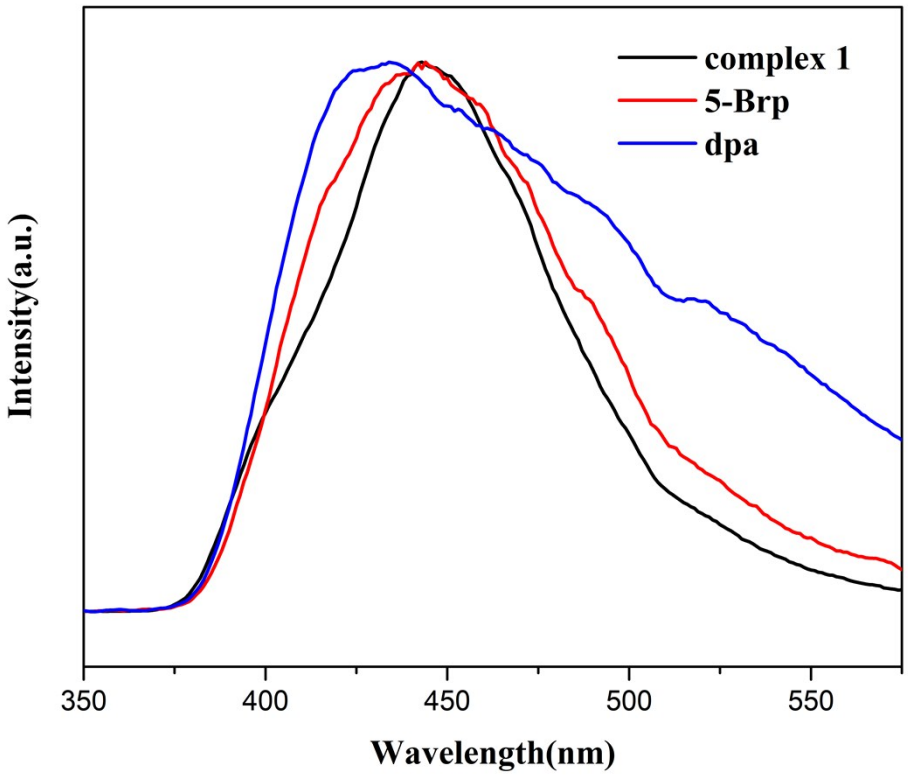

Fig. S4 Emission of **1**, 5-H_2Brp and dpa in ethanol (at λ_{ex}=346 nm).

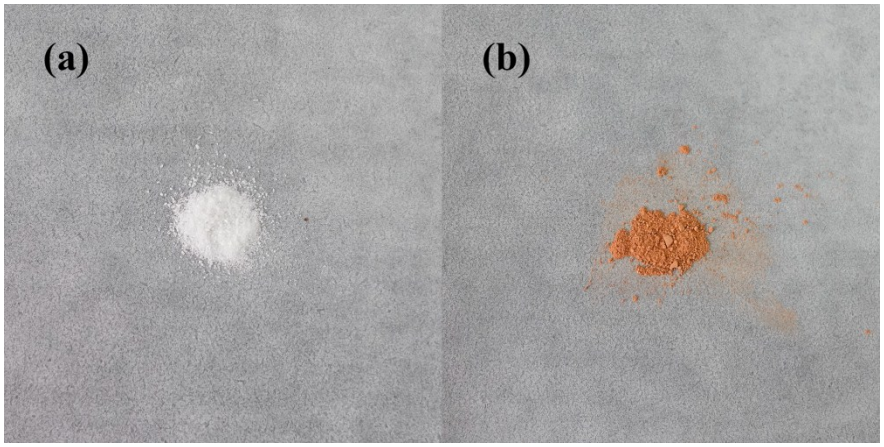

Fig. S5 Photograph of (a) **1** and (b) **1** immersed in 0.1 M solution of Fe^{3+} ions for 1 h.

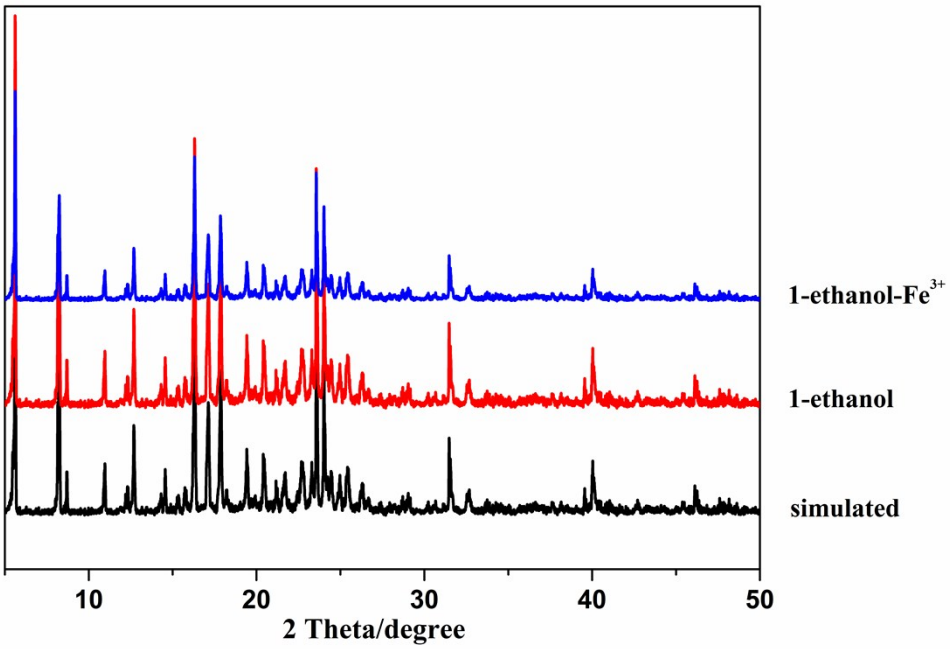

Fig. S6 The PXRD patterns of **1** after immersed into ethanol solution of Fe^{3+} ions.

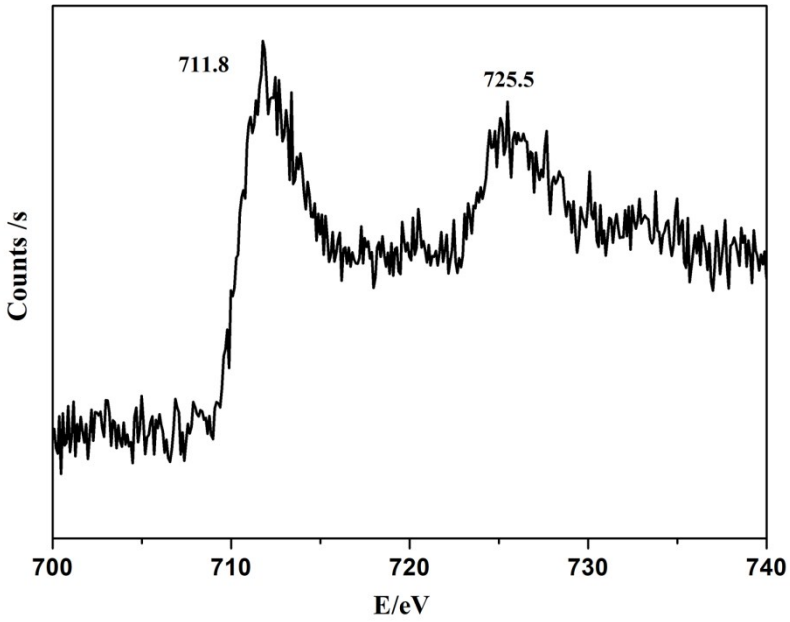

Fig. S7 Fe 2p XPS spectra after complex **1** was immersed in Fe^{3+} ions.

Fig. S8 Photograph before (left) and after (right) adding (a) **1**, (b) dpa, (c) 5-H_2Brp.

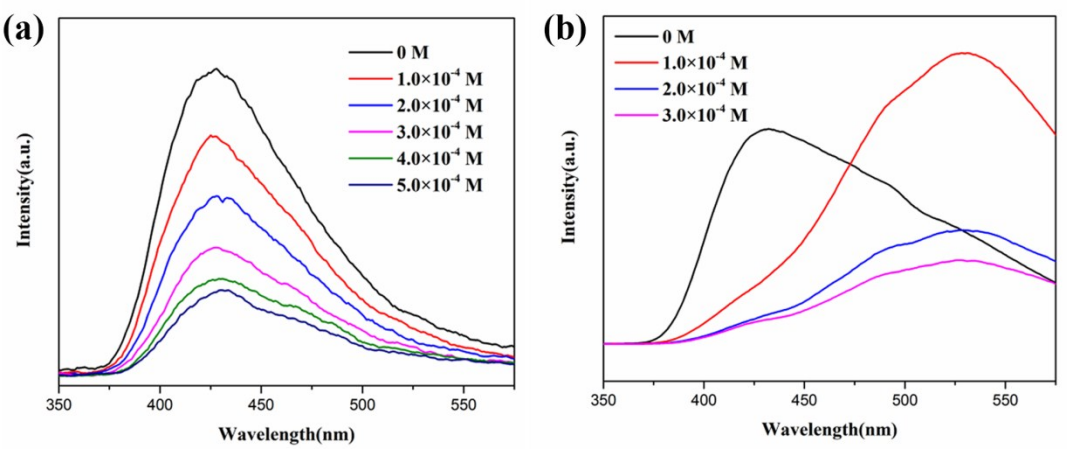

Fig. S9 Fluorescence of (a) 5-H_2Brp and (b) dpa with different [Fe^{3+}] in ethanol.

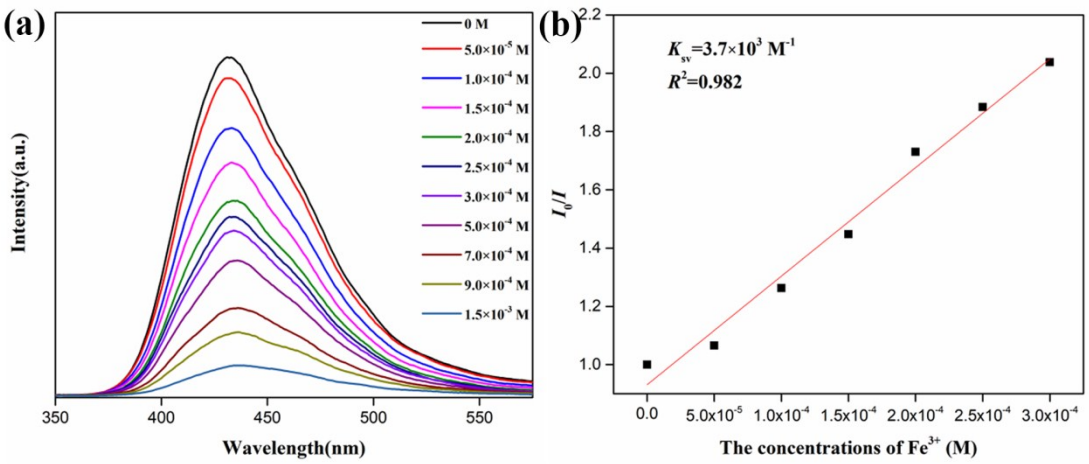

Fig. S10 (a) Fluorescence of 2 with different [Fe^{3+}] in ethanol (b) curve of K_{sv} (λ_{ex}=340 nm).

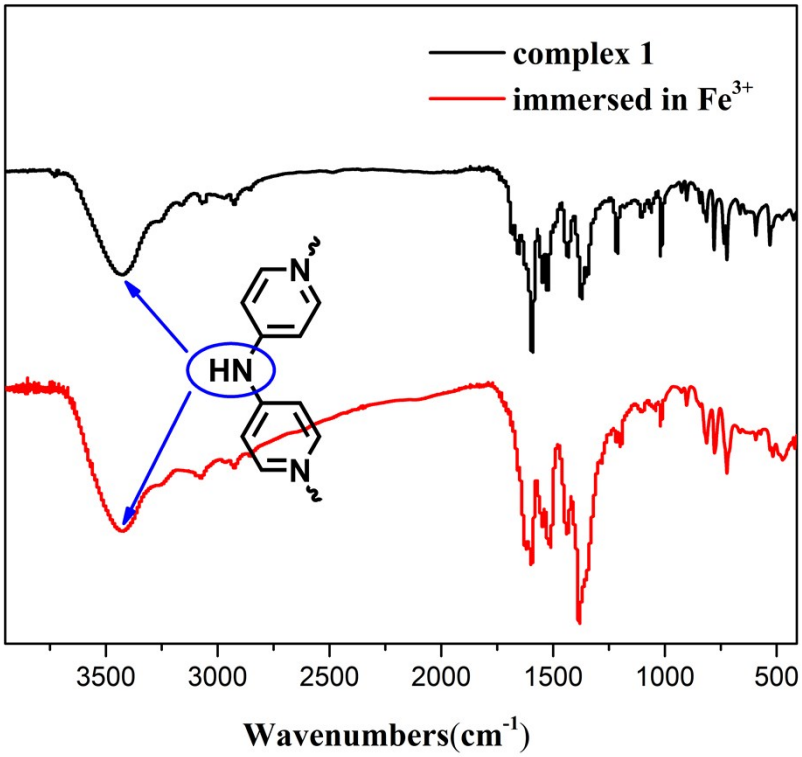

Fig. S11 FTIR spectra of **1** before and after immersed in Fe^{3+} ions.

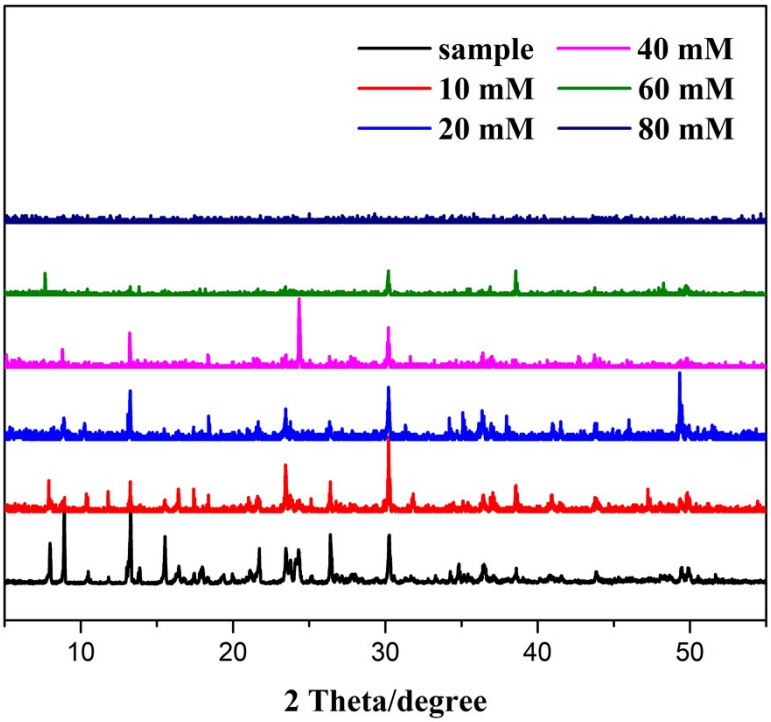

Fig. S12 PXRD of 20mg complex **1** after immersed in 2mL different [Fe^{3+}] aqueous solution for 24 hours.

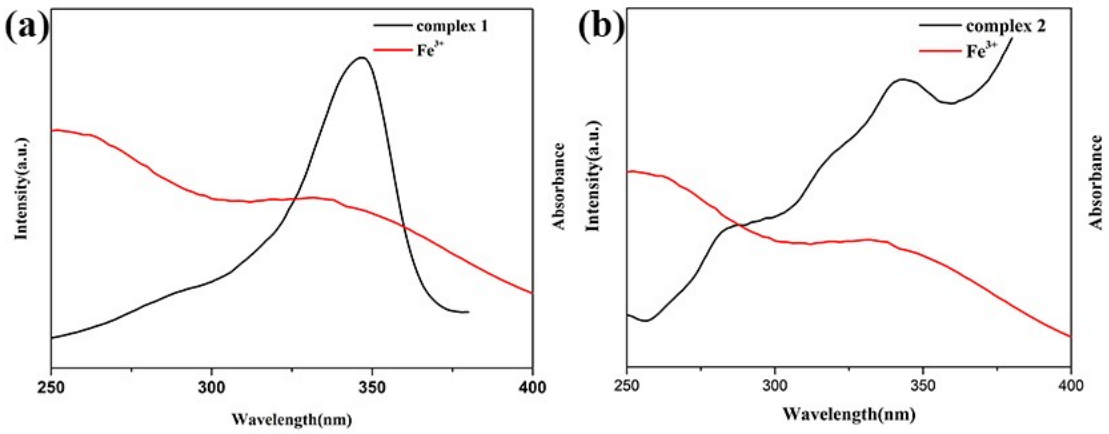

Fig. S13 UV absorbance spectra of Fe^{3+} ions and excitation spectra of (a) **1** and (b) **2**.

Table S1 The [Cd^{2+}] released to solution before and after **1** was immersed in Fe^{3+} ions.

Instrument	Agilent 7700X ICP-MS
Testing Results	
Determination of Element	Content (μg/mL)
Cd (water)	3.671658449
Cd (aqueous solution of Fe^{3+})	24.01234789

3mg of complex **1** was immersed in 10 mL water and aqueous solution of Fe^{3+} ions (0.01 M), respectively. The resulting solutions were centrifuged and supernatants were obtained to be determined by ICP-MS.

Table S2 Crystal data and structure refinement parameters for **1** and **2**.

	1	**2**
Empirical formula	$C_{19.5}H_{16.5}BrCdN_{3.5}O_{5.5}$	$C_{21}H_{19}BrCdN_2O_5$
Formula weight	580.17	571.69
Crystal system	monoclinic	monoclinic
Space group	C2/c	C2/c
a/Å	15.661(4)	14.340(2)
b/Å	13.297(3)	18.918(3)
c/Å	23.290(5)	16.582(3)
α/°	90	90
β/°	108.660(3)	100.615(2)
γ/°	90	90
Volume/Å^3	4595.0(18)	4421.3(13)
Z	8	8
ρ_{calc}g/cm^3	1.677	1.718
μ/mm^{-1}	2.727	2.829
F(000)	2280.0	2256.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.692 to 56.474	3.604 to 56.532
Index ranges	-20 ≤ h ≤ 15 -16 ≤ k ≤ 17 -29 ≤ l ≤ 30	-18 ≤ h ≤ 16 -21 ≤ k ≤ 24 -21 ≤ l ≤ 21
Reflections collected	15141	14786
Independent reflections	5324[R_{int} = 0.0367, R_{sigma} = 0.0487]	5158 [R_{int} = 0.0319, R_{sigma} = 0.0417]
Data/restraints/parameters	5324/246/344	5158/0/283
Goodness-of-fit on F^2	1.049	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0451, wR_2 = 0.1150	R_1 = 0.0350, wR_2 = 0.0729
Final R indexes [all data]	R_1 = 0.0724, wR_2 = 0.1299	R_1 = 0.0620, wR_2 = 0.0821
Largest diff. peak/hole / e Å^{-3}	1.78/-0.85	0.72/-0.58

Table S3 Bond Lengths for **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cd1	O4[1]	2.311(4)	O2	C8	1.238(6)
Cd1	O3[2]	2.313(3)	C9	C10	1.374(7)
Cd1	N2	2.307(4)	C10	C11	1.385(7)
Cd1	N1[3]	2.295(4)	C8	C6	1.514(6)
Cd1	O1	2.436(4)	C11	C12	1.399(7)
Cd1	O2	2.370(3)	C11	N3	1.398(6)
Br1	C4	1.889(4)	C5	C6	1.374(7)
O4	Cd1[1]	2.311(3)	C5	C4	1.394(7)
O4	C1	1.256(5)	C12	C13	1.363(7)
C1	O3	1.239(5)	N3	C14	1.392(6)
C1	C2	1.508(6)	C14	C18	1.381(7)
O3	Cd1[4]	2.313(3)	C14	C15	1.372(7)
N2	C9	1.343(6)	C17	C18	1.381(7)
N2	C13	1.343(6)	C15	C16	1.388(7)
C2	C3	1.394(7)	O6	C21	1.196(9)
C2	C7	1.390(6)	C19	N0AA	1.462(10)
C3	C4	1.384(7)	C20	N0AA	1.463(10)
N1	Cd1[5]	2.296(4)	N0AA	21	1.468(10)
N1	C17	1.340(7)	O6A	C21A	1.140(18)
N1	C16	1.345(7)	C21A	N4A	1.452(9)
C7	C6	1.400(6)	N4A	C19A	1.463(9)
O1	C8	1.262(6)	N4A	C20A	1.477(9)

[1] -*X*, 1-*Y*, -*Z*; [2] 1/2+*X*, -1/2+*Y*, +*Z*; [3] 1/2+*X*, 1/2-*Y*, 1/2+*Z*; [4] -1/2+*X*, 1/2+*Y*, +*Z*; [5] -1/2+*X*, 1/2-*Y*, -1/2+*Z*

Table S4 Bond Angles for **1.**

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O4[1]	Cd1	O3[2]	129.32(11)	N2	C9	C10	121.9(5)
O4[1]	Cd1	O1	144.96(12)	C9	C10	C11	120.6(4)
O4[1]	Cd1	O2	90.83(13)	O1	C8	C6	117.8(5)
O3[2]	Cd1	O1	85.26(11)	O2	C8	O1	122.4(4)
O3[2]	Cd1	O2	139.36(12)	O2	C8	C6	119.8(4)
N2	Cd1	O4[1]	87.56(13)	C10	C11	C12	117.1(4)
N2	Cd1	O3[2]	87.31(13)	C10	C11	N3	123.9(4)
N2	Cd1	O1	88.94(14)	N3	C11	C12	118.8(5)
N2	Cd1	O2	88.71(14)	C6	C5	C4	119.9(5)
N1[3]	Cd1	O4[1]	88.89(14)	C7	C6	C8	120.3(5)
N1[3]	Cd1	O3[2]	92.06(14)	C5	C6	C7	120.3(4)
N1[3]	Cd1	N2	174.84(14)	C5	C6	C8	119.4(4)
N1[3]	Cd1	O1	96.11(15)	C13	C12	C11	119.0(5)
N1[3]	Cd1	O2	95.08(14)	C14	N3	C11	126.7(5)
O2	Cd1	O1	54.23(12)	C3	C4	Br1	119.6(4)
C1	O4	Cd1[1]	177.0(3)	C3	C4	C5	120.3(5)
O4	C1	C2	118.9(4)	C5	C4	Br1	120.1(4)
O3	C1	O4	123.3(4)	N2	C13	C12	123.8(5)
O3	C1	C2	117.8(4)	C18	C14	N3	118.9(5)
C1	O3	Cd1[4]	105.2(3)	C15	C14	N3	123.1(5)
C9	N2	Cd1	121.8(3)	C15	C14	C18	117.7(5)
C13	N2	Cd1	120.5(3)	N1	C17	C18	123.0(5)
C13	N2	C9	117.6(4)	C17	C18	C14	119.6(5)
C3	C2	C1	118.2(4)	C14	C15	C16	119.8(5)
C7	C2	C1	122.1(4)	N1	C16	C15	122.5(5)
C7	C2	C3	119.7(4)	C19	N0AA	C20	123.5(17)
C4	C3	C2	120.0(4)	C19	N0AA	C21	115.9(17)
C17	N1	Cd1[5]	125.3(3)	C20	N0AA	C21	120.5(16)
C17	N1	C16	117.2(4)	O6	C21	N0AA	129(2)
C16	N1	Cd1[5]	117.4(4)	O6A	C21A	N4A	123.4(17)
C2	C7	C6	119.8(5)	C21A	N4A	C19A	126.0(12)
C8	O1	Cd1	89.8(3)	C21A	N4A	C20A	116.9(13)
C8	O2	Cd1	93.5(3)	C19A	N4A	C20A	117.1(12)

[1] -*X*, 1-*Y*, -*Z*; [2] 1/2+*X*, -1/2+*Y*, +*Z*; [3] 1/2+*X*, 1/2-*Y*, 1/2+*Z*; [4] -1/2+*X*, 1/2+*Y*, +*Z*; [5] -1/2+*X*, 1/2-*Y*, -1/2+*Z*

Table S5 Bond Lengths for **2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cd1	O1	2.244(2)	C16	C17	1.391(5)
Cd1	O2	2.638(3)	C17	C18	1.382(5)
Cd1	O3	2.216(2)	C18	C19	1.382(4)
Cd1	O5	2.346(3)	C18	C211	1.504(5)
Cd1	N1	2.372(3)	C21	C182	1.504(5)
Cd1	N2	2.285(2)	C5	C4	1.372(5)
Br1	C16	1.901(3)	C4	C3	1.383(5)
O1	C14	1.270(4)	C3	C2	1.372(5)
O2	C14	1.234(4)	C3	C63	1.511(5)
O3	C21	1.247(4)	C2	C1	1.385(5)
O4	C21	1.246(4)	C12	C13	1.378(5)
N1	C5	1.338(4)	C13	C9	1.379(5)
N1	C1	1.333(4)	C9	C10	1.371(5)
N2	C12	1.328(4)	C9	C8	1.508(4)
N2	C11	1.333(4)	C10	C11	1.381(4)
C14	C20	1.517(4)	C8	C7	1.508(5)
C20	C15	1.387(5)	C7	C6	1.538(5)
C20	C19	1.379(4)	C6	C34	1.511(5)
C15	C16	1.374(5)			

[1] +*X*, -*Y*, -1/2+*Z*; [2] +*X*, -*Y*, 1/2+*Z*; [3] -1/2+*X*, 1/2-*Y*, -1/2+*Z*; [4] 1/2+*X*, 1/2-*Y*, 1/2+*Z*

Table S6 Bond Angles for **2**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O1	Cd1	O2	52.98(8)	C16	C15	C20	119.2(3)
O1	Cd1	O5	90.02(10)	C15	C16	Br1	119.7(3)
O1	Cd1	N1	88.36(9)	C15	C16	C17	122.1(3)
O1	Cd1	N2	139.43(9)	C17	C16	Br1	118.2(3)
O3	Cd1	O1	130.24(10)	C18	C17	C16	118.5(3)
O3	Cd1	O2	176.70(9)	C17	C18	C19	119.4(3)
O3	Cd1	O5	80.82(12)	C17	C18	C21[1]	120.7(3)
O3	Cd1	N1	91.47(10)	C19	C18	C21[1]	119.9(3)
O3	Cd1	N2	90.15(10)	C20	C19	C18	121.9(3)
O5	Cd1	O2	98.91(11)	O3	C21	C18[2]	115.9(3)
O5	Cd1	N1	168.37(11)	O4	C21	O3	124.7(3)
N1	Cd1	O2	89.29(9)	O4	C21	C18[2]	119.4(4)
N2	Cd1	O2	86.58(9)	N1	C5	C4	123.1(3)
N2	Cd1	O5	93.76(10)	C5	C4	C3	120.2(4)
N2	Cd1	N1	94.96(9)	C4	C3	C6[3]	120.4(4)
C14	O1	Cd1	100.3(2)	C2	C3	C4	116.7(3)
C14	O2	Cd1	82.8(2)	C2	C3	C6[3]	122.8(4)
C21	O3	Cd1	114.7(2)	C3	C2	C1	120.2(3)
C5	N1	Cd1	119.3(2)	N1	C1	C2	122.9(3)
C1	N1	Cd1	123.8(2)	N2	C12	C13	123.4(3)
C1	N1	C5	116.9(3)	C12	C13	C9	119.7(3)
C12	N2	Cd1	119.5(2)	C13	C9	C8	118.8(3)
C12	N2	C11	117.1(3)	C10	C9	C13	116.9(3)
C11	N2	Cd1	123.2(2)	C10	C9	C8	124.2(3)
O1	C14	C20	116.4(3)	C9	C10	C11	120.4(3)
O2	C14	O1	123.6(3)	N2	C11	C10	122.6(3)
O2	C14	C20	119.9(3)	C9	C8	C7	117.3(3)
C15	C20	C14	120.8(3)	C8	C7	C6	112.1(3)
C19	C20	C14	120.2(3)	C3[4]	C6	C7	111.0(3)
C19	C20	C15	119.0(3)				

[1] +*X*, -*Y*, -1/2+*Z*; [2] +*X*, -*Y*, 1/2+*Z*; [3] -1/2+*X*, 1/2-*Y*, -1/2+*Z*; [4] 1/2+*X*, 1/2-*Y*, 1/2+*Z*