Supporting information

Three layer-structured cadmium coordination polymers based on flexible 5-(4-pyridyl)-methoxyl isophthalic acid: rapid synthesis and luminescence sensing

Table of content

Solvothermal syntheses of 1-3

[CdL(H_2O)]·2H_2O (**1**)**.** H_2L (0.014 g, 0.05 mmol) and $Cd(NO_3)_2·4H_2O$ (0.024 g, 0.1 mmol) were dissolved in the solution of DMF (3 mL), H_2O (3 mL) and HNO_3 (100 μl, 0.1 mmol), then the mixture was sealed in a 25 ml of glass bottle and heated at 90 °C for 72 h. Finally, the mixture was gradually cooled to room temperature, resulting in colorless block-like crystals that were isolated by washing with deionized water several times and dried in air. The yield of **1** was 90.6 % based on H_2L. Anal. Calcd for $C_{14}H_{15}NO_8Cd$: C, 38.39 %; H, 3.43 %; N, 3.20 %. Found: C 38.56 %; H, 3.34 %; N, 3.57 %.

[CdL(H_2O)(4,4'-bipy)$_{0.5}$]·H_2O (**2**). The mixture of $Cd(NO_3)_2·4H_2O$ (0.024 g, 0.1 mmol), H_2L (0.014 g, 0.05 mmol), 4,4'-bipy (0.0078 g, 0.05 mmol), H_2O (5 ml), DMF (1 ml) and HNO_3 (250 μl, 0.25 mmol) was added to a 25 ml of glass bottle, and was heated at 95 °C for 3 days. Then, the reaction mixture was slowly cooled to room temperature. Colorless crystals of **2** were collected from the final reaction system by filtration, washed several times with deionized water, and dried in air at ambient temperature. (Yield: 81.1 % based on H_2L). Anal. Calcd for $C_{19}H_{17}N_2O_7Cd$: C, 45.81 %; H, 3.42 %; N, 5.63 %. Found: C 45.36 %; H, 3.31%; N, 5.78%.

[CdL(H_2O)$_2$]·0.5H_2bdc (**3**). $Cd(NO_3)_2·4H_2O$ (0.024 g, 0.1 mmol), H_2L (0.014 g, 0.05 mmol) and terephthalic acid (0.008 g, 0.05 mmol) were successively dissolved in the solution of DMF (2 mL) and H_2O (4 mL). Then the mixture was sealed in a Teflon-lined stainless steel container and heated at 100 °C for 3 days, and then it was gradually cooled to room temperature, resulting in colorless block-like crystals that

were isolated by washing with deionized water and dried at room temperature. (Yield: 87.8 % based on H_2L). Anal. Calcd for $C_{18}H_{16}NO_9Cd$: C, 42.97 %; H, 3.18 %; N, 2.78 %. Found: C 43.06 %; H, 3.22 %; N, 2.65 %.

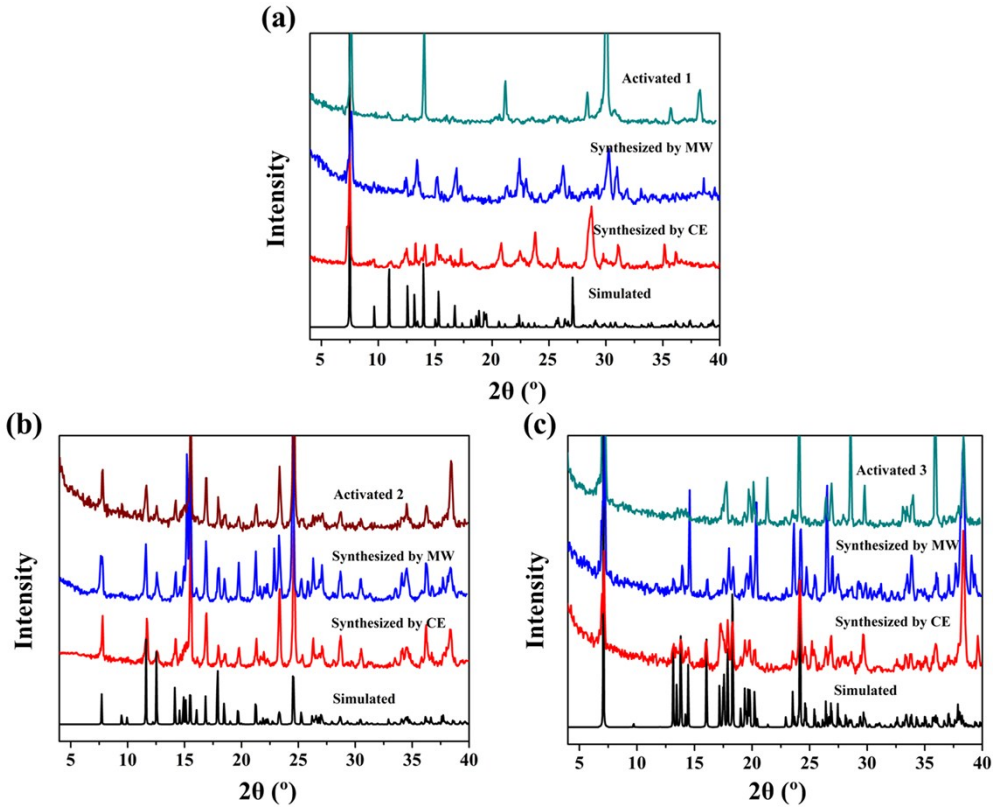

Fig. S1 The simulated and experimental PXRD patterns of **1** (a)**, 2** (b)**, 3** (c).

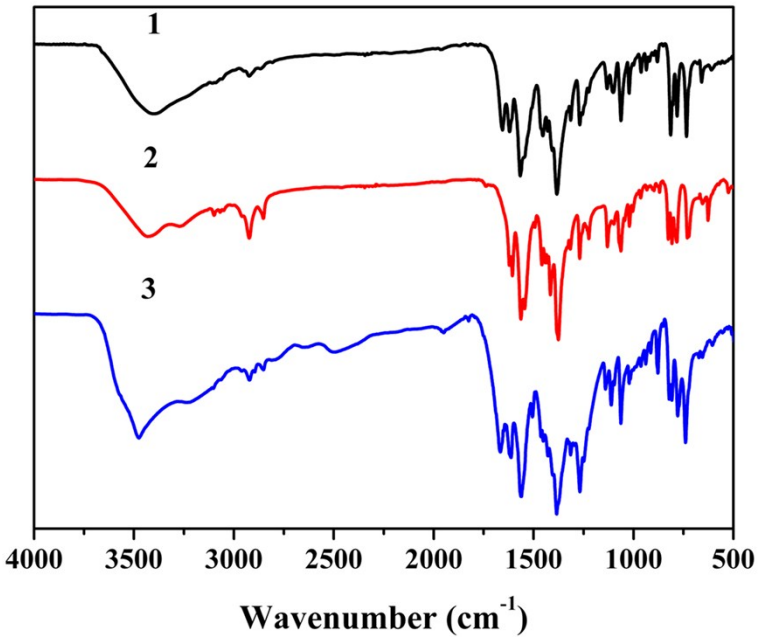

Fig. S2 IR spectra of **1**-**3.**

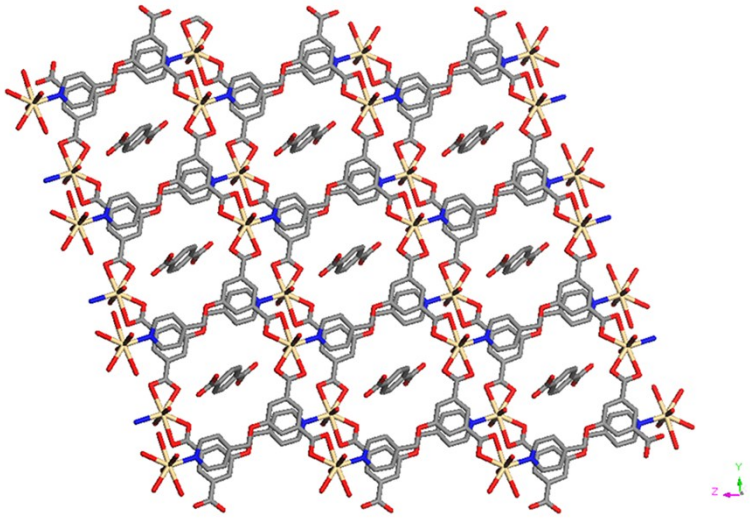

Fig. S3 The structure of **3** viewed along the *b* axis direction, showing the hexagonal windows and occluded with free H_2bdc molecules.

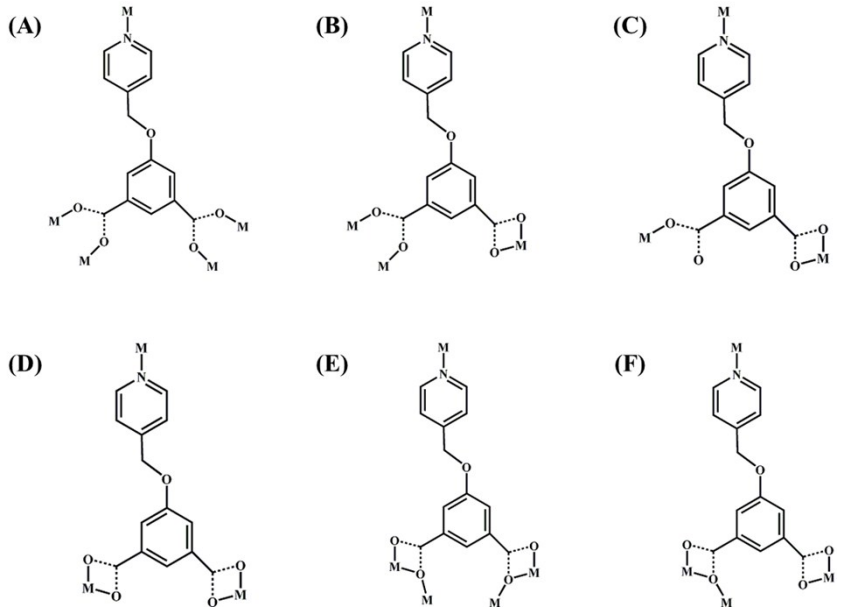

Fig. S4 Coordination modes of H_2L

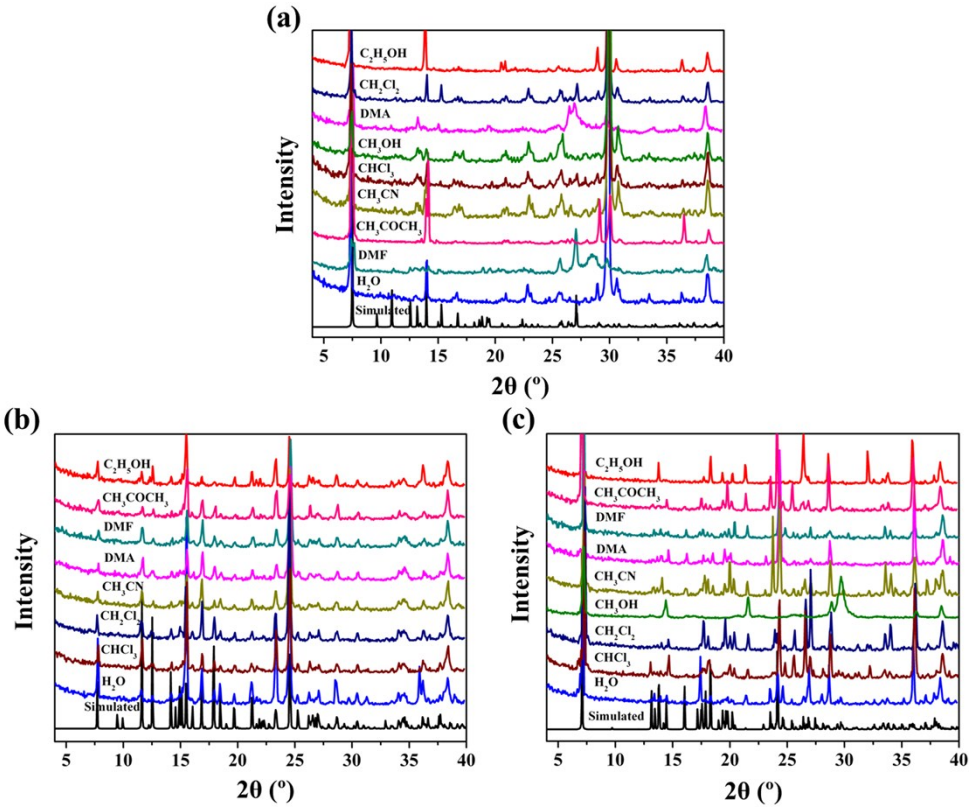

Fig. S5 PXRD patterns for **1** (a)**, 2** (b) and **3** (c) after soaking in various solvents.

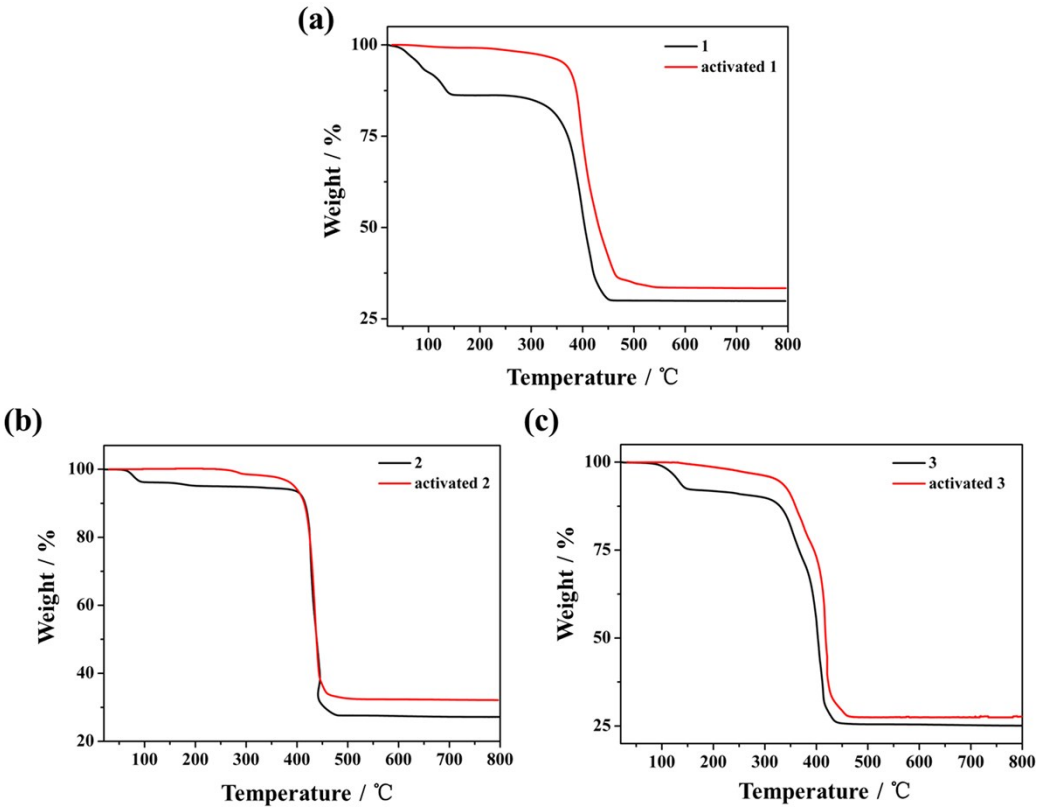

Fig. S6 TGA curves of **1**-**3** measured in air atmosphere.

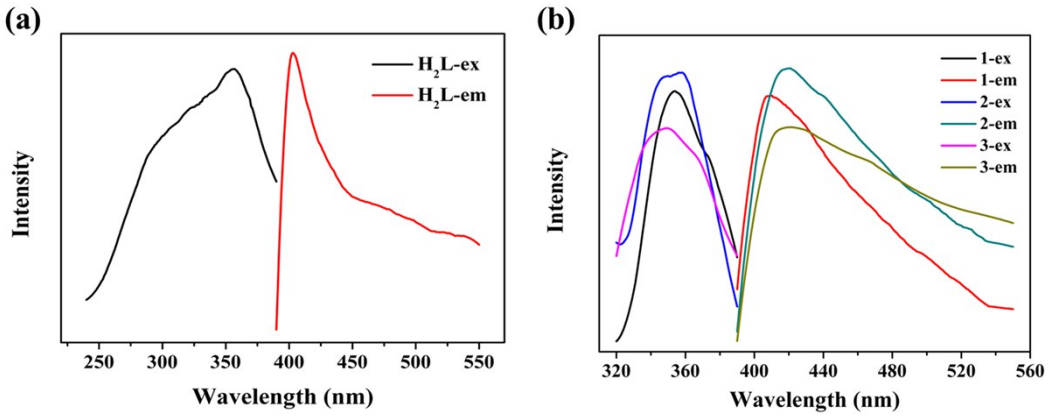

Fig. S7 The solid-state excitation and emission fluorescence spectra of H_2L ligand (a), **1**-**3** (b).

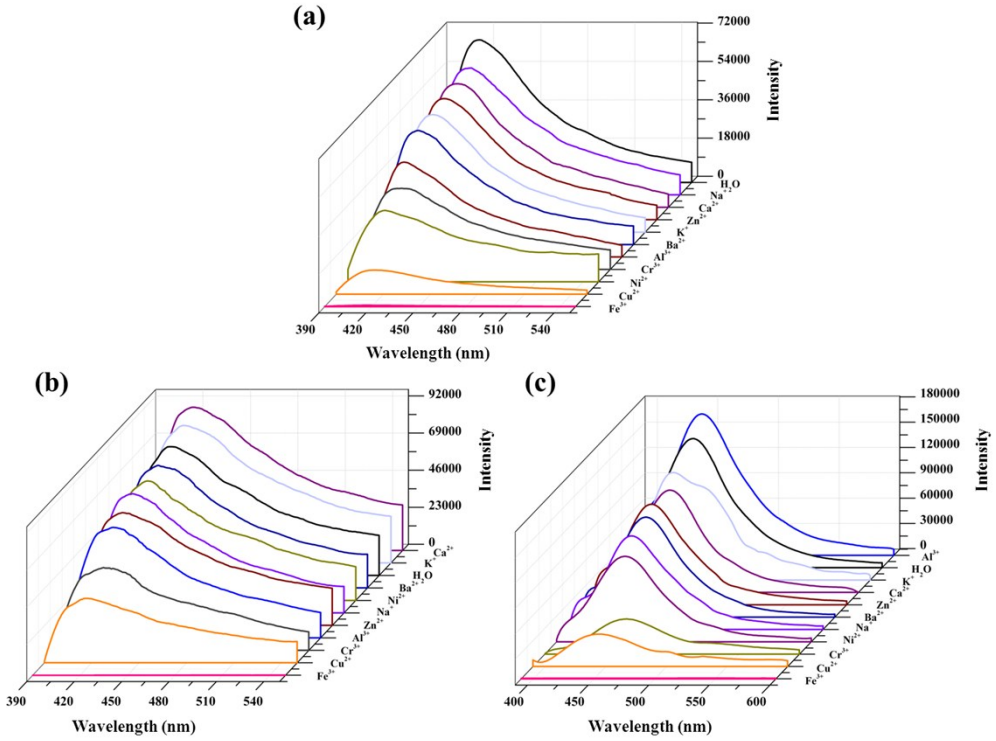

Fig. S8 The luminescent spectra of **1a** (a), **2a** (b) and **3a** (c) in aqueous solutions of diverse metal ions.

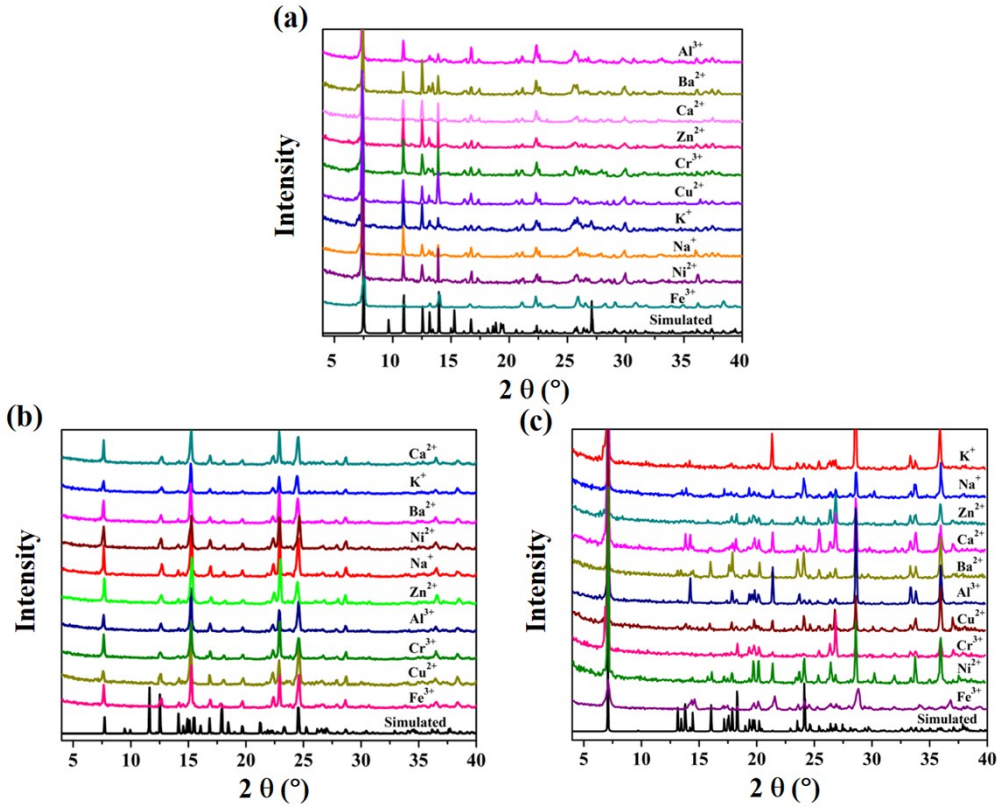

Fig. S9 PXRD patterns for **1a** (a), **2a** (b) and **3a** (c) after soaking in different metal ions aqueous solutions.

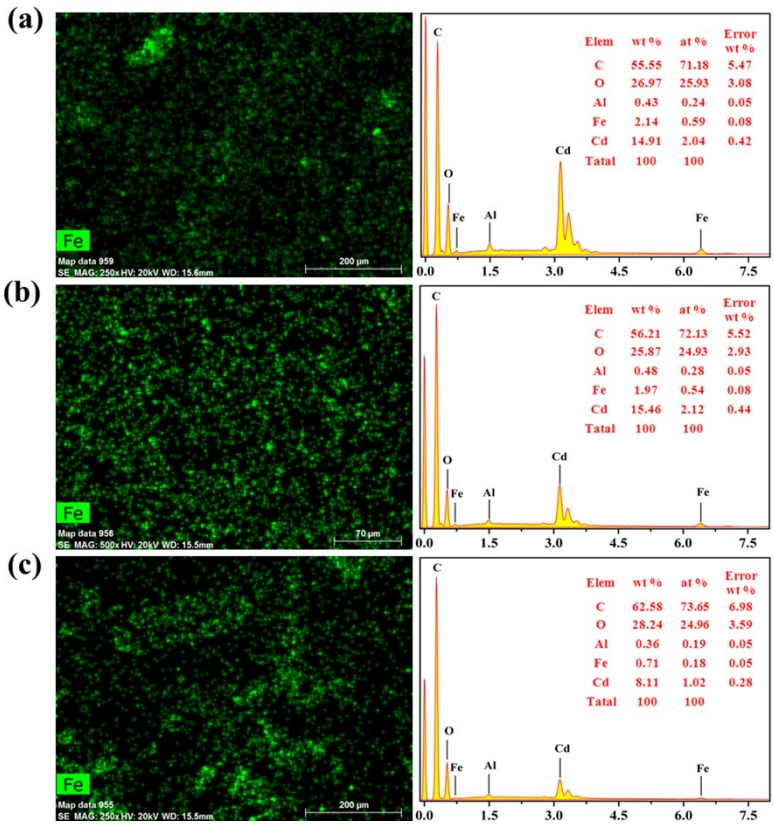

Fig. S10 The EDS-mapping images and the corresponding EDS spectra for Fe^{3+}@**1a** (a), Fe^{3+}@**2a** (b) and Fe^{3+}@**3a** (c), respectively.

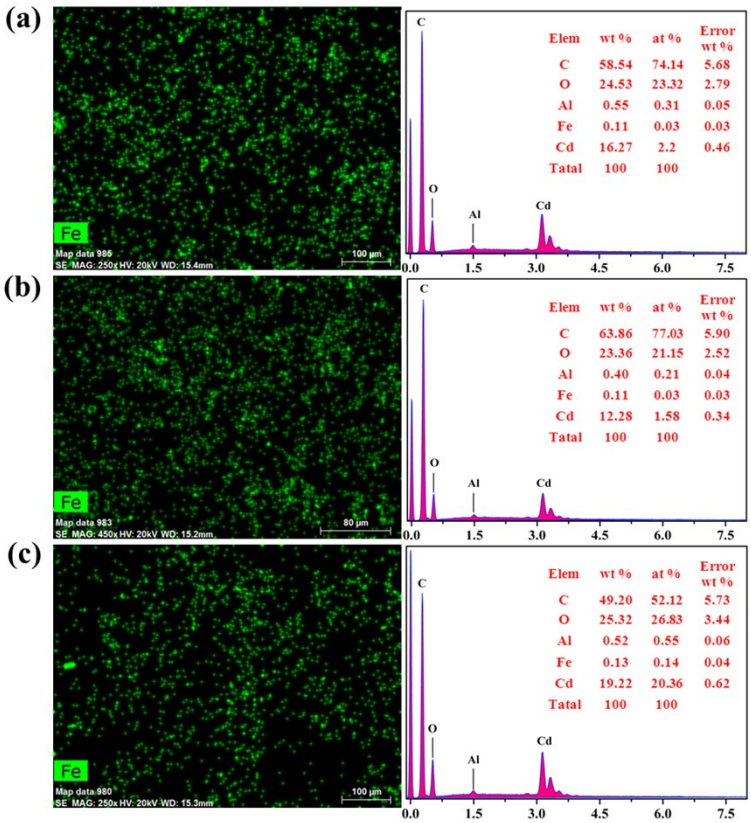

Fig. S11 The EDS-mapping images and the corresponding EDS spectra for Fe^{3+}@**1a** (a), Fe^{3+}@**2a** (b) and Fe^{3+}@**3a** (c) after washing with deionized water for several times.

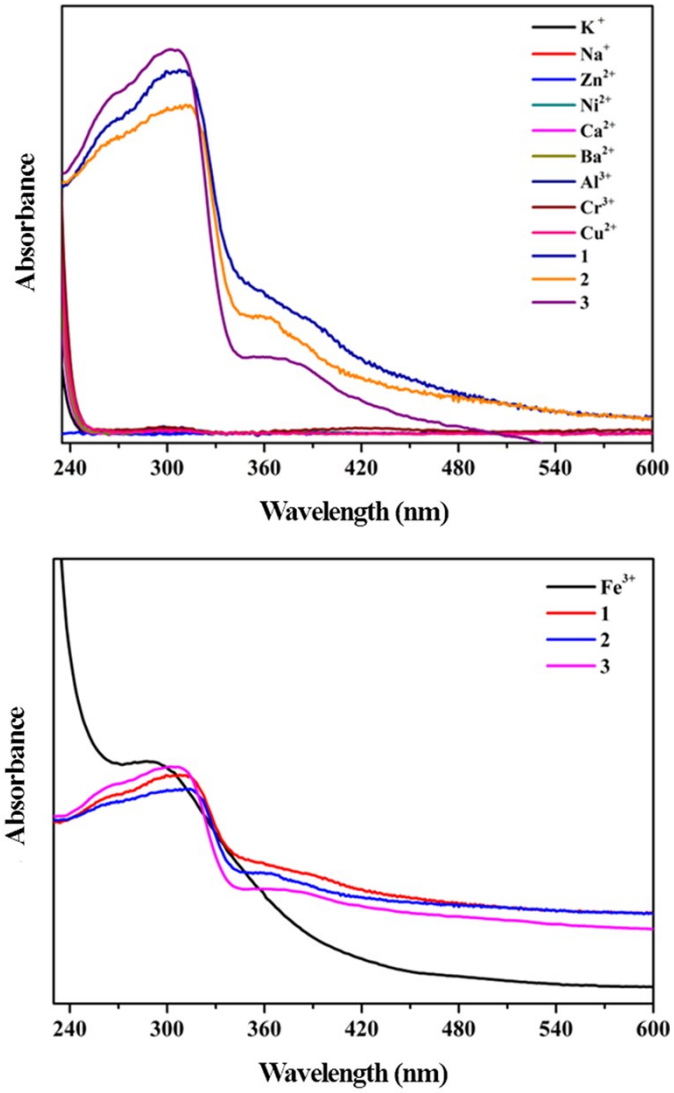

Fig. S12 The corrected UV-vis absorption spectra of **1-3** and various metal ions.

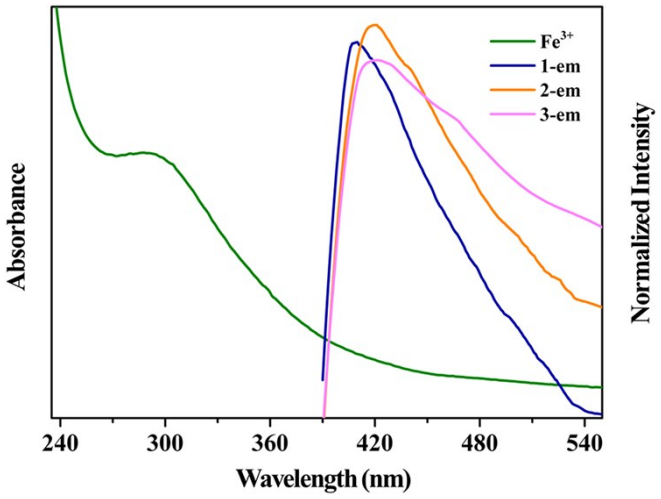

Fig. S13 The corrected UV-vis absorption spectra of Fe^{3+} aqueous solution and emission spectra of **1-3**.

Table S1 Crystallographic data and structure refinement for CPs **1-3.**

Compound	**1**	**2**	**3**
Formula	$C_{14}H_{11}CdNO_6$	$C_{19}H_{15}CdN_2O_7$	$C_{18}H_{16}NO_9Cd$
Formula weight	401.65	495.74	502.73
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1
a (Å)	7.5577(4)	8.1208(16)	7.6825(4)
b (Å)	9.9980(5)	10.241(2)	10.0737(4)
c (Å)	12.2600(6)	12.376(3)	13.2714(6)
α (°)	75.4320(10)	106.79(3)	70.5440(10)
β (°)	79.5900(10)	99.48(3)	89.008(2)
γ (°)	69.4910(10)	104.10(3)	74.231(2)
V (Å^3)	835.39(7)	924.6(3)	928.96(7)
Z	2	2	2
D_c (g·cm^{-3})	1.537	1.781	1.797
μ (mm^{-1})	1.325	1.228	1.229
F(000)	370	494	502
ϑ range (°)	2.22 - 25.11	3.26 - 24.15	2.23 - 34.20
Reflections collected	7280	5878	15317
Unique reflections	2955	2838	7639
R_{int}	0.0223	0.0519	0.0609
Data / restraints / parameters	2955 / 9 / 222	2838 / 9 / 270	7639 / 0 / 290
Gof	1.160	0.999	1.013
R_1,[I>2σ(I)]	0.0389	0.0472	0.0618
wR_1,[I>2σ(I)]	0.1277	0.0979	0.0849
R_1 (all data)	0.0424	0.0634	0.1312
R_2 (all data)	0.1305	0.1053	0.0996
CCDC No.	1851221	1851228	1851229

Table S2 Selected bond lengths [Å] and angles [°] for **1**-**3**.

1			
Cd(1)-O(1)	2.2696(19)	O(5)#2-Cd(1)-O(4)	81.82(9)
Cd(1)-N(1)#1	2.293(2)	O(1)-Cd(1)-O(6)#3	91.12(8)
Cd(1)-O(5)#2	2.301(2)	N(1)#1-Cd(1)-O(6)#3	89.07(7)
Cd(1)-O(4)	2.310(2)	O(5)#2-Cd(1)-O(6)#3	97.81(7)
Cd(1)-O(6)#3	2.419(2)	O(4)-Cd(1)-O(6)#3	172.15(8)
Cd(1)-O(3)	2.599(2)	O(1)-Cd(1)-O(3)	53.12(6)
Cd(1)-O(6)#2	2.610(2)	N(1)#1-Cd(1)-O(3)	86.49(7)
O(5)-Cd(1)#4	2.301(2)	O(5)#2-Cd(1)-O(3)	136.24(7)
O(6)-Cd(1)#3	2.419(2)	O(4)-Cd(1)-O(3)	81.41(8)
O(6)-Cd(1)#4	2.610(2)	O(6)#3-Cd(1)-O(3)	103.86(7)
N(1)-Cd(1)#5	2.293(2)	O(1)-Cd(1)-O(6)#2	132.68(7)
O(1)-Cd(1)-N(1)#1	138.32(8)	N(1)#1-Cd(1)-O(6)#2	86.24(7)
O(1)-Cd(1)-O(5)#2	89.39(7)	O(5)#2-Cd(1)-O(6)#2	52.60(7)
N(1)#1-Cd(1)-O(5)#2	131.83(8)	O(4)-Cd(1)-O(6)#2	103.23(8)
O(1)-Cd(1)-O(4)	96.72(9)	O(6)#3-Cd(1)-O(6)#2	70.77(7)
N(1)#1-Cd(1)-O(4)	85.43(9)	O(3)-Cd(1)-O(6)#2	171.03(6)

Symmetry transformations used to generate equivalent atoms:
#1 x-1, y, z+1; #2 x-1, y+1, z; #3 -x, -y+1, -z+2; #4 x+1, y-1, z; #5 x+1, y, z-1

2			
N(1)-Cd(1)#1	2.314(5)	O(5)#4-Cd(1)-O(1)	86.31(19)
Cd(1)-O(2)	2.308(4)	N(1)#5-Cd(1)-O(1)	90.6(2)
Cd(1)-N(1)#5	2.314(5)	O(2)-Cd(1)-N(2)	83.62(19)
Cd(1)-O(1)	2.339(6)	O(5)#4-Cd(1)-N(2)	87.20(18)
Cd(1)-N(2)	2.363(6)	N(1)#5-Cd(1)-N(2)	96.5(2)
Cd(1)-O(3)	2.561(4)	O(1)-Cd(1)-N(2)	172.57(18)
Cd(1)-O(4)#4	2.620(5)	O(2)-Cd(1)-O(3)	53.44(13)
O(4)-Cd(1)#3	2.620(5)	O(5)#4-Cd(1)-O(3)	138.11(15)
O(5)-Cd(1)#3	2.315(4)	N(1)#5-Cd(1)-O(3)	87.56(17)
O(2)-Cd(1)-O(4)#4	134.97(15)	O(1)-Cd(1)-O(4)#4	81.7(3)
O(2)-Cd(1)-O(5)#4	84.67(16)	O(1)-Cd(1)-O(3)	94.2(2)
O(3)-Cd(1)-O(4)#4	170.44(15)	N(2)-Cd(1)-O(4)#4	97.0(2)
O(5)#4-Cd(1)-N(1)#5	134.33(19)	N(1)#5-Cd(1)-O(4)#4	83.89(19)
O(2)-Cd(1)-N(1)#5	141.00(17)	N(2)-Cd(1)-O(3)	88.24(17)
O(2)-Cd(1)-O(1)	92.2(2)	O(5)#4-Cd(1)-O(4)#4	50.57(16)

Symmetry transformations used to generate equivalent atoms:
#1 x-1, y-1, z-1; #2 -x+2, -y+2, -z; #3 x, y-1, z; #4 x, y+1, z; #5 x+1, y+1, z+1

3			
N(1)-Cd(1)#1	2.288(2)	O(4)-Cd(1)-O(1)	93.26(10)
Cd(1)-N(1)#4	2.288(2)	N(1)#4-Cd(1)-O(6)#5	141.31(8)
Cd(1)-O(2)	2.291(3)	O(2)-Cd(1)-O(6)#5	99.51(12)
Cd(1)-O(4)	2.2980(19)	O(4)-Cd(1)-O(6)#5	79.70(7)
Cd(1)-O(1)	2.309(3)	O(1)-Cd(1)-O(6)#5	90.27(11)
Cd(1)-O(6)#5	2.329(2)	N(1)#4-Cd(1)-O(5)#5	87.40(8)
Cd(1)-O(5)#5	2.442(2)	O(2)-Cd(1)-O(5)#5	92.74(11)
Cd(1)-O(3)	2.630(2)	O(4)-Cd(1)-O(5)#5	133.17(7)
O(6)-Cd(1)#2	2.329(2)	O(1)-Cd(1)-O(5)#5	95.25(10)
O(5)-Cd(1)#2	2.442(2)	O(6)#5-Cd(1)-O(5)#5	54.35(7)
N(1)#4-Cd(1)-O(2)	86.65(11)	N(1)#4-Cd(1)-O(3)	87.07(8)
N(1)#4-Cd(1)-O(4)	139.00(8)	O(2)-Cd(1)-O(3)	86.88(11)
O(2)-Cd(1)-O(4)	85.81(10)	O(4)-Cd(1)-O(3)	52.32(7)
O(5)#5-Cd(1)-O(3)	174.46(7)	N(1)#4-Cd(1)-C(8)#5	114.55(9)
N(1)#4-Cd(1)-O(1)	87.45(10)	O(1)-Cd(1)-O(3)	84.56(10)
O(2)-Cd(1)-O(1)	169.83(12)	O(6)#5-Cd(1)-O(3)	131.16(7)

Symmetry transformations used to generate equivalent atoms:

#1 x, y, z-1; #2 x, y-1, z; #3 -x+1, -y+1, -z; #4 x, y, z+1; #5 x, y+1, z

Table S3 Comparisons between **1-3** and some reported coordination polymers.

compounds	crystal system	space group	dimension	coordination modes of H_2L	synthesis conditions	Ref
$[CoL]_n$	monoclinic	*P*2(1)/*n*	3D	A	9 ml H_2O， pH = 6.0-7.0， 130 ℃, 72 h	21
$[Ni_2L_2(H_2O)_3]_n$	monoclinic	*C*2/*c*	3D	C, D	2 ml DMF + 6 ml H_2O 100 ℃, 72 h	21
$[CoL(bimx)_{1/2}]_n$	monoclinic	*C*2/*c*	3D	B	2 ml DMF + 6 ml H_2O 100 ℃, 72 h	21
$[NiL(bimx)_{1/2}]_n$	monoclinic	*C*2/*c*	3D	B	2 ml DMF+6ml H_2O 100 ℃, 72 h	21
$[MnL(bimx)_{1/2}]_n$	monoclinic	*C*2/*c*	3D	B	3 ml DMF+6 ml H_2O 100 ℃, 72 h	21
$\{[CoL_2(bimb)(H_2O)_2]_3\cdot 2H_2O\}_n$	triclinic	*P*-1	2D	D	2 ml DMF+6 ml H_2O 100 ℃, 72 h	21
$[Mn_2L_2(H_2O)_2\cdot 2DMF\cdot 2H_2O]_n$	monoclinic	*P*21/*n*	3D	D	2ml DMF+6ml H_2O pH 6.0-7.0，100 ℃, 72 h	22
Cu(L2) ·xsolv	trigonal	*R-3 (148)*	3D	A	1.5 ml DMA + 0.5 ml + 50 μl H_2O 85 ℃, 12 h	23
Cu(L2) ·xsolv	orthorhombic	*Pbcn (60)*	3D	A	1.5 ml DMA + 0.5 ml EtOH 85 ℃, 12 h	23
$[DyAg(L)_2(H_2O)]n\cdot 2n(H_2O)$	triclinic	*P*-1	two-fold interpenetrated 3D framework	B, C	8 mL H_2O + 5 mL EtOH， 160 ℃, 72 h	24
$\{[Ln_2(L)_3(H_2O)_4]\cdot 10H_2O\}n$	orthorhombic	*Pnma*	3D	A, D	2 ml DMF + 8 ml H_2O 160 ℃, 72 h	25
$[Pb_2L_2]_n$	triclinic	*P*-1	3D pillared - layered structure	B, E	5 ml DMF+10 ml H_2O 160 ℃,60 h	26
$[CdL(H_2O)]\cdot 2H_2O$	triclinic	*P*-1	2D	F	3 ml H_2O +3 ml DMF 90 ℃,72 h	
$[CdL(H_2O)(4,4'\text{-bipy})_{0.5}]\cdot H_2O$	triclinic	*P*-1	two-fold interpenetrated 2D layer	D	5 ml H_2O +1 ml DMF 95 ℃,72 h	
$[CdL(H_2O)_2]\cdot 0.5H_2bdc$	triclinic	*P*-1	2D	D	4 ml H_2O +2 ml DMF 100 ℃,72 h	

Table S4 The comparison of K_{sv} between **1-3** and other reported probes for the detection of Fe^{3+}.

CPs	K_{sv} [M^{-1}]	Reference
Cd(II)-MOF	3.59×10^4	[21]
Pb_3O_2L	7.80×10^3	[23a]
PCN-604	8.53×10^3	[23b]
BUT-14	2.17×10^4	[23c]
BUT-15	1.66×10^4	[23c]
$[ZnL(H_2O)]\cdot(Me_2NH_2)\cdot DMF$	2.06×10^4	[23d]
Tb-MOF	3.714×10^4	[23e]
1	3.529×10^4	This work
2	3.619×10^4	This work
3	3.260×10^4	This work