

Cation-Exchange Porosity Tuning in a Dynamic 4d–4f–3d Framework for Ni^{II} Ion-Selective Luminescent Probe

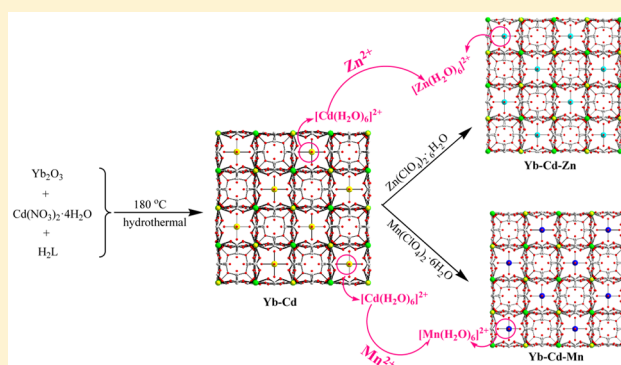
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S Supporting Information

ABSTRACT: A heterometallic complex $\{[\text{Yb}_2(\text{L})_6\text{Cd}_2][\text{Cd}(\text{H}_2\text{O})_6]\cdot 6\text{H}_2\text{O}\}_n$ (**Yb–Cd**) (H_2L = oxidiacetic acid) was synthesized under hydrothermal conditions. In **Yb–Cd**, each L chelates to one Yb^{3+} center and bonds to two Cd^{2+} ions in an anti-anti configuration. Yb and Cd atoms are arrayed alternatively and connected by O–C–O bridges to form a cubic octahedral cage as the secondary building unit. Consequently, topological NaCl nets with high symmetry in the cubic space group $Fd\bar{3}c$ have been constructed. The $[\text{Cd}(\text{H}_2\text{O})_6]^{2+}$ moieties lying in the porosity of anionic metal–organic framework (MOF) act as the thermodynamically stable species, required to balance the two negative charges of $[\text{Yb}_2(\text{L})_6\text{Cd}_2]^{2-}$ in **Yb–Cd**. Interestingly, when **Yb–Cd** was employed as a precursor and emerged in the aqueous solution of $\text{Mn}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ or $\text{Zn}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$, a reversible single-crystal-to-single-crystal transformation process driven by $[\text{Cd}(\text{H}_2\text{O})_6]^{2+}$ cations has been exhibited to generate the heterotrimetallic coordination polymer $\{[\text{Yb}_2(\text{L})_6\text{Cd}_2][\text{Mn}(\text{H}_2\text{O})_6]\cdot 6\text{H}_2\text{O}\}_n$ (**Yb–Cd–Mn**) or $\{[\text{Yb}_2(\text{L})_6\text{Cd}_2][\text{Zn}(\text{H}_2\text{O})_6]\cdot 6\text{H}_2\text{O}\}_n$ (**Yb–Cd–Zn**). To the best of our knowledge, **Yb–Cd–Mn** and **Yb–Cd–Zn** are the first examples representing 4d–4f–3d polymers based on multicarboxylic acid. Luminescent studies reveal that **Yb–Cd–Zn** may serve as a good candidate of Ni^{2+} a luminescent probe. To our knowledge, **Yb–Cd–Zn** represent the first example of the 4d–4f–3d framework to exhibit luminescent selectivity for Ni^{2+} .



INTRODUCTION

Over the past few decades, strong and continuous attention on metal–organic frameworks (MOFs) has been inspired by the aesthetics of crystalline architectures as well as potential applications in exchange,¹ catalysis,² gas storage,³ nonlinear optics,⁴ magnetism,⁵ luminescence,⁶ solvatochromic behavior,⁷ and so on. A key feature in MOFs is their porosity, which plays a significant role in the functional properties, typically in guest species recognition and adsorption.⁸ Most of the inorganic–organic hybrid materials with dynamic structural transformation behavior are of particular interest as coordination polymers and/or supramolecular entities, since they can exhibit several distinct polymeric architectures in response to external stimuli.^{9–15} The key to inducing characteristic crystal transformations is guest inclusion (common for various solvent molecules or templates)^{16–23} or guest exchange (mainly observed in the case of anion-exchange processes).^{24,25} Transformation of the overall structure of coordination polymers frequently occurs without destruction of the molecular skeleton or without dissolution and recrystallization of the materials, that is, transformation from one crystalline state to another. On the other hand, there are a few examples of induction of structural rearrangements in coordina-

tion polymers by physical stimuli besides heat,^{26–28} such as acidobasicity,²⁹ light,^{30–32} and magnetic and electric fields. Sometimes these conformational changes are reversible. In these cases, structural transformations can simply be classified as a breathing (contraction/expansion or shrinking/extending) transformation^{16–33} and conformation-change transformations (crystal-to-amorphous and crystal-to-crystal).^{23–25} In contrast, structural transformation of coordination polymers and supramolecular entities by a dissolution/reorganization process remains relatively understudied.³⁴ For example, Lee and co-workers described reversible polymerization and reversible conversion between folded and unfolded conformations of a coordination chain on counteranion exchange, which is driven by either depolymerization or conformational change. However, detailed studies of this process remain scarce.

Herein, we report a systematic study on a remarkable transition-metal cation-induced single-crystal-to-single-crystal (SC–SC) process that forms distinct metal carboxylate species. Previously, we reported a three-dimensional (3D) NaCl anionic

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Table 1. Crystallographic Data and Details of Refinements for Complexes Yb–Cd, Yb–Cd–Mn, and Yb–Cd–Zn

	Yb–Cd	Yb–Cd–Mn	Yb–Cd–Zn
formula	C ₂₄ H ₄₂ Cd ₃ O ₃₉ Yb ₂	C ₄₈ H ₇₈ Cd ₄ Mn ₂ O ₇₅ Yb ₄	C ₄₈ H ₇₈ Cd ₄ Zn ₂ O ₇₅ Yb ₄
<i>M</i> (g mol ⁻¹)	1637.85	3106.74	3127.60
cryst syst	cubic	cubic	cubic
space group	<i>Fd-3c</i>	<i>Fd-3c</i>	<i>Fd-3c</i>
temp.	293(2)	293(2)	293(2)
<i>a</i> (Å)	25.9723(6)	25.9261(11)	25.9261(11)
<i>b</i> (Å)	25.9723(6)	25.9261(11)	25.9261(11)
<i>c</i> (Å)	25.9723(6)	25.9261(11)	25.9261(11)
α (deg)	90	90	90
β (deg)	90	90	90
γ (deg)	90	90	90
<i>V</i> (Å ³)	17519.9(7)	17426.6(12)	17426.6(12)
<i>Z</i>	16	8	8
<i>F</i> (000)	12 512.0	11 904	11 984
ρ_{calcd} (Mg m ⁻³)	2.484	2.368	2.384
μ (mm ⁻¹)	5.782	5.610	5.870
data/restraints/params	651/1/60	366/6/59	513/0/57
GOF on <i>F</i> ²	1.150	1.100	1.058
<i>R</i> ₁ ^a (<i>I</i> = 2 σ (<i>I</i>))	0.0576	0.0592	0.0527
<i>wR</i> ₂ ^a (all data)	0.2651	0.2538	0.2481

$$^a R_1 = \sum ||F_o| - |F_c|| / |F_o|, \quad ^b wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^4]^{1/2}.$$

network $\{[\text{Sm}_2(\text{L})_6\text{Co}_2][\text{Co}(\text{H}_2\text{O})_6] \cdot 3\text{H}_2\text{O}\}_n$ (**Sm-Co**) (H_2L = oxidiacetic acid) in which $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ moieties serving as the thermodynamically stable species lie in the porosity of an anionic framework, required to balance the two negative charges of $[\text{Sm}_2(\text{L})_6\text{Co}_2]^{2-}$. For this study, oxidiacetic acid (L) as an ideal ligand was still chosen for constructing a 4d–4f–3d MOF $\{[\text{Yb}_2(\text{L})_6\text{Cd}_2][\text{Cd}(\text{H}_2\text{O})_6] \cdot 6\text{H}_2\text{O}\}_n$ (**Yb–Cd**) because (a) it is flexible, (b) it has multiple possible metal binding modes, and (c) its molecular coordination chemistry containing both transition- and lanthanide-metal ions is rarely developed.³⁵ Such ligand can be viewed as a relatively small dicarboxylic acid that is easily functionalized to generate a pentadentate coordination configuration that gives rise to thermodynamically and kinetically stable metal complexes of d and f block elements. More importantly, when **Yb–Cd** was employed as a precursor in the aqueous solution of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $[\text{Cd}(\text{H}_2\text{O})_6]^{2+}$ moieties residing in the one-dimensional (1D) channels of **Yb–Cd** can move freely out of the cavity and $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ or $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ ions occupy the position of $[\text{Cd}(\text{H}_2\text{O})_6]^{2+}$ to generate an isomorphous solvate of $\{[\text{Yb}_2(\text{L})_6\text{Cd}_2][\text{Mn}(\text{H}_2\text{O})_6] \cdot 6\text{H}_2\text{O}\}_n$ (**Yb–Cd–Mn**) or $\{[\text{Yb}_2(\text{L})_6\text{Cd}_2][\text{Zn}(\text{H}_2\text{O})_6] \cdot 6\text{H}_2\text{O}\}_n$ (**Yb–Cd–Zn**). The impetus for the recognition studies was to determine whether a reversible single-crystal-to-single-crystal transformation between $[\text{Cd}(\text{H}_2\text{O})_6]^{2+}$ in **Yb–Cd** and $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ in **Yb–Cd–Mn** or $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ in **Yb–Cd–Zn**. Experimental results demonstrate that typical ion-exchange reactions using $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ ions in **Yb–Cd–Mn** or $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ in **Yb–Cd–Zn** to replace $[\text{Cd}(\text{H}_2\text{O})_6]^{2+}$ ions of **Yb–Cd** in aqueous solution under mild conditions is possible. Luminescent measurements indicate that **Yb–Cd–Zn** represents the first example of a heterotrimetallic coordination polymer based on dicarboxylic acid as a luminescent probe of Ni^{2+} .

EXPERIMENTAL SECTION

General Remarks. All reagents are commercially available and used without further purification. Elemental analysis of carbon, nitrogen, and hydrogen was performed on a PerkinElmer 240 elemental analyzer.

Powder X-ray diffraction analysis was carried out on a D/Max-2500 X-ray diffractometer using Cu $K\alpha$ radiation. The photoluminescence spectra were recorded by a MPF-4 fluorescence spectrophotometer with a xenon arc lamp as the light source. The inorganic ion quantitative analyses were recorded on a Hitachi 180-80 Polarized Zeeman Atomic Absorption Spectrometer and Thermo Electron Corp., USA. FT-IR spectra were measured from KBr pellets in the range of 4000–400 cm^{-1} on a Bio-Rad FTS 135 spectrometer. TGA experiments were performed on a NETZSCH TG 209 instrument with a heating rate of 10 $^\circ\text{C min}^{-1}$.

Synthesis of $\{[\text{Yb}_2(\text{L})_6\text{Cd}_2][\text{Cd}(\text{H}_2\text{O})_6] \cdot 6\text{H}_2\text{O}\}_n$ (Yb–Cd**).** A mixture of Yb_2O_3 (0.0394 g, 0.1 mmol), $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.0925 g, 0.3 mmol), H_2L (0.0939 g, 0.7 mmol), and H_2O (12 mL) was put in a 20 mL acid digestion bomb and heated at 180 $^\circ\text{C}$ for 3 days. The crystal products were collected after washing with H_2O (2×5 mL) and diethyl ether (2×5 mL). Yield: 63% based on Yb_2O_3 . Anal. Calcd for $\text{C}_{12}\text{H}_{21}\text{Cd}_{1.5}\text{O}_{19.5}\text{Yb}$: C, 17.60; H, 2.58. Found: C, 17.94; H, 2.29. FT-IR data (cm^{-1}): 3497 (s), 3020 (w), 2917 (w), 1607 (s), 1441 (m), 1311 (m), 1134 (m), 1055 (m), 944 (m), 741 (w), 567 (w).

Synthesis of $\{[\text{Yb}_2(\text{L})_6\text{Cd}_2][\text{Mn}(\text{H}_2\text{O})_6] \cdot 6\text{H}_2\text{O}\}_n$ (Yb–Cd–Mn**).** A mixture of **Yb–Cd** (0.8190 g, 0.5 mmol) and $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.8097 g, 5 mmol) in H_2O (10 mL) was stirred for about 6 h; the crystals can retain their crystalline appearances. Well-shaped colorless block crystals suitable for X-ray diffraction analysis were isolated. Yield: 25%. Anal. Calcd for $\text{C}_{48}\text{H}_{78}\text{Cd}_4\text{Mn}_2\text{O}_{75}\text{Yb}_4$: C, 18.56; H, 2.53. Found: C, 18.42; H, 2.66. FT-IR data (cm^{-1}): 3497 (s), 3018 (w), 2918 (w), 1610 (s), 1439 (m), 1309 (m), 1136 (m), 1058 (m), 945 (m), 745 (w), 567 (w).

Synthesis of $\{[\text{Yb}_2(\text{L})_6\text{Cd}_2][\text{Zn}(\text{H}_2\text{O})_6] \cdot 6\text{H}_2\text{O}\}_n$ (Yb–Cd–Zn**).** A mixture of **Yb–Cd** (0.8190 g, 0.5 mmol) and $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.8620 g, 5 mmol) in H_2O (10 mL) was stirred for about 6 h; the crystals can retain their crystalline appearances. Well-shaped colorless block crystals suitable for X-ray diffraction analysis were isolated. Yield: 30%. Anal. Calcd for $\text{C}_{48}\text{H}_{78}\text{Cd}_4\text{O}_{75}\text{Yb}_4\text{Zn}_2$: C, 18.43; H, 2.51. Found: C, 18.64; H, 2.70. FT-IR data (cm^{-1}): 3501 (s), 3023 (w), 2917 (w), 1608 (s), 1440 (m), 1311 (m), 1135 (m), 1055 (m), 944 (m), 741 (w), 568 (w).

CAUTION! Although no problems were encountered in this study, transition-metal perchlorate complexes are potentially explosive and should be handled with proper precautions.

X-ray Crystallography. Single-crystal X-ray diffraction patterns for **Yb–Cd**, **Yb–Cd–Mn**, and **Yb–Cd–Zn** were collected on an APEX II CCD area detector and a Bruker Smart CCD diffractometer. A graphite crystal monochromator was equipped in the incident beam for data collection at temperatures of 292(2) K. The ω - Φ scan technique was

Table 2. Selected Bond Lengths [Angstroms] and Angles [degrees] for Yb–Cd, Yb–Cd–Mn, and Yb–Cd–Zn^a

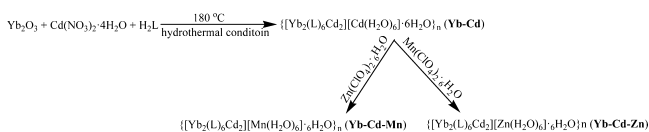
Yb–Cd					
Yb(1)–O(1)	2.331(13)	Yb(1)–O(3)	2.396(16)	Cd(1)–O(2)	2.276(14)
Cd(2)–O(4)	2.21(2)	O(1)#1–Yb(1)–O(1)#2	128.7(6)	O(1)#1–Yb(1)–O(1)#3	84.4(5)
O(1)#2–Yb(1)–O(1)#3	80.3(4)	O(1)#3–Yb(1)–O(1)	144.1(6)	O(1)#1–Yb(1)–O(3)#4	72.1(3)
O(1)#2–Yb(1)–O(3)#4	137.8(3)	O(1)#3–Yb(1)–O(3)#4	64.4(3)	O(3)#4–Yb(1)–O(3)	120.000(1)
O(2)#6–Cd(1)–O(2)	86.3(4)	O(2)#7–Cd(1)–O(2)	93.7(4)	O(2)–Cd(1)–O(2)#9	180.000(2)
O(4)#12–Cd(2)–O(4)#14	90.0	O(4)–Cd(2)–O(4)#14	90.000(2)		
Yb–Cd–Mn					
Yb(1)–O(2)#1	2.235(16)	Cd(2)–O(1)#6	2.345(18)	Cd(2)–O(3)	2.44(2)
Mn(1)–O(4)	2.157(19)	O(2)#1–Yb(1)–O(2)#2	87.1(4)	O(2)#1–Yb(1)–O(2)#4	92.9(4)
O(2)#2–Yb(1)–O(2)#4	179.999(3)	O(2)#3–Yb(1)–O(2)#4	92.9(4)	O(2)#1–Yb(1)–O(2)#5	180.0(2)
O(1)#6–Cd(2)–O(1)#7	129.8(8)	O(1)#6–Cd(2)–O(1)#8	86.8(7)	O(1)#7–Cd(2)–O(1)#8	78.4(5)
O(1)#6–Cd(2)–O(1)#9	144.8(8)	O(1)#7–Cd(2)–O(1)#9	78.4(5)	O(1)#8–Cd(2)–O(1)#10	129.9(8)
O(3)–Cd(2)–O(3)#6	120.000(1)	O(4)–Mn(1)–O(4)#11	90.000(1)	O(4)#12–Mn(1)–O(4)#13	179.999(1)
O(4)–Mn(1)–O(4)#15	180.0	O(1)#7–Cd(2)–O(3)	72.4(4)	O(1)#9–Cd(2)–O(3)	64.9(4)
O(1)#6–Cd(2)–O(3)	136.6(4)				
Yb–Cd–Zn					
Yb(1)–O(2)	2.224(8)	Cd(2)–O(1)	2.334(7)	Cd(2)–O(3)	2.396(8)
Zn–O(4)	2.183(14)	O(2)–Yb(1)–O(2)#1	92.6(2)	O(2)–Yb(1)–O(2)#2	179.998(2)
O(2)#1–Yb(1)–O(2)#2	87.4(2)	O(2)#1–Yb(1)–O(2)#4	87.4(2)	O(2)#3–Yb(1)–O(2)#4	180.000(1)
O(1)–Cd(2)–O(1)#6	85.8(3)	O(1)–Cd(2)–O(1)#7	79.2(2)	O(1)#6–Cd(2)–O(1)#7	129.4(3)
O(1)–Cd(2)–O(1)#8	144.5(3)	O(1)–Cd(2)–O(3)#9	137.11(16)	O(1)#7–Cd(2)–O(3)#9	72.23(16)
O(1)#8–Cd(2)–O(3)#9	64.70(17)	O(1)#10–Cd(2)–O(3)#9	72.23(16)	O(3)#9–Cd(2)–O(3)	120.0
O(4)#11–Zn–O(4)	90.0	O(4)–Zn–O(4)#12	180.0		

^aSymmetry transformations used to generate equivalent atoms. For **Yb–Cd**: #1 $x, -y + 3/4, -z + 3/4$; #2 $-x, y + 3/4, z - 3/4$; #3 $-x, -y, -z + 3/2$; #4 $-x + 3/4, y, -z + 3/4$; #5 $x + 3/4, -y, z - 3/4$; #6 $x, y + 1, z - 1$; #7 $-x, -y + 1, -z + 1$; #8 $x + 1, y, z - 1$; #9 $-x, -y, -z + 2$; #10 $-x + 1, -y, -z + 1$; #11 $-x + 5/4, -y + 5/4, z$; #12 $-x + 3/4, -y + 5/4, z + 1/2$; #13 $x, y - 1/2, z + 1/2$; #14 $-x + 5/4, -y + 3/4, z + 1/2$; #15 $x - 1/2, y, z + 1/2$. For **Yb–Cd–Mn**: #1 $-x + 2, -y + 3/2, -z + 3/2$; #2 $-x + 3/2, -y + 3/2, -z + 2$; #3 $-x + 2, -y + 1, -z + 2$; #4 $x - 1/2, y + 1/2, z$; #5 $x, y + 1/2, z - 1/2$; #6 $-x + 7/4, -y + 7/4, z$; #7 $x - 1/4, y + 1/4, -z + 2$; #8 $-x + 2, -y + 3/2, -z + 2$; #9 $-x + 2, y + 1/4, z - 1/4$; #10 $x, -y + 7/4, -z + 7/4$; #11 $-x + 1/4, -y + 3/4, z + 1/2$; #12 $-x + 3/4, -y + 3/4, z$; #13 $x + 1/2, y - 1/2, z$; #14 $x, y - 1/2, z + 1/2$; #15 $-x + 1/4, -y + 5/4, z$. For **Yb–Cd–Zn**: #1 $-x + 2, -y + 3/2, -z + 3/2$; #2 $-x + 2, -y + 1, -z + 2$; #3 $x - 1/2, y + 1/2, z$; #4 $-x + 3/2, -y + 3/2, -z + 2$; #5 $x, y + 1/2, z - 1/2$; #6 $x - 1/4, y + 1/4, -z + 2$; #7 $-x + 7/4, -y + 7/4, z$; #8 $-x + 2, -y + 3/2, -z + 2$; #9 $x, -y + 7/4, -z + 7/4$; #10 $-x + 2, z - 1/4, y + 1/4$; #11 $-x + 1/4, -y + 3/4, z + 1/2$; #12 $-x + 1/4, -y + 5/4, z$; #13 $x + 1/2, y - 1/2, z$; #14 $x, y - 1/2, z + 1/2$; #15 $-x + 3/4, -y + 3/4, z$.

employed. Direct methods were applied to solve the structures. Full-matrix least-squares methods using the SHELXL-97 and SHELXS-97 programs were used to refine the crystal structures.^{36,37} For all coordination complexes anisotropic thermal parameters were applied to all non-hydrogen atoms. Anomalous dispersion corrections were incorporated, and analytical expressions of neutral-atom scattering factors were also used. The crystallographic data, selected bond lengths, and bond angles of the complexes studied are listed in Tables 1 and 2.

RESULTS AND DISCUSSION

A mixture of Yb₂O₃, Cd(NO₃)₂·4H₂O, and H₂L in H₂O was sealed in a 20 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 3 days and then cooled to room temperature at a rate of 10 °C per hour to form colorless block crystals **Yb–Cd**. When **Yb–Cd** (0.5 mmol) was employed as a precursor and emerged in the aqueous solution of M(ClO₄)₂·6H₂O (M = Mn, Zn) (5 mmol) for about 6 h, the crystals can retain their crystalline appearances and a reversible single-crystal-to-single-crystal transformation process driven by [Cd(H₂O)₆]²⁺ cations has been exhibited to generate the heterotrimetallic coordination polymer {[Yb₂(L)₆Cd₂][Mn(H₂O)₆]₂·6H₂O}_n (**Yb–Cd–Mn**) or {[Yb₂(L)₆Cd₂][Zn(H₂O)₆]₂·6H₂O}_n (**Yb–Cd–Zn**), as illustrated in eq 1.



Combined with three FT-IR spectra of **Yb–Zn**, **Yb–Cd–Mn**, and **Yb–Cd–Zn** at 3497 or 3451 cm⁻¹ a broad band due to the O–H bond stretching in water is observed, due to the water molecules present in the 1D channel of 3D anionic frameworks. At about 1610 cm⁻¹, the O–H bending of water is also visible. The bands at about 3020 and 2918 cm⁻¹ are due to C–H stretching. The band at 1610 cm⁻¹ is related to the C=O stretching in a –COOH group, accompanied by the bands at 1440 (O–H bending) and 1311 cm⁻¹ (C–O stretching), further evidence of the presence of protonated –COOH groups, whereas the bands at about 944 cm⁻¹ may be ascribed to the plane bending vibration hydroxyl group.

Structural Descriptions. Single-crystal X-ray diffraction analysis shows that the 3D coordination network of colorless cubic **Yb–Cd** crystallizes in the cubic crystal system, space group *Fd-3c*. In **Yb–Cd**, the fundamental unit contains two crystallographically independent Cd^{II} ions. The octahedron coordination geometry around the CdI center consists of six O atoms from the carboxyl group of six L ligands. Each ligand chelates to one Yb atom and bonds to two Cd atoms in an anti-anti configuration, and each CdO₆ moiety connects six neighboring Yb^{III} ions through six L ligands (Figure 1a), leading to a unique three-dimensional (3D) MOF. The other Cd²⁺ ion exists in the form of a [Cd(H₂O)₆]²⁺ moiety and acts as the thermodynamically stable species, required to balance the two negative charges of [Yb₂(L)₆Cd₂]²⁻ in **Yb–Cd** (Figure 1b). It is interesting that the hydrogen bonds are linear, and the separations between O1...O2 and O2...O2A are 3.08 and 2.40 Å, respectively. As a result, a

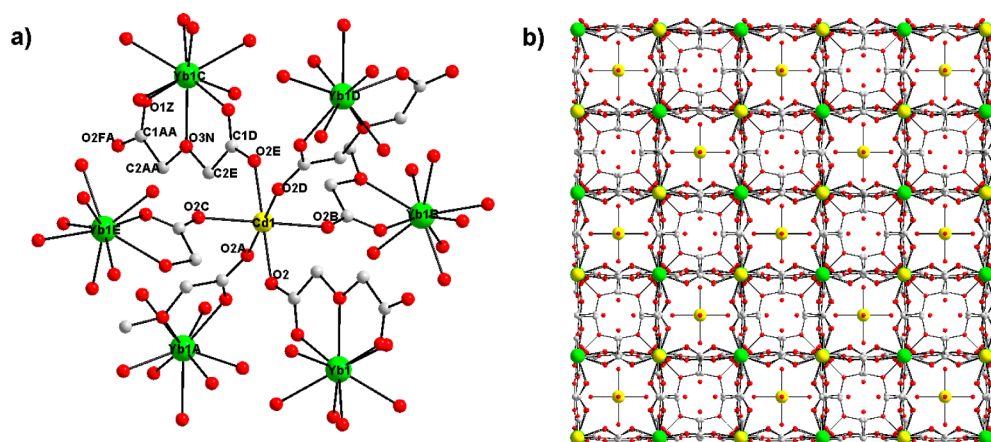
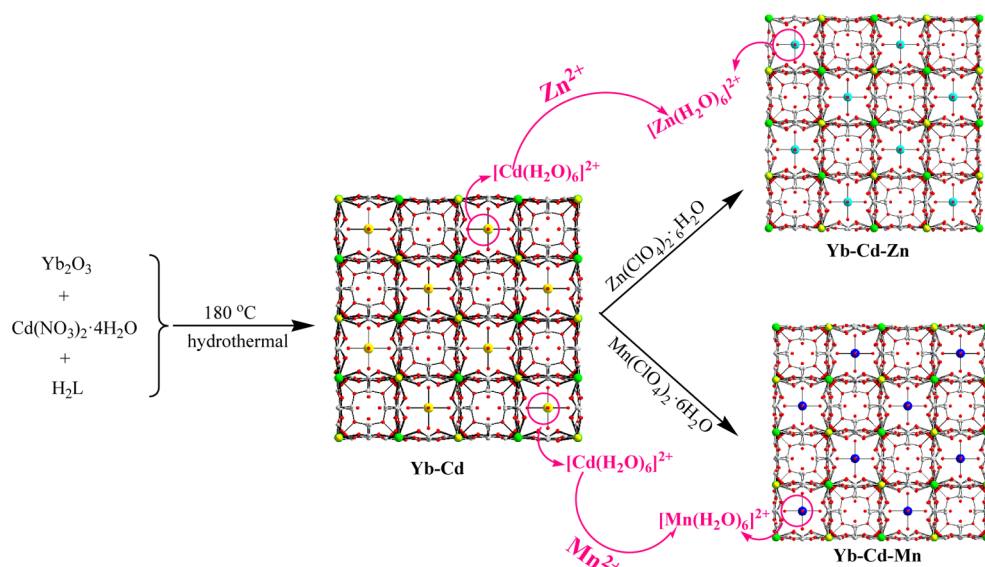


Figure 1. Coordination environments of Yb^{III} and Cd^{II} (a) and perspective view of 3D MOF (b) in Yb–Cd. Green, Yb; yellow, Cd; red, O; gray, C.

Scheme 1. Synthesis of Yb–Cd, Yb–Cd–Mn, and Yb–Cd–Zn



cubic supramolecular SBU with Cd₂–O···O···O···Cd₂ as sides is formed, and an interesting 2-fold interpenetrating 3D hydrogen-bonding supramolecular network has been constructed (Figure S1, Supporting Information). Such hydrogen-bonding roles are key and important for stabilizing the 3D supramolecular framework.

Ion-Exchange Properties in a SC–SC Fashion. SC–SC structural transformations, which involve cooperative movements of atoms in the solid state, have received considerable attention in recent years.³⁸ The SC–SC transformation is extremely useful and desirable, although it occurs relatively rarely, because it allows unequivocal assignment of the product obtained.³⁹ Usually, through the SC–SC transformation, new complexes, which cannot be obtained under conventional conditions, can be gained in a high yield.⁴⁰ Materials that show reversible structure transformation and a characteristic response toward specific external stimuli such as light,⁴¹ temperature,⁴² and guest molecules⁴³ are vitally important for applications in sensing, molecular capture, switches, and so on.⁴⁴

Provided that the solubility of the starting complex is sufficiently high, all components of the coordination polymer, namely, the anion, cation, and ligand, can be exchanged on contact with a solution phase of a competing component. The

solubility of coordination polymers is a key factor in the analysis of their reactivity, and this solubility depends strongly on the physical properties of the solvent and on its ability to bind metal cations constituting the backbone of the coordination polymer. The degree of reversibility of these cation-induced exchange transformations is determined by the radius of metal ions for the starting and resultant complexes, which in turn depend upon the choice of transition-metal cations. The extent of cation exchange is controlled effectively by the ratio of the concentrations of incoming ions to outgoing ions in the liquid phase. These observations can be rationalized in terms of a dynamic equilibrium of ion-exchange reactions coupled with crystalline products.

On the basis of these observations, a general view has formed that ion-exchange processes in coordination polymers take place through a solid-state diffusion mechanism.^{45–52} Such a solid-state mechanism implies that ion exchange proceeds through the diffusion of free ions within channels of coordination polymer crystals or microcrystals.^{53,54}

It is reasonable for us to conceive that [Cd(H₂O)₆]²⁺ serves as a template in the assembly of the 3D network. The ability of [Co(H₂O)₆]²⁺ to serve as a counterion in complexes has been reported;⁵⁵ however, cases of [Cd(H₂O)₆]²⁺ acting as a template

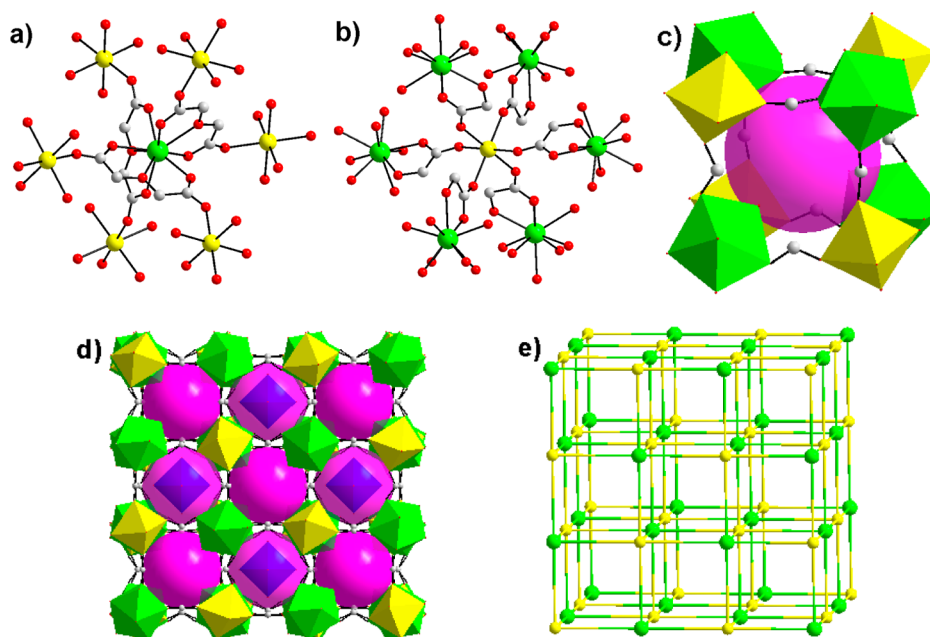


Figure 2. Coordination environments of Yb^{III} ion (a) and Cd^{II} ion (b) in Yb–Cd–Mn. Cubic cage building block (c); 3D framework (d) showing the packing of the cages and Yb/Cd/Mn metal centers represented by polyhedron; a uninodal primitive cubic (*pcu*) net with a point (Schläfli) symbol {4¹².6³} (e). Green, Yb; yellow, Cd; red, O; gray, C; blue, Mn.

in the cavity of the network remain rare. Inspired by the aforementioned progress in the study of anion- or solvent-exchange properties and organic-group-functionalized aromatic guest-loaded host–guest complex in a SC–SC fashion,⁵⁶ within this area, we examined the exchangeable nature of the extra-framework [Cd(H₂O)₆]²⁺ cations as a way to modulate the porous structure of this material. After gently stirring colorless block crystals of Yb–Cd (0.5 mmol) in the aqueous solution containing 5 mmol of Mn(ClO₄)₂·6H₂O or Zn(ClO₄)₂·6H₂O for about 6 h, the crystals can retain their crystalline appearances. A remarkable SC–SC transformation was observed, and another isomorphous 3D framework with encapsulating [Mn(H₂O)₆]²⁺ or [Zn(H₂O)₆]²⁺ moieties was obtained, as evidenced by the inorganic ion quantitative analysis result (see Supporting Information) and single-crystal structure of {[Yb₂(L)₆Cd₂][Mn(H₂O)₆·6H₂O]_n (Yb–Cd–Mn) or {[Yb₂(L)₆Cd₂][Zn(H₂O)₆·6H₂O]_n (Yb–Cd–Zn), as illustrated in Scheme 1. To the best of our knowledge, Yb–Cd–Mn and Yb–Cd–Zn represent the first two examples of ion-induced 4d–4f–3d heterotrimetallic frameworks encapsulating [Mn(H₂O)₆]²⁺ or [Zn(H₂O)₆]²⁺ as template moieties in the 1D channels of a primitive cubic network. The impetus for the recognition studies was to determine whether a reversible SC–SC transformation between [Mn(H₂O)₆]²⁺ in Yb–Cd–Mn or [Zn(H₂O)₆]²⁺ in Yb–Cd–Zn and [Cd(H₂O)₆]²⁺ in Yb–Cd could be realized. Experimental results demonstrate that typical ion-exchange reactions using [Mn(H₂O)₆]²⁺ ions in Yb–Cd–Mn or [Zn(H₂O)₆]²⁺ in Yb–Cd–Zn to replace [Cd(H₂O)₆]²⁺ ions of Yb–Cd in aqueous solution under mild conditions is possible. In addition, we examined the plausible modulation of its porous network by means of ion-exchange processes of the extra-framework cations. The results show that the ion-exchange processes on these systems lead to profound changes in the luminescent properties. The radius of Cd²⁺, Mn²⁺, and Zn²⁺ is 95, 67, and 74 pm, respectively. Among these ions, Mn²⁺ and Zn²⁺ ions with comparatively smaller size can move freely in the 1D cavity of the 3D anionic framework. Also, it seems reasonable

that it would be difficult to break up the framework and exchange other ions whose radius is larger than that of Cd²⁺ such as Ca²⁺ and Ba²⁺ (100 pm) for Cd²⁺. The ion-exchange process also failed between the smaller size of Co²⁺ or Fe²⁺ and Cd²⁺, possibly due to the absence of hydrogen bonding between [M(H₂O)₆]²⁺ and H₂O as the inorganic templates in the cavity of 3D anionic frameworks. Thus, the products of Yb–Cd–Mn and Yb–Cd–Zn in the above ion-exchange experiments are reasonable.

Single-crystal X-ray diffraction confirmed that Yb–Cd–Mn and Yb–Cd–Zn are isostructural, and therefore, only Yb–Cd–Mn is described in detail herein. Yb–Cd–Mn crystallizes in the high-symmetry cubic space group *Fd-3c*. The asymmetric unit of Yb–Cd–Mn is comprised of two distinct motifs and 1/8 lattice water molecule. Motif I contains a Yb(III) ion, a Cd(II) ion, and 0.5 L ligand; motif II consists of a Mn(II) ion coordinated with six water molecules (Figure S2a, Supporting Information). The Cd(II) ion is coordinated by six O atoms from six separated L ligands, giving rise to a [CdO₆] octahedral geometry (Figure S2b, Supporting Information). The metal coordination sphere of the Yb(III) ion has been completed with eight O atoms from three L anions, and the Yb–O bond lengths are ranging from 2.346(18) to 2.44(2) Å (Figure S2c, Supporting Information). Each L anion chelates to one Yb(III) metal center via three O atoms, and the remaining two carboxylate O atoms link two Cd(II) ions (Figure S2d, Supporting Information). Hence, each Yb(III) ion connects six neighboring Cd(II) ions through three L ligands (Figure 2a), while each Cd(II) ion connects six Yb(III) ions through six L ligands (Figure 2b). The alternative linkage between Cd(II) and Yb(III) ions results in the formation of a fantastic cage-like (Figure 2c) three-dimensional (3-D) framework with a Yb...Cd distance of 6.45(3) Å (Figure 2d). From a topological viewpoint, every Cd(II) and Yb(III) ion can be simplified to a six-connected node and the ligands act as the linkers. Therefore, the overall framework of 1 can be viewed as a uninodal primitive cubic (*pcu*) net (Figure 2e) with a point (Schläfli) symbol {4¹².6³} and a vertex symbol [4.4.4.4.4.4.4.4.4.4.4.4.*.*] calculated with TOPOS software.⁵⁷

As shown in Figure 2c, the cage possesses a geometry of a regular cube with four $[\text{CdO}_6]$ and four $[\text{YbO}_8]$ units in turn locating at eight vertices and the $\text{O}(1)-\text{C}(1)-\text{O}(1)$ bridges which is part of the L ligand playing as the edges. Adjacent cages are connected by sharing faces. What should be noted is that the guest moieties in the neighboring cages are somewhat different. Every two neighboring cages contain a free $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ octahedron in **Yb–Cd–Mn** instead of $[\text{Cd}(\text{H}_2\text{O})_6]^{2+}$ ones in **Yb–Cd** to compensate for the negative charge of the framework and the other cage without the $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ is only filled by solvated water molecules. The disposition and arrangement of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ and water molecules found in the cages may be markedly affected as the result of the confined channel space and the charge of the framework. Furthermore, these guests are incorporated into the framework with hydrogen bonds; the $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ and water molecules link to each other through H bonds $\text{O}(4)\cdots\text{O}(5)\cdots\text{O}(5)\cdots\text{O}(4)$ to define a 2-fold interpenetrating 3-D supramolecular framework (Figure S3, Supporting Information). The removal of all guests would create an accessible free volume of 5252.3 \AA^3 or 30.1% of the volume of the unit cell estimated by PLATON software.⁵⁸

Luminescent Properties. Near-infrared luminescent Ln(III) complexes or coordination polymers (Ln = Nd, Er, Yb, and Ho) are attracting increasing attention for their potential uses in telecommunication, laser systems, medical diagnostics, fluoroimmunoassays, etc.⁵⁹ However, as the lanthanide $f-f$ transitions are Laporte forbidden, inducing low absorption coefficients, the photophysical properties of lanthanide ions are very dependent on their environment.⁶⁰ Overcoming the inherent weakness, a suitable organic ligand with an antenna effect introduced into a Ln(III) complex can allow the intrinsic low absorption coefficient of the Ln(III) ion to be effectively overcome.⁶¹ Another new strategy used for improving NIR Ln(III) emission is to employ a transition-metal complex (d block) as a sensitizer for Ln(III) emission,⁶² i.e., choosing a suitable organic ligand to bridge the d-block chromophore and Ln(III) luminophore into a d–f heterometallic complex to achieve sensitized NIR luminescence from Ln(III) through the d–f energy transfer. The d-block metal ions introduced into lanthanide complexes may conceivably play two different roles in the luminescence properties of Ln^{3+} ions. They may enhance the luminescence via $d \rightarrow f$ energy transfer,⁶³ or they may quench the luminescence via $f \rightarrow d$ energy transfer.⁶⁴ For example, chromogenic Cd components have been used as sensitizers for lanthanide luminescence following ligand $\rightarrow f$ and $d \rightarrow f$ energy transfers (i.e., via LMCT excited states).⁶⁵ In the studies of d–f heterometallic complexes with NIR emission, most of the work focuses on the 3d–4f, 4d–4f, and 5d–4f heterometallic complexes.⁶⁶ However, the 3d–4d–4f heterotrimetallic complexes remain underdeveloped. In order to probe further the relationship between luminescence property and structure, preparing multiseries of d–f heterometallic complexes with novel structures and NIR luminescence will be an important task for chemists. In this work, the direct interaction and influence of the 3d or 4d orbital of the Cd(II) or Zn(II) ion with the 4f orbital of Yb(III) ion would cause the 4f energy level (especially the lower energy state) to be tuned and finally tune the NIR emission of the Yb(III) ion.

Aromatic organic molecules and inorganic–organic hybrid coordination complexes were investigated for their photoluminescent properties and potential applications as luminescent materials, such as light-emitting diodes (LEDs).⁶⁷ Owing to the ability of adjusting the emission strength and wavelength of

organic materials, construction of inorganic–organic coordination complexes through judicious incorporation of transition-metal centers and conjugated organic spacers can be an efficient strategy for synthesizing new kinds of photoluminescent materials. As we know, a double bond is constituted by σ and π bonds, and the emissions of the organic ligands are usually ascribed to the $\pi^* \rightarrow n$ or $\pi \rightarrow \pi^*$ transitions.⁶⁸ Compared to the amount of efforts on the photophysical or magnetic behavior of 3d–4f heteronuclear complexes from the compartmental multicarboxylic acid ligands,⁶⁹ research on luminescent 4d–4f–3d heterotrinuclear complex has never been researched nearly as extensively; in particular, limited single-crystal X-ray diffraction studies have been reported for those classic complexes. Nonetheless, the self-assembly process of the typical dicarboxylic acid is complicated and strictly related to the detailed reaction conditions, besides the diverse quadridentate and pentadentate coordination codes adopted. Moreover, to the best of our knowledge, there is no report of the self-assembly of three-dimensional 4d–4f–3d complexes from such flexible oxidiacetic acid and study of their luminescent properties to date. Inspired by the previous progress in exploring Ln–Mn (Eu, Tb, Dy) nanoporous polymers as $\text{Zn}^{2+}/\text{Mg}^{2+}$ -selective luminescent probes,^{69a,b} we wonder whether adopting the ligand of oxidiacetic acid instead of 4-hydroxypyridine-2,6-dicarboxylic acid and pyridine-2,6-dicarboxylic acid to obtain multidimensional coordination polymers associated with 4d–4f–3d metals would also serve as a luminescent probe of some other transition-metal ion.

The luminescent properties of **Yb–Cd–Mn** and **Yb–Cd–Zn** were studied in DMF solution. After our careful observation, crystals of **Yb–Cd–Mn** and **Yb–Cd–Zn** are soluble in DMF. In **Yb–Cd–Zn**, the $\text{Cd}\cdots\text{Yb}$ and $\text{Zn}\cdots\text{Yb}$ separation is 6.482 and 5.613 Å, respectively, much longer than that in $[(\text{YbL})_2(\text{H}_2\text{O})\text{Cl}(\text{OAc})_2]_2[\text{ZnCl}_4]_2$ (**4**).⁷⁰ Thus, the 4d and 3d orbitals of the Cd(II) and Zn(II) ion and 4f orbital of the Yb(III) ion may more effectively interact and influence each other, which probably causes the inner levels of the system of **Yb–Cd–Zn** to be tuned.

The free ligand H_2L exhibits an absorption band at 333 nm ($\lambda_{\text{ex}} = 270 \text{ nm}$), as illustrated in Figure S4, Supporting Information. The absorptions of the complexes are significantly stronger than the free ligand, which is advantageous for the ligand center to absorb energy for sensitizing the lanthanide luminescence. Upon irradiation at $\lambda_{\text{ex}} = 360 \text{ nm}$, for **Yb–Cd–Zn**, there is only one narrow sharp emission band ranging from 975 to 1025 nm (Figure 3, $\lambda_{\text{max}} = 998 \text{ nm}$), which is assigned to the ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ transition of the Yb(III) ion. Compared with the theoretical emission band ($\lambda = 970 \text{ nm}$)⁷¹ and that of reported Yb(III) complexes,⁷² the emission band of **Yb–Cd–Zn** has a red shift, which may be mainly attributed to formation of the coordination polymer except for the consequence of ligand field effects.

Interestingly, the emission intensity of **Yb–Cd–Mn** decreased gradually upon addition of 1–3 equiv (1×10^{-3} , 2×10^{-3} , $3 \times 10^{-3} \text{ M}$) of Ca^{2+} , Mg^{2+} , Ni^{2+} , or Zn^{2+} ions (from CaCl_2 , MgCl_2 , NiCl_2 , or ZnCl_2) with respect to **Yb–Cd–Mn** (Figure 4). In particular, upon the addition of Cd^{2+} and Co^{2+} (from CdCl_2 and CoCl_2), the rapid emission intensity sharply decreased. As illustrated in Figure 4, the highest band at 995 nm is ca. one-third as intense as the corresponding peak in DMF solution without 1 equiv of Cd^{2+} or Co^{2+} ion into the system. Continued adding 2–3 equiv of Cd^{2+} or Co^{2+} , the results show that the intensity of the luminescent peaks is almost zero.

Most importantly, the emission intensity of **Yb–Cd–Zn** increases significantly upon adding 1–3 equiv of Ni^{2+} (1×10^{-3} ,

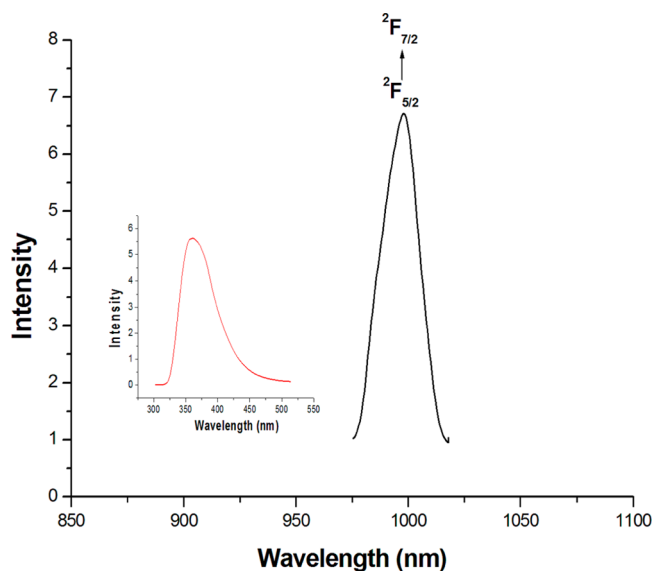


Figure 3. NIR emission (black) and excitation (inserted red) spectra of **Yb–Cd–Zn** in DMF solution (10^{-3} M) at room temperature.

2×10^{-3} , and 3×10^{-3} M) from NiCl_2 with respect to **Yb–Cd–Zn**. The highest peak at 998 nm is at least twice as intense as the corresponding band in solution without Ni^{2+} . To make a further understanding of this phenomenon, the same experiments were performed for the introduction of Ca^{2+} , Co^{2+} , and Mg^{2+} ions into the system. The addition of the Ni^{2+} ion may change the level of the excited state of the $[\text{Cd}(\text{L})_3]^{2+}$ moiety, resulting in a more efficient energy transition to Yb^{3+} ion. The emission intensity decreased gradually in the presence of 1–3 equiv of Ca^{2+} , Co^{2+} , or Mg^{2+} ions (Figure 5), while upon addition of Cd^{2+} (from CdCl_2), the rapid emission intensity sharply decreased. As illustrated in Figure 4, the highest band at 998 nm is ca. one-third as intense as the corresponding peak in DMF solution without 1 equiv of Cd^{2+} ion into the system, in particular for Zn^{2+} , which promptly quenches the luminescence of **Yb–Cd–Zn**. To the best of our knowledge, this is the first report of 3D

heterotrimetallic polymers containing lanthanide ions based on multicarboxylic acid as a luminescent probe of Ni^{2+} .

Thermal Stabilities and Powder X-ray Diffraction Studies. The thermogravimetric analysis (TGA) curves (Figure S4, Supporting Information) show that the guest and coordinated water molecules are removed in the temperature range 25–200 °C for **Yb–Cd**, **Yb–Cd–Mn**, and **Yb–Cd–Zn**, indicating strong hydrogen-bonding interactions exist in these 3D anionic framework. At 370 °C, the coordination networks of **Yb–Cd**, **Yb–Cd–Mn**, and **Yb–Cd–Zn** begin to decompose. Above 400 °C, all of these three frameworks collapse because the organic ligands have been removed. To the best of our knowledge, complexes that could be stable up to 400 °C are quite rare. We further investigated whether the framework would break down upon removal of uncoordinated H_2O . Water molecules can be removed by heating **Yb–Cd**, **Yb–Cd–Mn**, and **Yb–Cd–Zn** at 140 °C for 12 h. PXRD spectra of hydrated and dehydrated **Yb–Cd**, **Yb–Cd–Mn**, and **Yb–Cd–Zn** are almost identical (Figures S5–S8, Supporting Information), which suggests that the crystal lattice remains intact after the uncoordinated water molecules are removed. The powder X-ray diffraction (PXRD) spectra further confirm the high thermal stability of the 3D network of **Yb–Cd**, **Yb–Cd–Mn**, and **Yb–Cd–Zn**.

CONCLUSION

In summary, a novel 4d–4f heterometallic complex $\{[\text{Yb}_2(\text{L})_6\text{Cd}_2][\text{Cd}(\text{H}_2\text{O})_6] \cdot 6\text{H}_2\text{O}\}_n$ (**Yb–Cd**) (H_2L = oxidiacetic acid) was synthesized under hydrothermal conditions. The $[\text{Cd}(\text{H}_2\text{O})_6]^{2+}$ moieties located in the porosity of the anionic framework serve as the thermodynamically stable species, required to balance the two negative charges of $[\text{Yb}_2(\text{L})_6\text{Cd}_2]^{2-}$. Interestingly, when **Yb–Cd** was employed as a precursor and emerged in the aqueous solution of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, a reversible single-crystal to single-crystal (SC–SC) transformation process driven by $[\text{Cd}(\text{H}_2\text{O})_6]^{2+}$ cations has been exhibited to generate two 4d–4f–3d heterotrimetallic coordination polymers $\{[\text{Yb}_2(\text{L})_6\text{Cd}_2][\text{Mn}(\text{H}_2\text{O})_6] \cdot 6\text{H}_2\text{O}\}_n$ (**Yb–Cd–Mn**) and $\{[\text{Yb}_2(\text{L})_6\text{Cd}_2][\text{Zn}$

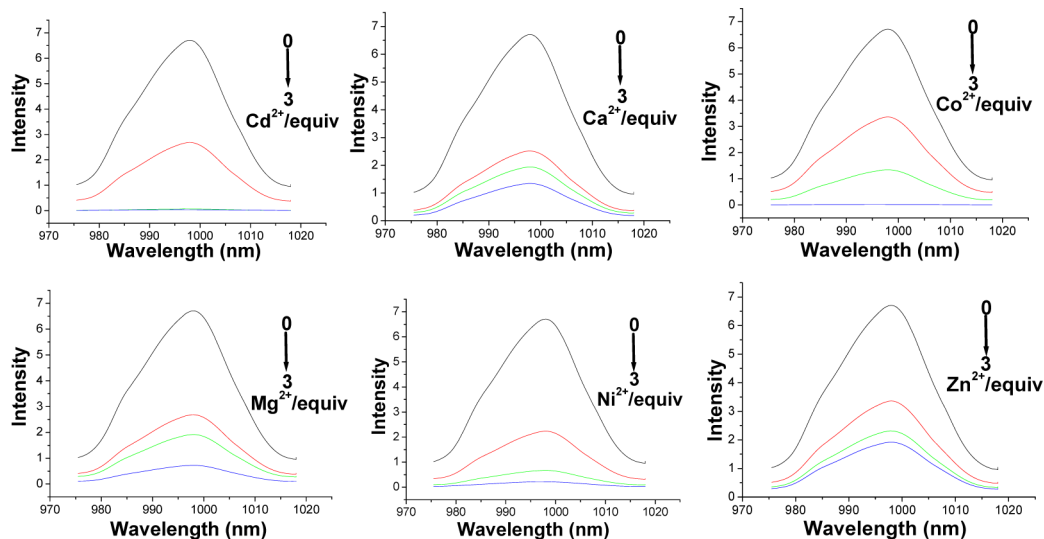


Figure 4. Emission spectra of complex **Yb–Cd–Mn** in DMF (10^{-3} M) at room temperature (excited at 400 nm) in the presence of 0–3 equiv of Cd^{2+} (top left), Ca^{2+} (top middle), Co^{2+} (top right), Mg^{2+} (bottom left), Ni^{2+} (bottom middle), and Zn^{2+} (bottom right). Black, no addition; red, 1 equiv; green, 2 equiv; blue, 3 equiv.

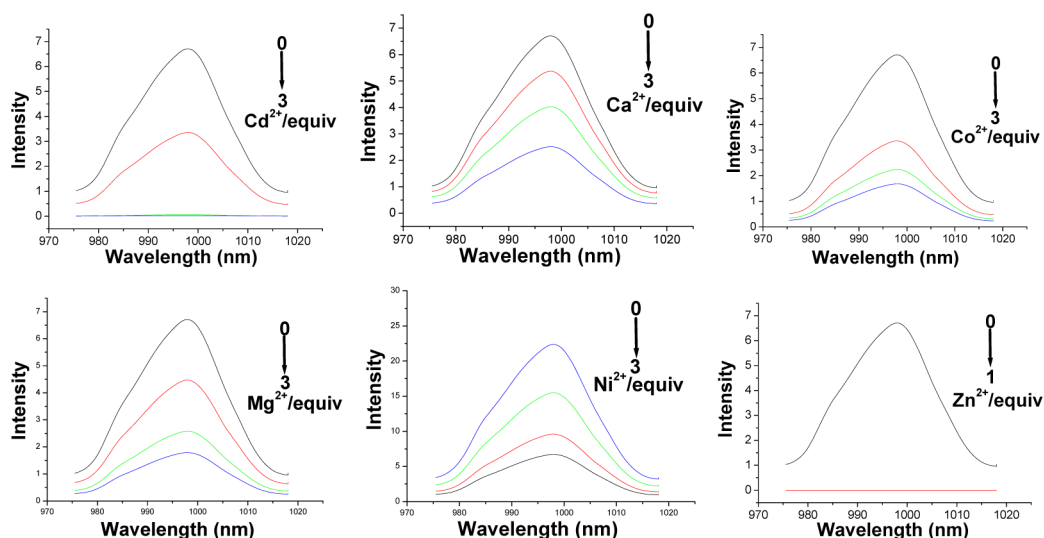


Figure 5. Emission spectra of complex Yb-Cd-Zn in DMF (10^{-3} M) at room temperature (excited at 400 nm) in the presence of 0–3 equiv of Cd^{2+} (top left), Ca^{2+} (top middle), Co^{2+} (top right), Mg^{2+} (bottom left), Ni^{2+} (bottom middle), and Zn^{2+} (bottom right). Black, no addition; red, 1 equiv; green, 2 equiv; blue, 3 equiv.

$(\text{H}_2\text{O})_6 \cdot 6\text{H}_2\text{O}]_n (\text{Yb-Cd-Zn})$. Luminescent studies reveal that Yb-Cd-Zn may serve as a good candidate of Ni^{2+} luminescent probe. To the best of our knowledge, Yb-Cd-Zn represents the first example of a heterotrimetallic coordination polymer based on dicarboxylic acid as a luminescent probe of Ni^{2+} .

■ ASSOCIATED CONTENT

Supporting Information

Listings of X-ray crystallographic files (CIF) for Yb-Cd , Yb-Cd-Mn , and Yb-Cd-Zn , structure drawings, inorganic quantitative analysis reports, powder X-ray diffraction (PXRD) patterns of Yb-Cd , Yb-Cd-Mn , and Yb-Cd-Zn , TGA plots. This material is available free of charge via the Internet at <http://pubs.acs.org>. Crystallographic data have been assigned to the following deposition CCDC numbers: CCDC-1013812 (Yb-Cd), CCDC-1013793 (Yb-Cd-Mn), and CCDC-1013792 (Yb-Cd-Zn). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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