Syntheses, structures and luminescent properties of a series of 3D lanthanide coordination polymers with tripodal semirigid ligand

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ABSTRACT

Reactions of the tripodal bridging ligand 5-(4-carboxy–phenoxy)-isophthalic acid (abbreviated as H_3cpia) with lanthanide salts lead to the formation of a family of different coordination polymers, that is, $[Ln(cpia)(H_2O)_2]_n \cdot nH_2O$ ($Ln = $Ce ($\mathbf{1}$), Pr ($\mathbf{2}$), Nd ($\mathbf{3}$), Sm ($\mathbf{4}$), Eu ($\mathbf{5}$), Gd ($\mathbf{6}$), Dy ($\mathbf{7}$), Er ($\mathbf{8}$), Tm ($\mathbf{9}$) and Y ($\mathbf{10}$)) in the presence of formic acid or diethylamine, which are characterized by elemental analysis, IR spectrum, thermogravimetric analysis (TGA), XRPD spectrum and single-crystal X-ray diffraction. Compounds $\mathbf{1}$–$\mathbf{10}$ are isostructural and exhibit three-dimensional microporous frameworks. Furthermore, the photoluminescent properties of $\mathbf{4}$, $\mathbf{5}$ and $\mathbf{7}$ have been studied in detail.

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1. Introduction

In recent years, a new class of ordered, three-dimensional extended solids composed of metal ions and organic linkers, known as metal-organic frameworks (MOFs), has emerged as a promising materials with potential applications as sensors, gas adsorption, magnetic materials, porous materials, nonlinear optics and heterogeneous catalysis [1–18]. The multicarboxylic ligands have been widely used as bridging ligands to construct MOFs with diverse structures and topologies, owing to their various coordination modes, strong coordination ability, chemical stability and structure rigidity [19–25]. However, most of the work has so far focused on the assembly of the d-block metal-organic open frameworks [19–29], while the analogous chemistry of the lanthanides remains less developed [30–36]. This is due to the tendency of the lanthanide ions for high and variable coordination numbers, which favors to construct condensed structures with or without guest species. To date, systematic investigation on lanthanide-based materials with luminescent properties has been rarely documented [37]. Thus, exploring the chemistry of lanthanide-based coordination polymers remains an interesting and challenging topic in syntheses chemistry and material science alike.

Accordingly, our aim was to synthesize novel lanthanide-organic open frameworks by using the semirigid ligand H_3cpia: (i) two rigid benzene rings of H_3cpia are connected by a rotatable –O– group, which allows the ligand with subtle conformational adaptation; (ii) the

additional strong coordinating ability of carboxylate arms is expected to exhibit more varied coordinating patterns in the construction of coordination frameworks. Herein, we report the syntheses, structures, and luminescent properties of ten new lanthanide-organic coordination polymers, $[Ln(cpia)(H_2O)_2]_n \cdot nH_2O$ ($Ln = $Ce ($\mathbf{1}$), Pr ($\mathbf{2}$), Nd ($\mathbf{3}$), Sm ($\mathbf{4}$), Eu ($\mathbf{5}$), Gd ($\mathbf{6}$), Dy ($\mathbf{7}$), Er ($\mathbf{8}$), Tm ($\mathbf{9}$) and Y ($\mathbf{10}$)). The structures of compounds $\mathbf{1}$–$\mathbf{10}$ are isomorphic and display three-dimensional microporous frameworks. All the compounds were characterized by elemental analysis, X-ray crystallography and thermogravimetric analysis. The photoluminescence of $\mathbf{4}$, $\mathbf{5}$ and $\mathbf{7}$ were investigated in the solid state at room temperature.

2. Experimental

2.1. Materials and measurements

The starting materials 5-(4-carboxyphenoxy)isophthalic acid (H_3cpia) was synthesized according to the procedure described in the literature [38] and characterized by IR spectrum. The $EuCl_3 \cdot xH_2O$ was prepared by the reaction of Eu_2O_3 and HCl, and $Dy(NO_3)_3 \cdot xH_2O$ was prepared by the reaction of Dy_2O_3 and HNO_3, respectively. All other chemicals were obtained from commercial sources and were used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded in the range 4000–400 cm^{-1} on an Alpha Centaurt FT/IR spectrophotometer using KBr pellets. Thermogravimetric analyses of the samples were

performed using a Perkin-Elmer TG-7 analyzer heated from room temperature to 900 °C under nitrogen atmosphere at the heating rate of 5 °C min^{-1}. Solid-state fluorescence spectra for compounds **4**, **5** and **7** were recorded on a Cary Eclipse spectrofluorometer (Varian) equipped with a xenon lamp and quartz carrier at room temperature. X-ray powder diffraction measurements were performed on a Siemens D5005 diffractometer with Cu$K\alpha$ ($\lambda = 1.5418$ Å) radiation in the range 5–50° at 293 K. The XRPD patterns for **1–10** are presented in Fig. S3. The diffraction peaks of both simulated and experimental patterns match well, indicating that the phase purities of compounds **1–10**.

2.2. Syntheses

The preparations of compounds **1–10** are divided into three groups, differing mainly in the reaction materials.

2.2.1. Syntheses of compounds 1–4

The four compounds were prepared using an analogous method. In general, a mixture of H$_3$cpia (0.5 mmol) and Ln(NO$_3$)$_3$·6H$_2$O (0.5 mmol) was dissolved in distilled water (10 mL) with stirring for 30 min after addition of three drops formic acid, and then transferred and sealed in a 23 mL Teflon lined stainless steel container, which was heated at 120 °C for 72 h. After the autoclave was cooled to room temperature at 10 °C min^{-1}, light yellow block crystals suitable for X-ray crystallography were obtained.

[Ce(cpia)(H$_2$O)$_2$]$_n$·nH$_2$O (**1**). Light yellow block crystals washed with distilled water, and air-dried to give **1** in 90% yields (based on Ce). Elemental analysis: Anal. Calc. for C$_{15}$H$_{13}$O$_{10}$Ce (493.25): C 36.52; H 2.66. Found: C 36.48; H 2.62%. IR (KBr, cm^{-1}, Fig. S4a): 3375 (m), 3250 (m), 1624 (m), 1595 (s), 1535 (s), 1460 (m), 1393 (s), 1248 (m), 1211 (m), 917 (w), 862 (w), 779 (s), 715 (s).

[Pr(cpia)(H$_2$O)$_2$]$_n$·nH$_2$O (**2**). Light yellow block crystals washed with distilled water, and air-dried to give **2** in 83% yields (based on Pr). Elemental analysis: Anal. Calc. for C$_{15}$H$_{13}$O$_{10}$Pr (494.05): C 36.47; H 2.65. Found: C 36.50; H 2.68%. IR (KBr, cm^{-1}, Fig. S4b): 3420 (s), 1621 (s), 1597 (m), 1538 (m), 1462 (m), 1394 (s), 1249 (m), 1212 (m), 916 (w), 863 (w), 779 (m), 715 (m).

[Nd(cpia)(H$_2$O)$_2$]$_n$·nH$_2$O (**3**). Light yellow block crystals washed with distilled water, and air-dried to give **3** in 85% yields (based on Nd). Elemental analysis: Anal. Calc. for C$_{15}$H$_{13}$O$_{10}$Nd (497.35): C 36.22; H 2.63. Found: C 36.17; H 2.67%. IR (KBr, cm^{-1}, Fig. S4c): 3387 (m), 1621 (m), 1596 (m), 1538 (s), 1461 (m), 1395 (s), 1249 (m), 1211 (m), 918 (w), 863 (w), 779 (m) and 715 (m).

[Sm(cpia)(H$_2$O)$_2$]$_n$·nH$_2$O (**4**). Light yellow block crystals washed with distilled water, and air-dried to give **4** in 87% yields (based on Sm). Elemental analysis: Anal. Calc. for C$_{15}$H$_{13}$O$_{10}$Sm (503.45): C 35.79; H 2.60. Found: C 35.74; H 2.63%. IR (KBr, cm^{-1}, Fig. S4d): 3414 (m), 1623 (m), 1597 (s), 1541 (s), 1460 (m), 1396 (s), 1250 (m), 1212 (m), 919 (w), 864 (w), 779 (m) and 715 (m).

2.2.2. Syntheses of compounds 5 and 9

A mixture of EuCl$_3$·xH$_2$O or TmCl$_3$·6H$_2$O (0.5 mmol) and H$_3$cpia (0.5 mmol) was dissolved in distilled water (10 mL) with stirring for 30 min after addition of three drops of diethylamine, and then transferred and sealed in a 23 mL Teflon lined stainless steel container, which was heated at 120 °C for 72 h. After the autoclave was cooled to room temperature at 10 °C min^{-1}, colorless block crystals suitable for X-ray crystallography were obtained.

[Eu(cpia)(H$_2$O)$_2$]$_n$·nH$_2$O (**5**). Colorless block crystals washed with distilled water, and air-dried to give **5** in 81% yields (based on Eu). Elemental analysis: Anal. Calc. for C$_{15}$H$_{13}$O$_{10}$Eu (505.05): C 35.67; H 2.59. Found: C 35.70; H 2.60%. IR (KBr, cm^{-1}, Fig. S4e): 3422 (s), 3075 (m), 1626 (m), 1599 (s), 1546 (m), 1462 (m), 1396 (s), 1251 (m), 1212 (m), 918 (w), 864 (w), 779 (s) and 714 (m).

[Tm(cpia)(H$_2$O)$_2$]$_n$·nH$_2$O (**9**). Colorless block crystals washed with distilled water, and air-dried to give **9** in 75% yields (based on Tm). Elemental analysis: Anal. Calc. for C$_{15}$H$_{13}$O$_{10}$Tm (522.05): C 34.51; H 2.51. Found: C 34.47; H 2.55%. IR (KBr, cm^{-1}, Fig. S4i): 3425 (s), 3079 (w), 1653 (m), 1600 (m), 1560 (s), 1454 (m), 1392 (s), 1255 (m), 1213 (m), 925 (w), 866 (w), 778 (m) and 717 (m).

2.2.3. Syntheses of compounds 6–8 and 10

A mixture of Ln(NO$_3$)$_3$·6H$_2$O (0.5 mmol) and H$_3$cpia (0.5 mmol) was dissolved in distilled water (10 mL) with stirring for 30 min after addition of three drops of diethylamine, and then transferred and sealed in a 23 mL Teflon lined stainless steel container, which was heated at 120 °C for 72 h. After the autoclave was cooled to room temperature at 10 °C min^{-1}, colorless block crystals suitable for X-ray crystallography were obtained.

[Gd(cpia)(H$_2$O)$_2$]$_n$·nH$_2$O (**6**). Colorless block crystals washed with distilled water, and air-dried to give **6** in 88% yields (based on Gd). Elemental analysis: Anal. Calc. for C$_{15}$H$_{13}$O$_{10}$Gd (510.35): C 35.30; H 2.57. Found: C 35.35; H 2.61%. IR (KBr, cm^{-1}, Fig. S4f): 3395 (w), 3076 (w), 1626 (m), 1598 (m), 1546 (m), 1462 (m), 1397 (s), 1251 (m), 1212 (m), 918 (w), 864 (w), 780 (s) and 715 (s).

[Dy(cpia)(H$_2$O)$_2$]$_n$·nH$_2$O (**7**). Colorless block crystals washed with distilled water, and air-dried to give **7** in 76% yields (based on Dy). Elemental analysis: Anal. Calc. for C$_{15}$H$_{13}$O$_{10}$Dy (515.65): C 34.94; H 2.54. Found: C 34.99; H 2.60%. IR (KBr, cm^{-1}, Fig. S4g): 3425 (s), 3077 (w), 1627 (s), 1550 (s), 1463 (m), 1398 (s), 1252 (m), 1213 (m), 920 (w), 865 (w), 780 (m) and 715 (m).

[Er(cpia)(H$_2$O)$_2$]$_n$·nH$_2$O (**8**). Colorless block crystals washed with distilled water, and air-dried to give **8** in 75% yields (based on Er). Elemental analysis: Anal. Calc. for C$_{15}$H$_{13}$O$_{10}$Er (520.35): C 34.62; H 2.52. Found: C 34.66; H 2.55%. IR (KBr, cm^{-1}, Fig. S4h): 3426 (s), 3078 (w), 1628 (m), 1550 (m), 1463 (m), 1397 (s), 1252 (w), 976 (m), 920 (m), 865 (m), 779 (m) and 714 (m).

[Y(cpia)(H$_2$O)$_2$]$_n$·nH$_2$O (**10**). Colorless block crystals washed with distilled water, and air-dried to give **10** in 68% yields (based on Y). Elemental analysis: Anal. Calc. for C$_{15}$H$_{13}$O$_{10}$Y (442.05): C 40.76; H 2.96. Found: C 40.68; H 2.90%. IR (KBr, cm^{-1}, Fig. S4j): 3413 (s), 3079 (m), 1628 (m), 1600 (m), 1556 (m), 1463 (m), 1399 (s), 1253 (m), 1214 (m), 922 (w), 866 (m), 780 (m) and 716 (m).

2.3. X-ray crystallography

Single crystal X-ray diffraction data for compounds **1–10** were recorded on a Bruker APEXII CCD diffractometer with graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å) at 293 K. Absorption corrections were applied using multi-scan technique. All the structures were solved by Direct Method of SHELXS-97 [39] and refined by full-matrix least-squares techniques using the SHELXL-97 program [40] within WINGX [41]. Hydrogen atoms on the H$_3$cpia ligands were placed on calculated positions and included in the refinement riding on their respective parent atoms. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Those hydrogen atoms attached to lattice water molecules were not located. CCDC numbers 78,8771–788,780 contain the supplementary crystallographic data for this paper. The crystal data and structure refinement results of compounds **1–10** are shown in Table 1. The selected bond lengths of compounds **1–10** are listed in Table S1.

3. Results and discussion

3.1. Synthesis

Compounds **1–10** were prepared in good yields by the reactions of Ln^{3+} cations and H$_3$cipa in the presence of formic acid or diethylamine. Without the introduction of formic acid or diethylamine, the lower

Table 1
Crystal data and structure refinement for compounds **1–10**.

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{15}H_{13}O_{10}Ce$	$C_{15}H_{13}O_{10}Pr$	$C_{15}H_{13}O_{10}Nd$	$C_{15}H_{13}O_{10}Sm$	$C_{15}H_{13}O_{10}Eu$
M_w	493.25	494.05	497.35	503.45	505.05
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.4230(8)	9.3980(19)	9.3700(7)	9.3410(10)	9.3410(7)
b (Å)	9.9470(8)	9.911(2)	9.9020(7)	9.8650(12)	9.8490(8)
c (Å)	11.4190(10)	11.422(2)	11.4290(9)	11.4150(12)	11.4220(9)
α (deg)	93.6330(10)	93.965(3)	93.9420(10)	94.0330(10)	94.0760(10)
β (deg)	98.0920(10)	98.131(3)	98.0750(10)	98.3320(10)	98.5770(10)
γ (deg)	110.6490(10)	110.782(2)	110.6920(10)	110.8090(10)	110.9270(10)
V (Å^3)	984.17(14)	976.4(3)	974.11(13)	964.41(19)	961.69(13)
Z	2	2	2	2	2
D_c (mg m^{-3})	1.664	1.680	1.696	1.734	1.744
Abs. coeff. (mm^{-1})	2.358	2.541	2.711	3.091	3.308
Reflns collected	4951	4777	4895	4774	4815
Independent reflns	3416	3345	3376	3327	3328
θ range (deg)	1.81–24.99	1.82–25.00	1.81–25.00	1.82–25.00	1.82–25.00
GOF on F^2	0.997	1.028	1.001	1.007	1.005
R_{int}	0.0134	0.0225	0.0145	0.0153	0.0147
R_1[a]	0.0337	0.0467	0.0326	0.0348	0.0316
wR_2(all data)[b]	0.1107	0.1448	0.1072	0.1150	0.1070

	6	**7**	**8**	**9**	**10**
Empirical formula	$C_{15}H_{13}O_{10}Gd$	$C_{15}H_{13}O_{10}Dy$	$C_{15}H_{13}O_{10}Er$	$C_{15}H_{13}O_{10}Tm$	$C_{15}H_{13}O_{10}Y$
M_w	510.35	515.65	520.35	522.05	442.05
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.3310(9)	9.3410(8)	9.3490(12)	9.3560(6)	9.3530(16)
b (Å)	9.8410(9)	9.8130(9)	9.8000(13)	9.7960(7)	9.7960(16)
c (Å)	11.4230(11)	11.3950(10)	11.3790(15)	11.4150(8)	11.3880(19)
α (deg)	94.2240(10)	94.2470(10)	94.441(2)	94.7990(10)	94.340(2)
β (deg)	98.5100(10)	99.0870(10)	99.3050(10)	99.6140(10)	99.407(2)
γ (deg)	110.9520(10)	111.2590(10)	111.5270(10)	111.7380(10)	111.455(2)
V (Å^3)	959.65(16)	951.37(15)	946.4(2)	945.98(11)	947.6(3)
Z	2	2	2	2	2
D_c (mg m^{-3})	1.766	1.800	1.826	1.833	1.549
Abs. coeff. (mm^{-1})	3.502	3.974	4.481	4.737	3.125
Reflns collected	4811	4772	4765	4781	4700
Independent reflns	3324	3305	3287	3289	3254
θ range (deg)	1.82–25.00	1.83–24.99	1.83–25.00	1.83–25.00	1.83–24.95
GOF on F^2	0.994	0.993	1.002	1.020	1.005
R_{int}	0.0173	0.0171	0.0177	0.0154	0.0260
R_1[a]	0.0366	0.0327	0.0355	0.0297	0.0632
wR_2 (all data)[b]	0.1184	0.1040	0.1156	0.1037	0.2155

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

yields and worse purities would be obtained. Interestingly, compounds **1–6** can be synthesized when formic acid or diethylamine were added in the reaction systems. For **1–4**, the yields are higher when formic acid was added compared with diethylamine under the similar conditions; whereas, for **5** and **6**, the yields are higher when diethylamine was added compared with formic acid under the similar conditions. From the parallel experiments, it is clearly to see that compounds **1–6** can be obtained and are stable in a relatively broad pH range, indicating that compounds **1–6** are not sensitive to the pH values. Compounds **7–10** can be prepared in high yields and purities when diethylamine is introduced. When formic acid was added to the reaction mixture, the expected products cannot be obtained. The parallel experiments indicating that the addition of formic acid or diethylamine is a key factor for enhancing the yields and purities of the title compounds but have no influence on the final structure of compounds **1–10**.

3.2. Structure description

X-ray crystal structure analyses revealed that compounds **1–10** are isostructural only with slight differences in bond lengths and

bond angles and crystallize in the low-symmetry triclinic space group $P\bar{1}$. Therefore, only the structure of **3** is described in detail. The asymmetric unit of **3** contains one crystallographically unique Nd^{3+} cation, one cpia ion, two coordinated water and one lattice water molecules (see Fig. 1a). As shown in Fig. 1b, Nd is nine-coordinated with slightly distorted tri-capped trigonal prism configurations: seven carboxylate oxygen (O_{COO^-}) atoms from five cpia ligands and two terminal water molecules (Nd(1)–O(1)=2.498(4), Nd(1)–O(2)=2.570(4), Nd(1)–O(3)#1=2.354(4), Nd(1)–O(4)#2=2.356(4), Nd(1)–O(5)#3=2.502(4), Nd(1)–O(6)#3 =2.862(4), Nd(1)–O(6)#4=2.434(4), Nd(1)–O(1w)=2.560(4), Nd(1)–O(2w)=2.509(4) Å, #1: $-x$, $-y$, $1-z$; #2: x, $1+y$, $1+z$; #3: $1-x$, $1-y$, $1-z$; #4: x, y, $1+z$). The Nd–O bond lengths are all within the normal ranges as reported in the literatures [42,43]. The average lengths of Ln–O bonds in compounds **1–9** are 2.550, 2.529, 2.516, 2.492, 2.484, 2.477, 2.457, 2.443 and 2.439 Å, respectively, in accordance with the effect of the lanthanide contraction. The average length of Y–O bonds in **10** is 2.448 Å, which is close to average distance of Er–O bonds in compound **8**. Two adjacent Nd(III) atoms, separated by an Nd···Nd distance of 4.425 Å, are
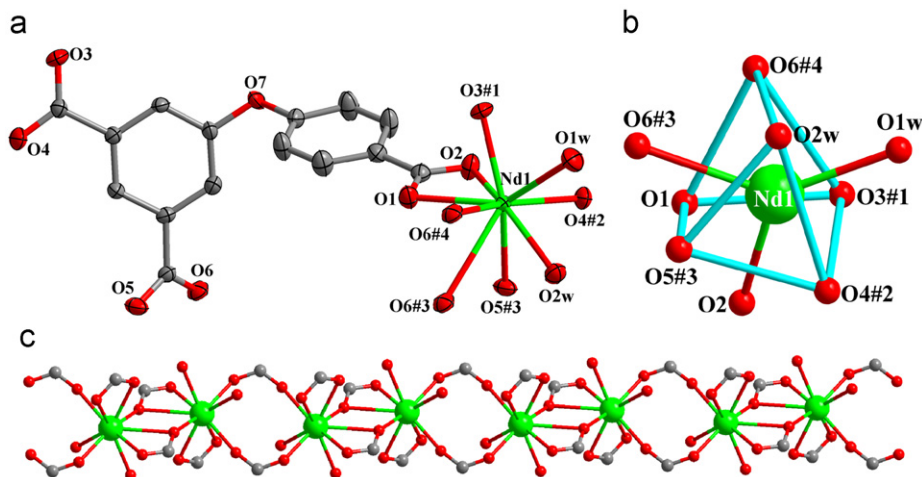
Fig. 1. (a) Perspective view of the coordination geometry of the Nd atom in **1**. (b) The tri-capped trigonal prism coordination configuration of Nd^{3+} ion. (c) Infinite rod-shaped building blocks of neodymium chain. Green, red and gray spheres represent Nd, O and C atoms, respectively. Hydrogen atoms are not shown for clarity. Symmetry codes: #1, $-x, -y, 1-z$; #2, $x, 1+y, 1+z$; #3, $1-x, 1-y, 1-z$; #4, $x, y, 1+z$ (for interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

bridged by two carboxylate groups to give a bimetallic unit $[Nd_2(COO)_2(COO)_2(H_2O)_4]$ which was further linked by another four μ_2-COO groups to give rise to a 1D neodymium chain (Fig. 1c).

The binding mode of the carboxylates ligand observed in **3** is depicted in Fig. S1a and the dihedral angle between the two benzene rings is 71.5° (Fig. S1b). One cpia anion coordinates to five Nd(III) cations. Such connectivity mode gives rise to a three-dimensional network of **3**, in which has a one-dimensional channel structure with dimensions of 9.46×11.42 Å^2 parallel to the *b*-axis (Fig. S2). If cipa ions are considered as four-connected nodes (Fig. 2a) and double-core neodymium units are considered as eight-connected nodes (Fig. 2b), the overall structure of **3** is a 3D (4,8)-connected fluorite topology framework (Fig. 2c). The Schläfli symbol for **3** is $(4^6)_2(4^{12} \cdot 6^{12} \cdot 8^4)$. Up to date, only a few examples of fluorite topology have been observed in MOFs [44–50]. Previous examples of (4,8)-connected frameworks are very rare, and they are reminiscent of the binary inorganic compounds fluorite (CaF_2), one of the most important and preferred structure for AB_2 type compounds.

3.3. Thermogravimetric analyses (TGA)

To examine the thermal stabilities of the as-synthesized compounds, the thermogravimetric analyses were performed with a flowing nitrogen atmosphere for compounds **1**, **4**, **6** and **8** from room temperature to 900 °C at the heating rate of 5 °C min^{-1} (Fig. S5). The TG curves of **1**, **4**, **6** and **8** exhibit two steps of weight loss. The first weight loss of 11.14%, 10.85%, 10.37% and 10.15% (calc. 10.95%, 10.73%, 10.59% and 10.39%) from room temperature to around 180 °C corresponds to the loss of lattice water and coordinated water. Then, only a little further weight loss was observed until approximately 500 °C for **1**, **4**, **6** and **8**. The second weight loss from 500 to approximately 750 °C is attributed to the decomposition of organic ligands. The remaining weight of 33.89%, 34.87%, 35.32% and 37.03% corresponds to the percentage (calc. 33.27%, 34.63%, 35.51% and 36.76%) of Ce_2O_3, Sm_2O_3, Gd_2O_3 and Er_2O_3, respectively.

3.4. Fluorescence properties

Taking into account the excellent luminescent properties of Sm(III), Eu(III) and Dy(III), the luminescence of **4**, **5** and **7** containing samarium, europium and dysprosium ion were investigated, respectively.

Under the excitation of 403 nm, compound **4** has shown a strong visible emission in the orange-red region. The emission spectra of compound **4** are depicted in Fig. S6, which can be assigned to the $^4G_{5/2} \rightarrow {}^6H_J$ ($J = 5/2$, 7/2, 9/2 and 11/2) emission transitions at 559, 597, 645 and 708 nm, respectively. This kind of visible emission phenomenon were observed in the published literatures [51,52].

The emission spectrum of compound **5** (see Fig. 3a) at room temperature upon excitation at 394 nm and exhibits the characteristic transition of Eu(III) ions, which can be attributed to $^5D_0 \rightarrow {}^7F_J$ ($J = 0$, 1, 2, 3, 4) transitions, i.e., 580 nm ($^5D_0 \rightarrow {}^7F_0$), 592 nm ($^5D_0 \rightarrow {}^7F_1$), 616 nm ($^5D_0 \rightarrow {}^7F_2$), 653 nm ($^5D_0 \rightarrow {}^7F_3$) and 698 nm ($^5D_0 \rightarrow {}^7F_4$). The symmetry-forbidden $^5D_0 \rightarrow {}^7F_0$ transition, observed as a weak peak at 580 nm, reveals the presence of the Eu(III) site with low symmetry [37,53,54]. The $^5D_0 \rightarrow {}^7F_2$ transition is clearly stronger than the $^5D_0 \rightarrow {}^7F_1$ transition, the intensity ratio of ca. 3.0 for $I_{(^5D \rightarrow {}^7F)}/I_{(^5D \rightarrow {}^7F)}$ suggests the absence of an inversion center at the Eu(III) site, which is consistent with the result of the single-crystal X-ray analysis. The most intense transition is $^5D_0 \rightarrow {}^7F_2$, which implies the red luminescence of **6**. No emission bands from the ligands or LMCT are observed, indicating that the ligands transfer the excitation energy efficiently to the Eu(III).

The two emission groups for compound **7** in the range 300–400 and 450–700 nm are shown in Fig. 3b. The emissions at 481, 575 and 657 nm are attributable to the characteristic emission of $^4F_{9/2} \rightarrow {}^6H_J$ ($J = 15/2$, 13/2 and 11/2) transitions of the Dy^{3+} ion [53–55]. It is obvious that the intensity of the blue emission, corresponding to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition, is slightly stronger than that of the yellow one. The large broad blue-shift band ranging 300–400 nm could be assigned to the emission of ligand-to-metal charge transfer (LMCT) [54,55]. The intensity of the metal-centered transitions is strong relative to that of the broad LMCT band, which implies that direct metal excitation is comparable with the sensitized process, as the extinction coefficients of the metal emission are much lower than that of the ligands.

4. Conclusions

In conclusion, a series of new 3D coordination polymers with lanthanide ions have been successfully synthesized under hydrothermal conditions using a tripodal carboxylate ligand. The luminescent investigations reveal that compounds **5** and **7** exhibit
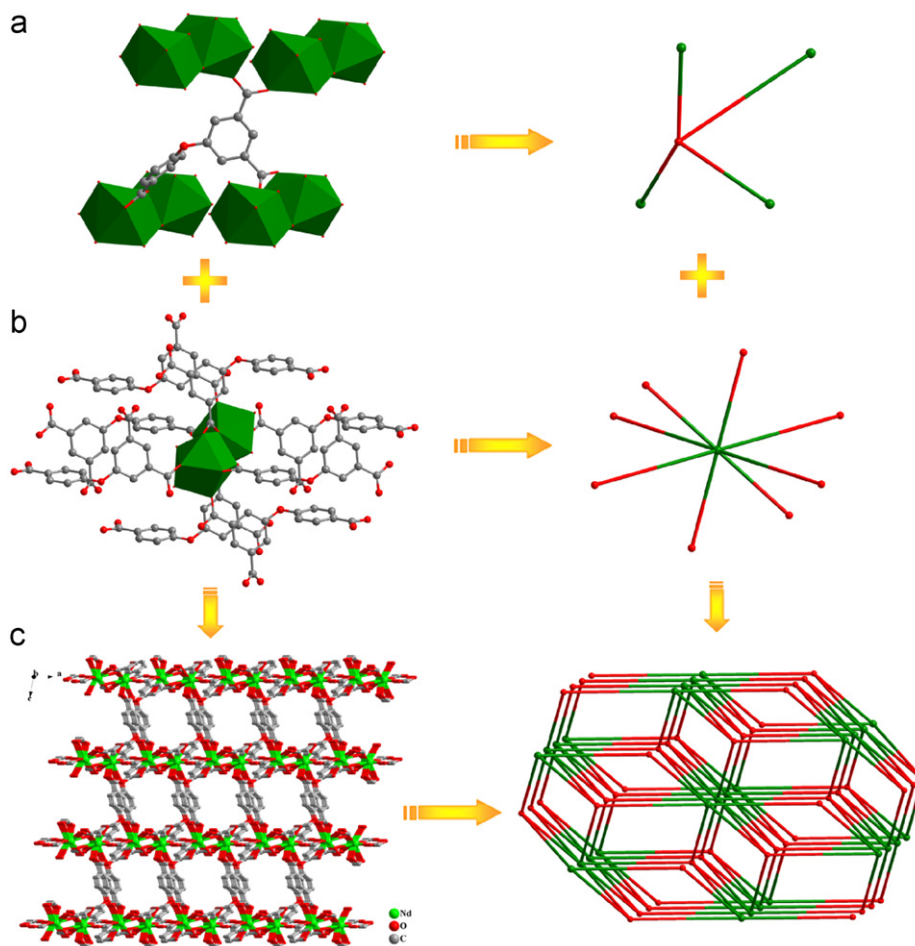
Fig. 2. (a, b) Ball-and-stick and schematic representations of 4-connected and 8-connected nodes, respectively. (c) The 3D framework of **3** and the schematic diagram showing the $(4^6)_2(4^{12} \cdot 6^{12} \cdot 8^4)$ network (red and green spheres represent four- and eight-connected nodes, respectively)(for interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).
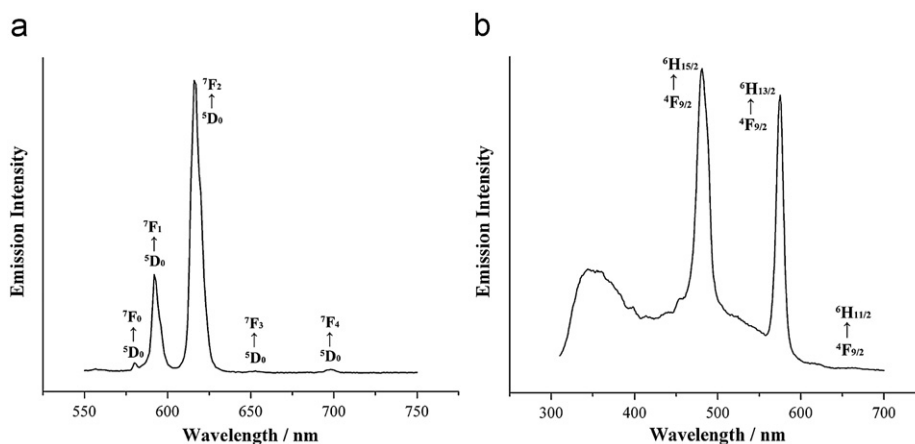

Fig. 3. Emission spectrum of compounds **5** (a: $\lambda_{ex} = 394$ nm) and **7** (b: $\lambda_{ex} = 277$ nm) in the solid state at room temperature.

characteristic red and blue luminescence of Eu^{3+} and Dy^{3+}, respectively, which indicate that these two compounds may be promising as fluorescent materials. The results of the present study suggest that the combination of multicarboxylate-containing ligand with suitable metal centers might be a promising strategy for the construction of MOFs with a specific structure and topology. We are now going on with our investigation of the system and expect that more results will be obtained in the future.

Appendix A. Supplementary Material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2010.11.012.

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