



New anion-templated 3D heterobimetallic open frameworks based on lanthanide-carboxylate layers and copper pillars

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ABSTRACT

A series of new three-dimensional (3D) lanthanide–transition metal (4*f*–3*d*) heterobimetallic open frameworks, $[Ln_2(1,2\text{-bdc})_2(\text{H}_2\text{O})_2\text{Cu}(\text{inic})_2](\text{ClO}_4)$ ($Ln = \text{Eu}$ (**1**), Tb (**2**), Nd (**3**) and Sm (**4**); 1,2-bdc = 1,2-benzenedicarboxylate; Hinic = isonicotinic acid) have been hydrothermally synthesized and characterized by elemental analysis, IR, TG and single-crystal X-ray diffraction analysis. Compounds **1–4** are isostructural. They possess a new anion-templated 3D heterobimetallic open framework, which is observed for the first time in the $\{Ln/TM/\text{bdc}/\text{inic}\}$ ($TM = \text{transition metal}$) system. Compounds **1** and **2** exhibit the characteristic fluorescent properties of $\text{Eu}(\text{III})$ and $\text{Tb}(\text{III})$, respectively.

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1. Introduction

The design and synthesis of novel lanthanide–transition metal (4*f*–3*d*) heterobimetallic compounds have received much attention in recent years owing to their fascinating structural topologies and potential applications in luminescence, magnetism, catalysis, adsorption and separation [1–16]. A general synthetic strategy in this area is the use of lanthanide and transition metal ions assembled with ligands containing mixed O- and N-donors [9–16]. So far, many discrete lanthanide–transition metal clusters have been successfully synthesized based on the above strategy [17–35]. In comparison, the design and synthesis of three-dimensional (3D) heterobimetallic open frameworks is still a challenging project due to a series of factors, such as the high and variable coordination modes of lanthanide ions with low stereochemical preference, and the competitive reaction between lanthanide and transition metal ions for the organic ligands [36–38]. In this subfield, the use of mixed 1,2- or 1,3-benzenedicarboxylate (abbreviated as 1,2-bdc and 1,3-bdc) and isonicotinic acid (abbreviated as inic) ligands in 4*f*–3*d* reaction system provides an effective route. Several new 3D heterobimetallic 4*f*–3*d* and 4*f*–4*d* coordination frameworks have been reported [36–41]. In this reaction system, 1,2-bdc and 1,3-bdc can be viewed as arch-like ligands (see Scheme S1) and they can easily combine lanthanide ions to form low-dimensional lantha-

nide-carboxylate chains or layers [36–41]. Meanwhile, the N-donor of the linear inic ligand possesses a strong tendency to bond to transition metal ions with low coordination numbers such as $\text{Cu}(\text{I})$ and $\text{Ag}(\text{I})$. Thus effective bridges are created to link the lanthanide-carboxylate subunits into 3D heterobimetallic frameworks [42–44]. More recently, it is also found that some anions (e.g. Cl^- , Br^- and I^-) introduced into this reaction system can act as linkers and microtune the topology of these 3D open frameworks [39].

During our research on the 4*f*–3*d* heterobimetallic reaction system with mixed 1,2-bdc and inic ligands, the perchlorate anions were deliberately introduced in order to explore their potentially templating roles [45] in forming new 3D coordination frameworks. In this paper, we report a series of new 3D heterobimetallic compounds synthesized by the hydrothermal technique, $[Ln_2(1,2\text{-bdc})_2(\text{H}_2\text{O})_2\text{Cu}(\text{inic})_2](\text{ClO}_4)$ ($Ln = \text{Eu}$ (**1**), Tb (**2**), Nd (**3**) and Sm (**4**)). Compounds **1–4** exhibit a new 3D heterobimetallic 4*f*–3*d* open framework templated by the perchlorate anions. The photoluminescent properties of these four compounds were studied.

2. Experimental

2.1. Materials and measurement

All chemicals purchased were of reagent grade and used without further purification. Elemental analyses (C, N and H) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Eu,

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Tb, Nd, Sm and Cu were measured with a Leaman inductively coupled plasma (ICP) spectrometer. FT/IR spectra were recorded in the range 4000–400 cm^{-1} on an Alpha Centaur FTIR spectrophotometer using KBr pellets. TG analyses were performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of $10^\circ\text{C min}^{-1}$. Photoluminescence spectra were measured using a FL-2T2 instrument (SPEX, USA) with a 450-W xenon lamp monochromatized by double grating (1200 gr mu^{-1}). All measurements were performed at room temperature.

2.2. Hydrothermal synthesis of $[\text{Ln}_2(1,2\text{-bdc})_2(\text{H}_2\text{O})_2\text{Cu}(\text{inic})_2](\text{ClO}_4)$ ($\text{Ln} = \text{Eu}$ (**1**), Tb (**2**), Nd (**3**) and Sm (**4**))

Compound **1** was synthesized from a mixture of Eu_2O_3 (0.176 g, 0.5 mmol), H₂inic (0.246 g, 2.0 mmol), 1,2-H₂bdc (0.168 g, 1 mmol), CuCl (0.020 g, 0.2 mmol), NaClO_4 (0.07 g, 0.5 mmol) and H_2O (10 mL). This mixture was adjusted to $\text{pH} = 1.50$ by the addition of 1 M NaOH and stirred for 20 min. Then the above mixture was transferred into a Teflon-lined autoclave (20 mL) and kept at 170°C for 5 days. After the reaction mixture had been slowly cooled at a rate of 10°C h^{-1} to room temperature, yellow block-like crystals of **1** were obtained. The products were collected by filtration, washed with distilled water and dried in a desiccator at room temperature (yield: 54% based on Eu). Elemental analysis for $\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_{18}\text{ClCuEu}_2$ ($M_r = 1075.37$) (**1**): calcd: C 31.27%, H 1.87%, N 2.60%, Cu 5.91%, Eu 28.26%; found: C 31.21%, H 1.81%, N 2.55%, Cu 5.97%, Eu 28.34%. Selected IR data (KBr pellet, cm^{-1}): 3349 (s), 3189 (br), 1560 (s), 1504 (s), 1435 (s), 1397 (s), 1228 (m), 1153 (m), 1089 (s), 966 (w), 870 (s), 841 (s), 763 (s), 695 (s), 649 (w), 623 (m), 598 (w), 577 (w), 439 (s).

Compounds **2–4** were prepared with the similar procedure of **1** except that Eu_2O_3 was replaced by Tb_4O_7 (0.374 g, 0.5 mmol), Nd_2O_3 (0.168 g, 0.5 mmol) and Sm_2O_3 (0.174 g, 0.5 mmol), respectively. Yellow block-like crystals of **2–4** were obtained with the yield of 42%, 39% and 38% based on the lanthanide, respectively. Elemental analysis for $\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_{18}\text{ClCuTb}_2$ ($M_r = 1089.31$) (**2**): calcd: C 30.87%, H 1.85%, N 2.57%, Cu 5.83%, Tb 29.18%; found: C 30.81%, H 1.78%, N 2.52%, Cu 5.92%, Tb 29.24%. Selected IR data (KBr pellet, cm^{-1}): 3347 (s), 3194 (br), 1562 (s), 1505 (s), 1435 (s), 1398 (s), 1269 (w), 1227 (m), 1153 (m), 1090 (s), 966 (w), 871 (s), 842 (s), 806 (w), 763 (s), 695 (s), 649 (w), 623 (m), 599 (w), 578 (w), 440 (s). Elemental analysis for $\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_{18}\text{ClCuNd}_2$

($M_r = 1059.93$) (**3**): calcd: C 31.73%, H 1.90%, N 2.64%, Cu 6.00%, Nd 27.22%; found: C 31.65%, H 1.82%, N 2.56%, Cu 6.09%, Nd 27.29%. Selected IR data (KBr pellet, cm^{-1}): 3350 (s), 3190 (br), 1562 (s), 1530 (m), 1505 (s), 1436 (s), 1398 (s), 1229 (m), 1155 (m), 1089 (s), 966 (w), 870 (s), 841 (s), 763 (s), 695 (s), 649 (w), 623 (m), 598 (w), 577 (w), 471 (w), 439 (s), 406 (m). Elemental analysis for $\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_{18}\text{ClCuSm}_2$ ($M_r = 1072.15$) (**4**): calcd: C 31.37%, H 1.88%, N 2.61%, Cu 5.93%, Sm 28.05%; found: C 31.30%, H 1.83%, N 2.51%, Cu 6.04%, Sm 28.11%. Selected IR data (KBr pellet, cm^{-1}): 3348 (s), 3196 (br), 1563 (s), 1531 (s), 1506 (s), 1437 (s), 1400 (s), 1269 (w), 1228 (m), 1155 (m), 1091 (s), 966 (w), 870 (s), 842 (s), 763 (s), 695 (s), 649 (w), 623 (m), 600 (w), 578 (w), 472 (w), 440 (s), 407 (w).

Caution! Perchlorate salts are potentially explosive and should be handled in small quantities and with adequate precautions.

2.3. X-ray crystallography study

Crystallographic data for compounds **1–4** were collected at 150 K with a Rigaku *R*-axis Rapid IP diffractometer using graphite monochromatic $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) and IP technique. Empirical absorption corrections (ψ scan) were applied. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXTL 97 crystallographic software package [46,47]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. H atoms on their parent C atoms were fixed in geometrically calculated positions, while H atoms on the water molecules cannot be located in the difference Fourier maps but included in the final molecular formula directly. Further details of the X-ray structural analysis are given in Table 1. Selected bond lengths and angles of **1** are listed in Table 2. The bond lengths and angles of **2–4** are listed in Tables S1–S3.

3. Results and discussion

3.1. Synthesis

In our research on the 4f–3d–inic–bdc synthetic system, various anionic templates were deliberately used in order to explore their potentially templating roles in forming new 3D coordination frameworks. Usually, the size and the charge of

Table 1
Crystal data and structural refinement of compounds **1–4**

	1	2	3	4
Empirical formula	$\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_{18}$ ClCuEu_2	$\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_{18}$ ClCuTb_2	$\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_{18}$ ClCuNd_2	$\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_{18}$ ClCuSm_2
Formula weight	1075.37	1089.31	1059.93	1072.15
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/m$	$C2/m$	$C2/m$	$C2/m$
<i>a</i> (Å)	36.815(7)	36.706(7)	36.997(7)	36.840(7)
<i>b</i> (Å)	6.9805(14)	6.9945(14)	7.0551(14)	7.0063(14)
<i>c</i> (Å)	6.2024(12)	6.1881(12)	6.2045(12)	6.1988(12)
β (deg)	97.42(3)	97.42(3)	97.75(3)	97.45(3)
Volume (Å ³)	1580.6(5)	1575.4(5)	1604.7(5)	1586.5(5)
<i>Z</i>	2	2	2	2
Calculated density (mg m^{-3})	2.260	2.229	2.194	2.244
Absorption coefficient (mm^{-1})	4.760	5.275	4.015	4.490
<i>F</i> (000)	1036	1012	1024	1032
<i>R</i> (int)	0.0785	0.0943	0.0717	0.1339
Goodness-of-fit on F^2	1.084	1.070	1.083	1.080
Final R^a indices [$I > 2\sigma(I)$] (all data)	0.0464	0.0529	0.0480	0.0750
wR_2^b (all data)	0.1059	0.1316	0.1344	0.1780

^a $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$.

^b $wR_2 = \sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2)^{1/2}$.

anions have obvious influence on the structural topologies of final 3D “host” frameworks, which has been extensively proved in other synthetic system [45,50]. In this case, NaClO₄ was introduced in the reaction system since ClO₄⁻ is a useful and effective template to obtain single-crystal compounds [52–56]. And a series of new 3D 4f–3d heterobimetallic open framework “hosts”, compounds **1–4**, were obtained. It is noteworthy that no crystals can be obtained without adding NaClO₄. Attempts to synthesize new compounds with similar 3D heterobimetallic “hosts” via different anionic “guest” templates such as BF₄⁻, PF₆⁻ and NO₃⁻ have resulted in no crystal products yet. Further, a series of anions with different charges such as SO₄²⁻, PO₄³⁻ and various polyoxometalates [48–51] were also employed in order to get new cationic heterobimetallic scaffolds, no crystalline compounds were isolated either. It is supposed that since the size and charge of anions were changed, the length, coordination modes and charges of organic bridging ligands should also be adjusted so as to realize above ideas. This synthetic research is still in progress.

3.2. Crystal structure of compounds **1–4**

Single-crystal X-ray diffraction analysis reveals that compounds **1–4** crystallize in the monoclinic space group *C2/m* and exhibit the isostructural feature. The basic structural unit of **1** is shown in Fig. 1. There are one independent Eu center and one Cu

Table 2

Selected bond lengths [Å] and angles [deg] of compound **1**

Eu(1)–O(1WA)	2.362(6)	Eu(1)–O(1)	2.428(9)
Eu(1)–O(2)	2.447(10)	Eu(1)–O(3B)	2.446(8)
Eu(1)–O(4A)	2.362(6)	Eu(1)–O(5)	2.580(6)
Eu(1)–O(5C)	2.580(6)	Eu(1)–O(5D)	2.489(6)
Eu(1)–O(5E)	2.489(6)	Cu(1)–N(1)	1.898(7)
Cu(1)–N(1F)	1.898(7)		
O(1WA)–Eu(1)–O(1)	116.5(2)	O(1)–Eu(1)–O(5D)	80.68(15)
O(1)–Eu(1)–O(2)	52.3(3)	O(1)–Eu(1)–O(5)	145.8(2)
O(1)–Eu(1)–O(3B)	80.8(3)	O(1)–Eu(1)–O(5E)	80.68(15)
O(4A)–Eu(1)–O(1)	116.5(2)	O(1)–Eu(1)–O(5C)	145.78(19)
N(1F)–Cu(1)–N(1)	180.0(10)		

Symmetry transformations used to generate equivalent atoms: A $-x+1/2, y+1/2, -z+2$; B $x, y, z-1$; C $x, -y+1, z$; D $-x+1/2, -y+1/2, -z+1$; E $-x+1/2, y+1/2, -z+1$; F $-x+1, -y+1, -z$.

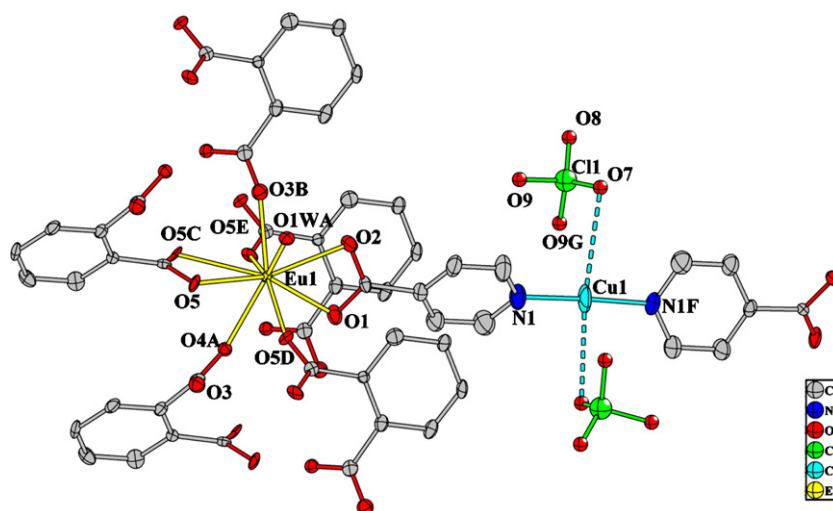
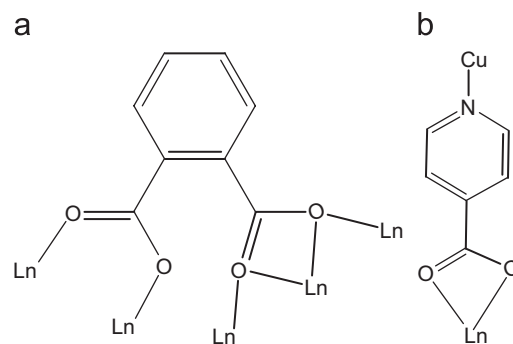


Fig. 1. ORTEP plot of the basic structural unit of **1** with 50% probability ellipsoids showing the coordination environment of Eu and Cu centers. All hydrogen atoms are omitted for clarity. Symmetry transformations codes: A $-x+1/2, y+1/2, -z+2$; B $x, y, z-1$; C $x, -y+1, z$; D $-x+1/2, -y+1/2, -z+1$; E $-x+1/2, y+1/2, -z+1$; F $-x+1, -y+1, -z$; G $x, -y, z$.



Scheme 1. The coordination modes of (a) 1,2-bdc ligand and (b) inic ligand.

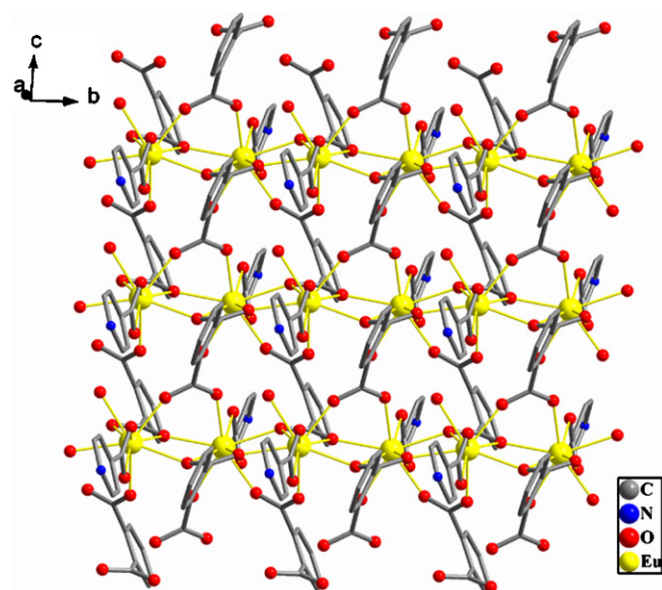


Fig. 2. Ball-and-stick representation of the 2D Eu-carboxylate layer viewed along *a*-axis.

center in the unit cell. The Eu center exhibits a nine-coordinated environment with one aqua ligand, two O ligands deriving from one inic ligand and six O ligands originating from five bdc ligands. The bond lengths of Eu–O are in the range of 2.362(6)–2.580(6) Å and the bond angles of O–Eu–O vary from 49.6(3)° to 150.8(4)°. The Cu center is coordinated with two N ligands deriving from two inic ligands. The distance of Cu–N is 1.898(7) Å and the angle of N–Cu–N is 180.0(10)°. Further, there are very weak coordination interactions between Cu center and perchlorate anions. The distances of Cu–O range from 2.923(3) to 3.322(3) Å. Bond valence sum calculations confirm that the oxidation states of Eu and Cu are 3+ and 1+, respectively [57,58]. In **1**, the inic ligand can be viewed as a bridge, which links one Cu and one Eu center

together. The 1,2-bdc ligand exhibits a pentadentate chelating-bridging coordination mode, connecting with five Eu centers (see Scheme 1).

Based on the above connection modes, the adjacent Eu centers in **1** are linked into a one-dimensional (1D) chain with an edge-sharing mode along the *b*-axis (as shown in Fig. S1). Further, the 1,2-bdc ligands act as bridges to join the adjacent Eu chains together, forming a two-dimensional (2D) layer on [100] plane (as shown in Fig. 2). It is noteworthy that such a 2D layer displays a new arrangement mode in the lanthanide–benzenedicarboxylate system. More interestingly, the inic ligands are connected by the Cu centers to form linear pillars and these Cu(I)–inic pillars support the 2D lanthanide–carboxylate layers into a 3D host open frameworks with 1D channels along the *c*-axis. The channel size is about 6.98 × 8.62 Å. The guest ClO₄[−] anions are sealed into these channels (see Fig. 3). It is found that such an anion-templated 3D host framework is observed for the first time in the heterobimetallic 4*f*–3*d* coordination framework system.

3.3. IR spectra

In the IR spectra of **1** (see Fig. S5(a)), the characteristic bands of carboxylate groups are shown in the range 1637–1538 cm^{−1} for

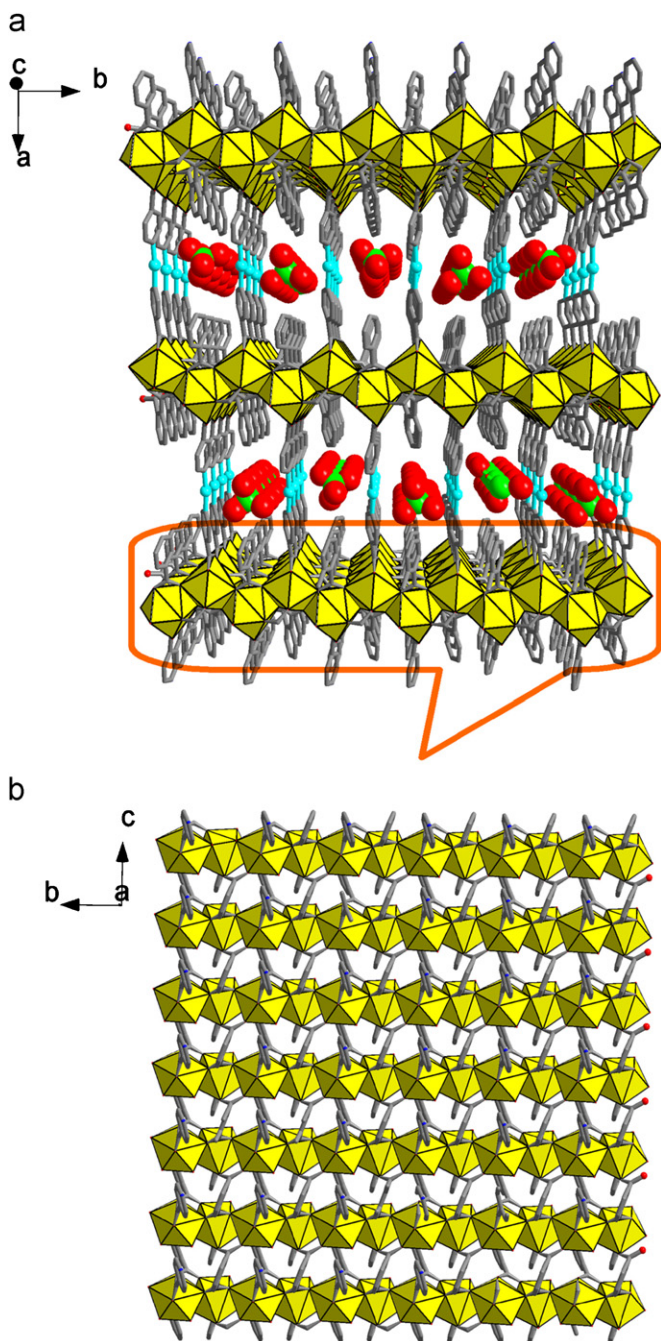


Fig. 3. (a) View of the anion-templated 3D host framework based on the Eu-carboxylate layers and Cu-inic pillars along *c*-axis. (b) View of the 2D Eu-carboxylate layer along *a*-axis.

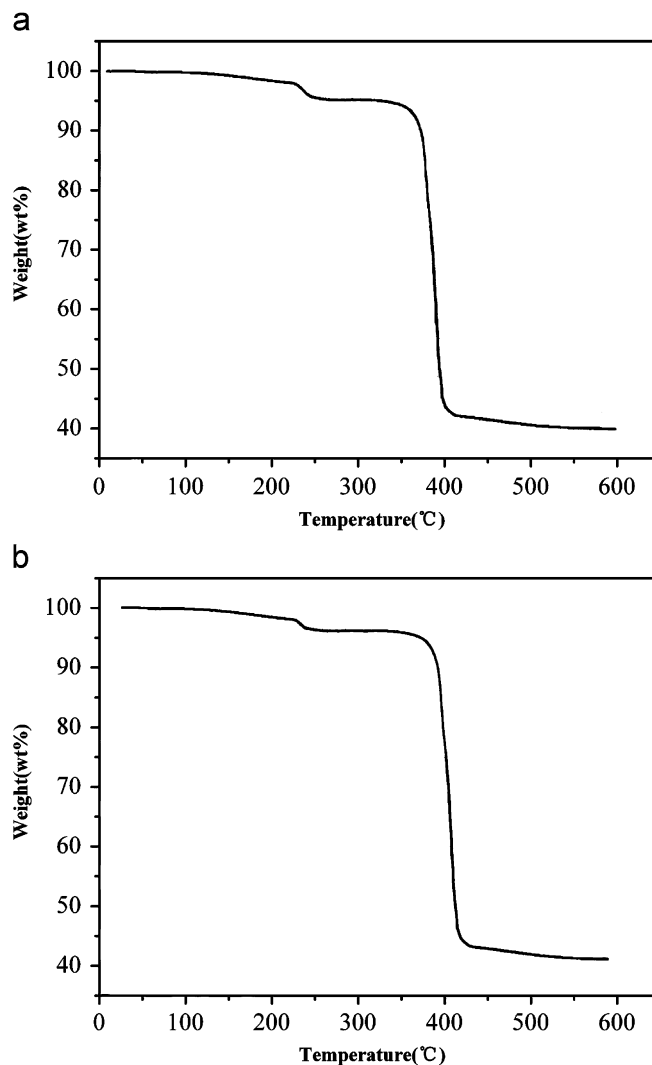


Fig. 4. TG curves of (a) compounds **1** and (b) **2**.

asymmetric stretching and $1441\text{--}1396\text{ cm}^{-1}$ for symmetric stretching [50]. The absence of strong peaks around 1720 cm^{-1} indicates that all carboxylic groups are deprotonated [50,59,60].

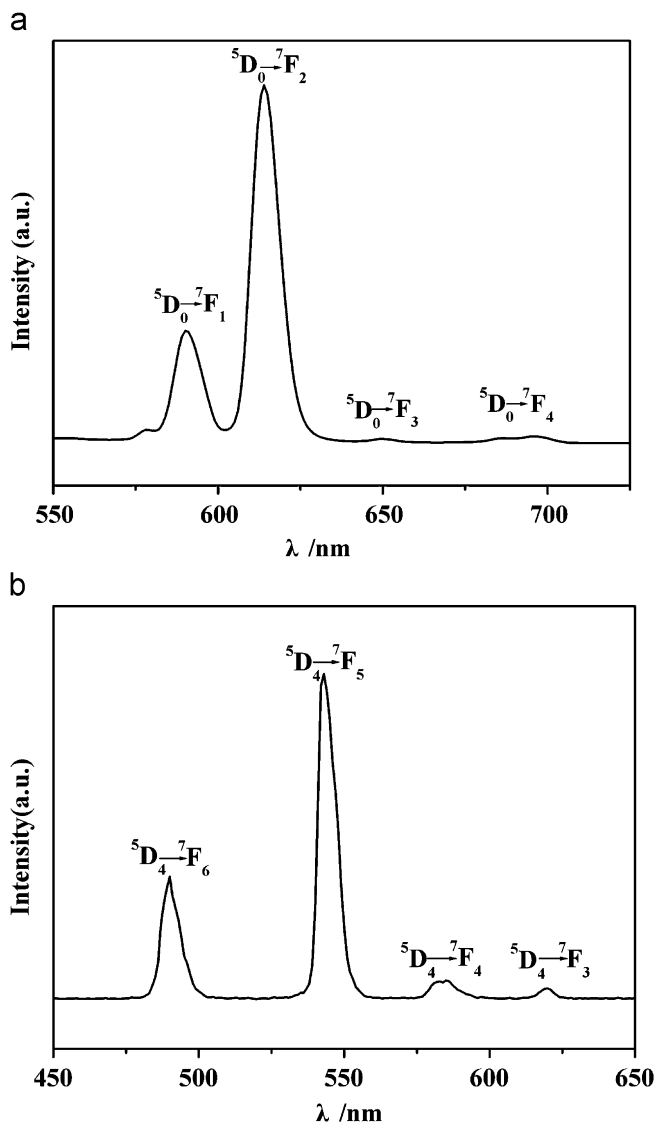


Fig. 5. Solid-state emission spectra of (a) **1** (excited at 397 nm) and (b) **2** (excited at 272 nm) at room temperature.

Weak absorption peaks observed at $3045\text{--}2988\text{ cm}^{-1}$ are attributed to the $\nu_{\text{C-H}}$ of the pyridyl group. The band at 3349 cm^{-1} is assigned to the coordinating water molecules. The IR spectra of compounds **1–4** exhibit similar features (as shown in Figs. S5(a), (b) and S6(c), (d)).

3.4. Thermal analysis

In the TG curve of compound **1** (see Fig. 4(a)), the first minor weight loss of 4.05% in the temperature range $100\text{--}260\text{ }^{\circ}\text{C}$ corresponds to the release of coordinated water molecules. The second weight loss of 55.34% in the temperature range $350\text{--}550\text{ }^{\circ}\text{C}$ is attributed to the release of inic, 1,2-bdc and perchlorate anions. The whole weight loss (59.39%) is in good agreement with the calculated value (59.88%). The TG curve of compound **2** (see Fig. 4(b)) also exhibits two weight loss steps. The first weight loss of 3.60% occurs between 100 and $260\text{ }^{\circ}\text{C}$, corresponding to the loss of coordinated water molecules. The latter weight loss of 53.92% appears in the temperature range of $350\text{--}550\text{ }^{\circ}\text{C}$ and is ascribed to the loss of inic, 1,2-bdc and perchlorate anions. The whole weight loss (57.52%) is consistent with the calculated value (58.38%). The TG curves of compounds **3–4** exhibit similar features (as shown in Figs. S7(c) and (d)) (Fig. 5).

3.5. Fluorescent properties

Taking into account the excellent luminescent properties of lanthanide compounds, the solid-state luminescent properties of **1–4** were investigated at room temperature. It is found that compound **1** showed the characteristic emission bands of the Eu^{3+} ion when measured from 450 to 750 nm with an excitation wavelength of 397 nm. Compound **1** exhibits a strong emission band at 613 nm, a medium emission band at 590 nm, and two weak bands at 650 and 696 nm (Fig. 5(a)), which are attributed to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ transitions of Eu^{3+} ion, respectively. The high intensity of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition at 613 nm implies the red luminescence of **1**. Compound **2** emits green light under excitation of 272 nm and gives a typical Tb^{3+} emission spectrum (Fig. 5(b)), that is, a medium emission band at 489 nm (${}^5\text{D}_4 \rightarrow {}^7\text{F}_6$), a strongest emission band at 542 nm (${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$), two weak emission bands at 584 nm (${}^5\text{D}_4 \rightarrow {}^7\text{F}_4$) and 620 nm (${}^5\text{D}_4 \rightarrow {}^7\text{F}_3$). All these emission bands are in agreement with those of Eu^{3+} and Tb^{3+} complexes in previous reports [61,62]. However, the luminescent properties of compounds **3** and **4** cannot be detected in current experimental conditions.

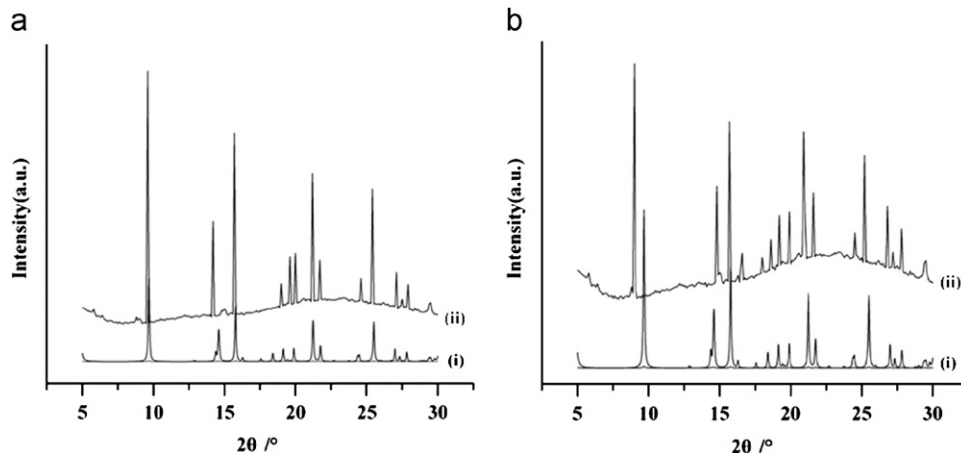


Fig. 6. Simulated and experimental XRPD patterns of **1** (a) and **2** (b). In each plot, (i) is the simulated XRPD and (ii) is the experimental XRPD at room temperature.

3.6. X-ray powder diffraction for **1** and **2**

In order to check the phase purity of these compounds, the X-ray powder diffraction (XRPD) of compounds **1** and **2** were checked at room temperature. As shown in Fig. 6, the peak positions of simulated and experimental XRPD patterns are in agreement with each other, indicating the good phase purity of the compounds. The differences in intensity may be due to the preferred orientation of the crystalline powder samples. The compounds **3** and **4** were synthesized in the same conditions, so they can obtain similar results of XRPD.

4. Conclusions

In summary, a series of new heterobimetallic 4f–3d compounds, $[Ln_2(1,2\text{-bdc})_2(\text{H}_2\text{O})_2 \text{Cu}(\text{inic})_2](\text{ClO}_4)$ ($Ln = \text{Eu}$ (**1**), Tb (**2**), Nd (**3**), Sm (**4**)), have been hydrothermally synthesized. The introduction of an anionic template ClO_4^- leads to a new 3D host framework based on the new lanthanide-carboxylate layers and copper-isonicotinate pillars. The successful preparation of compounds **1–4** suggest that novel high-dimensional 4f–3d heterobimetallic open frameworks could be designed and synthesized by the choice of suitable organic O- and N-donor ligands as well as a series of anionic templates with different charges and sizes. Further, the strong luminescent properties of compounds **1** and **2** may have potential applications in photo-active materials.

5. Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC reference numbers 664755, 664756, 664757 and 664758 for compounds **1–4**, respectively. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223/336 033; e-mail: deposit@ccdc.cam.ac.uk).

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2008.03.027

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