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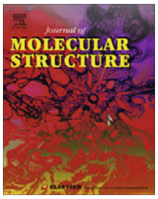

Synthesis, crystal structures and properties of a series of three-dimensional lanthanide coordination polymers with the rigid and flexible mixed dicarboxylate ligands of 1,4-benzene dicarboxylic acid and succinic acid

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ABSTRACT

A series of new lanthanide coordination polymers, with the formula [Ln(Suc)$_{0.5}$(*p*-BDC)] (Ln = Eu (**1**), Sm (**2**), Tb (**3**), Pr (**4**), Ho (**5**); H$_2$Suc = succinic acid; *p*-H$_2$BDC = 1,4-benzene dicarboxylic acid), have been synthesized under hydrothermal condition and all of them have been structurally characterized. X-ray diffraction analyses reveal that complexes **1–5** are isostructural and crystallized in orthorhombic space group *Pbca*. One-dimensional infinite inorganic edge-sharing polyhedra chains formed by lanthanide ions and tetradentate carboxyl groups of succinic acid ligands, link to each other through the carbon atoms of succinic acid ligands and phenyl groups of the 1,4-benzene dicarboxylic acid ligands, to lead to a three-dimensional framework structure. In addition, the phase purities of the bulk samples were identified by X-ray powder diffraction. The photoluminescent properties of **1** and **3** were discussed in detail.

1. Introduction

Crystal engineering based on metal-organic frameworks (MOFs) has attracted intensive interest because of their elegant framework topologies as well as their potential applications in gas storage, catalysis, optical and magnetic applications [1–10]. To our knowledge, there are many factors important for the rational design of MOFs, such as the shape and binding mode of multicarboxylate, geometry of metal ions, the spacer linking the binding sites, and so on [11,12]. So, systematic research is a challenge for understanding the role of these factors in the formation of MOFs. In this aspect, multicarboxylate ligands which are usually employed in the architectures for lanthanide-containing MOFs, have received considerable study due to their availability and potential for the tailored design of the frameworks [13–18]. So far, much work is focused on using single rigid multicarboxylate ligands (1,4-benzenedicarboxylic acid, 1,3,5-benzenetriacetic acid and 1,2,4,5-benzenetetracarboxylic acid, etc.) or flexible multicarboxylate ligands (succinic acid, glutaric acid, adipic acid, etc.) to prepare lanthanide-containing MOFs [19–28]. However, lanthanide-containing MOFs with the rigid and flexible mixed multicarboxylate ligands are less developed [29–32].

For enriching this research field, we chose 1,4-benzene dicarboxylic acid and succinic acid as the rigid and flexible mixed multicarboxylate ligands to synthesize a new series of lanthanide coordination polymers. The rigid 1,4-benzene dicarboxylic acid ligand seems to be promising to control and adjust open and stable framework in which there are two carboxyl groups with a 180° angle as well as conjugated aromatic rings [33–36]. On the other hand, the flexible succinic acid with the flexibility and conformational freedom may bend and rotate when it coordinates to the metal center, and cause the structural diversity with unique structures and useful properties [37,38,24]. This assembly leads to a intricate three-dimensional framework structure. Herein, we report the preparation and crystal structures of Ln–Suc–*p*-BDC coordination polymers, [Ln(Suc)$_{0.5}$(*p*-BDC)] (Ln = Eu (**1**), Sm (**2**), Tb (**3**), Pr (**4**), Ho (**5**); Suc = succinic acid; *p*-H$_2$BDC = 1,4-benzene dicarboxylic acid). The luminescent properties have also been investigated.

2. Experimental

2.1. Materials and physical measurements

All chemicals purchased were of reagent grade or better and were used without further purification. Lanthanide chloride salts were prepared via dissolving lanthanide oxides with 12 M HCl

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while adding a bit of H_2O for Tb_4O_7 and then evaporating at 100 °C until the crystal film formed. C and H analyses were made on a Perkin-Elmer 240 C automatic analyzer at the analysis center of Liaoning Normal University. Infrared (IR) spectra were recorded on JASCO FT/IR-480 PLUS Fourier Transform spectrophotometer with pressed KBr pellets in the range 200–4000 cm^{-1}. The luminescence spectra were reported on a JASCO FP-6500 spectrofluorimeter (solid) in the range of 200–850 nm. Content of Lanthanide was analyzed on a Plasma-Spec(I)-AES model ICP spectrometer. The powder X-ray diffraction (PXRD) data were collected on a Bruker Advance-D8 with Cu Kα radiation, in the range $5° < 2\theta < 60°$, with a step size of $0.02°(2\theta)$ and an acquisition time of 2s per step.

2.2. Synthesis of [Eu(Suc)$_{0.5}$(p-BDC)] (**1**)

The complex was prepared by hydrothermal reaction. $EuCl_3$ $6H_2O$ (0.20 g, 0.55 mmol), succinc acid (H_2Suc, 0.10 g, 0.85 mmol), 1,4-benzene dicarboxylic acid (p-H_2BDC, 0.10 g, 0.60 mmol), and H_2O (10 ml) were mixed in 25 ml beaker. The pH value was adjusted to 6.5 with ethylenediamine. After stirring for 2 h, the mixture was sealed in the bomb and heated at 180 °C for four days, then cooled at 10 °C/3 h to 100 °C, followed by slow cooling to room temperature. After filtration, the product was washed with distilled water and then dried at room temperature. Yield: 73% (based on Eh(III)). Elemental analysis for **1**: $C_{10}H_6O_6Eu$ ($Mr = 374.11$). Calcd: C, 32.11; H, 1.61; Eu, 40.62. Found: C, 32.13; H: 1.63; Eu, 40.60. IR data (KBr pellet, $\nu[cm^{-1}]$): 3057, 2924, 2854, 1617, 1577, 1541, 1502, 1466, 1402, 1316, 1289, 1165, 1105, 1013, 967, 887, 823, 791, 748, 683, 573, 539, 514.

2.3. Synthesis of [Ln(Suc)$_{0.5}$(p-BDC)] (Ln = Sm (**2**), Tb (**3**), Pr (**4**), Ho(**5**))

Complexes **2**–**5** were synthesized by a method similar to that of **1** except $EuCl_3$ $6H_2O$ was replaced by $LnCl_3$ $6H_2O$ (Ln = Sm, Tb, Pr, Ho, 0.55 mmol), and the reaction was heated at 160 °C for 7 days for **3**–**5**. Yield: 68% (based on Sm), 78% (based on Tb), 64% (**4**), and 61% (**5**). Elemental analysis for **2**: $C_{10}H_6O_6Sm$ ($Mr = 372.50$). Calcd: C, 32.24; H,1.62; Sm, 40.37. Found: C, 32.27; H: 1.64; Sm, 40.35; for **3**: $C_{10}H_6O_6Tb$ ($Mr = 381.07$). Calcd: C, 31.52; H, 1.59; Tb, 41.71. Found: C, 31.53; H: 1.56; Tb, 41.74; for **4**: $C_{10}H_6O_6Pr$ ($Mr = 363.05$): Calcd: C, 33.08; H, 1.67; Pr, 38.81. Found: C, 33.05; H: 1.69; Pr, 38.84; for **5**: $C_{10}H_6O_6Ho$ ($Mr = 387.08$): Calcd: C, 31.03; H, 1.56; Ho, 42.61. Found: C, 31.05; H: 1.53; Ho, 42.65. IR data (KBr pellet, cm^{-1}) for **2**: 3057, 2923, 2854, 1617, 1576, 1540, 1502, 1465, 1402, 1315, 1290, 1252, 1165, 1105, 1013, 966, 887, 823, 791, 748, 683, 572, 539, 515; for **3**: 3057, 2923, 2854, 1620, 1578, 1542, 1502, 1467, 1402, 1314, 1289, 1251, 1164, 1105, 1013, 968, 887, 824, 791, 749, 685, 576, 541, 515; for **4**: 3057, 2925, 2854, 1614, 1574, 1536, 1402, 1303, 1214, 1166, 1050, 999, 905, 886, 821, 790, 747, 681, 647, 570, 513; for **5**: 3057, 2926, 2853, 1621, 1579, 1542, 1405, 1314, 1290, 1252, 1163, 1107, 1013, 970, 905, 886, 825, 791, 748, 687, 579, 543, 516.

2.4. X-ray crystallography

Suitable single crystals of five complexes were mounted on glass fibers for X-ray measurement. Reflection data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer for complex **2** and Rigaku R-AXIS RAPID IP diffractometer for complexes **1,** and **3**–**5** with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Crystal structures were solved by the direct method. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on the basis of the difference Foutier map for all the complexes. All calculations were performed using the program SHELX-97 program [39]. The crystallographic data and experimental details of the data collection and the structure refinement are given in Table 1. Selected bond lengths and angles of complexes **1**–**5** are listed in Table 2.

3. Results and discussion

The title compound was synthesized in the hydrothermal reaction of $LnCl_3$ $6H_2O$ with 1,4-benzenedicarboxylic acid, succinc acid. X-ray powder diffraction analysis of complex **1**–**5** shows that the X-ray powder diffraction data are in agreement with that of calculated on the basis of the structural data (Fig. 1), that is, **1**–**5** have been obtained successfully as pure crystalline phases.

3.1. Description of crystal structures

Single-crystal X-ray structural analyses revealed that the frameworks of **1–5** are isostructural. Therefore, complex **1** is taken as an example to present and discuss the structure in detail.

Table 1
Crystallographic data for **1**–**5**.

	1	**2**	**3**	**4**	**5**
Formula	$C_{10}H_6O_6Eu$	$C_{10}H_6O_6Sm$	$C_{10}H_6O_6Tb$	$C_{10}H_6O_6Pr$	$C_{10}H_6O_6Ho$
M ($g\,mol^{-1}$)	374.11	372.50	381.07	363.06	387.08
Temperature (K)	298(2)	298(2)	298(2)	298(2)	298(2)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pbca*	*Pbca*	*Pbca*	*Pbca*
a (Å)	13.956(3)	14.0029(17)	13.895(3)	14.102(3)	13.807(3)
b (Å)	6.8726(14)	6.8928(8)	6.8249(14)	6.9727(14)	6.7801(14)
c (Å)	21.829(4)	21.883(3)	21.746(4)	21.982(4)	21.691(4)
V (Å^3)	2093.7(7)	2112.1(4)	2062.2(7)	2161.5(7)	2030.6(7)
Z	8	8	8	8	8
D_c (g/cm^3)	2.374	2.343	2.455	2.231	2.532
μ(Mo Kα)/cm^{-1}	6.004	5.573	6.872	4.520	7.806
$F(000)$	1416	1408	1432	1384	1448
GOF	1.170	1.010	1.098	1.156	1.061
R^a	0.0207	0.0306	0.0209	0.0294	0.0210
	(0.0227)^b	(0.0471)^b	(0.0237)^b	(0.0315)^b	(0.0244)^b
$wR_2{}^a$	0.0511	0.0587	0.0477	0.0793	0.0499
	(0.0518)^b	(0.0654)^b	(0.0490)^b	(0.0817)^b	(0.0513)^b
$\Delta(\rho)$ (e/Å^{-3})	0.997, −1.110	1.471, −0.832	0.796, −0.698	1.331, −1.348	0.910, −0.579

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2/[\Sigma(w(F_o^2)^2]^{1/2}$; $[F_o > 4\sigma(F_o)]$.

[b] Based on all data.

Table 2
Selected bond lengths (Å) and angles (°) for **1–5**.

Complex **1**					
Eu—O5	2.284(2)	Eu—O1	2.333(2)	Eu—O6	2.349(2)
Eu—O4	2.366(2)	Eu—O3A	2.441(2)	Eu—O2B	2.497(2)
Eu—O3	2.528(2)	Eu—O2	2.576(2)		
O5—Eu—O1	86.08(8)	O5—Eu—O6	104.93(8)	O1—Eu—O6	151.12(9)
O5—Eu—O4	75.35(9)	O1—Eu—O4	134.69(9)	O6—Eu—O2B	126.07(8)
O5—Eu—O3	166.10(8)	O1—Eu—O3	96.95(8)	O3A—Eu—O3	113.87(6)
O2B—Eu—O3	64.51(7)	O5—Eu—O2	143.11(8)	O3—Eu—O2	50.63(7)
Complex **2**					
Sm—O5	2.300(3)	Sm—O1	2.345(3)	Sm—O6	2.361(3)
Sm—O4	2.376(3)	Sm—O3A	2.457(3)	Sm—O2B	2.498(3)
Sm—O3	2.538(3)	Sm—O2	2.590(3)		
O5—Sm—O1	86.08(8)	O5—Sm—O6	104.93(8)	O1—Sm—O6	151.12(9)
O5—Sm—O4	75.35(9)	O1—Sm—O4	134.69(9)	O6—Sm—O2B	126.07(8)
O5—Sm—O3	166.10(8)	O1—Sm—O3	96.95(8)	O3A—Sm—O3	113.87(6)
O2B—Sm—O3	64.51(7)	O5—Sm—O2	143.11(8)	O3—Sm—O2	50.63(7)
Complex **3**					
Tb—O5	2.259(2)	Tb—O1	2.306(2)	Tb—O4	2.320(2)
Tb—O6	2.341(2)	Tb—O3A	2.420(2)	Tb—O2B	2.482(2)
Tb—O3	2.501(2)	Tb—O2	2.551(2)		
O5—Tb—O1	85.69(8)	O5—Tb—O4	104.65(9)	O1—Tb—O4	151.73(9)
O5—Tb—O6	75.62(9)	O1—Tb—O6	134.40(9)	O4—Tb—O2B	126.01(8)
O5—Tb—O3	165.91(8)	O1—Tb—O3	97.49(9)	O3A—Tb—O3	113.99(6)
O2B—Tb—O3	64.28(8)	O5—Tb—O2	142.84(8)	O3—Tb—O2	51.08(8)
Complex **4**					
Pr—O5	2.345(2)	Pr—O1	2.396(2)	Pr—O4	2.406(2)
Pr—O6	2.411(2)	Pr—O3A	2.499(3)	Pr—O2B	2.535(2)
Pr—O3	2.579(2)	Pr—O2	2.643(2)		
O5—Pr—O1	86.87(9)	O5—Pr—O4	105.55(8)	O1—Pr—O4	149.40(10)
O5—Pr—O6	75.34(9)	O1—Pr—O6	135.28(10)	O4—Pr—O2B	126.36(8)
O3A—Pr—O2B	155.66(8)	O5—Pr—O3	167.19(9)	O1—Pr—O3	95.84(10)
O3A—Pr—O3	113.01(7)	O2B—Pr—O3	65.15(8)	O3—Pr—O2	49.35(8)
Complex **5**					
Ho—O5	2.232(2)	Ho—O1	2.285(2)	Ho—O4	2.299(2)
Ho—O6	2.319(2)	Ho—O3A	2.401(3)	Ho—O2B	2.465(2)
Ho—O3	2.472(2)	Ho—O2	2.521(2)		
O5—Ho—O1	85.43(8)	O5—Ho—O4	104.41(9)	O1—Ho—O4	152.11(8)
O5—Ho—O6	75.88(9)	O1—Ho—O6	134.25(9)	O4—Ho—O2B	125.95(8)
O5—Ho—O3	165.84(8)	O1—Ho—O3	97.59(9)	O3A—Ho—O3	114.08(6)
O2B—Ho—O3	63.98(8)	O5—Ho—O2	142.43(8)	O3—Ho—O2	51.53(8)

Symmetry codes: A: $-x + 1/2, y - 1/2, z$; B: $-x + 1/2, y + 1/2, z$ for **1**, **4**; A: $-x + 1/2, y + 1/2, z$; B: $-x + 1/2, y - 1/2, z$ for **3**; A: $-x + 3/2, y + 1/2, z$; B: $-x + 3/2, y - 1/2, z$ for **2**, **5**.

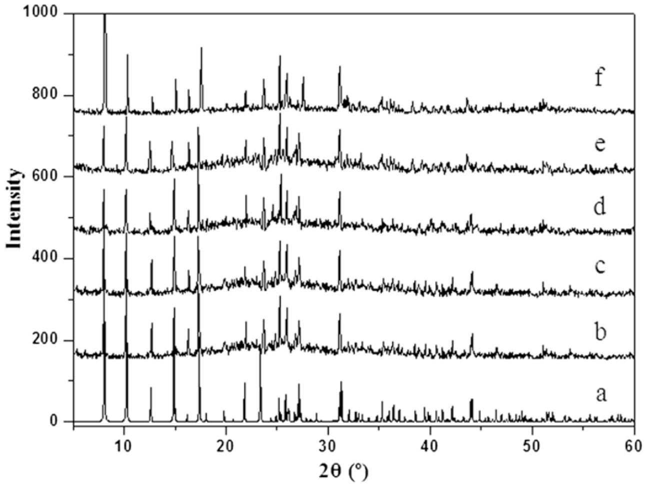


Fig. 1. The powder XRD patterns: (a) the simulated PXRD pattern calculated from single-crystal structure of complex **1**; (b) experimental PXRD for complex **1**; (c) experimental PXRD for complex **2**; (d) experimental PXRD for complex **3**; (e) experimental PXRD for complex **4**; (f) experimental PXRD for complex **5**.

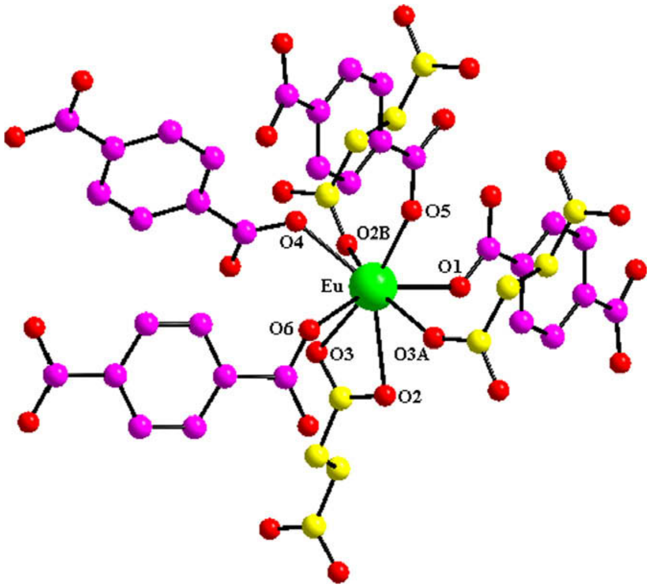
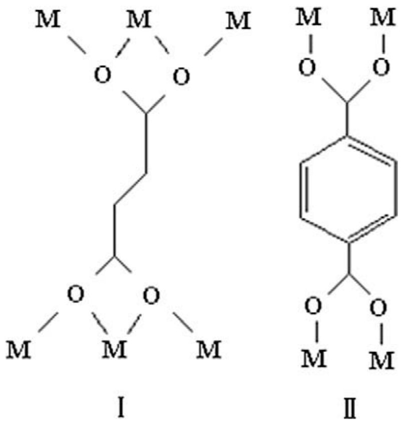


Fig. 2. Coordination environment of Eu in complex **1** with non-hydrogen atoms drawn by diamond. Carbon atoms of Suc ligands are yellow for being different from those of *p*-BDC ligands (purple). Symmetry codes: A: $-x + 1/2, y - 1/2, z$; B: $-x + 1/2, y + 1/2, z$.

Complex **1** shows a three-dimensional framework, in which the asymmetric unit contains one eight-coordinated europium ion, half a Suc ligand and a *p*-BDC ligand. The coordination mode of the europium ions (Eu) are shown in Fig. 2. The eight oxygen atoms coordinated with Eu are from two dimonodentate carboxyl groups (O1 and O2B) and one chelating bidentate carboxyl group (O2 and



Scheme 1. Coordination modes of the Suc (I) and *p*-BDC (II) Ligands in **1**–**5**.

O3) from Suc ligand, and four dimonodentate carboxyl groups (O1, O5, O7, and O9) from *p*-BDC ligand. The distances of Eu—O_{Suc} (from succinic acid) and $\text{Eu—O}_{p\text{-BDC}}$ (from 1,4-benzene dicarboxylic acid) are in the ranges of 2.441(2)–2.576(2), and 2.284(2)–2.366(2) Å, respectively, all of which are comparable to those reported for other europium–oxygen donor complexes [31,40]. For Suc ligand, its coordination mode in complex **1** is rare, compared to those reported Ln–Suc complexes [37,38,24]. Both carboxylate groups of each Suc ligand exhibit only one kind of coordination mode: μ_3–η^2–η^2-bridging (namely one oxygen atom of the carboxylate group connects two metal ions, the other one connects also two metal ions and the carboxylate group coordinates to three metal ions) (Scheme 1, I). And the Suc ligand assumes a anti conformation with the torsion angle of C8–C9–C9E–C8E being 180.0°, which is similar

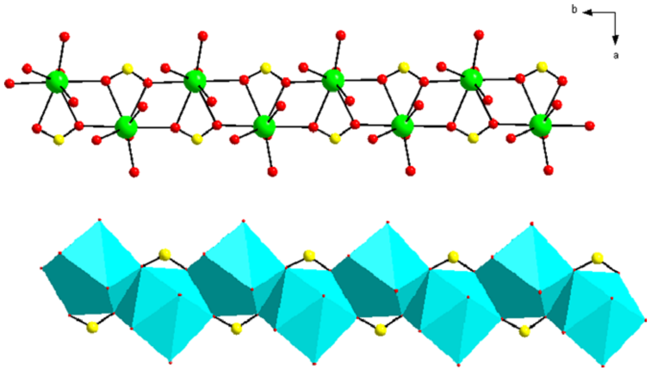


Fig. 3. A polyhedra chain (sharing edges) formed by Eu and its corresponding centrosymmmtric atoms through the tetradentate carboxylate bridging interactions of Suc ligands. Hydrogen atoms are omitted for clarity.

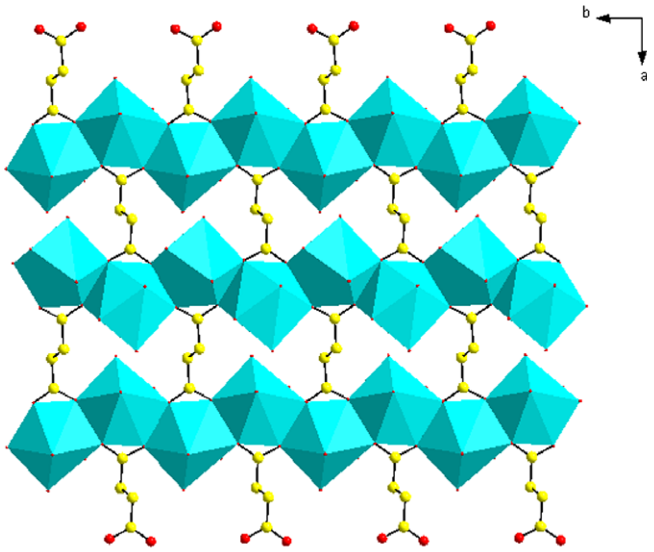


Fig. 4. Two-dimensional layer structure formed polyhedra chains linked to each other by the Suc ligands on [1 1 0] plane. Hydrogen atoms and parts of *p*-BDC ligands are omitted for clarity.

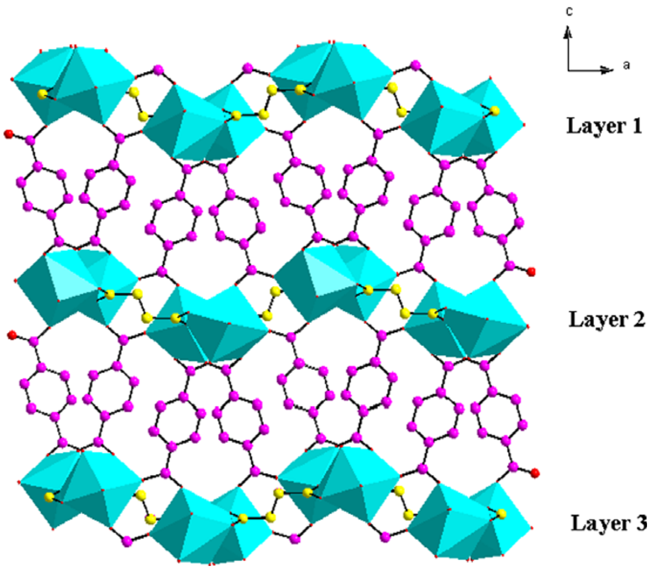


Fig. 5. The layers link to each other by *p*-BDC ligands to form 3D framework.

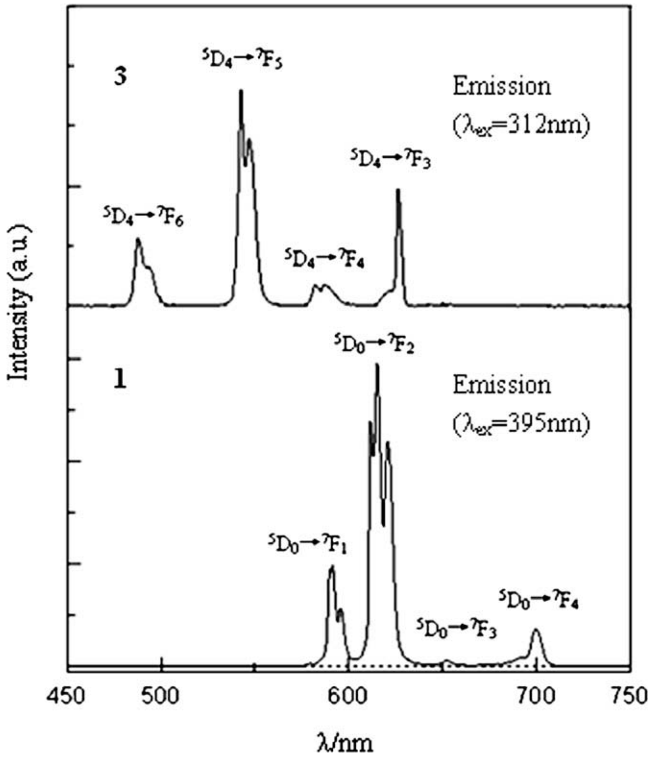


Fig. 6. Room-temperature solid-state photoluminescence spectra of complexes **1** (bottom) and **3** (top).

Table 3
The detailed attribution of IR for **1**–**5**.

	1	2	3	4	5
$\nu_{s(COO)^-}$	1402	1402	1402	1402	1405
$\nu_{as(COO)^-}$	1541	1540	1542	1536	1542
$\nu_{C=C}$ of vibration of benzene ring	1617	1617	1620	1614	1621
$\nu_{=C-H}$ of benzene	3057	3057	3057	3057	3057
$\delta_{=C-H}$ out of the face of benzene	823	823	824	822	825
1,4-Substitutions of the benzene ring	683, 748	683, 748	685, 749	681, 747	687, 748
ν_{C-H} vibrational modes of –CH_2– groups	2854, 2924	2854, 2923	2854, 2923	2854, 2925	2853, 2926

to that of reported complexes, such as the torsion angle in complex $[Eu_2(Suc)_3(H_2O)_2]_n$ is 179.2 ° [24]. For *p*-BDC ligand, each of two carboxylate groups of it adopts a μ_2–η^1–η^1-bridging (namely one oxygen atom of the carboxylate group connects one metal ion, the other one connects also one metal ion and the carboxylate group coordinates to two metal ions) (Scheme 1, II).

To deeply understand the structures of frameworks and coordinated carboxylate molecular conformation, it would be important to explore the connection ways of the metal centers and carboxylate ligands. In complex **1**, Lanthanide metal center atoms (Eu) and its corresponding centrosymmetric atoms are linked through bridging tetradentate carboxyl groups of Suc ligands to form a one-dimensional (1D) infinite edge-sharing EuO_8 polyhedra chain along the [0 1 0] direction (Fig. 3). These polyhedra chains connect each other by the carbon atoms of Suc ligands on the [1 1 0] plane to form a 2D layer structure (Fig. 4). As a good rigid linker, two carboxyl groups and a phenyl group of *p*-BDC ligand play an important fixing role in the structure of **1**. For both carboxyl groups of each *p*-BDC ligand, one links two adjacent Eu atoms of one polyhedra chain to fix the structure of the chain itself, the other links two adjacent Eu atoms of two adjacent chains to fix the connection of chains. Along the [1 0 0] direction, the coordination ways of *p*-BDC ligands appear inverted alternately in pairs. Furthermore, the layers are linked by phenyl groups of *p*-BDC ligands into a 3D framework structure (Fig. 5).

3.2. Photoluminescent properties

The solid-state luminescent properties of complexes **1** and **3** were investigated at room temperature. When excited at 395 nm for **1** and 312 nm for **3**, they emit red light (**1**) and green luminescence (**3**) at room temperature (Fig. 6). The emission peaks of the complexes correspond to the transitions from $^5D_0 \rightarrow {}^7F_n$ (n = 1, 2, 3 and 4) transitions at 590, 618, 652, and 700 nm for the Eu(III) ion in **1** and $^5D_4 \rightarrow {}^7F_n$ (n = 6, 5, 4, and3) transitions at 490, 544, 583, and 621 nm for the Tb(III) ion in **3**. Among these emission lines, the most striking red emissions ($^5D_0 \rightarrow {}^7F_2$) for complex **1** and green luminescence ($^5D_4 \rightarrow {}^7F_5$) for complex **3** were observed in their emission spectra. The luminescent characters of them are similar to those of $[Ln_2\ (Suc)_{0.5}(B\text{-}C)_3(OH)_2]$ (Ln = Tb, Eu) [31].

3.3. IR spectrum

The complexes **1–5** display the similar IR spectral shape. For complex **1**, peaks appearing at 1402 and 1540 cm^{-1} should be assigned to the symmetric and asymmetric stretching vibrations of the carboxyl groups. The bands at 1617, 3057, 823, 748 and 683 cm^{-1} are attributed to the aromatic skeleton vibration of the benzene ring, $\upsilon_{=C-H}$ of benzene, $\delta_{=C-H}$ out of the face of benzene, and the 1,4-substitutions of the benzene ring, respectively. The bands of 2854 and 2923 cm^{-1} are characteristic of the υ_{C-H} vibration modes of –CH_2– groups within the carbon chain of succinic acid. The absence of strong bands ranging from 1690 to 1730 cm^{-1} indicates that the ligands are deproponated. The detailed attribution of IR for complexes **1–5** is listed in Table 3.

4. Conclusions

Five new three-dimensional isostructural complexes $[Ln(Suc)_{0.5}(p\text{-BDC})]$ (Ln = Eu(**1**), Sm(**2**), Tb(**3**), Pr(**4**), Ho(**5**)) have been synthesized under hydrothermal condition. X-ray diffraction analyses reveal that they are crystallized in the orthorhombic space group *Pbca*. The 3D framework structures of complexes **1–5** are formed by *p*-BDC ligands connecting the 2D layers of lanthanide ions and Suc ligands. At room temperature, complexes **1** and **3** emit red and green luminescence, respectively, and no solvent molecule is directly connected to the framework of them, so it would be a useful feature to produce functional luminescent materials considering the quenching effect of –OH oscillators on luminescence.

5. Supplementary material

Crystallographic data for the four complexes in this paper have been deposited at the Cambridge Crystallographic data center, CCDC Nos. 687565, 687564, 694475, 687567, 694476 are for complexes **1–5**, 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 Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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