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Syntheses and characterization of novel lanthanide adamantine–dicarboxylate coordination complexes

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ABSTRACT

Hydrothermal reactions of 1,10-phenanthroline (phen), 1,3-adamantanedicarboxylic acid (H_2L) and lanthanide chlorides yielded six compounds: [*Ln*(L)(HL)(phen)] (*Ln* = Pr, **1**; Nd, **2**), [*Ln*(L)(HL)(phen)(H_2O)] (Sm, **3**; Eu, **4**), [Tb(L)(HL)(phen)(H_2O)]$_2 \cdot 2H_2O$ (**5**), [Er_3(L)$_4$(OH)(phen)]$_2$ (**6**). Compounds **1**–**4** are structurally featured by one-dimensional polymeric chains; 5 hold binuclear structure constructed from eight-coordinated lanthanide center LnN_2O_6 of distorted bicapped trigonal prism bridged by dicarboxylate ligands; 6 shows that erbium ions are in mono and bicapped trigonal prismatic geometries, respectively, which are further connected by μ_3-OH to give rise to trinuclear structure. Thermogravimetric analyses of **1**, **3** and **5** were performed. Fluorescent measurements of **4** and **5** were carried out, respectively.

1. Introduction

Design and syntheses of lanthanide complexes are of great interest due to their various topological networks and crystal packing motifs as well as potential applications in fluorescent probes, magnetic materials, catalysts, molecular sensors [1–13]. In virtue of the large radii and high coordination number of lanthanide metals, the assembly of lanthanide complexes may encounter many difficulties and great challenges in terms of controlling their shapes and dimensions. However, the fascinating structures and special properties of lanthanide complexes have attracted increasing attention of scientists, and extensive investigation has been reported in the recent years [14–26].

It has been documented that the geometries and properties of organic ligands exert great effect on structural frameworks of lanthanide complexes, thus much effort has been devoted to modify the building blocks and to control the assembled motifs for desired products through the selection of different organic ligands. Previous studies have shown that rigid bridging ligands containing multicarboxylate groups are versatile ones for constructions of the robust networks or other porous coordination polymers [27–35]. As known, lanthanide ions have high affinity for hard donor atoms, and ligands with oxygen or hybrid oxygen–nitrogen atoms, especially multicarboxylate ligands are usually employed in construction for lanthanide complexes. 1,3-adamantanedicarboxylic acid possesses intriguing coordination behaviors and potential hydrogen-bond interactions, such as asymmetric geometry and multiple coordination sites. However, former studies on the coordination chemistry of 1,3-adamantanedicarboxylic acid are mainly focused on transition metals [36–38], and those on lanthanide matals were very limited [39]. Recently we began to use adamantanedicarboxylic acid as organic ligand to synthesize lanthanide complexes, aiming at studying the coordination chemistry of lanthanide adamantanedicarboxylic acid as well as at obtaining some novel structures. By means of hydrothermal technique, six new lanthanide complexes have successfully prepared with 1,3-adamantanedicarboxylic acid. This paper will report about the syntheses and characterizations of a series of lanthanide adamantine–dicarboxylate complexes, [*Ln*(L)(HL)(phen)] (*Ln* = Pr, **1**; Nd, **2**), [*Ln*(L)(HL)(phen)(H_2O)] (Sm, **3**; Eu, **4**), [Tb(L)(HL)(phen)(H_2O)]$_2 \cdot 2H_2O$ (**5**), [Er_3(L)$_4$(OH)(phen)]$_2$ (**6**).

2. Experimental section

2.1. Materials and methods

Except $LnCl_3 \cdot nH_2O$, which was prepared in our laboratory, all chemicals of reagent grade were commercially available and used without further purification. Elemental analyses(C, H and N) were performed using a Perkin-Elmer 2400 CHNS/O analyzer. The infrared spectrum of KBr pellets in the range 4000–400 cm^{-1} was recorded on a Shimadzu FTIR-8900 spectrometer.

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Thermogravimetric measurements were carried out from room temperature to 1000 °C for **1**, to 800 °C for **3** and **5** on preweighed samples in nitrogen stream using a Seiko Exstar6000 TG/DTA6300 apparatus with a heating rate of 10 °C/min. All the excitation and emission spectra were measured with an Aminco Bowman Series 2 instrument with a xenon arc lamp as the excitation light source for the solid-state samples at room temperature.

2.2. Preparation of complexes

2.2.1. Synthesis of [Pr(L)(HL)(phen)] (*1*)

Pale green powder of $PrCl_3 \cdot nH_2O$ was obtained by slow evaporation of a solution of Pr_2O_3 dissolved in HCl (10 mL) under water boiling condition. A mixture of 1,3-adamantanedicarboxylic acid (H_2L, 0.30 mmol, 0.0673 g), the above-prepared $PrCl_3 \cdot nH_2O$ (0.106 g) and 1,10-phenanthroline (phen, 0.30 mmol, 0.0595 g) in water (10 mL) was stirred for 1.0 h, and then sealed in a 23 mL Teflon-lined stainless autoclave, which was heated at 170 °C for six days and thereafter cooled slowly at 10 °C/h to room temperature, and pale green crystals were seperated by filtering and washing with absolute ethanol (Yield 40%, based on Pr_2O_3). Anal. Cacd (%) for $C_{36}H_{37}N_2O_8Pr$ (766.61): C 56.40, H 4.86, N 3.65. Found (%): C 56.85, H 4.97, N 3.59. IR(ν cm^{-1}): 3396ms, 3055vw, 2903s, 2849s, 1684vs, 1608vs, 1518vs, 1408vs, 847s, 731s.

2.2.2. Synthesis of [Nd(L)(HL)(phen)] (*2*)

Pale red crystal were prepared analogously to **1** except using Nd_2O_3 instead of Pr_2O_3 (Yield 35%). Anal. Cacd (%) for $C_{36}H_{37}N_2O_8Nd$ (769.94): C 56.16, H 4.84, N 3.64. Found (%): C56.19, H 4.71, N 3.58. IR (ν cm^{-1}): 3422ms, 3080vw, 2883s, 2847s, 1697vs, 1589vs, 1518vs, 1408vs, 851s, 731s.

2.2.3. Synthesis of [Sm(L)(HL)(phen)(H_2O)] (*3*)

Yellow powder of $SmCl_3 \cdot nH_2O$ was obtained by slow evaporation of a solution of Sm_2O_3 (0.150 mmol, 0.0525 g) dissolved in HCl (10 mL) under water boiling condition. A mixture of 1,3-adamantanedicarboxylic acid (0.30 mmol, 0.0673 g), the above-prepared $SmCl_3 \cdot nH_2O$ and 1,10-phenanthroline (0.30 mmol, 0.0595 g) in water (10 mL) was stirred for 30 min, and then sealed in a 23 mL Teflon-lined stainless autoclave, which was heated at 160 °C for three days and thereafter cooled slowly to room temperature, and pale yellow crystals were seperated by filtering and washing (Yield 30%, based on Sm_2O_3). Anal. Cacd (%) for $C_{36}H_{39}N_2O_9Sm$ (794.07): C 54.45, H 4.95, N 3.53. Found (%): C 55.01, H 4.81, N 3.64. IR(ν cm^{-1}): 3402ms, 3080w, 2902s, 1685vs, 1610vs, 1514vs, 1408vs, 848s, 729s.

2.2.4. Synthesis of [Eu(L)(HL)(phen)(H_2O)] (*4*)

Colorless crystals were prepared analogously to **3** except using Eu_2O_3 instead of Sm_2O_3 (Yield 45%). Anal. Cacd (%) for $C_{36}H_{39}N_2O_9Eu$ (796.67): C 54.34, H 4.94, N 3.52. Found (%): C54.57, H 4.82, N 3.48. IR (ν cm^{-1}): 3410ms, 3059vw, 2902s, 2849s, 1684vs, 1612vs, 1522vs, 1418vs, 847s, 730s.

2.2.5. Synthesis of [Tb(L)(HL)(phen)(H_2O)]$_2$···2H_2O (*5*)

Pale green powder of $TbCl_3 \cdot nH_2O$ was obtained by slow evaporation of a solution of Tb_4O_7 (0.07 mmol, 0.0549 g) dissolved in HCl (5 mL) under water boiling condition. A mixture of 1,3-adamantanedicarboxylate (0.30 mmol, 0.0672 g), $TbCl_3 \cdot nH_2O$ nd 1,10-phenanthroline (0.30 mmol, 0.0595 g) in water (10 mL) was stirred for 30 min, and sealed in a 23 mL Teflon-lined stainless autoclave, which was heated at 170 °C for three days and thereafter cooled slowly to room temperature, and Pale green crystals were seperated by filtering and washing (Yield 30%). Anal. Cacd (%) for $C_{36}H_{41}N_2O_{10}Tb$ (820.65): C 52.69, H 5.04, N 3.41. Found (%): C 52.78, H 5.13, N 3.36. IR (ν cm^{-1}): 3410ms, 3059vw, 2902s, 2849s, 1684vs, 1612vs, 1522vs, 1418vs, 847s, 729s.

2.2.6. Synthesis of [Er_3(L)$_4$(OH)(phen)]2 (*6*)

Pale red crystals were prepared similarly to **5** except using Er_2O_3 instead of Y_2O_3 (Yield 15%). Anal. Cacd (%) for $C_{120}H_{130}N_4O_{34}Er_6$ (3175.92): C 45.38, H 4.13, N 1.76; Found: C 45.51, H 4.06, N 1.79; IR (ν cm^{-1}): 3410ms, 3059vw, 2902s, 2849s, 1684vs, 1612vs, 1522vs, 1418vs, 847s, 731s.

2.3. X-ray crystallography

Suitable crystals of **1**–**6** were selected under a polarizing microscope and fixed with epoxy cement on respective fine glass fibers which were then mounted on a RIGAKU RAXIS-RAPID diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) for cell determination and subsequent data collection for in the range of $3.22 \leqslant \theta \leqslant 27.48°$. Empirical absorption corrections were applied using the SADABS program. SHELXS-97 and SHELXL-97 programs were used for structure solution and refinement [40,41]. The structures were solved by using direct methods and followed by successive Fourier and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters by full-matrix least-squares technique and all hydrogen atoms with isotropic displacement parameters. Detailed information about the crystal data and structure determination is summarized in Table 1. Selected interatomic distances and bond angles are given in Tables 2–7 (See in Supporting Materials). Crystallographic data (excluding structure factors) for complexes **1**–**6** in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publications.

3. Results and discussion

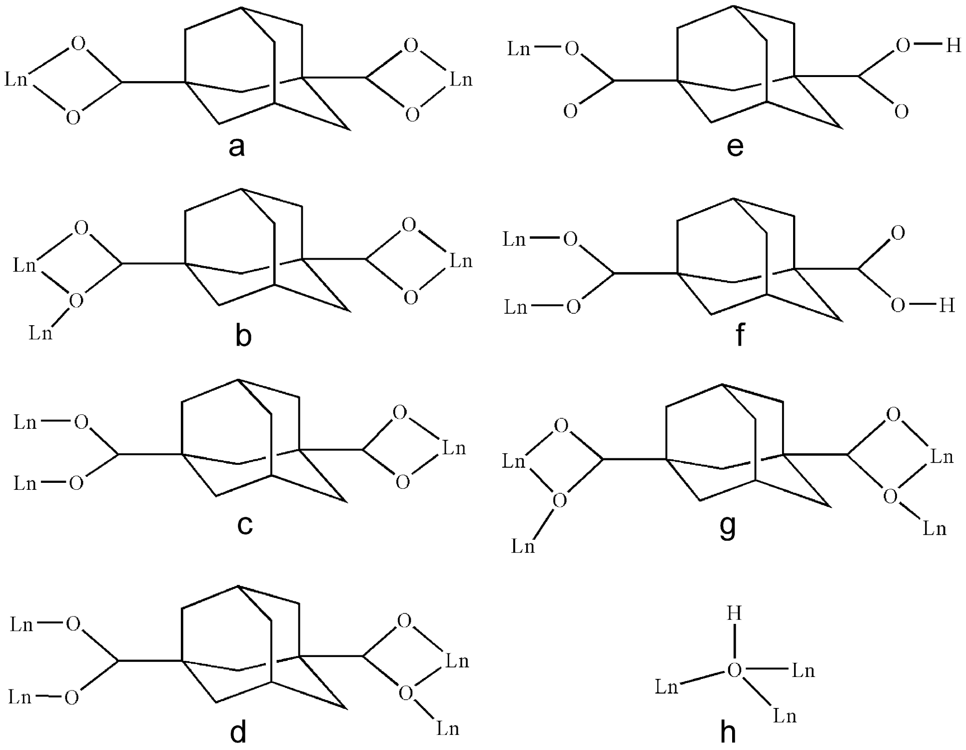
3.1. Syntheses of the complexes

Owing the hydrophobility of the adamantane framework, 1,3-adamantanedicarboxylic acid was found to be uneasily dissolved in common solvents such as H_2O, MeOH, EtOH, THF, etc. under ambient condition, therefore, the reactions of the dicarboxylatic acid with lanthanide chlorides were carried out under the similar hydrothermal conditions in order to obtain new complexes with novel networks. Six lanthanide metal-organic complexes suitable for single crystal X-ray diffraction were obtained. 1,3-adamantanedicarboxylates function as linkers in various fashions (monodentate, bidente bridging, bidentate chelate, bidente chelating–bridging etc.) through its carboxylate groups in these complexes (Scheme 1), demonstrating its versatility in construction of the robust network or porous functional materials [36–39]. The structural analyses show that *Ln*(III) ions are the nine-coordinated modes in **1** and **2**, the eight-coordinated modes in **3**, **4** and **5**, the 8/7-coordinated fashions in **6**, respectively. On the other hand, complexes **1**, **2**, **3** and **4** possess one-dimensional chain frameworks, however, complex **5** is binuclear structure, and complex **6** has double chains extended by two inequivalved structural units. The different geometries and structures may result from the effects of the lanthanide contraction on crystal structural formation, which would offer a helpful route to design and synthesize lanthanide compounds with the special structural networks.

Table 1
Crystallographic data for **1–6**

	1	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{36}H_{37}N_2O_8Pr$	$C_{36}H_{37}NdN_2O_8$	$C_{36}H_{39}N_2O_9Sm$	$C_{36}H_{39}EuN_2O_9$	$C_{36}H_{41}N_2O_{10}Tb$	$C_{120}H_{130}Er_6N_4O_{34}$
Formula mass	766.59	769.92	794.04	795.65	820.63	3175.84
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a	11.167(2)	11.141(2)	11.153(2)	11.133(2)	8.636(2)	12.805(3)
b	12.407(3)	12.403(3)	12.329(3)	12.312(3)	13.573(3)	18.094(4)
c	13.292(3)	13.302(3)	12.651(3)	12.681(3)	14.579(3)	26.128(5)
α (deg)	109.38(3)	109.36(3)	109.04(3)	109.13(3)	94.59(3)	80.69(3)
β (deg)	98.54(3)	98.57(3)	97.19(3)	97.31(3)	96.33(3)	86.39(3)
γ (deg)	110.16(3)	110.20(3)	99.83(3)	99.72(3)	92.30(3)	84.09(3)
V (Å^3)	1557.4(5)	1553.7(5)	1589.5(5)	1587.2(5)	1691.0(6)	5936.2(2)
Z	2	2	2	2	2	2
ρ (Mg/m^3)	1.635	1.646	1.659	1.665	1.612	1.777
μ (mm^{-1})	1.623	1.730	1.909	2.038	2.513	4.274
F (000)	780	782	806	808	832	3116
θ range (deg)	3.02–27.48	3.02–27.48	3.04–27.48	3.04–27.48	3.02–27.48	3.04–27.48
Reflns collected	15337	15251	15768	15453	16764	54559
Reflns independent	7068	7009	7237	7168	7671	25969
Reflns observed	6789	6423	6872	6663	6824	18087
R1 [$I \geqslant 2\sigma(I)$]	0.0188	0.0427	0.0300	0.0320	0.0276	0.0611
R1 (all data)	0.0202	0.0468	0.0318	0.0357	0.0344	0.0940
GOF	1.190	1.095	1.192	1.161	1.074	1.002

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



Scheme 1. Linking fashions of the adamantanedicarboxylate groups.

3.2. *Description of the crystal structures*

X-ray diffraction studies reveal that the asymmetric unit of complex **1** contains one Pr(III) ion, one phen ligand and two kinds of coordiantion styles of 1,3-adamantanedicarboxylate ligand (HL^{1-}, L^{2-}). As shown in Fig. 1a, the nine-coordinated Pr(III) ion is in a tricapped trigonal antiprism LnN_2O_7 defined by seven oxygen atoms of the different 1,3-adamantanedicarboxylate and two N atoms of one phen ligand with Pr–O distances ranging from 2.408 to 2.742 Å (average 2.512 Å), Pr–N distances of 2.674 and 2.700 Å (average 2.687 Å). For adamantane–dicarboxylate ligand of each structural unit, L^{2-} acts as a μ_3-bridge to link three Pr(III) ion with one carboxylate group adopting a bidentate chelate mode coordinating to one praseodymium ion and the other adopting a bidente chelating–bridging mode connecting two praseodymium ion (Scheme 1b) [42,43]; HL^{1-}, the monoprotonated adamantanedicarboxylate, links two praseodymium ions through the carboxylate group acting as a bidentate bridge mode and the protonated end remains uncoordinated (Scheme 1f). Two adjacent praseodymium ions are held together to form a dimeric subunit

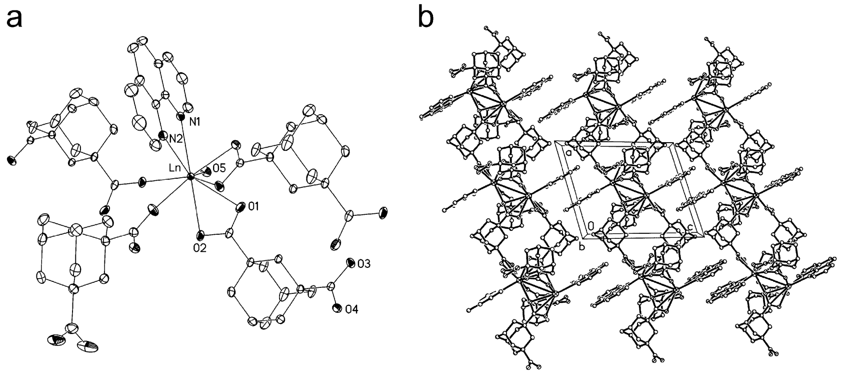


Fig. 1. (a) ORTEP view of coordination environments of *Ln*(III) ion with 30% displacement ellipsoids and (b) two dimensional layer structure projected along *b* axis in **1** and **2**.

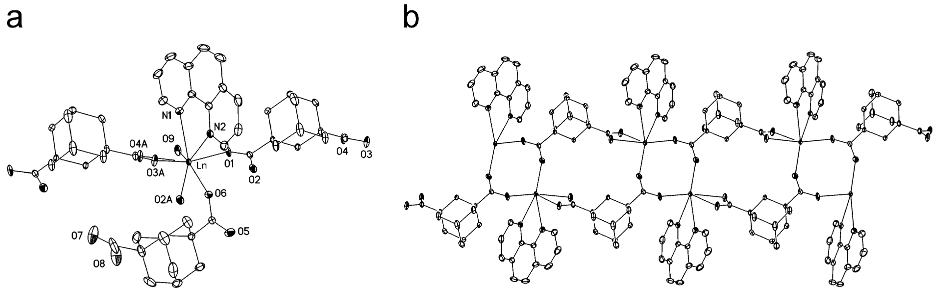


Fig. 2. (a) ORTEP view of coordination environments of *Ln*(III) ion with 30% displacement ellipsoids and (b) a fragment of a double chain along *c* axis in **3** and **4**.

$[Pr_2(L)_2(HL)_2(phen)_2]$ by the carboxylates with Pr–Pr distance of 3.96 Å, implying no significant direct interaction between metal ions.

$[Pr_2(L)_2(HL)_2(phen)_2]$ can be viewed as the basic building block for the whole structure of **1**. Each pair of such blocks are bridged by adamantanedicarboxylate bridging, giving rise to a double chain. The chains are further connected through strong offset face-to-face $\pi\cdots\pi$ stacking interaction with a mean interplanar distance of 3.25 Å between the adjacent aromatic rings to generate two-dimensional network (Fig. 1b). Complex **1** finally forms three-dimensional packing structure by hydrogen bond of the carboxylate oxygen atoms with $O\cdots O$ distance 2.658 Å and $\angle(O\text{–}H\cdots O) = 161^\circ$, as well as weak $C\text{–}H\cdots O$ and $C\text{–}H\cdots N$ interactions with $C\cdots O = 3.385$ Å and $\angle(C\text{–}H\cdots O) = 149^\circ$; $C\cdots N = 3.349$ Å, and $\angle(C\text{–}H\cdots N) = 155^\circ$, respectively (Fig. S10).

Complex **2**, being isomorphous to **1**, possesses one-dimensional network by covalent bonding. The Nd–O distances fall in a range from 2.393–2.742 Å (average 2.509 Å), and Nd–N from 2.660 to 2.685 Å (average 2.673 Å), which slightly shorter than oens in **1**, resulting from the effect of lanthanide contraction.

Complexes **3** and **4** are allomers with one-dimensional chain structure by covalent bonding. Two kinds of coordination modes of adamantanedicarboxylate (HL^{1-}, L^{2-}) are present in the structre: L^{2-} acts as μ_3-bridge to link three *Ln*(III) ion, in which one carboxylate group adopts a bidentate chelate mode coordinating to one lanthanide ion while the other adopts a bidente bridging mode connecting two lanthanide ion (Scheme 1c) [42–45]; and HL^{1-}, the protonated adamantanedicarboxylate, links only one lanthanide ion through the carboxylate group acting as a monodentate mode while the protonated one remains uncoordinated to metal ion (Scheme 1e). As shown in Fig. 2a, the Sm(III) or Eu(III) ion is in a eight-coordinated geometry defined by four oxygen atoms from L^{2-}, one oxygen from the HL^{1-}, one aqua oxygen atom and two nitrogen atoms from phen ligand, forming a distorted bicapped trigonal prism LnN_2O_6 with the metal to ligating atom distances Sm–O = 2.297–2.512 Å, Sm–N = 2.633–2.659 Å in 3; Eu–O = 2.2291–2.499 Å, Eu–N = 2.620–2.643 Å in 4. $[Ln_2(L)_2(phen)_2]$, being as dimeric subunits, are formed by carboxylate linkers, which are reproduced through adamantanedicarboxylate bridging, giving rise to a double chain structure (Fig. 2b). The chains are further extended into two-dimensional network through hydrogen bonds between the carboxylate and aqua oxygen atoms with distance $O\text{–}H\cdots O = 2.647\text{–}2.878$ Å and $\angle(O\text{–}H\cdots O) = 150^\circ$, as well as weak $C\text{–}H\cdots O$ interaction with $C\text{–}H\cdots O = 3.352$ Å and $\angle(C\text{–}H\cdots O) = 147^\circ$ in 3;

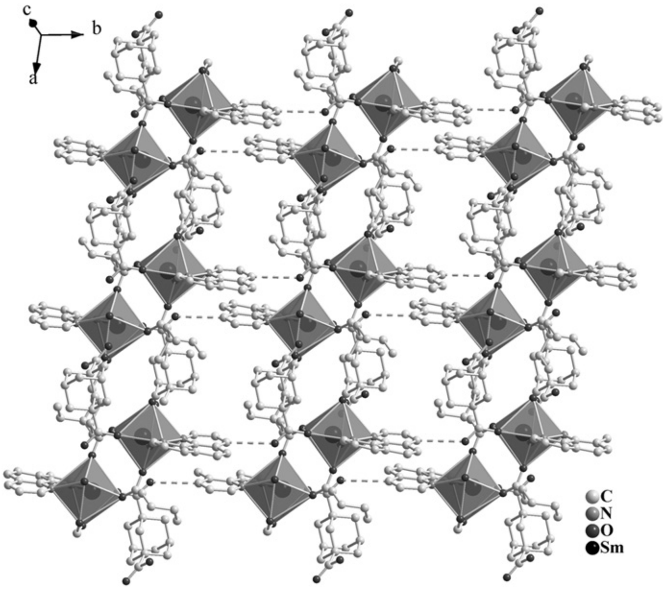


Fig. 3. Two-dimensional network through hydrogen bonds in **3** and **4**.

O–H···O = 2.643–2.873 Å, ∠(O–H···O) = 149 = 178°, C–H···O = 3.339 Å and ∠(C–H···O) = 147° in 4, respectively (Fig. 3).

Complex **5** possesses binuclear structural motifs constructed by Tb(III) ions, phen, water molecule and adamantanedicarboxylate (HL^{1-}, L^{2-}). As shown in Fig. 4, the Tb(III) ion is in a eight-coordinated fashion by four oxygen atoms from L^{2-}, one oxygen from HL^{1-}, one oxygen from a coordination water and two nitrogen atoms from a phen ligand, forming a distorted bicapped trigonal prism TbN_2O_6 with distances Tb–O = 2.248–2.445 Å, Tb–N = 2.525–2.577 Å. The adamantanedicarboxylate ligands display two types of linking modes in the structures: L^{2-} acts as a μ_2-bridge to connect two Tb(III) ions with each carboxylate chelating one lanthanide ion (Scheme 1a); HL^{1-}, the protonated adamantanedicarboxylate, links a lanthanide ion by the deprotonated carboxylate group acting as a monodentate mode while the protonated end remains uncoordinated (Scheme 1e). Different kinds of hydrogen bondings are observed in 5: (a) hydrogen bondings between uncoordinated water molecule/coordinated water molecule (O···O distances: 2.552 Å); (b) uncoordinated water molecule/carboxylate oxygen atoms (O···O distances: 2.665, 2.698 Å); (c) coordinated water molecules/carboxylate oxygen atoms (O···O distance: 2.743 Å); The presence of the extensive hydrogen bonding interaction results in formation of one-dimensional chains, which further grow into two-dimensional layer-like network by offset face-to-face π···π stacking interaction with a mean interplanar distance of 3.383 Å between adjacent phen ligands belonging to neighboring chains (Fig. 5).

Compound **6** contains two types of crystallographic distinct units (A and B), each of which is composed of three Er(III) ions, one OH, one phen and four adamantanedicarboxylate ligands (Fig. 6). In asymmetry unit A, Er(III) ions have different coordination environments: Er1 and Er2 are eight-coordinated dodecahedron ErO_8 by one hydroxy oxygen atom, and seven carboxylate oxygen atoms with distances Er–O = 2.208–2.759 Å; Er3 is in seven-coordinated mode by two nitrogen atoms of phen, one hydroxy oxygen atom, four oxygen atoms of different adamantanedicarboxylates, forming capped octahedron with distances Er—O = 2.190–2.346 Å, Er–N = 2.494 and 2.531 Å, respectively; three Er(III) ions grow into an interesting trimeric unit $Er_3N_2O_{17}$ through sharing a common vertex of the polyhedra. In asymmetry unit B, Er4, Er6 and Er5 are similar to Er1, Er2 and Er3 in terms of cooridination modes. The adamantanedicarboxylate ligands exhibit two types of linking modes to bridge erbium ions in the structure: (a) the adamantane–dicarboxylate acts as μ_3-bridge to link three erbium ions, in which one carboxylate adopts a chelate mode coordinating to one erbium ion while the other adopts a bridging mode connecting two erbium ions (Scheme 1c); (b) acts as μ_4-bridge to link four erbium ions, in which one carboxylate adopts a bridging mode coordinating to two erbium ions while the other adopts a chelate bridging mode connecting two erbium ions (Scheme 1d). The OH-group acts as μ_3-bridge linking three erbium ions (Scheme 1h) with distances Er–O = 2.268, 2.349, 2.354 Å, Er–Er = 3.776–4.160 Å in the unit A; Er–O = 2.254, 2.345, 2.349 Å, Er–Er = 3.725–4.135 Å in the unit B, indicating no substantial interaction among erbium ions. The asymmetry units A and B grow into one-dimensional chains by covalent bonding, respectively, and are finally extended into three-dimensional supramolecular network by Van der Waals forces and weak C–H···O interacion with distances C···O = 3.34–3.42 Å (Fig. S11).

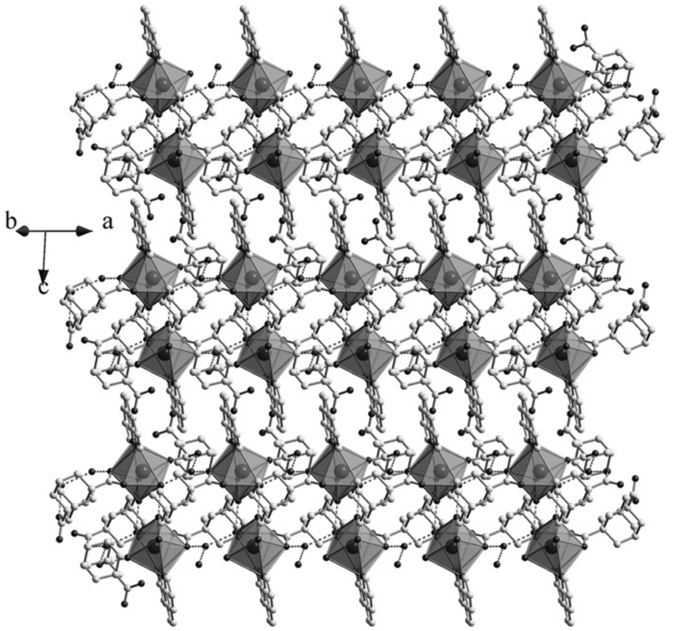


Fig. 5. Two-dimensional framework in **5**.

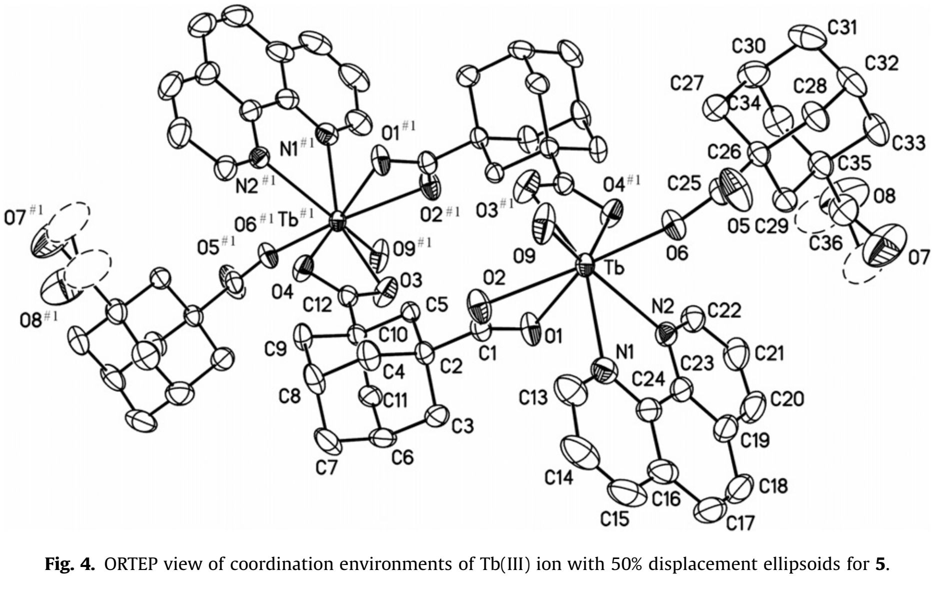


Fig. 4. ORTEP view of coordination environments of Tb(III) ion with 50% displacement ellipsoids for **5**.

3.3. Thermogravimetric analysis (TGA)

TGAs for complexes **1**, **3** and **5**, have been measured under a flow of nitrogen gas. The DTA curves of complex **1** display two endothermic peaks at 150 and 222 °C, respectively, which indicated that the complex undergo the chemical reactions or physical process at corresponding temperature. The first weight loss of 23.0% (calcd: 23.4%) over 150–298 °C corresponds well to the loss of one phen per formula unit [Pr(L)(HL)(phen)]. Upon further heating, one endothermic peak was observed at 570 °C with the final residue of 22.4% at 979 °C, presumably being Pr_2O_3 (calcd: 21.5%). For **3**, DTA studies show four endothermic peaks at 192, 330, 470 and 581 °C, respectively. The first weight loss of 2.14% (calcd: 2.26%) over 179–224 °C could be contributed to the dehydration of $[Sm(C_{12}H_{14}O_4)(C_{12}H_{15}O_4)(phen)(H_2O)]$. The second weight loss of 39.8% (calcd: 40.1%) from 310 to 345 °C results from release of one $C_{12}H_{15}O_4^-$ ligand and 0.5 molecular phen per molecular unit. The final decomposition product, is presumably Sm_2O_3, 19.8% (calcd: 20.7%) heating upon to 720 °C. For **5**, DTA studies show four endothermic peaks at 120, 200, 319 and 490 °C, respectively. The first weight loss of 4.35% (calcd: 4.39%) from 60 to 228 °C is due to the loss of two water per formula unit $[Tb(L)(HL)(phen)(H_2O)]_2 \cdot 2H_2O$; the second weight loss of 25.5% (calcd: 22.2%) from 260 to 364 °C corresponds to the loss of one phen per formula unit. The final decomposition product is assumed to be Tb_3O_4, 20.0% (calcd: 21.9%).

3.4. Fluorescence properties

Complex **4** in solid-state displays three fluorescent emission peaks at 580 (weak), 592 (mediate) and 614 nm (strong) upon photoexcitation at 341 nm, respectively (Fig. 7). The photoluminescence emission may be assigned to the excitated radiative decay of europium ions: 614 nm attributed to $^5D_0 \rightarrow {}^7F_2$, 592 nm attributed to $^5D_0 \rightarrow {}^7F_1$, and 580 nm attributed to $^5D_0 \rightarrow {}^7F_0$ energy transitions by 4*f*–4*f* orbits [46–49], which are consistent with the known characteristic peaks of europium ions, indicating that the effect of the photoluminescence of organic ligands could be negligible in compound **4**.

As shown in Fig. 8, compound **5** presents four fluorescent emission peaks: 491 nm ($^5D_4 \rightarrow {}^7F_6$, strong), 545 nm ($^5D_4 \rightarrow {}^7F_5$, very strong), 585 nm ($^5D_4 \rightarrow {}^7F_4$, weak) and 623 nm ($^5D_4 \rightarrow {}^7F_3$, very

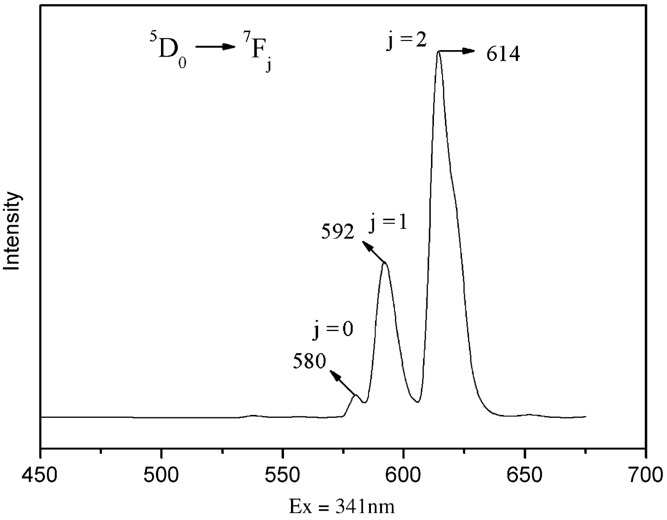


Fig. 7. The solid-state luminescent spectrum for **4**.

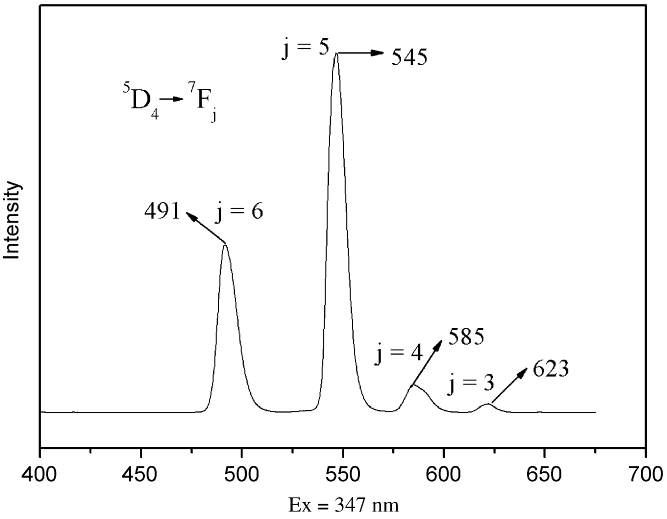


Fig. 8. The solid-state luminescent spectrum for **5**.

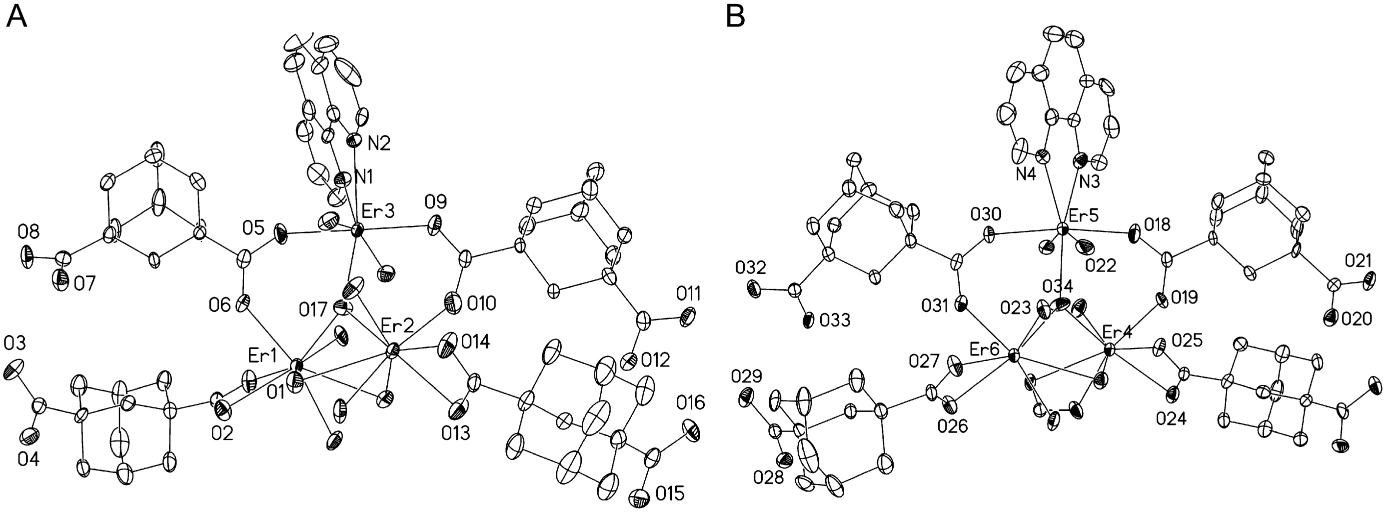


Fig. 6. Local coordination environment of erbium ions with 30% displacement ellipsoids in **6**.

weak), respectively, in the solid state upon photoexcitation at 347 nm. The strong luminescence emission at 545 nm may result from supersensitive effect of the terbium ion. The peak positions of fluorescent emission of the Tb-compound are consistent with the known ones for free terbium ions, indicating that the effect of the photoluminescence of organic ligands could be negligible in compound **5**.

4. Conclusions

In summary, six new lanthanide metal-organic frameworks have been synthesized by hydrothermal reactions, and the complexes exhibit the different frameworks. The diverse structures imply subtle effects of lanthanide ion radii on crystal structural formation. Complex **5** illustrates remarkable thermal stability and strong photoluminescent emission at the solid state. The contribution may afford useful information for the construction of lanthanide photoluminescent materials.

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Appendix A. Supporting information available

X-ray crystallographic files for compounds **1**–**6** in CIF format, IR spectra for **1**–**6**, TGA spectra for 1, 3 and 5. CCDC number 683833-683838 for **1**–**6** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44 1223/336 033; E-mail: deposit@ccdc.cam.ac.uk].

Appendix B. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2008.09.018.

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