

Synthesis, structure and luminescent properties of coordination polymers with 1,2-benzenedicarboxylic acid and a series of flexible dicarboxylate ligands†

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Received 5th August 2009, Accepted 5th October 2009

First published as an Advance Article on the web 19th October 2009

DOI: 10.1039/b916127a

A series of lanthanide coordination polymers, namely, $[\text{Ln}(\text{ox})_{0.5}(\text{phth})(\text{H}_2\text{O})_2] \cdot 0.5\text{H}_2\text{O}$ ($\text{Ln} = \text{Tb}$ (**1**), Sm (**2**); H_2ox = oxalic acid; H_2phth = 1,2-benzenedicarboxylic acid), $[\text{Ln}(\text{mal})_{0.5}(\text{phth})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}$ (**3**), Sm (**4**); H_2mal = maleic acid), $[\text{Pr}_3(\text{mal}')(\text{phth})_3(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ (**5**) ($\text{H}_2\text{mal}'$ = malic acid) $[\text{Eu}(\text{ad})_{0.5}(\text{phth})(\text{H}_2\text{O})_2]$ ($\text{Ln} = \text{Eu}$ (**6**), Sm (**7**); H_2ad = adipic acid), $[\text{Pr}_2(\text{ad})(\text{phth})_2(\text{H}_2\text{O})_4]$ (**8**) have been synthesized hydrothermally from the self-assembly of the lanthanide ions (Ln^{3+}) with different types of flexible dicarboxylate ligands and the rigid 1,2-benzenedicarboxylate ligand. All coordination polymers were characterized by elemental analysis, IR spectroscopy, and single-crystal X-ray diffraction. Structural analyses reveal that the networks of all eight complexes exhibit a variety of coordination modes at the metal centers. The thermal stabilities for **1**, **3**, **5**, **6**, **8**, photoluminescent properties for **1–4** and **6–7** were examined, and the results show that the complexes seem to be good candidates for novel hybrid inorganic–organic photoactive materials with excellent thermal stability.

Introduction

Nowadays, there has been increasing research on the crystal engineering of metal–organic frameworks (MOFs) for their unusual topology frameworks as well as their potential applications, such as: gas storage, catalysis, optical and magnetic applications.^{1–10} In this aspect, considerable work has been done to produce useful functional materials and frameworks with special topologies.^{11–14} In the synthetic process of lanthanide-based MOFs, it is found that the diversity of the coordination modes of the carboxylate groups to metal atoms influence the molecular packing arrangement of the complexes. In particular, coordination polymers consisted of just rigid multicarboxylate ligands (benzenic acids, 1,2,4,5-benzenetetracarboxylic acid,¹⁵ 1,3-benzenedicarboxylic acid (*m*-phthalic),¹⁶ 1,4-benzenedicarboxylic acid (*p*-phthalic),¹⁷ or single flexible multicarboxylate ligands (succinic acid, glutaric acid, adipic acid, *etc.*) have been studied, but lanthanide-containing MOFs with both rigid and flexible mixed multicarboxylate ligands are less developed.^{14,18–20} As we know, through competition among oxygen atoms from F (flexible) and R (rigid) for the lanthanide ions, the introduction of a flexible ligand into the system of a rigid ligand with lanthanide

ions leads to the formation of unforeseen lanthanide complexes, which are the so-called third generation coordination polymers with dynamic frameworks and striking functions. Recently, our group has been focusing ourselves on synthesizing a series of lanthanide coordination polymers with two types of carboxylates (rigid and flexible) and past research works have been reported: (i) $[\text{Ln}_2(\text{Suc})_{0.5}(\text{BC})_3(\text{H}_2\text{O})_2]$ ($\text{Ln} = \text{Tb}$, Eu , Sm , Pr ; H_2Suc = succinic acid; HBC = benzoic acid);¹⁹ (ii) $[\text{Ln}(\text{Suc})_{0.5}(p\text{-BDC})]$ ($\text{Ln} = \text{Eu}$, Sm , Nd , Pr , Ho ; H_2Suc = succinic acid; *p*- H_2BDC = 1,4-benzenedicarboxylic acid).²¹ $[\text{Ln}(\text{ad})_{0.5}(2,5\text{-pydc})(\text{H}_2\text{O})]$ ($\text{Ln} = \text{Eu}$, Pr , Nd , Sm , Tb ; H_2ad = adipic acid; 2,5- H_2pydc = 2,5-pyridinedicarboxylic acid).²² In order to have a further understanding on the influence of aliphatic acids with different number of carbon atoms on directed synthesis and molecular packing configuration, a series of flexible acids were used with 1,2-benzenedicarboxylic acid, as the rigid ligand which seems to be promising not only to control and adjust the open and stable framework, but also acts as a bridging ligand in various coordination modes.²³ To the best of our knowledge, only a few Ln-phthalate complexes have been reported, and they can sum up as two kinds, such as: (i) Ln-phen-phthalate, $\{[\text{Nd}_2(\text{phth})_3(\text{phen})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}$, $\{[\text{Ho}_2(\text{phth})_3(\text{phen})(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}\}_n$,²⁴ $\{\text{Sm}_3(\text{phth})_4(\text{phen})_2(\text{NO}_3)\}_n$,²⁵ $\text{Tb}_2(\text{phth})_2(\text{Hphth})_2(\text{phen})_2(\text{H}_2\text{O})_4$ ²⁶ and (ii) Ln-phth-M, $[\text{Nd}(\text{H}_2\text{O})(1,2\text{-bdc})\text{Ag}(\text{inic})_2](\text{ClO}_4)$, (*inic* = isonicotinic acid).²⁷ Among the complexes reported, they all contain just one type of carboxylic compound (rigid) as the ligand with different coordination modes. Considering the flexible acid; it may bend and rotate when it coordinates to the metal centers, causing structural diversity and producing useful properties.^{28–30} Although there are no lack of lanthanide coordination polymers with binary mixed dicarboxylate ligands, those with rigid and flexible dicarboxylate as mixed ligands are still rare,^{18,19} especially the luminescent properties of lanthanide coordination polymer containing both rigid and flexible as mixed ligands. Considering the factors above, it is necessary to

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† Electronic supplementary information (ESI) available: Tables listing selected bond lengths and bond angles and figures showing coordination environments of the Sm, chain structure, network structure, packing structure, and XRD patterns of complexes **2**, **4** and **7**. CCDC reference numbers 725100 (**1**), 725101 (**2**), 725102 (**3**), 725103 (**4**), 725104 (**5**), 725105 (**6**), 725106 (**7**) and 725107 (**8**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b916127a

investigate the influence on the structure and luminescent properties of lanthanide coordination polymer containing both rigid and flexible ligands. In our experiment, we chose 1,2-benzenedicarboxylic acid as the rigid ligand; oxalic, maleic and adipic acid as the flexible ligands to synthesize a new family of lanthanide coordination polymers. Herein, we report our work aimed at developing of (R + F) based lanthanide-containing MOFs: eight lanthanide-containing hybrid coordination polymers: [Tb(ox)_{0.5}(phth)(H₂O)₂]·0.5H₂O (**1**), [Sm(ox)_{0.5}(phth)(H₂O)₂]·0.5H₂O (**2**), [Eu(mal)_{0.5}(phth)(H₂O)₂]·H₂O (**3**), [Sm(mal)_{0.5}(phth)(H₂O)₂] (**4**), [Pr(mal')(phth)₃(H₂O)₂]·H₂O (**5**), [Eu(ad)_{0.5}(phth)(H₂O)₂] (**6**), [Sm(ad)_{0.5}(phth)(H₂O)₂] (**7**) and [Pr₂(ad)(phth)₂(H₂O)₄] (**8**), displaying diverse structural motifs, were successfully produced by the aggregation of lanthanide ions, an R ligand (1,2-benzenedicarboxylic acid), and a series of F ligands (oxalic acid, maleic acid and adipic acid). It is surprising that an unusual chemical rearrangement from maleic acid to malic acid occurs in the formation of **5**. In addition, the thermal stability of the **1**, **3**, **5**, **6** and **8** and luminescent properties of the **1–4**, **6** and **7** were primary evaluated by using thermogravimetric analysis and luminescent spectra.

Experimental

All chemicals purchased were of reagent grade or better and were used without further purification. Lanthanide chloride salts were prepared by dissolving lanthanide oxides with 12 M HCl while adding a bit of H₂O₂ for Tb₄O₇, and then evaporating at 100 °C until the crystal film formed. Lanthanide nitrate salts were prepared the same procedure as the chloride salts. The infrared spectra were recorded on a JASCO FT/IR-480 PLUS Fourier Transform spectrometer with pressed KBr pellets in the range 200–4000 cm⁻¹. The luminescence spectra were reported on a JASCO FP-6500 spectrofluorimeter (solid). The elemental analyses were carried out on a Perkin Elmer 240C automatic analyzer. Thermogravimetric analyses (TGA) were performed under N₂ atmosphere at 1 atm with a heating rate of 10 °C min⁻¹ on a Perkin Elmer Diamond TG/DTA. X-Ray powder diffraction (XRD) data were collected on a Bruker Advance-D8 with Cu Kα radiation, in the range 5° < 2θ < 60°, with a step size of 0.02° (2θ) and an acquisition time of 2 s per step.

Synthesis of [Tb(ox)_{0.5}(phth)(H₂O)₂]·0.5H₂O (**1**)

The complex was prepared by a hydrothermal reaction. A mixture of TbCl₃·6H₂O (0.12 g, 0.32 mmol), oxalic acid (0.10 g, 1.06 mmol), 1,2-benzenedicarboxylic acid (H₂phth, 0.10 g, 0.55 mmol), ethylenediamine (0.20 mL), and H₂O (12 mL) was sealed in a Teflon-lined autoclave and heated at 180 °C for four days, then cooled at 10 °C every 3 h to 100 °C, followed by slowly cooling to room temperature. White block crystals of **1** were obtained in *ca.* 56.87% yield (based on Tb). Anal. calcd for C₉H₉O_{8.5}Tb (412.09): C 26.23, H 2.20. Found: C 26.28, H 2.14. IR data (KBr pellet, ν/cm⁻¹): 3368, 1668, 1523, 1498, 1435, 1153, 881, 857, 798, 775, 714, 658, 583, 398.

Synthesis of [Sm(ox)_{0.5}(phth)(H₂O)₂]·0.5H₂O (**2**)

The complex was prepared by a hydrothermal reaction. A mixture of SmCl₃·6H₂O (0.12 g, 0.33 mmol), oxalic acid (0.10 g,

1.06 mmol), 1,2-benzenedicarboxylic acid (H₂phth, 0.10 g, 0.55 mmol), ethylenediamine (0.20 mL), and H₂O (12 mL) was sealed in a Teflon-lined autoclave and heated at 180 °C for four days, then cooled at 10 °C every 3 h to 100 °C, followed by slow cooling to room temperature. White block crystals of **2** were obtained in *ca.* 60.15% yield (based on Sm). Anal. calcd for C₉H₉O_{8.5}Sm (403.51): C 26.79, H 2.25. Found: C 25.83, H 2.31. IR data (KBr pellet, ν/cm⁻¹): 3368, 1668, 1523, 1498, 1435, 1153, 881, 857, 798, 775, 714, 658, 583, 398.

Synthesis of [Eu(mal)_{0.5}(phth)(H₂O)₂]·H₂O (**3**)

A mixture of EuCl₃·6H₂O (0.12 g, 0.33 mmol), maleic acid (H₂mal, 0.10 g, 0.82 mmol), and 1,2-benzenedicarboxylic acid (0.10 g, 0.55 mmol), H₂O (12 mL) and 1 mol L⁻¹ KOH 0.5 mL, was sealed in a Teflon-lined autoclave and heated at 180 °C for three days, then cooled at 10 °C every 3 h to 100 °C, followed by slow cooling to room temperature. White block crystals of **3** were obtained in *ca.* 56.78% yield (based on Eu). Anal. calcd for C₁₀H₁₁O₉Eu (427.15): C 32.78, H 2.58. Found: C 32.56, H 2.71. IR data (KBr pellet, ν/cm⁻¹): 3425, 1552, 1404, 879, 851, 778, 717, 696, 454, 381.

Synthesis of [Sm(mal)_{0.5}(phth)(H₂O)₂]·H₂O (**4**)

The procedure was the same as that for **3** except that EuCl₃·6H₂O was replaced by SmCl₃·6H₂O (0.12 g, 0.33 mmol). Light yellow block crystals for **4** were obtained in *ca.* 62.34% yield (based on Sm). Anal. calcd for C₁₀H₁₁O₉Sm (425.54): C 32.90, H 2.61. Found: C 32.79, H 2.69. IR data (KBr pellet, ν/cm⁻¹): 3423, 1621, 1446, 1395, 1297, 1176, 1077, 1018, 927, 828, 730, 660, 415.

Synthesis of [Pr₃(mal')(phth)₃(H₂O)₃]·H₂O (**5**)

The complex was prepared by hydrothermal reaction. A mixture of Pr(NO₃)₃·6H₂O (0.12 g, 0.28 mmol), maleic acid (H₂mal, 0.10 g, 0.82 mmol), and 1,2-benzenedicarboxylic acid (0.10 g, 0.55 mmol), 1 mol L⁻¹ KOH (0.5 mL), and H₂O (12 mL) was sealed in a Teflon-lined autoclave and heated at 180 °C for two days then 160 °C for one day, then cooled at 10 °C every 3 h to 100 °C, followed by slow cooling to room temperature. Light green block crystals for **5** were obtained in *ca.* 57.25% yield (based on Pr). Anal. calcd for C₂₈H₂₃O₂₁Pr₃ (1118.19) C 35.06, H 2.06. Found: C 35.10, H 2.22. IR data (KBr pellet, ν/cm⁻¹): 3481, 1531, 1405, 1121, 970, 863, 747, 696, 458, 235.

Synthesis of [Eu(ad)_{0.5}(phth)(H₂O)₂] (**6**)

A mixture of EuCl₃·6H₂O (0.12 g, 0.33 mmol), adipate acid (H₂ad, 0.10 g, 0.68 mmol), and 1,2-benzenedicarboxylic acid (H₂phth, 0.10 g, 0.55 mmol), triethylamine (0.5 mL), and H₂O (12 mL) was sealed in a Teflon-lined autoclave and then heated at 160 °C for three days, then cooled at 10 °C every 3 h to 100 °C, followed by slow cooling to room temperature. White block crystals for **6** were obtained in *ca.* 58.19% yield (based on Eu). Anal. calcd for C₁₁H₁₂O₈Eu (424.17): C 36.31, H 2.83. Found: C 36.25, H 2.68. IR data (KBr pellet, ν/cm⁻¹): 3210, 2955, 1544, 1401, 1320, 1213, 936, 876, 847, 777, 712, 450, 364.

Synthesis of [Sm(ad)_{0.5}(phth)(H₂O)₂] (7)

The procedure was the same as that for **6** except that EuCl₃·6H₂O was replaced by SmCl₃·6H₂O (0.12 g 0.33 mmol). Light yellow block crystals for **7** were obtained in ca. 60.3 yield (based on Sm) Anal. Calcd for C₁₁H₁₂O₈Sm (422.56): C, 36.44; H, 2.84 Found: C, 36.38; H, 2.65. IR data (KBr pellet, ν/cm⁻¹): 3417, 2955, 2930, 1525, 1400, 1319, 1212, 876, 777, 657, 446, 304.

Synthesis of [Pr₂(ad)(phth)₂(H₂O)₄] (8)

The procedure was the same as that for **6** except that the EuCl₃·6H₂O was replaced by PrCl₃·6H₂O (0.12 g 0.38 mmol)

temperature was heated at 160 °C for two days and then 180 °C for one day. Green block crystals for **8** were obtained. Yield: 60.54% (based on Pr). Anal. calcd for C₂₂H₂₄O₁₆Pr₂(826.23): C 37.28, H 2.90. Found: C 37.32, H 2.77. IR data (KBr pellet, ν/cm⁻¹): 3432, 2963, 2928, 1149, 1087, 918, 841, 755, 562, 434.

X-Ray crystallographic determination

Suitable single crystals of eight 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 with graphite monochromatized Mo Kα radiation

Table 1 Crystallographic data for complexes **1–4**

Formula	C ₉ H ₉ O _{8.5} Tb	C ₉ H ₉ O _{8.5} Sm	C ₁₀ H ₁₁ O ₉ Eu	C ₁₀ H ₁₁ O ₉ Sm
<i>M</i> /g mol ⁻¹	412.09	403.51	427.15	425.54
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>P2₁/n</i>	<i>P2₁/n</i>
<i>a</i> /Å	19.504 (2)	19.694(3)	11.673(2)	11.703(2)
<i>b</i> /Å	5.9798(5)	6.0192(9)	5.969 (1)	5.9725(12)
<i>c</i> /Å	20.422 (2)	20.467(3)	18.456(4)	18.446(4)
α/°	90	90	90	90
β/°	110.868 (1)	110.995(2)	97.65(3)	97.62(3)
γ/°	90	90	90	90
<i>V</i> /Å ³	2225.6(3)	2265.1(6)	1274.5(4)	1278.0(4)
<i>Z</i>	8	8	4	4
<i>D_c</i>	2.460	2.366	2.226	2.212
Crystal size/mm	0.231 × 0.061 × 0.044	0.69 × 0.13 × 0.11	0.214 × 0.239 × 0.280	0.19 × 0.10 × 0.09
<i>F</i> (000)	1568	1544	824	820
μ(Mo Kα)/mm ⁻¹	6.393	5.222	4.963	4.637
θ/°	2.13–25.00	2.13–29.02	3.52–27.48	3.51–27.48
Reflections collected	5257	5301	11 096	11 718
Independent reflections (<i>I</i> > 2σ(<i>I</i>))	1953	1988	2885	2922
Parameters	152	153	186	182
Δ(ρ)/e Å ⁻³	0.673 and –0.792	0.564 and –0.720	1.379 and –1.203	1.306 and –1.310
Goodness of fit	1.065	1.056	1.361	1.217
<i>R</i> ^a	0.0227 (0.0261) ^b	0.0185 (0.0207) ^b	0.0482 (0.0568) ^b	0.0421 (0.0534) ^b
<i>wR</i> ₂ ^a	0.0513 (0.0531) ^b	0.0442 (0.0452) ^b	0.0884 (0.0904) ^b	0.1086 (0.1131) ^b

^a *R* = Σ||*F*_o| – |*F*_c||/Σ|*F*_o|, *wR*₂ = {Σ[w(*F*_o² – *F*_c²)²]/Σ[w(*F*_o²)²]}^{1/2}; [*F*_o > 4σ(*F*_o)]. ^b Based on all data.

Table 2 Crystallographic data for complexes **5–8**

Formula	C ₂₈ H ₂₃ O ₂₁ Pr ₃	C ₁₁ H ₁₂ O ₈ Eu	C ₁₁ H ₁₂ O ₈ Sm	C ₂₂ H ₂₄ O ₁₆ Pr ₂
<i>M</i> /g mol ⁻¹	1118.19	424.17	422.56	826.23
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P2₁/n</i>	<i>P2₁/n</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	11.542(2)	13.362(3)	13.354(9)	6.2994(13)
<i>b</i> /Å	13.199(3)	5.9634(13)	5.977(4)	8.9181(18)
<i>c</i> /Å	13.687(3)	15.641(3)	15.640(10)	12.448(3)
α/°	115.50(3)	90	90	77.22(3)
β/°	91.29(3)	93.626(3)	93.532(9)	78.95(3)
γ/°	115.05(3)	90	90	71.00(3)
<i>V</i> /Å ³	1650.5(6)	1243.8(5)	1246.0(14)	639.4(2)
<i>Z</i>	2	4	4	1
<i>D_c</i>	2.250	2.265	2.253	2.146
Crystal size/mm	0.088 × 0.101 × 0.192	0.152 × 0.106 × 0.162	0.11 × 0.10 × 0.07	0.192 × 0.122 × 0.118
<i>F</i> (000)	1072	820	816	402
μ(Mo Kα)/mm ⁻¹	4.450	5.079	4.749	3.845
θ/°	2.99–27.48	1.94–25.00	1.95–24.99	1.69–25.00
Reflections collected	16 241	5920	5847	3415
Independent reflections (<i>I</i> > 2σ(<i>I</i>))	7460	2187	2194	2745
Parameters	419	178	172	342
Δ(ρ)/e Å ⁻³	1.354 and –0.811	0.886 and –0.751	3.747 and –1.995	0.498 and –0.767
Goodness of fit	1.102	0.978	1.067	1.061
<i>R</i> ^a	0.0303 (0.0383) ^b	0.0355 (0.0543) ^b	0.0586 (0.0784) ^b	0.0226 (0.0229) ^b
<i>wR</i> ₂ ^a	0.0629 (0.0657) ^b	0.0639 (0.0698) ^b	0.1403 (0.1490) ^b	0.0577 (0.0580) ^b

^a *R* = Σ||*F*_o| – |*F*_c||/Σ|*F*_o|, *wR*₂ = {Σ[w(*F*_o² – *F*_c²)²]/Σ[w(*F*_o²)²]}^{1/2}; [*F*_o > 4σ(*F*_o)]. ^b Based on all data.

Table 3 Selected bond lengths (Å) for complexes **1**, **3**, **5**, **6** and **8**.^a

Complex 1					
Tb1–O2W	2.366(4)	Tb1–O1	2.373(3)	Tb1–O1W	2.387(4)
Tb1–O6 ^{#1}	2.414(4)	Tb1–O5	2.441(4)	Tb1–O3 ^{#2}	2.443(4)
Tb1–O2 ^{#3}	2.453(3)	Tb1–O4 ^{#2}	2.461(3)	Tb1–O1 ^{#3}	2.594(4)
Complex 3					
Eu–O3 ^{#1}	2.384(4)	Eu–O1W	2.402(5)	Eu–O2W	2.409(5)
Eu–O5	2.429(5)	Eu–O2	2.437(4)	Eu–O1	2.475(4)
Eu–O4 ^{#2}	2.487(4)	Eu–O6	2.522(4)	Eu–O3 ^{#2}	2.591(4)
Complex 5					
Pr1–O15	2.366(3)	Pr1–O12 ^{#1}	2.479(4)	Pr1–O13	2.491(3)
Pr1–O9 ^{#1}	2.516(3)	Pr1–O2	2.517(3)	Pr1–O7 ^{#2}	2.527(3)
Pr1–O8 ^{#2}	2.568(4)	Pr1–O1	2.645(3)	Pr1–O12	2.658(3)
Pr1–O11	2.747(4)	Pr2–O14	2.673(3)	Pr2–O4 ^{#3}	2.368(4)
Pr2–O5 ^{#2}	2.417(4)	Pr2–O17 ^{#4}	2.430(4)	Pr2–O6	2.435(3)
Pr2–O10 ^{#1}	2.485(4)	Pr2–O13	2.549(3)	Pr2–O9 ^{#1}	2.665(4)
Pr3–O15	2.380(3)	Pr3–O11	2.416(3)	Pr3–O3	2.424(4)
Pr3–O16 ^{#5}	2.520(3)	Pr3–O16	2.526(3)	Pr3–O1	2.549(3)
Pr3–O3W	2.557(4)	Pr3–O2W	2.628(4)	Pr3–O1W	2.663(4)
Complex 6					
Eu1–O3 ^{#1}	2.391(5)	Eu1–O2W	2.394(5)	Eu1–O1W	2.423(5)
Eu1–O2	2.438(4)	Eu1–O1	2.445(5)	Eu1–O5	2.453(5)
Eu1–O4 ^{#2}	2.462(5)	Eu1–O6	2.487(5)	Eu1–O3 ^{#2}	2.693(4)
Complex 8					
Pr1–O2W	2.447(8)	Pr1–O5	2.451(9)	Pr1–O8 ^{#1}	2.465(7)
Pr1–O3 ^{#2}	2.486(5)	Pr1–O10	2.505(7)	Pr1–O9	2.550(8)
Pr1–O1W	2.564(7)	Pr1–O2	2.600(5)	Pr1–O1	2.662(5)
Pr2–O4 ^{#2}	2.329(8)	Pr2–O12 ^{#3}	2.482(10)	Pr2–O1	2.490(5)
Pr2–O11 ^{#3}	2.502(7)	Pr2–O4W	2.523(8)	Pr2–O3W	2.503(10)
Pr2–O7 ^{#1}	2.531(6)	Pr2–O6 ^{#4}	2.532(5)	Pr2–O8 ^{#1}	2.840(6)

^a Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 2, -z$; #2 $x, y + 1, z$; #3 $-x + 1/2, -y + 3/2, -z$ for **1**; #1 $x, y + 1, z$; #2 $-x + 2, -y + 1, -z$ for **3**; #1 $-x + 1, -y, -z + 1$; #2 $-x + 2, -y, -z + 1$; #3 $x + 1, y, z$; #4 $-x + 2, -y + 1, -z + 1$; #5 $-x + 1, -y + 1, -z + 1$ for **5**; #1 $x, y - 1, z$; #2 $-x + 2, -y + 1, -z + 1$ for **6**; #1 $x, y + 1, z$; #2 $x + 1, y, z$; #3 $x - 1, y + 1, z - 1$; #4 $x - 1, y + 1, z$ for **8**.

($\lambda = 0.71073$ Å). All absorption corrections were performed using SADABS program.³¹ Crystal structures were solved by the direct method. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of organic multi-polycarboxylate ligands and water molecules for the eight complexes were fixed at calculated positions with isotropic thermal parameters and Fourier maps. While, the hydrogen atoms of lattice water in complexes **3** have not been located. All calculations were performed using SHELXL-97 program.³² Crystal data and details of the data collection and the structure refinement of complexes **1–4** and **5–8** are given in Table 1 and 2, respectively. The selected bond lengths and bond angles of complexes **1**, **3**, **5**, **6** and **8** are listed in Table 3.

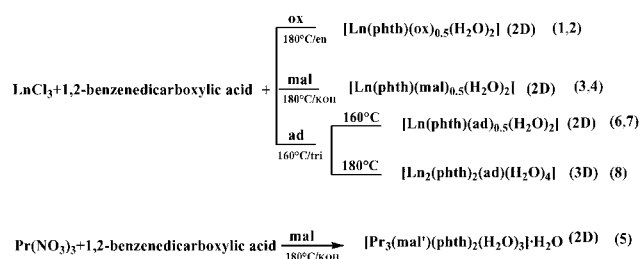
Results and discussion

Synthesis

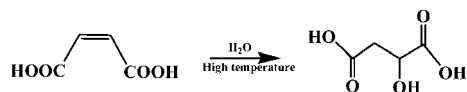
To the best of our knowledge, though there are various lanthanide coordination polymers contain binary mixed dicarboxylate ligands reported, those with rigid and flexible dicarboxylates as

mixed ligands are still rare, especially the complexes with different flexible acids (oxalic acid, maleic acid, adipic acid). In the reaction system, the physical and chemical properties of aromatic (rigid) acid and aliphatic (flexible) acid are different, so it is crucial to meet the coordinated conditions of both the flexible and rigid ligands to make them coordinate to Ln^{3+} at one time.

By a hydrothermal method, we have obtained complexes **1–5** at 180 °C, **6** and **7** at 160 °C, **8** at 160 °C for two days and 180 °C for one day. Originally, we tried to synthesize these complexes using different templates: triethylamine, ethylenediamine, KOH at 160 °C, but only Ln–phth–ad complexes are obtained with triethylamine (complexes **6** and **7**). It is essential to find suitable reaction conditions for making the other flexible acid ligands coordinate to Ln^{3+} . We then tried to adjust the temperature to 180 °C, when ethylenediamine was used as template for Ln–phth–ox system, complexes **1** and **2** were obtained, while when KOH was used for the Ln–phth–mal system, complexes **3** and **4** were obtained. It is worth noting that the temperature affects structures of the complexes, e.g. for the Ln–phth–ad system, the original reaction was carried out at different



Scheme 1 The reaction equations of the complexes.



Scheme 2 The course of the oxidizing reaction with maleic acid.

temperatures (from 160 to 180 °C) and complex **8** was obtained. When PrCl_3 was replaced by $\text{Pr}(\text{NO}_3)_3$ as the starting material, complex **5** was obtained. Therefore, the reaction conditions play an important role, including the starting material, template, temperature *etc.* in the syntheses of complexes **2**, **4** and **7**. The lanthanide ions and the rigid ligands are same, however different templates are needed to synthesize the corresponding complexes (Scheme 1). In addition, it is found that structures of complexes **1** and **2** are isomorphous and similar to that reported complex $[\text{La}_2(\text{ox})(\text{phth})_2(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$.⁴² Beside the above we have also investigated the favour reaction environment of single linker, and it is found that in this system Ln-phth coordination polymers could be formed more easily than that of Ln-ad under similar reaction conditions.

In the course of preparing complex **5**, an unusual rearrangement was found (Scheme 2), in which the maleic acid was oxidized at high temperatures. Similar trends were found in complexes $[\text{Zn}(\text{Hmal})(1,10\text{-phen})(\text{H}_2\text{O})_n]$, $[\text{Cu}(\text{Hmal})(2,2\text{-bipy})]_n \cdot 3\text{H}_2\text{O}$,⁴⁰ $[\text{Zn}_2(\text{mal})(1,10\text{-phen})\text{Cl}]_n$ and $[\text{Cd}(\text{fma})(2,2\text{-bpy})(\text{H}_2\text{O})_n]$,⁴¹ which was testified by us many times. It is interesting that the higher the temperature is, the more complicated the structure of the complexes becomes. A similar phenomenon has been found before.³⁹

Additionally, the compositions of **1–8** were confirmed by elementary analysis, IR spectra, and the phase purities of the bulk samples were identified by X-ray powder diffraction. (ESI, Fig. S1–S5.)†

The IR spectra of complexes **1–8** were examined, and the related characteristic bands are listed in the Table 4. The IR

spectra of complexes **1** and **2**, **3** and **4**, **6** and **7** are similar. The characteristic bands of carboxylate groups are shown in the range of 1531–1668 cm^{-1} for asymmetric stretching and 1404–1523 cm^{-1} for symmetric stretching. The bands at 2928 to 2963 cm^{-1} are characteristic of the $\nu_{\text{C-H}}$ vibration modes of the $-\text{CH}_2-$ groups within the carbon chain of the flexible acid. The broad bands at *ca.* 3210–3481 cm^{-1} are attributed to the $\nu_{\text{O-H}}$ vibrations of coordination water.

Structural description of complexes 1–8

X-Ray diffraction reveals that polymers **1–2**, **3–4** and **6–7** are isomorphous. Polymers **5** and **8** are different. Here, complexes **1**, **3**, **5**, **6** and **8** are taken as the examples to describe the structures in detail.

$[\text{Ln}(\text{ox})_{0.5}(\text{phth})(\text{H}_2\text{O})_2] \cdot 0.5\text{H}_2\text{O}$ (Ln = Tb (**1**) Sm (**2**))

Now, we will pay our attention and presentation to complex **1**. In structure unit, $[\text{Tb}(\text{ox})_{0.5}(\text{phth})(\text{H}_2\text{O})_2] \cdot 0.5\text{H}_2\text{O}$ contains one nine coordinated terbium ion, one phth ligands, half a ox ligand, two coordinated water molecules and half lattice water, which lies on the two-fold axis. The coordination mode of the terbium ion is shown in Fig. 1. Tb is coordinated with nine oxygen atoms from two chelating bidentate carboxyl groups (O1#3, O2#3, O3#2, O4#2), one di-monodentate carboxyl group from phth ligands (O1), two di-monodentate carboxyl groups from oxalic acid (O5 and O6#1), and two coordinated water molecules (O1w and O2w). The Tb–O_{carboxylate} bond distances are in range of

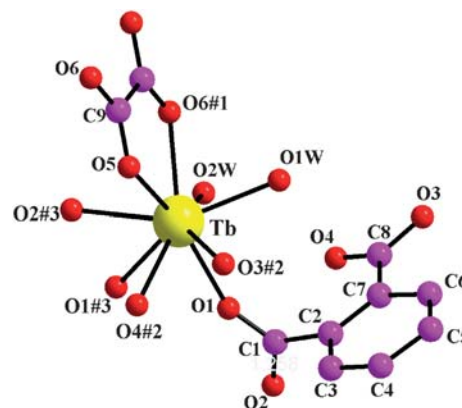


Fig. 1 The coordination environment of Tb in complex **1**. (Symmetry codes: #1: $-x + 1, -y + 2, -z$; #2: $x, y + 1, z$; #3: $-x + 1/2, -y + 3/2, -z$).

Table 4 The detailed attribution of IR (cm^{-1}) for complexes **1**, **3**, **5**, **6** and **8**

Complexes	1	3	5	6	8
$\nu_{\text{as}}(\text{COO}^-)$	1668	1621	1531	1544	1543
$\nu_{\text{s}}(\text{COO}^-)$	1523	1446,1395	1405	1431	1404
$\nu_{\text{C}=\text{C}}$ of vibration of benzene ring	1581	1568	1587,1551	1566	1498,1458
$\nu_{\text{C}=\text{H}}$ of benzene	3066	3078	3062	3070	3042
$\nu_{\text{C}-\text{C}}$ of benzene	658–857	660–828	657–848	658–847	657–841
The substitutions of the benzene ring	775–1092	760–1077	747–1040	777–1087	768–1087
$\nu_{\text{C}-\text{H}}$ vibration modes of $-\text{CH}_2-$ groups				2955	2963,2928
$\nu_{\text{O}-\text{H}}$	3368	3423	3388,3481	3210	3432

2.373–2.594 Å, and 2.366–2.387 Å for Tb–O_{water}, all of which are comparable to those reported for other Tb–oxygen donor complexes.³³ For phth ligand, the coordination modes of both carboxylate groups are as follows (Fig. 8a): (i) one of the carboxylate group adopts a $\mu_1\text{-}\eta^1\text{-}\eta^1$ -bridging (namely one oxygen atom of the carboxylate group connects one Tb atom, the other one connects also the same Tb atom, and the carboxylate group coordinates to one metal atom) coordination mode; (ii) the other one adopts a $\mu_2\text{-}\eta^2\text{-}\eta^1$ -bridging coordination mode (namely one oxygen atom of the carboxylate group connects two Tb atoms, the other one connects one Tb atom and the carboxylate group coordinates to two metal atoms).

In order to have a deep understanding of the frameworks structures and coordinated carboxylate molecular conformation, it would be important to explore the way the metal centers connect to the carboxylate ligands. In complex **1**, the lanthanide metal center atoms (Tb) and its corresponding centrosymmetric atoms were linked through the bridging carboxylate groups of phth ligands to form an infinite Tb-phth chain Fig. 2a, in which the adjacent Tb...Tb contacts are 4.226 Å and 6.505 Å. The chains are further linked by oxalic acids to form a 2D network Fig. 2b. The 2D packing structure is shown in Fig. 3. The structure of complex **2** is similar to that of **1** as shown in the ESI (Fig. S6).†

[Ln(mal)_{0.5}(phth)(H₂O)₂]·H₂O (Ln = Eu (**3**) Sm (**4**))

An X-ray diffraction study performed on complex **3** reveals that each structural unit contains one nine coordinated Eu(III) atom,

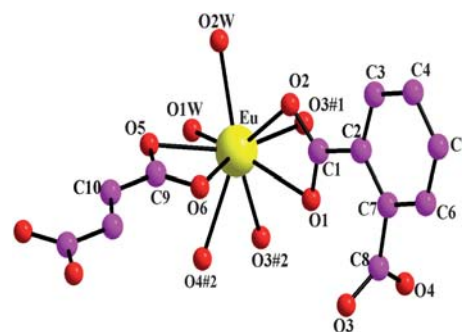


Fig. 4 The coordinated environment of Eu in complex **3**. (Symmetry codes: #1: $x, y + 1, z$; #2: $-x + 2, -y + 1, -z$.)

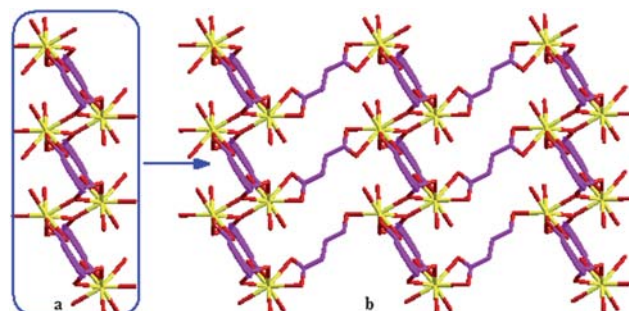


Fig. 5 (a) The Eu-phth infinite chain. (b) The 2D network of complex **3**.

half a mal ligand, a phth ligand, two coordinated water molecules and one lattice water molecule. In complex **3**, the Eu atom is coordinated with nine oxygen atoms, five are from three phth ligands (O1–O2, O3#1, O3#2 and O4#2), two are from one mal ligand (O5 and O6) and two are from water molecules (O1w and O2w) (Fig. 4). The Eu–O_{carboxylate} bond distances are in the range of 2.384–2.591 Å, and 2.402–2.409 Å for Eu–O_{water}, all of which are comparable to those reported for other Eu–oxygen donor complexes.^{34–37} The Eu atoms are bridged by phth ligands

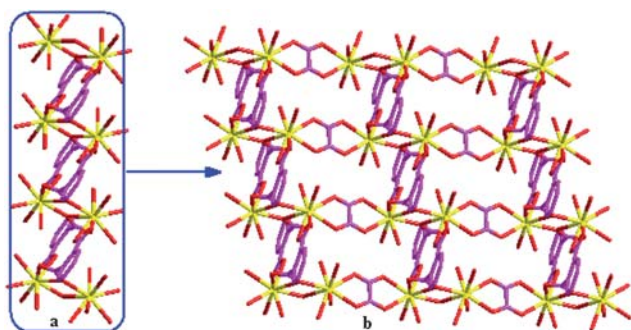


Fig. 2 (a) An infinite Tb-phth chain. (b) 2D network of complex **1**.

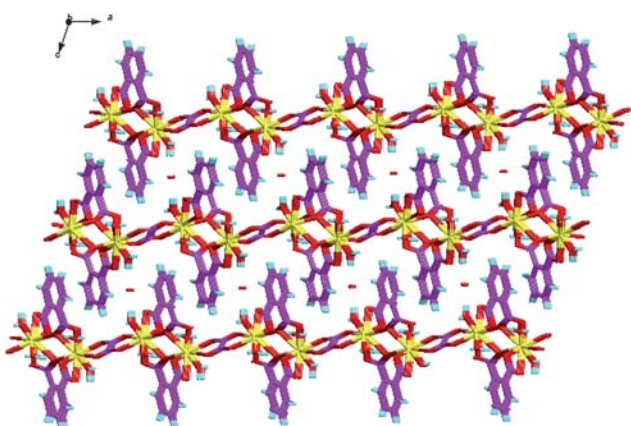


Fig. 3 The packing structure of complex **1**. (The hydrogen atoms of free water have not been added.)

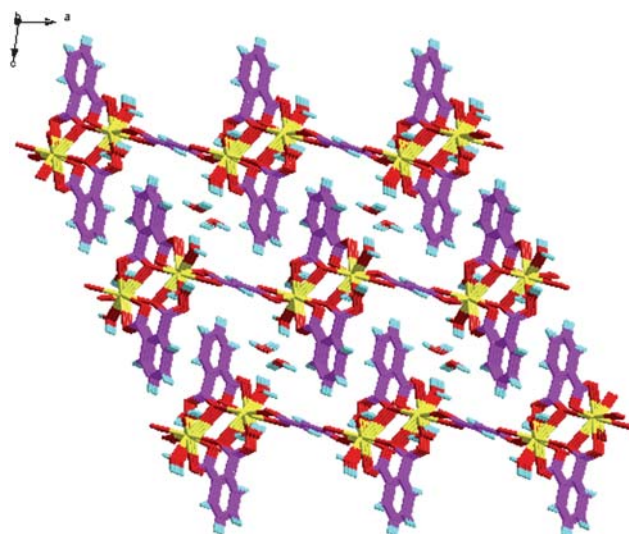


Fig. 6 The 2D packing structure of complex **3**.

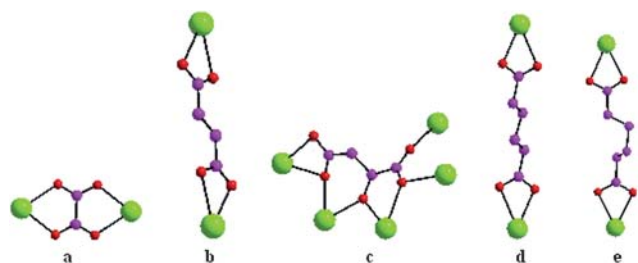


Fig. 7 The coordinated ways of the aliphatic carboxylate in the construction of the complexes.

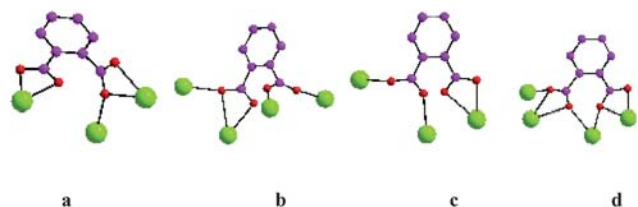


Fig. 8 The coordination modes of phth ligands.

forming an infinite Eu-phth chain structure (Fig. 5a). The coordination modes of both phth and mal ligands are shown in (Fig. 7b and Fig. 8a). The Eu-phth chains are further linked by mal ligands to generate a 2D network in *ac* plane (Fig. 5b). The structure of complex **3** (Fig. 6) and the coordination modes of the phth ligands are similar to that of **1**, except the lattice water molecules. It should be pointed out that in **1** and **3**, although H₂ox and H₂mal differ in the number of C atoms in their alkyl chains, they show quite similar chain structures. However, there are also differences existence between these two coordination polymers. Such as: the numbers of the free water molecule, the coordinated ways of the flexible acids. (Fig. 7a, b).

It is obvious that in the structures of complexes **3–4** a transformation has occurred in the form of the *cis*-maleate anion becoming *trans*-fumarate. This transformation is used for the industrial synthesis of fumaric acid and has been observed in cobalt coordination chemistry.⁴³

[Pr₃(mal')(phth)₃(H₂O)₃]·H₂O (**5**)

Complex **5** is a trinuclear complex, the asymmetric unit is completed by three Pr atoms, two phth ligands, one malate ligand and three coordinated water molecules. The coordinated modes of Pr1, Pr2 and Pr3 are shown in Fig. 9. Pr1 is ten coordinated by eight oxygen atoms from four phth ligands (O1, O2, O7#2, O8#2, O9#1, O11, O12 and O12#1), two oxygen atoms (O15 and O13) from mal' ligand; the eight oxygen atoms coordinated with Pr2, five (O4#3, O5#2, O6, O9#1 and O10#1) are from four phth ligands, three (O13, O14 and O17#4) are from two mal' ligands, while Pr3 is coordinated with nine oxygen atoms, three (O1, O3 and O11) are from two phth ligands, three (O15, O16 and O16#5) are from mal' ligands and three (O1w–O3w) are from coordinated water molecules. Pr1, Pr2 and Pr3 were bridged by the oxygen atoms from mal ligands to form an infinite Pr-mal chain (Fig. 10a). At the same time, a Pr-phth chain (Fig. 10b) could be observed, too. Along the [100]

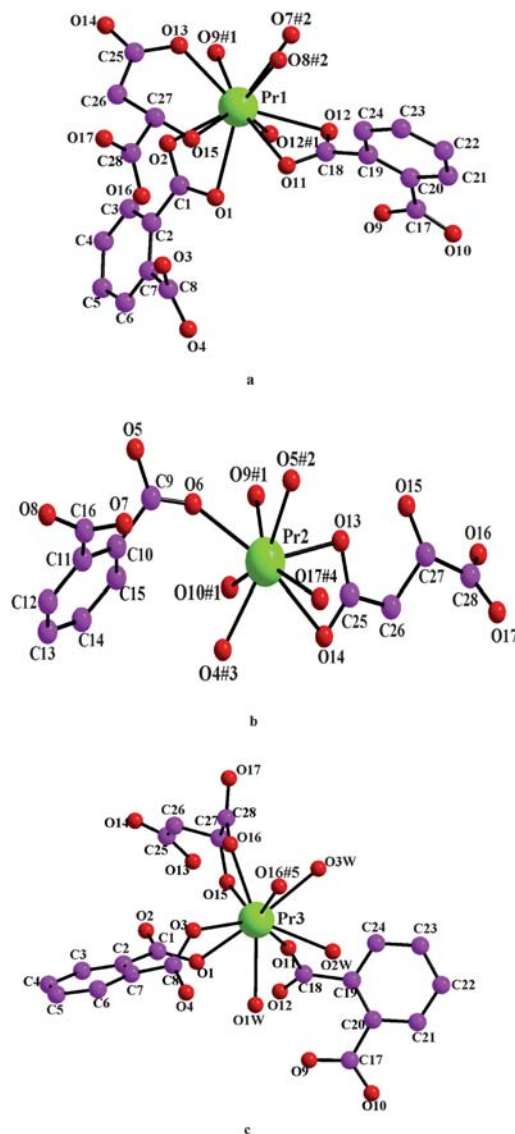


Fig. 9 Coordination environments of (a) Pr1, (b) Pr2, (c) Pr3 in complex **5** (Symmetry codes follow: #1: $-x + 1, -y, -z + 1$; #2: $-x + 2, -y, -z + 1$; #3: $x + 1, y, z$; #4: $-x + 2, -y + 1, -z + 1$; #5: $-x + 1, -y + 1, -z + 1$.)

direction, the chains are linked by the bridging oxygen atoms from phth and mal into 2D layers structure. (Fig. 11). And it is remarkable that the coordinated modes of both the phth (Fig. 8d) and the mal ligands (Fig. 7c) in **5** are obviously different from most of the reported complexes.^{24–27,38}

[Ln(ad)_{0.5}(phth)(H₂O)₂] (Ln = Eu (**6**), Sm (**7**))

To examine the influence of the flexibility of the aliphatic acid on the assembly of the frameworks, H₂ad was introduced. Consequently, the complex [Eu(ad)_{0.5}(phth)(H₂O)₂] formed. It has a 2D network, which contains one nine-coordinated europium atom, half a adipate ligand, one 1,2-benzenedicarboxylate ligand and two coordinated water molecules, its coordination mode is similar to that of **1** and **3**, except for the free water molecules. The coordination environments of the europium atom (Eu) is shown in Fig.12. Each Eu is coordinated with nine oxygen atoms, five

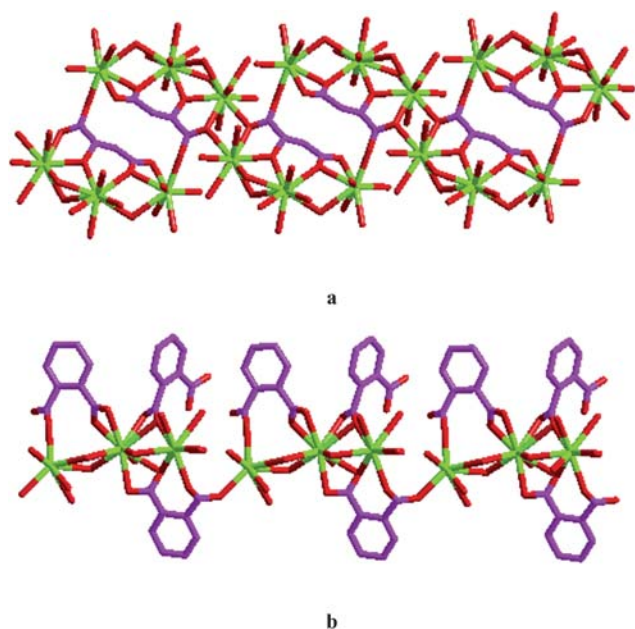


Fig. 10 (a) The Pr-mal' chain. (b) The Pr-phth chain in complex 5.

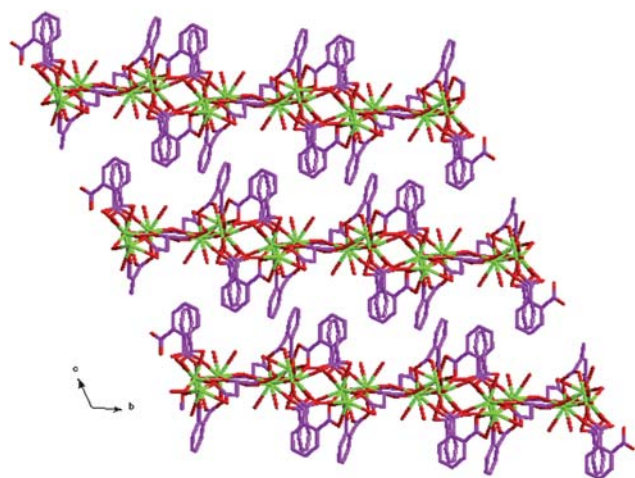


Fig. 11 The 2D packing structure of complex 5.

from three phth ligands (O1–O2, O3#1, O3#2 and O4#2) and two from one chelating bidentate carboxylate group (O5 and O6) of adipate group, and two from coordinated water molecules (O1w, O2w). The distances of Eu–O_{ad} (from adipate acid), Eu–O_{phth} (from 1,2-benzenedicarboxylic acid) and Eu–O_w (from water molecules) are in the ranges of 2.453(5)–2.487(5) Å, 2.391(5)–2.693(4) Å, and 2.394(5)–2.423(5) Å, respectively, especially the bond length of Eu–O2 (2.693(4) Å) is obviously longer than the normal Eu–O bond length reported, but the rest are comparable to those reported for other europium–oxygen donor complexes.^{18,19,31} For the adipate ligand, both carboxylate groups of each adipate exhibit only one kind of coordination mode: $\mu_1\text{-}\eta^1\text{-}\eta^1$ -bridging (namely one oxygen atom of the carboxylate group connects one metal ion, the other one connects also one metal atom and the carboxylate group coordinates to one metal atom, Fig. 7d). As for 1,2-benzenedicarboxylate acids, both carboxylate groups exhibit two kinds of

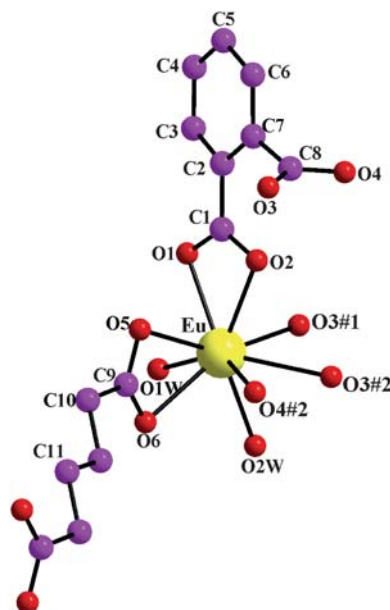


Fig. 12 The coordination environment of Eu in complex 6. (Symmetry codes follow: #1: $x, y - 1, z$; #2: $-x + 2, -y + 1, -z + 1$.)

coordination modes, one of two carboxylate groups adopts a $\mu_2\text{-}\eta^1\text{-}\eta^2$ -bridging fashion (namely one oxygen atom of the carboxylate group connects one metal atom, the other one connects two metal atoms and the carboxylate group coordinates to two metal atoms), the other one adopts $\mu_1\text{-}\eta^1\text{-}\eta^1$ -bridging fashion (namely one oxygen atom of the carboxylate group connects one metal atom, the other one connects also one metal atom and the carboxylate group coordinates to one metal atom, Fig. 8a).

In complex 6, the lanthanide metal center atoms (Eu) and their corresponding centrosymmetric atoms are linked through the carboxylate groups of phthalate ligands forming a 1D infinite Eu-phthalate chain along the [001] direction (Fig. 13a). In the chains, we may remark that the metal centers are grouped in pairs by the carboxyl groups of phth ligand. For both carboxyl groups of each phthlate ligand, one link two adjacent Eu atoms, and another connects another Eu atom further away (Fig. 8a). As a good bridging ligand, the adipate acid linked these chains to one another to form a 2D layer structure (Fig. 13b). A clearer 2D structure of Eu-phth-ad can be observed along [010] direction (Fig. 14).

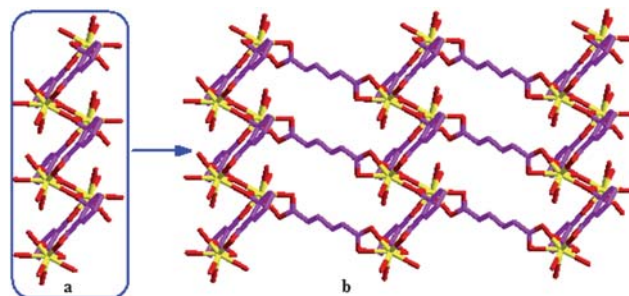


Fig. 13 (a) The 1D chain linked by 1,2-benzenedicarboxylic acid. (b) 1D chain linked by adipate forming a 2D structure.

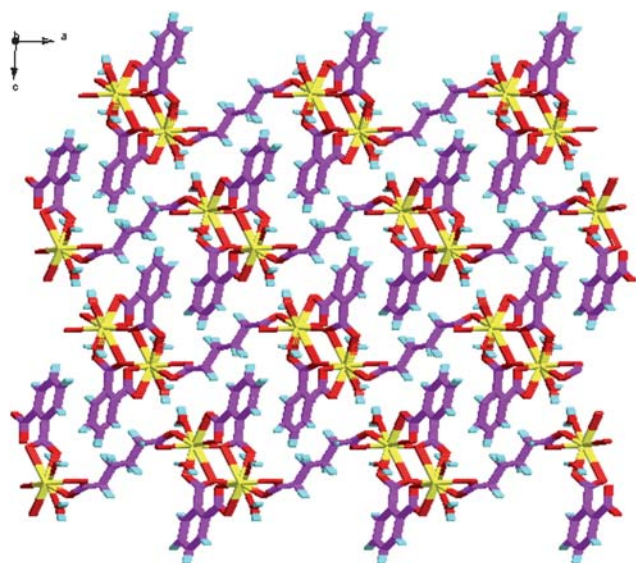


Fig. 14 The 2D structure of complex **6** viewed along the [010] direction.

The structure of complex **8** reveals that it is a 3D framework, crystallizing in triclinic space group $P\bar{1}$. The asymmetric unit $[\text{Pr}_2(\text{ad})(\text{phth})_2(\text{H}_2\text{O})_4]$ contains two nine-coordinated Pr ions, two 1,2-benzenedicarboxylate and one adipate acid ligands, and four coordinated water molecules. The coordination modes of two praseodymium ions (Pr1 and Pr2) are the same and are shown in Fig. 15. Pr1 is coordinated with nine oxygen atoms from one chelating bidentate carboxyl group (O1 and O2) and three monodentate carboxyl groups (O3#2, O5 and O8#1) from 1,2-benzenedicarboxylate ligand, one chelating bidentate carboxyl group (O9 and O10) from adipate ligand, and two coordination water molecules (O1w and O2w). The distances of $\text{Pr1}-\text{O}_{\text{phth}}$ (from 1,2-benzenedicarboxylate acid), $\text{Pr1}-\text{O}_{\text{ad}}$ (from adipate acid) and $\text{Pr1}-\text{O}_{\text{w}}$ (from water molecule) are in the ranges of 2.451(9)–2.486(5) Å, 2.505(7)–2.662(5) Å and 2.447(8)–

2.564(7) Å, respectively. The bonds of $\text{Pr}-\text{O}_{\text{phth}}$ are similar to those of other complexes.^{19,21,22} However, it is noteworthy that the bond length of $\text{Pr2}-\text{O8\#1}$ (2.840(6) Å) is longer than related lanthanide complexes. The bonds of $\text{Pr}-\text{O}_{\text{ad}}$ are similar to that reported complexes.²² The coordination modes of adipate are the same as complex **6**, however, the distorted angles of adipate ligand are different: 180° for **6**, 71.86° for **8** (shown in Fig. 7d, e); while as for the coordination modes of 1,2-benzenedicarboxylate ligand, it is different from **6** (Fig. 8b) as follows: (i) one of carboxylate groups adopts a $\mu_2-\eta^1-\eta^1$ -bridging (namely one oxygen atom of the carboxylate group connects one metal ion, the other one connects also one metal atom and the carboxylate group coordinates to two metal atoms) coordination mode; (ii) the other one adopts a $\mu_2-\eta^2-\eta^1$ -bridging (namely one oxygen atom of the carboxylate group connects two metal atoms, the other one connects one metal atom and the carboxylate group coordinates to two metal atoms) coordination mode.

On the basis of these connection modes of organic polycarboxylate ligands, a binuclear unit is built up by two edge-shared polyhedra units Pr_2O_{18} shown in Fig. 16a. The distance between adjacent Pr ions is 4.235 Å and 6.299 Å, respectively. It is interesting that the edge-shared polyhedra units Pr_2O_{18} are further linked to each other through seven oxygen atoms from four carboxylate groups of two 1,2-benzenedicarboxylate acid groups forming a 1D chain structure along the [001] direction Fig. 16b, and the remained oxygen atoms connect each 1D chains to form an infinite 2D Ln-Phth layer along [001] direction Fig. 16c. When viewed along [100] direction, the 2D layer is connected by the bridging adipate, to form a 3D structure, as shown in Fig. 17.

This body of work completes the series of lanthanide complexes with aliphatic dicarboxylic acids of varying lengths and eight complexes have been synthesized, which can be divided into five groups as follows: **1–2**, **3–4**, **5**, **6–7** and **8**. For the purpose of clarity, we will give the comparison of the eight complexes step by step: (1) the structure of the complexes: **1–7**

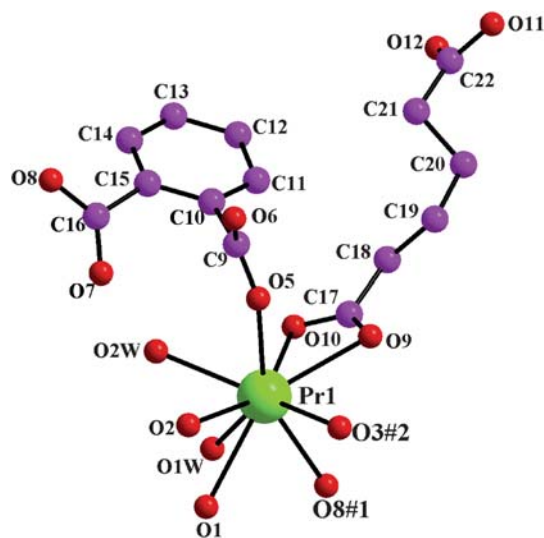


Fig. 15 The coordination environment of Pr1 in complex **8**. (Symmetry codes follow: #1: $x, y + 1, z$; #2: $x + 1, y, z$.)

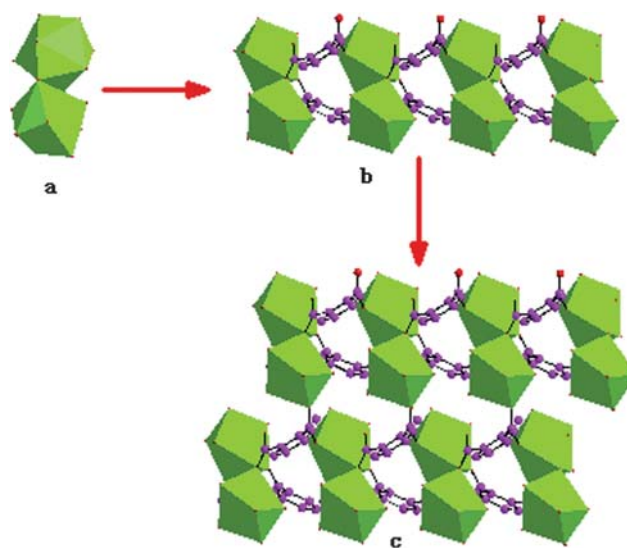


Fig. 16 (a) The edge sharing Pr_2O_{18} unit. (b) The infinite chain of Pr-phth in complex **8**. (c) The planar structure of Pr-phth built by the infinite chains in **8**.

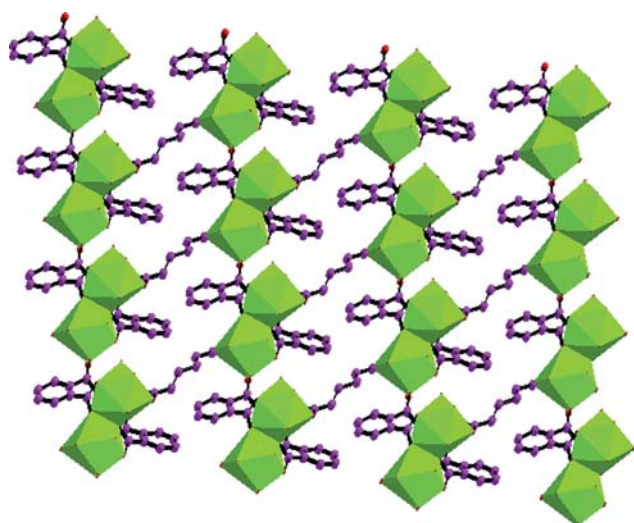


Fig. 17 The 3D framework of complex 8.

exhibit a 2D structure, while **8** has a 3D structure. Structure analysis reveals that, complexes **1–4** and **6**, **7** exhibit similar 2D frameworks except that the alkyl chains are different. While **5** and **8** are different, for **5** it is a trinuclear complex, with phth and oxidized mal ligands, the coordination modes of both ligands are different from **3** and **4**; **8** is a 3D dinuclear complex, with different coordination modes of phth. By comparison of **6**, **7** and **8**, it is found that the coordination modes of the rigid ligand may have an effect on the dimension of the complexes, because they can adopt different coordination fashion leading to different packing arrangements of the frameworks. The flexible dicarboxylate ligands may decide the type of the conformation units to make the whole framework more stable; (2) for the bond distances: it is found that the longer chains of the flexible acids are, the longer lengths of Eu–O_{water} and Eu–O_{flexible} are; however, the Eu–O_{phth} (the carboxylate from rigid acids) are shorter; while for the bond angle, the trends seem not as distinct as the trends of the bond length in complexes **1–4**, and **6**, **7**. Beside that in the construction of these complexes, the rigid ligand can control the type of the complexes, while the flexible ligand mainly makes the structures more stable.

Thermal properties

Thermogravimetric analysis (TGA) was carried out in the interest of studying the thermal behaviours of the different flexible ligands effects on the complexes. Fig. 18 shows the TG curves for **1**, **3**, **5**, **6** and **8** at a heating rate of 10 °C min^{−1} under an N₂ atmosphere. The TGA of **1** shows the first step weight loss (15.42%) at 62–370 °C, corresponding to the loss of half a lattice water molecule, two coordinated water molecules and one CO₂ molecule (calcd: 16.26%); and after that, from 370–650 °C, the second step weight loss (49.56%), corresponding to the loss of one phth ligand (calcd: 49.02%). For **3** in the TG plot, there are four main weight losses: the first, from 50 °C to 131 °C, corresponds to the release of the lattice water molecule (calcd: 4.21%, observed: 3.69%), and the second weight loss is due to the loss of the two coordinated water molecules (calcd: 8.43%, observed: 8.29%), the third weight loss is the loss of half mal ligand (calcd:

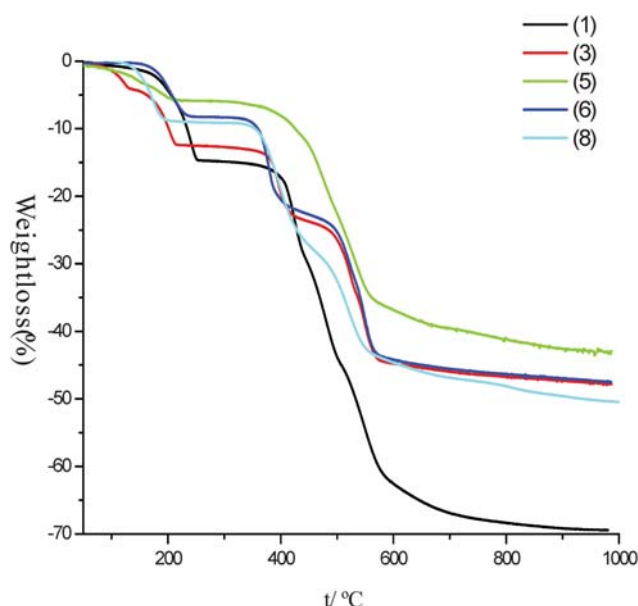


Fig. 18 TG curves for **1** (black), **3** (red), **5** (green), **6** (blue) and **8** (cyan).

11.00%, observed: 10.36%), the fourth weight loss is the loss of one phth ligand (calcd: 21.07%, observed: 21.81%). As for compound **5**, the initial weight loss in the range 50–332 °C corresponds to the loss of the lattice water and three coordinated water molecules (calcd: 6.44%, observed: 5.60%), and the second weight loss in the range 332–567 °C corresponds to the loss of the C₄O₅H₃ (calcd: 28.53%, observed: 29.16%), As for **6**, the release of two coordinated water molecules is observed (calcd: 8.49%, observed: 7.4%) in the temperature range 52–231 °C, and after that from 231–499 °C due to the weight loss of half ad ligand (calcd: 18.39%, observed: 17.40%), the third weight loss corresponds to the loss of one phth ligand (calcd: 21.22%, observed: 20.82%). For **8** the initial weight loss in the range 111–198 °C corresponds to the loss of four water molecules (calcd: 8.71%, observed: 8.69%), the second weight loss in the range 198–428 °C corresponds to the loss of the one ad ligand (calcd: 15.49%, observed: 16.18%), and the third weight loss in the range 428–691 °C corresponds to the loss of the one phth ligand (calcd: 21.79%, observed: 21.84%). Hence, we can see that although the structures of complexes **1**, **3** and **6** are similar, different flexible ligands coordinated to metal ions have an influence on the courses of thermal decomposition of complexes.

Photoluminescent properties

The luminescent behaviours of complexes **1–4**, **6** and **7** were investigated in solid state at room temperature. Excited at 396 nm, **3**, **6** exhibited red luminescence (Fig. 19d and 19e), with emissions characterizing ⁵D₁ → ⁷F₂, ⁵D₀ → ⁷F_n (n = 1–4) transitions at 579, 592, 616, 651, and 696 nm. The strongest emission of the ⁵D₀ → ⁷F₂ transition at 616 nm is four times stronger than the second one of the ⁵D₀ → ⁷F₁ transition at 592 nm, indicating non-centrosymmetric Eu³⁺ site in **4**, **6**, as the structure revealed. From the strongest emission it is clear that the emission of **6** is obviously stronger than **3** in the same slit width (3 : 1). **1** emits green light when excited at 260 nm with emissions at 490, 543,

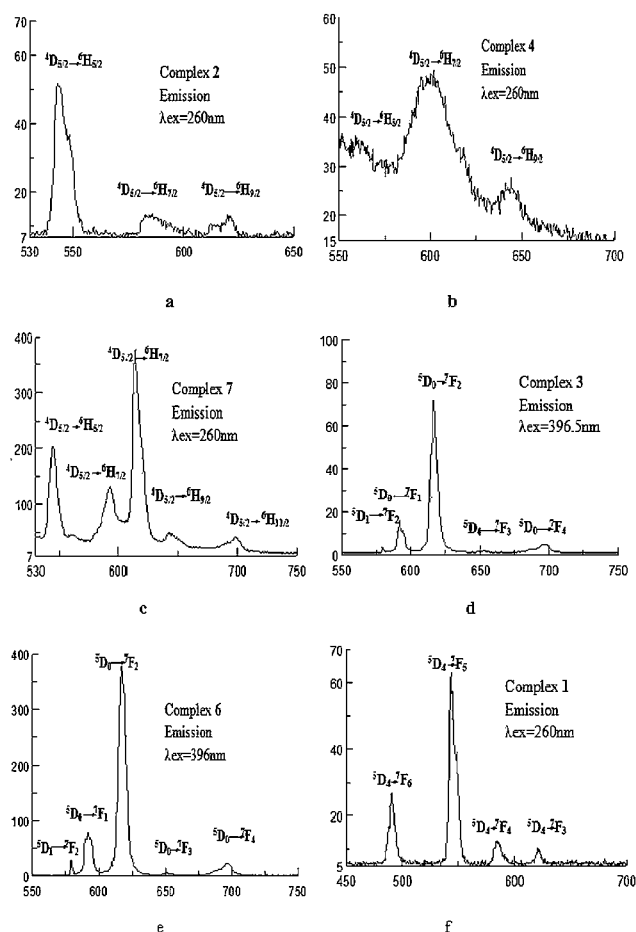


Fig. 19 Room-temperature solid-state photoluminescence spectra 1–4 and 6–7.

584, and 622 nm assigned to $^5D_4 \rightarrow ^7F_n$ ($n = 6-3$) transitions of Tb (Fig. 19f).

For clarity, the luminescent properties of Sm(III) complexes are given for comparison (Fig. 19a, 19b and 19c). Complexes 2, 4 and 7 emit pink light at room temperature. 2 is excited at 260 nm with a band width of 1 nm (E_x), while at band width of 3 nm (E_x) for 4 and 7. So the intensity order of strongest peaks is $2 > 7 > 4$. Complexes 2 and 4 exhibit similar shapes of the emission spectrum. When excited at 260 nm the two complexes exhibited a pink luminescence (Fig. 19a and 19b), with emissions characterizing $^4D_{5/2} \rightarrow ^6H_n$ ($n = 5/2-9/2$) transitions at 543, 584, 620 nm for 2, at 561, 599, 645 nm for 4. For 7 four characteristic transition peaks namely $^4D_{5/2} \rightarrow ^6H_{5/2}$ (545 nm), $^4D_{5/2} \rightarrow ^6H_{7/2}$ (592 nm and 614 nm), $^4D_{5/2} \rightarrow ^6H_{9/2}$ (643 nm) and $^4D_{5/2} \rightarrow ^6H_{11/2}$ (699 nm) are found also.

Conclusions

Eight lanthanide polymers with different architectures, complexes 1–8 have been synthesized using hydrothermal conditions. X-Ray diffraction analyses reveal that 1–4, 6 and 7 exhibit the similar two-dimensional (2D) architecture. Five different types of the eight complexes can be isolated based on five groups of the crystal structure and the flexible ligands, that is

two Ln-phth-ox complexes(2D), two Ln-phth-mal (2D), one Ln-phth-mal' (2D), two Ln-phth-ad (2D) one Ln-phth-ad (3D). For complexes 1–8, in general, the structures are all composed of one-dimensional linkers with Ln ions and 1,2-benzenedicarboxylic acid, which are further linked by flexible ligands to form the 2D or 3D structure. By comparing the structures of the complexes with different flexible acids, it shows that they have effects on the Ln–O bond length, and it is further informed that the flexible can only reinforce the frameworks, however the rigid ligand decide the type of the frameworks, because they can adopt different coordination modes to lead to different arrangement of frameworks packing. For example, for 6 and 8, with the different coordination modes, the dimension of the structures changes from 2D to 3D. In addition, complex 1, 3 and 6 emit green and red luminescence, respectively and complex 2, 4 and 7 emit pink luminescence at room temperature. They could be anticipated as potential fluorescent materials.

Acknowledgements

This work was supported by the grants of the National Natural Science Foundation of China (grant no. 20771051 and 20633050), and the Education Foundation of Liaoning Province in China (grant no. 2007T093) for financial assistance.

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