

Synthesis, structures and photoluminescence of three terbium(III) dicarboxylate coordination polymers

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Three polymeric terbium(III) complexes of 4,4'-oxybis(benzoic acid) (H_2oba) have been hydrothermally synthesised with different metal : carboxylate ratios or in the presence of an additional chelate ligand 2,2'-bipyridine (2,2'-bpy) and characterised by single-crystal X-ray diffraction. In $[Tb(oba)(Hoba)(H_2O)_2] \cdot H_2O$, **1**, the metal atoms are bridged by the oba/Hoba carboxylate groups into one-dimensional covalent chains, which are further interconnected by the oba ligands to produce a two-dimensional brick-wall network. In $[Tb_2(oba)_3(H_2O)_4]$, **2**, the metal atoms are bridged by the oba/Hoba carboxylate groups into one-dimensional covalent chains different from those in **1**, which are further interconnected by the oba ligands to produce a two-dimensional condensed network. In the structure of $[Tb_2(oba)_3(2,2'-bpy)_2]$, **3**, there are centrosymmetrical tetrakis(μ -carboxylate)-bridged Tb(III) dimeric structural subunits, which are interlinked by the oba ligands into a three-dimensional framework. The three compounds exhibit interesting photoluminescence at room temperature. The results show that different metal : carboxylate ratios can influence the polymeric structures and that the presence of 2,2'-bpy ligand alters not only the topology of the framework from two-dimensional to three-dimensional, but also the photoluminescent properties in both intensity and lifetime.

Introduction

The rational design and synthesis of coordination polymer materials has recently attracted much attention for their varied topologies and potential applications.^{1–3} So far most of the work has been focused on coordination polymers containing transition metal ions^{1–9} rather than lanthanide ions.^{10–17} Lanthanide(III) ions are very attractive luminescent centres for their high colour purity and long lifetimes of the excited states based on the 4f electronic transitions, and their complexes have potential applications in fluorescent probes and conversion or amplification of light.^{18–20} It has also been noted that photoluminescent intensities of lanthanide complexes are strongly dependent on their organic compositions.^{21–23} On the other hand, although lanthanide(III) monocarboxylates have been widely studied,^{24,25} only limited reports on the construction of polymeric lanthanide(III) dicarboxylates have been uncovered,^{26–29} which are usually very stable and exhibit luminescent properties. So far no systematic investigation on the structures and properties of lanthanide(III) dicarboxylates with different metal : carboxylate ratios has been carried out. Moreover, the effect of auxiliary ligands on the structures and properties, especially luminescence, is also very interesting to us. We report herein the hydrothermal synthesis, crystal structures and photoluminescent properties of three new terbium dicarboxylate coordination polymers, namely the two-dimensional brick-wall network $[Tb(oba)(Hoba)(H_2O)_2] \cdot H_2O$, **1**, [$H_2oba = 4,4'$ -oxybis(benzoic acid)], the two-dimensional condensed network $[Tb_2(oba)_3(H_2O)_4]$, **2**, and the three-dimensional network $[Tb_2(oba)_3(2,2'-bpy)_2]$, **3**, (2,2'-bpy = 2,2'-bipyridine). Our results show significant influences of the metal : carboxylate ratios and the addition of auxiliary chelate ligands on the structures and photoluminescent properties.

Experimental

Materials and methods

All chemicals were purchased from commercial sources and used without further purification. The C, H and N microanalyses were carried out with a Perkin–Elmer 240 elemental analyser. The solid-state excitation and emission spectra were acquired on a Hitachi F-4500 spectrofluorometer. In a typical experiment, the solid sample of **1**, **2** or **3** was layered on a quartz plate and the same laser beam with wavelength 294 nm was used to excite the samples to measure the solid-state excitation spectra. The laser beam was generated by a cavity-dumped dye laser (Model 3000, Spectra Physics) and synchronously pumped by a CW Nd:YAG laser. The luminescence lifetime measurements were performed with an EMG 201-MSD excimer laser with a wavelength of 308 nm and a Tektronix TDS3032 oscilloscope.

Synthesis

[Tb(oba)(Hoba)(H₂O)₂] · H₂O, 1. Tb(NO₃)₃ · 5H₂O (0.2 mmol), H₂oba (0.4 mmol), Et₃N (0.8 mmol or 1.6 mmol) and water (10 mL) were mixed in a Teflon-lined Parr stainless vessel (23 mL). After the solution was heated at 140 °C for 4 days and then cooled to room temperature, colourless block crystals of **1** were obtained in 67% yield after washing by water and acetone. Anal. calcd for C₂₈H₂₃O₁₃Tb, **1**: C 46.30, H 3.19%. Found: C 46.36, H 3.11%.

[Tb₂(oba)₃(H₂O)₄], 2. Tb(NO₃)₃ · 5H₂O (0.2 mmol), H₂oba (0.3 mmol), Et₃N (0.6 mmol) and water (10 mL) were mixed in a Teflon-lined Parr stainless vessel (23 mL). After the solution was heated at 140 °C for 4 days and then cooled to room

temperature, colourless plate-like crystals of **2** were obtained in 58% yield after washing by water and acetone. Anal. calcd for $C_{42}H_{32}O_{19}Tb_2$, **2**: C 43.52, H 2.78%. Found: C 43.41, H 2.86%.

[Tb(oba)₃(2,2'-bpy)₂], 3. Tb(NO₃)₃·5H₂O (0.2 mmol), 2,2'-bpy (0.2 mmol), H₂oba (0.4 mmol), Et₃N (0.8 mmol) and water (10 mL) were mixed in a Teflon-lined Parr stainless vessel (23 mL). After the solution was heated at 140 °C for 4 days and then cooled to room temperature, yellow block crystals of **3** were obtained in 55% yield after washing by water and acetone. Anal. calcd for $C_{62}H_{40}N_4O_{15}Tb_2$, **3**: C 53.23, H 2.88, N 4.01%. Found: C 53.17, H 2.81, N 4.05%.

X-Ray crystallography

Diffraction intensities for the three complexes were collected at 297 K on a Bruker Smart 1 K CCD (for **1** and **2**; sizes $0.28 \times 0.20 \times 0.16$ and $0.21 \times 0.11 \times 0.02$ mm³, respectively) and a Siemens R3m diffractometer (for **3**, size $0.38 \times 0.30 \times 0.26$ mm³) using graphite-monochromated MoK α ($\lambda = 0.71073$ Å) radiation.

For each complex, determinations of the crystal class, orientation matrix, and cell dimensions were performed according to the established procedures, and Lorentz polarization and absorption corrections using SADABS (for **1** and **2**; transmission factors 0.789–1.00, 0.568–0.934)³⁰ and Ψ -scan data (for **3**; transmission factors 0.571–0.757) were applied.³¹

Most of the non-hydrogen atoms in each crystal structure were located with direct methods, and subsequent Fourier syntheses were used to derive the remaining non-hydrogen atoms using the SHELXS-97 program package.³² All of the non-hydrogen atoms were refined anisotropically, and all of the hydrogen atoms were held stationary and included in the final stage of full-matrix least-squares refinement based on F^2 using the SHELXL-97 program package.³³ Drawings were produced with the SHELXTL program package.³⁴ The crystallographic data for **1** to **3** are listed in Table 1. Selected bond lengths and bond angles are given in Table 2.

CCDC reference numbers 156112, 156113 and 182825. See <http://www.rsc.org/suppdata/nj/b1/b109869a/> for crystallographic data in CIF or other electronic format.

Results and discussion

Crystal structures

Each independent crystallographic unit of **1**, comprises one Tb(III) atom, one oba, one monoprotonated oba (Hoba) and

two aqua ligands, as well as one lattice water molecule. The oba ligand acts in a bis-bidentate coordination mode to ligate four metal atoms, whereas the Hoba ligand functions in a mono-bidentate mode to chelate a metal atom. The carboxylate C–O bonds are very similar [C–O = 1.255(4)–1.276(3) Å], while the pair of carboxy C–O bonds in the uncoordinated end of Hoba are significantly different due to the protonation [C–O = 1.221(4) and 1.325(4) Å]. The O–C–O bond angles are usually *ca.* 123°, while the smallest one [119.9(2)°] corresponds to the chelate carboxylate group, as expected. As shown in Fig. 1(a), each Tb(III) atom in this structure is coordinated by two oxygen atoms from two monodentate carboxylate ends of oba ligands, two oxygen atoms from a chelate carboxylate end of an oba ligand, two oxygen atoms from two Hoba ligands and two aqua oxygen atoms to furnish an eight-fold coordination. The Tb–O bond lengths vary from 2.315(2) to 2.592(2) Å and the O–Tb–O bond angles range from 52.10(6) to 155.07(8)°. Each pair of adjacent Tb(III) atoms is alternately bridged by a pair of the oba μ -carboxylate ends into one-dimensional covalent chains running along the *b* axis with an adjacent Tb···Tb spacing of 4.795(1) Å, which are interconnected by these oba/Hoba ligands to produce a two-dimensional network parallel to the *ab* plane [Fig. 1(b)]. Besides the chelate coordination of its carboxylate end, the carboxylic end of Hoba is uncoordinated and forms two hydrogen bonds with one aqua ligand [O1···O2w 2.675(3) Å] and a coordinated oba carboxylate oxygen atom [O2···O4 2.843(3) Å] from an adjacent layer. These hydrogen bonds, together with π – π stacking interactions between the phenyl rings from adjacent layers furnish the final three-dimensional architecture.

As we all know, hydrothermal products are usually influenced by many factors such as the pH, solvent, and molar ratio of starting reagents.^{35–39} In contrast, the pH of the reaction system for the generation of **1** is not crucially important. After addition of excess Et₃N (pH \approx 8) into the reaction system, we isolated the same product as proved by single-crystal X-ray diffraction.

When we strictly controlled the molar ratio of terbium salt and H₂oba at 2 : 3, the two-dimensional condensed network **2** was generated under similar conditions for the preparation of **1**. In the structure of **2** there are three crystallographically independent oba molecules exhibiting three different coordination modes, namely bis-monodentate, chelate-bidentate and bidentate-tridentate. The carboxylate C–O bond lengths [1.235(9)–1.283(9) Å] and O–C–O bond angles [120.1(5)–125.2(6)°] are analogous to the corresponding values found in **1**, in which somewhat unusual are one of the monodentate carboxylate group having virtually identical C–O bonds [1.249(8) and 1.253(9) Å] and the tridentate carboxylate group

Table 1 Crystal data and structure refinement for **1**, **2** and **3**

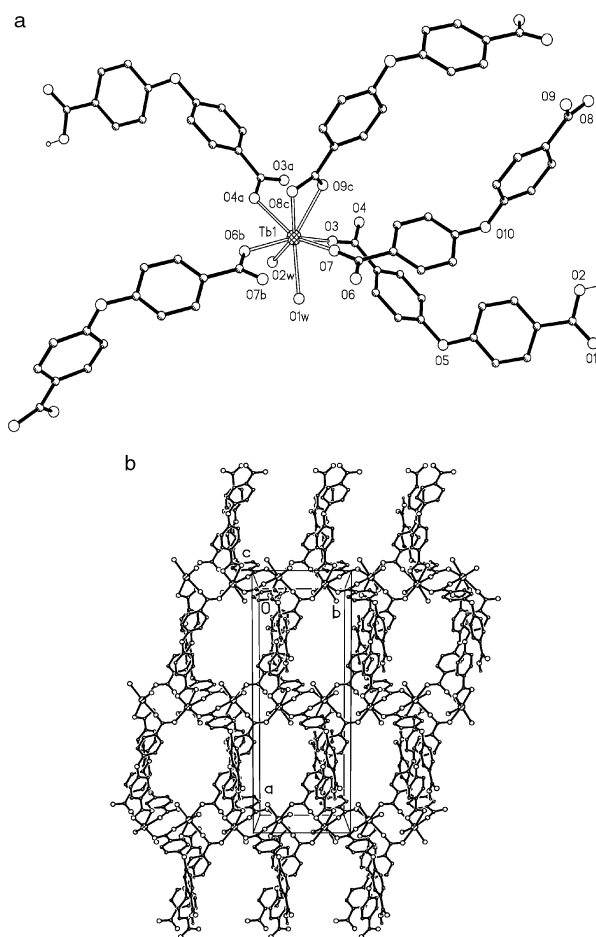
	$C_{28}H_{17}O_{10}Tb \cdot 3H_2O$	$C_{42}H_{24}O_{15}Tb_2 \cdot 4H_2O$	$C_{62}H_{40}N_4O_{15}Tb_2$
Empirical formula	$C_{28}H_{17}O_{10}Tb \cdot 3H_2O$	$C_{42}H_{24}O_{15}Tb_2 \cdot 4H_2O$	$C_{62}H_{40}N_4O_{15}Tb_2$
FW	726.39	1158.52	1398.82
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$ (no.15)	$P2_1/c$ (no.4)	$C2/c$ (no.15)
<i>a</i> /Å	27.154(5)	8.5937(9)	30.896(11)
<i>b</i> /Å	9.530(2)	29.016(3)	10.183(7)
<i>c</i> /Å	21.903(4)	16.505(2)	20.432(13)
β /deg	97.57(3)	90.279(2)	118.75(2)
<i>U</i> /Å ³	5619(2)	4115.5(8)	5636(6)
<i>Z</i>	8	4	4
<i>T</i> /K	293(2)	293(2)	293(2)
μ /mm ^{−1}	2.586	3.491	2.562
Unique reflections	8103	8932	4520
Observed reflect. [<i>I</i> $2\sigma(I)$]	5562	7552	3526
<i>R</i> _{int}	0.0199	0.0291	0.0314
<i>R</i> ₁ [<i>I</i> $2\sigma(I)$] ^a	0.0256	0.0471	0.0388
<i>wR</i> ₂ ^a (all data)	0.0589	0.1559	0.0996

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

Table 2 Selected bond lengths (Å) and angles (°) for **1**, **2** and **3**^a

1			
Tb(1)–O(3)	2.315(2)	Tb(1)–O(9b)	2.398(2)
Tb(1)–O(7)	2.322(2)	Tb(1)–O(4c)	2.440(2)
Tb(1)–O(6a)	2.328(2)	Tb(1)–O(1w)	2.443(2)
Tb(1)–O(2w)	2.393(2)	Tb(1)–O(8b)	2.592(2)
O(3)–Tb(1)–O(7)	87.60(7)	O(6a)–Tb(1)–O(9b)	127.68(7)
O(3)–Tb(1)–O(6a)	155.07(7)	O(2w)–Tb(1)–O(9b)	127.39(7)
O(7)–Tb(1)–O(6a)	105.27(7)	O(3)–Tb(1)–O(4c)	107.92(7)
O(3)–Tb(1)–O(2w)	71.26(7)	O(7)–Tb(1)–O(4c)	147.79(7)
O(7)–Tb(1)–O(2w)	137.26(7)	O(6a)–Tb(1)–O(4c)	72.32(7)
O(6a)–Tb(1)–O(2w)	85.18(7)	O(2w)–Tb(1)–O(4c)	74.95(7)
O(3)–Tb(1)–O(9b)	75.21(7)	O(9b)–Tb(1)–O(4c)	78.37(7)
O(7)–Tb(1)–O(1w)	72.02(7)	O(4c)–Tb(1)–O(1w)	135.88(7)
O(6a)–Tb(1)–O(1w)	79.50(7)	O(3)–Tb(1)–O(8b)	125.48(6)
O(2w)–Tb(1)–O(1w)	69.39(7)	O(7)–Tb(1)–O(8b)	70.96(7)
O(9b)–Tb(1)–O(1w)	144.91(7)	O(6a)–Tb(1)–O(8b)	79.32(7)
O(2w)–Tb(1)–O(8b)	151.09(7)	O(4c)–Tb(1)–O(8b)	77.14(7)
O(9b)–Tb(1)–O(8b)	52.10(6)	O(1w)–Tb(1)–O(8b)	130.14(6)
O(7)–Tb(1)–O(9b)	78.70(7)	O(3)–Tb(1)–O(1w)	84.52(7)
2			
Tb(1)–O(8a)	2.279(5)	Tb(1)–O(1)	2.412(5)
Tb(1)–O(7)	2.291(5)	Tb(1)–O(2w)	2.429(7)
Tb(1)–O(13b)	2.333(6)	Tb(1)–O(1w)	2.444(6)
Tb(1)–O(14a)	2.380(5)		
Tb(2)–O(12)	2.540(4)	Tb(2)–O(4w)	2.411(5)
Tb(2)–O(3c)	2.304(4)	Tb(2)–O(3w)	2.421(5)
Tb(2)–O(9a)	2.344(5)	Tb(2)–O(12c)	2.503(4)
Tb(2)–O(6)	2.346(5)	Tb(2)–O(11)	2.504(4)
O(8a)–Tb(1)–O(7)	82.9(2)	O(13b)–Tb(1)–O(1)	86.7(2)
O(8a)–Tb(1)–O(13b)	163.2(2)	O(14a)–Tb(1)–O(1)	74.6(2)
O(7)–Tb(1)–O(13b)	92.8(2)	O(8a)–Tb(1)–O(2w)	119.7(3)
O(8a)–Tb(1)–O(14a)	81.4(2)	O(7)–Tb(1)–O(2w)	74.6(2)
O(7)–Tb(1)–O(14)	132.8(2)	O(13b)–Tb(1)–O(2w)	74.3(3)
O(13b)–Tb(1)–O(14a)	112.8(2)	O(14a)–Tb(1)–O(2w)	75.4(2)
O(8a)–Tb(1)–O(1)	88.7(2)	O(1)–Tb(1)–O(2w)	134.3(2)
O(8a)–Tb(1)–O(1w)	79.1(3)	O(8a)–Tb(1)–O(13a)	122.9(2)
O(7)–Tb(1)–O(1w)	75.5(2)	O(7)–Tb(1)–O(13a)	141.7(2)
O(13b)–Tb(1)–O(1w)	84.0(3)	O(13b)–Tb(1)–O(13a)	69.6(2)
O(14a)–Tb(1)–O(1w)	142.6(2)	O(14a)–Tb(1)–O(13a)	43.7(2)
O(1)–Tb(1)–O(1w)	73.4(2)	O(1)–Tb(1)–O(13a)	66.7(2)
O(2w)–Tb(1)–O(1w)	141.9(2)	O(2w)–Tb(1)–O(13a)	67.8(2)
O(7)–Tb(1)–O(1)	148.9(2)	O(1w)–Tb(1)–O(13a)	132.6(2)
O(3c)–Tb(2)–O(9a)	90.0(2)	O(6)–Tb(2)–O(3w)	76.4(2)
O(3c)–Tb(2)–O(6)	139.8(2)	O(4w)–Tb(2)–O(3w)	134.3(2)
O(9a)–Tb(2)–O(6)	99.3(2)	O(3c)–Tb(2)–O(12d)	73.43(2)
O(3c)–Tb(2)–O(4w)	73.2(2)	O(9a)–Tb(2)–O(12d)	92.7(2)
O(9a)–Tb(2)–O(4w)	77.6(2)	O(6)–Tb(2)–O(12)	144.0(2)
O(6)–Tb(2)–O(4w)	70.8(2)	O(4w)–Tb(2)–O(12d)	145.2(2)
O(3c)–Tb(2)–O(3w)	143.7(2)	O(3w)–Tb(2)–O(12d)	73.3(2)
O(9a)–Tb(2)–O(3w)	77.4(2)	O(3c)–Tb(2)–O(12)	106.54(2)
O(3c)–Tb(2)–O(11)	80.94(2)	O(9a)–Tb(2)–O(12)	149.30(2)
O(9a)–Tb(2)–O(11)	159.06(2)	O(6)–Tb(2)–O(12)	84.64(2)
O(6)–Tb(2)–O(11)	76.42(2)	O(4w)–Tb(2)–O(12)	131.57(2)
O(4w)–Tb(2)–O(11)	81.83(2)	O(3w)–Tb(2)–O(12)	74.01(1)
O(3w)–Tb(2)–O(11)	120.40(1)	O(12d)–Tb(2)–O(12)	68.71(1)
O(12d)–Tb(2)–O(11)	102.77(1)	O(11)–Tb(2)–O(12)	51.49(1)
3			
Tb(1)–O(6a)	2.298(4)	Tb(1)–O(4b)	2.410(5)
Tb(1)–O(7)	2.362(4)	Tb(1)–O(3b)	2.465(5)
Tb(1)–O(2a)	2.353(5)	Tb(1)–N(1)	2.603(6)
Tb(1)–O(1)	2.379(5)	Tb(1)–N(2)	2.607(5)
O(6a)–Tb(1)–O(7)	124.7(2)	O(4b)–Tb(1)–O(3b)	53.6(2)
O(6a)–Tb(1)–O(2)	73.3(2)	O(6a)–Tb(1)–N(1)	81.1(2)
O(7)–Tb(1)–O(2a)	79.6(2)	O(7)–Tb(1)–N(1)	141.3(2)
O(6a)–Tb(1)–O(1)	80.9(2)	O(2a)–Tb(1)–N(1)	138.9(2)
O(7)–Tb(1)–O(1)	79.8(2)	O(1)–Tb(1)–N(1)	76.4(2)
O(2a)–Tb(1)–O(1)	128.6(2)	O(4b)–Tb(1)–N(1)	102.7(2)
O(6a)–Tb(1)–O(4b)	137.7(2)	O(3b)–Tb(1)–N(1)	71.1(2)
O(7)–Tb(1)–O(4b)	77.6(2)	O(6a)–Tb(1)–N(2)	137.8(2)
O(2a)–Tb(1)–O(4b)	77.6(2)	O(7)–Tb(1)–N(2)	80.8(2)
O(1)–Tb(1)–O(4b)	141.0(2)	O(2a)–Tb(1)–N(2)	148.9(2)
O(6a)–Tb(1)–O(3b)	89.8(2)	O(1)–Tb(1)–N(2)	70.6(2)
O(7)–Tb(1)–O(3b)	129.4(2)	O(4b)–Tb(1)–N(2)	74.7(2)
O(2a)–Tb(1)–O(3b)	77.1(2)	O(3b)–Tb(1)–N(2)	97.2(2)
O(1)–Tb(1)–O(3b)	147.3(2)	N(1)–Tb(1)–N(2)	62.6(2)

^a Symmetry codes: for **1**: (a) $-x, -y+1, -z$; (b) $-x-1/2, -y+1/2, -z$; (c) $-x, -y, -z$; for **2**: (a) $-x+1/2, y+1/2, -z+1/2$; (b) $x+1/2, -y-1/2, z+1/2$; (c) $x-1/2, -y+1/2, z-1/2$; (d) $-x, -y, -z$; for **3**: (a) $-x+3/2, -y+3/2, -z+1$; (b) $x-1/2, y-1/2, z$; (c) $x+1/2, y+1/2, z$.

**Fig. 1** Perspective views of (a) the coordination environment of the Tb(III) atom and (b) two-dimensional network in **1** viewed along the *c* axis.

having a small O–C–O bond angle [120.1(5)°] similar to the chelate ones. As illustrated in Fig. 2(a), there are two types of metal environments in **2**. Tb1 is coordinated by four oxygen atoms from four bidentate oba carboxylate ends, one oxygen atom from a bis-monodentate oba ligand, and two aqua oxygen atoms to furnish a seven-fold coordination with the Tb1–O bond lengths in the range 2.279(5) to 2.444(6) Å and the O–Tb1–O bond angles in the range 51.5(1) to 163.2(2)°. Tb2 is ligated by one oxygen atom from a bis-monodentate oba ligand, two oxygen atoms from two bis-bidentate oba ligands, three oxygen atoms from two tridentate carboxylate ends and two aqua oxygen atoms to furnish an eight-fold coordination with the Tb2–O bond lengths in the range 2.304(4) to 2.540(4) Å and the O–Tb2–O bond angles in the range 73.2(2) to 159.1(2)°. Each pair of adjacent Tb1...Tb1, Tb1...Tb2 and Tb2...Tb2 are alternately bridged by a pair of μ -carboxylate ends from the bis-bidentate oba ligands, a pair of μ -carboxylate ends from bidentate-tridentate oba ligands, and a pair of μ_3 -carboxylate ends from bidentate-tridentate oba ligands into one-dimensional covalent chains running along the *c* axis, in which the adjacent Tb1...Tb1, Tb1...Tb2 and Tb2...Tb2 separations are 4.523(2), 5.271(2) and 4.160(2) Å, respectively. These one-dimensional covalent chains are further interconnected by the organic oba bridges to produce two-dimensional networks parallel to the *bc* plane [Fig. 2(b)]. These two-dimensional layers are stacked into the three-dimensional molecular architecture through hydrogen bonds [O1w...O4 2.842(9) Å, O3w...O4(2) 2.730(9) Å, O3w...O2 2.792(9) Å, O4w...O11 2.783(9) Å], edge-to-face interactions⁴⁰ between the aromatic rings from adjacent layers and van der Waals interactions.

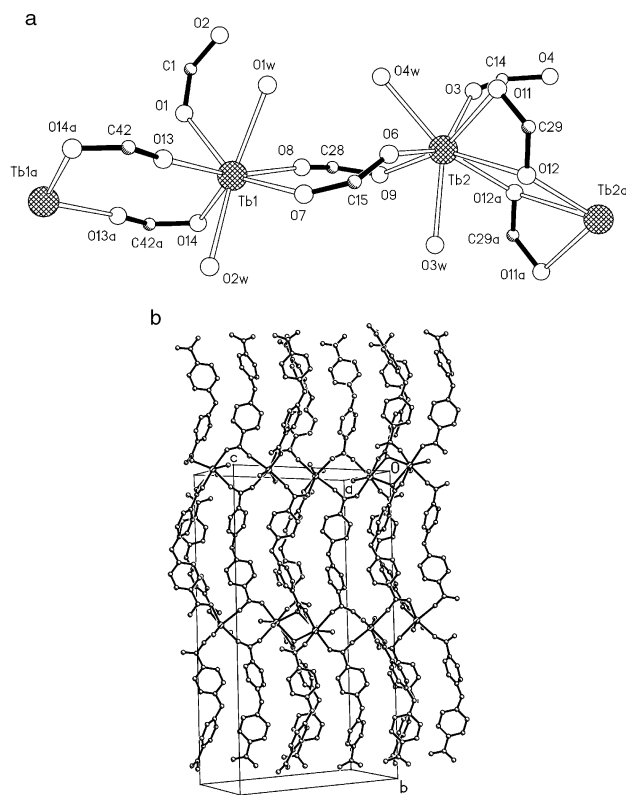


Fig. 2 Perspective views of (a) the coordination environment of the Tb(III) atom and (b) two-dimensional network in **2** viewed along the *b* axis.

Compound **3** was obtained by addition of 2,2'-bpy as an aromatic chelate ligand into the reaction system used to produce **1**. Different from those in the above structures, the oba ligands in **3** act in either the chelate-bidentate or bis-bidentate modes. As expected, the carboxylate C–O bond lengths [C–O = 1.255(7)–1.275(7) Å] and O–C–O bond angles [bridging: *ca.* 125°; chelate: 120.6(6)°] are analogous to the corresponding values found in **1**. As illustrated in Fig. 3(a), the Tb(III) centre

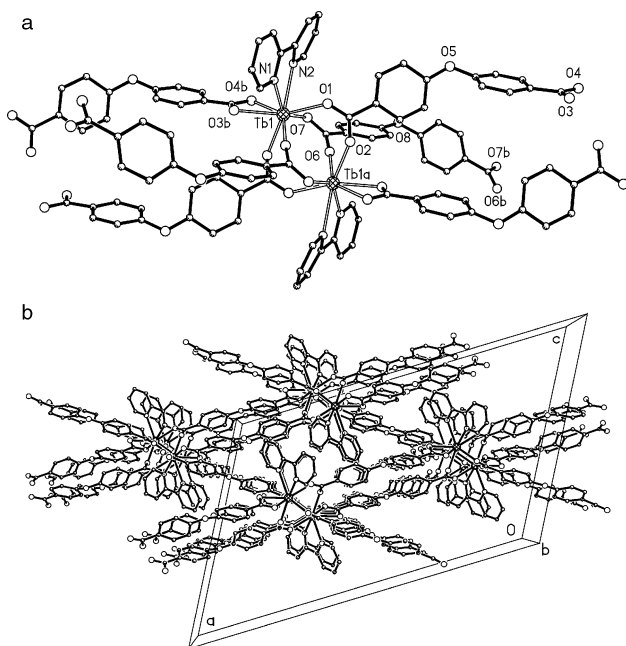
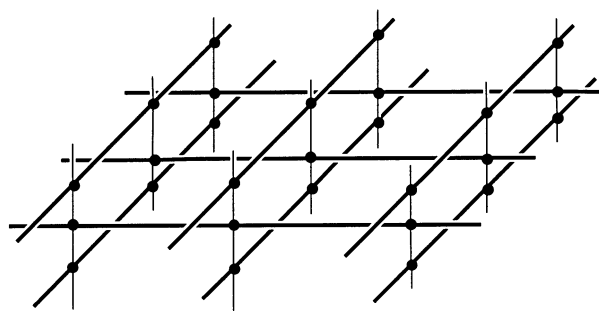


Fig. 3 Perspective views of (a) the coordination environment of the Tb(III) atom and (b) three-dimensional network in **3** viewed along the *b* axis.



Scheme 1 Schematic presentation of the topology in **3**. The dot represents the metal dimer, the thick line represents a pair of oba ligands in the chelate-bidentate mode, and the thin line represents an oba ligand in the bis-bidentate mode.

in this structure is also eight-coordinated by four oxygen atoms from four bidentate bridging oba carboxylate ends of oba ligands, two oxygen atoms from a chelate oba carboxylate end of an oba ligand, as well as two nitrogen atoms from a chelate 2,2'-bpy. The Tb–O bond lengths vary from 2.300(5) to 2.463(4) Å, Tb–N bond lengths vary from 2.608(6) to 2.611(6) Å, and bond angles range from 53.6(2) to 147.4(2)°, as shown in Table 2. A centrosymmetrical tetrakis(carboxylate-*O,O'*)-bridged Tb(III) dimeric structural subunit is now formed with a metal-metal separation of 4.220(3) Å. These dimers are cross-linked by the oba ligands into a three-dimensional framework featuring a rhombic net motif in the *b* axis direction [Fig. 3(b)], within the rhombic “channel” the 2,2'-bpy ligands are located and chelate to the metal atoms. The topology is shown in Scheme 1. The crystal structure of **3** shows that the ligation of an auxiliary 2,2'-bpy ligand not only excludes coordination of aqua ligands, but also results in a highly different topology. It should be mentioned that, with addition of 2,2'-bpy as an aromatic chelate ligand into the reaction system of **2**, the same product (**3**) was isolated and proved by single-crystal X-ray diffraction.

Luminescent properties

1, **2** and **3** in the solid state all emit the characteristic bright colour of Tb(III) when excited with UV light at room temperature, as shown in Fig. 4. Their emission spectra are essentially identical except for the intensity. The emission peaks at 490, 545, 585, and 625 nm can be assigned to $^5D_4 \rightarrow ^7F_n$ ($n = 6, 5, 4, 3$) transitions, respectively. Qualitatively, the intensities are in the order of **3** > **1** > **2**, which is in consistent with the aromatic ring : metal ratios. The difference between the excitation spectra of **1** and **2** might possibly be attributed to the different configurations of the oba ligands. Based on the crystal structures, the co-planarity between the carboxy and phenyl groups of each benzoate group of the organic ligands is different; in **1**, the O–C–C–C torsion angles vary in the range of 2.6–18.7°; whereas in **2**, the corresponding torsion angles vary in the range of 2.6–35°. Hence, the greater co-planarity of the benzoate groups in solid **1** may increase the $\pi \rightarrow \pi^*$ absorption at high wavelength, resulting in the shoulder band. Meanwhile, the maximum absorption wavelength of **3** is red-shifted quite significantly in comparison to those of **1** and **2** due to the contribution of 2,2'-bpy. The fluorescent delay curves of $^5D_4 \rightarrow ^7F_5$ for Tb(III) in **1**, **2** and **3** were also measured, showing that the lifetimes of Tb(III) are respectively 0.82, 0.79 and 1.05 ms. Although we were unable to determine the quantum yields for these compounds due to the insoluble nature of these polymers, our observations of an increase in lifetime for **3** may be attributed to the co-ligand effect of 2,2'-bpy in **3**, which suggests efficient energy transfer from 2,2'-bpy to the central Tb(III) ion.

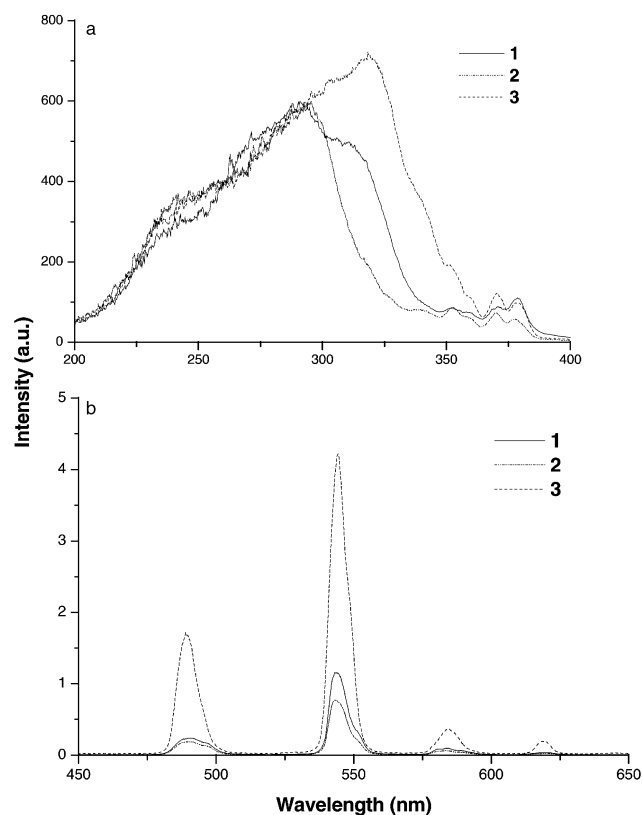


Fig. 4 The (a) excitation and (b) emission spectra of **1**, **2** and **3**.

Conclusions

Three terbium coordination polymers have been generated under hydrothermal conditions. Our results show that different metal : carboxylate ratios can influence the polymeric structures and that the presence of 2,2'-bpy ligand alters not only the topology of the framework from two-dimensional to three-dimensional, but also the photoluminescent properties in both intensity and lifetime. These observations suggest a possible route for construction of intensive luminescent lanthanide(III) coordination polymers with long lifetimes.

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