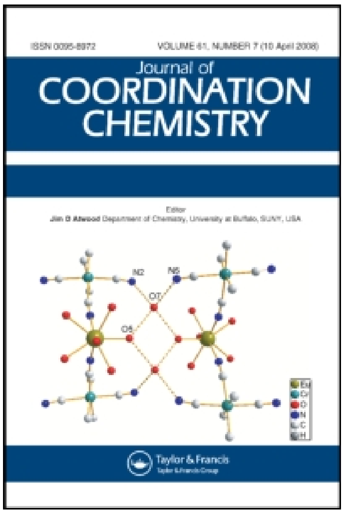

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Synthesis and characterization of two 3-D polymeric lanthanide complexes constructed from 1,2,4,5-benzenetetracarboxylic acid

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Synthesis and characterization of two 3-D polymeric lanthanide complexes constructed from 1,2,4,5-benzenetetracarboxylic acid

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Two 3-D porous coordination polymers, $[\mathrm{Nd}({}^{a}\mathrm{btec})_{2/4}({}^{b}\mathrm{btec})_{2/4}(\mathrm{H_2O})]_n$ (**1**) and $[\mathrm{NdYb}({}^{c}\mathrm{btec})_{2/4}({}^{d}\mathrm{btec})_{2/4}({}^{e}\mathrm{btec})_{2/4}(\mathrm{H_2O})_4]_n$ (**2**), have been prepared by the hydrothermal method at 160°C. Both complexes were characterized by elemental analyses, photoluminescence spectra, and single-crystal X-ray diffraction.

Keywords: Coordination polymer; Hydrothermal method; Photoluminescence spectra; 1,2,4,5-Benzenetetracarboxylic acid

1. Introduction

Porous coordination polymers with open channels have potential applications in the heterogeneous catalysts, separation, preparation of sensors, and storage materials [1–5]. Benzene carboxylate compounds [6, 7] have given rise to a large number of coordination polymers with interesting structural, physical, and chemical properties [8–14]. Of the many benzenecarboxylate compounds prepared and characterized, we are interested in those of the 1,2,4,5-benzenetetracarboxylic acid. Variations in binding modes for the construction of coordination polymers have developed rapidly, owing to their interesting molecular topologies and crystal packing motifs along with the potential applications as functional materials [15–17]. Herein, we report the synthesis and characterizations of two 3-D polymeric complexes

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constructed by 1,2,4,5-benzenetetracarboxylic acid; different coordination modes are discussed.

2. Experimental

2.1. *General*

All chemicals are commercially available and used as received. Elemental analyses were carried out on a Perkin Elmer 2400 element analyzer. IR spectra were obtained on an EQUINOX55 FTIR spectrometer. Solid-state photoluminescent spectra were carried out on a 970CRT fluorescence spectrophotometer at room temperature.

2.2. *Synthesis of complexes*

2.2.1. $[\mathrm{Nd}(^{a}\mathrm{btec})_{2/4}(^{b}\mathrm{btec})_{2/4}(\mathrm{H_2O})]_n$ (1). A mixture of $NdCl_3 \cdot 6H_2O$ (0.0713 g, 0.2 mmol), 1,2,4,5-benzenetetracarboxylic acid (0.0300 g, 0.1 mmol), $CoCl_2 \cdot 6H_2O$ (0.0480 g, 0.2 mmol), and 10 mL water was stirred for 30 min and then heated in a stainless steel reactor with Teflon liner at 160°C for 72 h. After cooling at $10^{\circ}\mathrm{C\,h^{-1}}$, violet crystals were obtained. Yield: 60%. Anal. Calcd for $C_{10}H_4O_9Nd$: C, 29.13; H, 0.98. Found: C, 28.79; H, 1.01. IR (KBr pellet, $\mathrm{cm^{-1}}$): 3462(vs), 1599(s), 1543(s), 1391(vs), 1300(s), 1122(m), 876(m), 835(s), 765(m), 587(s), 515(s).

2.2.2. $[\mathrm{NdYb}(^{c}\mathrm{btec})_{2/4}(^{d}\mathrm{btec})_{2/4}(^{e}\mathrm{btec})_{2/4}(\mathrm{H_2O})_4]_n$ (2). A mixture of $NdCl_3 \cdot 6H_2O$ (0.0360 g, 0.1 mmol), 1,2,4,5-benzenetetracarboxylic acid (0.0300 g, 0.1 mmol), $Yb(NO_3)_3 \cdot 6H_2O$ (0.047 g, 0.1 mmol), and 10 mL water was stirred for 30 min and then heated in a stainless steel reactor with Teflon liner at 160°C for 72 h. After cooling at $10^{\circ}\mathrm{C\,h^{-1}}$, light violet crystals were obtained. Yield: 53%. Anal. Calcd for $C_{15}H_{11}NdO_{16}Yb$: C, 23.57; H, 1.45. Found: C, 23.80; H, 1.12. IR (KBr pellet, $\mathrm{cm^{-1}}$): 3446(vs), 1617(s), 1542(s), 1502(s), 1388(vs), 1139(m), 878(m), 826(s), 764(s), 584(s), 513(s).

2.3. *X-ray crystal structure determination*

Determination of the unit cell and data collection were performed on a Bruker SMART APEX CCD X-ray diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Semiempirical absorption corrections were applied using SADABS. The crystallography details for the structure determinations of **1** and **2** are presented in table 1. Selected bond lengths and angles are listed in tables 2 and 3.

Table 1. Crystal data and structure refinement parameters for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{10}H_4NdO_9$	$C_{15}H_{11}NdO_{16}Yb$
Formula weight	412.38	764.52
Temperature (K)	293(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	*P-1*	*P-1*
Unit cell dimensions (Å, °)		
a	6.4146(9)	9.6784(19)
b	9.3821(13)	11.058(10)
c	9.5654(13)	11.385(2)
α	88.409(10)	105.11(3)
β	74.380(10)	90.23(3)
γ	76.624(10)	113.98(3)
Volume (Å^3), Z	539.00(13), 2	1066.4(4), 2
Calculated density (mg cm^{-3})	2.547	2.381
Absorption coefficient (mm^{-1})	4.87	6.88
$F(000)$	394	718
θ range for data collection (°)	2.2–28.2	2.1–26.2
Reflections collected	4134	4236
Independent reflection	1997 [R(int) = 0.010]	3908 [R(int) = 0.026]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.013$, $wR_2 = 0.033$	$R_1 = 0.031$, $wR_2 = 0.069$
R indices (all data)	$R_1 = 0.013$, $wR_2 = 0.033$	$R_1 = 0.035$, $wR_2 = 0.071$

Table 2. Selected bond lengths and angles for **1**.

Nd1–O2^{i}	2.3880(18)	O2^{i}–Nd1–O9	139.74(7)
O7–Nd1^{ii}	2.5121(16)	O1–Nd1–O9	66.51(6)
Nd1–O1	2.4397(17)	O2^{i}–Nd1–O7^{ii}	81.04(6)
Nd1–O9	2.4567(19)	Nd1–O8^{iii}	2.5164(17)
O8–Nd1^{v}	2.5164(17)	Nd1–O3^{iv}	2.5427(17)
Nd1–O7^{ii}	2.5121(16)	Nd1–O5	2.5444(17)
O8–Nd1^{ii}	2.6113(17)	Nd1–O6	2.5725(16)
O1–Nd1–O7^{ii}	72.50(6)	O8^{iii}–Nd1–O3^{iv}	85.70(6)
O9–Nd1–O7^{ii}	102.52(7)	O2^{i}–Nd1–O5	72.57(6)
O2^{i}–Nd1–O8^{iii}	145.52(6)	O1–Nd1–O5	142.29(6)
O1–Nd1–O8^{iii}	136.52(6)	O9–Nd1–O5	130.30(7)
O9–Nd1–O8^{iii}	70.32(6)	O7^{ii}–Nd1–O5	122.66(5)
O7^{ii}Nd1–O8^{iii}	113.09(5)	O8^{iii}–Nd1–O5	73.48(6)
O2^{i}–Nd1–O3^{iv}	88.69(7)	O3^{iv}–Nd1–O5	70.67(5)
O1–Nd1–O3^{iv}	87.18(6)	O2^{i}–Nd1–O6	73.36(6)
O9–Nd1–O3^{iv}	73.73(7)	O1–Nd1–O6	137.31(6)
O7^{ii}–Nd1–O3^{iv}	158.81(6)	O9–Nd1–O6	146.53(6)

Symmetry codes: $^{i}-x+1, -y+1, -z+1$; $^{ii}-x+1, -y+1, -z$; $^{iii}x+1, y, z$; $^{iv}x+1, y-1, z$; $^{v}x-1, y, z$.

3. Results and discussion

3.1. *Synthesis*

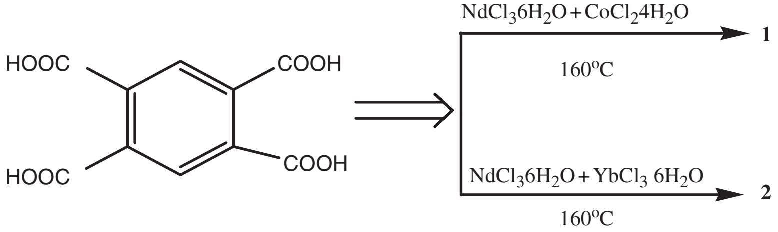
Complexes **1** and **2** were synthesized from 1,2,4,5-benzenetetracarboxylic acid, and $NdCl_3 \cdot 6H_2O$ or $NdCl_3 \cdot 6H_2O$ and $Yb(NO_3)_3 \cdot 6H_2O$ under the hydrothermal condition. In the synthesis of **1**, $CoCl_2 \cdot 6H_2O$ was added as a reactant, but Co(II) did not

Table 3. Selected bond lengths and angles for **2**.

Nd1–O5	2.414(4)	Nd2–O7	2.353(4)
Nd1–O9	2.417(5)	Nd2–O3W	2.379(5)
Nd1–O1W	2.431(4)	Nd2–O4	2.393(4)
Nd1–O3	2.435(4)	Nd2–O8	2.465(4)
Nd1–O1^{i}	2.477(4)	Nd2–O3	2.488(4)
Nd1–O2W	2.506(5)	O1–Yb1^{i}	2.477(4)
Nd1–O2^{i}	2.658(4)	O1–Nd1^{i}	2.477(4)
Nd2–O12^{ii}	2.202(5)	O2–Yb1^{i}	2.658(4)
Nd2–O10	2.238(4)	O2–Nd1^{i}	2.658(4)
Nd2–O4W	2.262(5)	O6–Yb1^{i}	2.345(4)
O12–Yb2^{ii}	2.202(5)	O2–Yb1^{i}	2.658(4)
Nd2–O12^{ii}	2.202(5)	O2–Nd1^{i}	2.658(4)
Nd2–O10	2.238(4)	O6–Yb1^{i}	2.345(4)
Nd2–O4W	2.262(5)	O6–Nd1^{i}	2.345(4)
Nd2–O7	2.353(4)	O12–Yb2^{ii}	2.202(5)
Nd2–O3W	2.379(5)	O2–Yb1^{i}	2.658(4)
Nd2–O4	2.393(4)	O3–Nd1–O2^{i}	139.63(14)
Nd2–O8	2.465(4)	O1–Nd1–O2^{i}	116.26(13)
Nd2–O3	2.488(4)	O1^{i}–Nd1–O2^{i}	50.71(14)
O1–Nd1^{i}	2.477(4)	O2W–Nd1–O2^{i}	63.44(14)
O5–Nd1–O1^{i}	73.44(13)	O12^{ii}–Nd2–O3	80.68(17)
O9–Nd1–O1^{i}	122.58(14)	O4W–Nd2–O3	131.84(18)
O1W–Nd1–O1^{i}	143.92(14)	O7–Nd2–O3	72.80(14)
O6^{i}–Nd1–O2W	71.54(16)	O8–Nd2–O3	115.27(14)
O5–Nd1–O2W	130.05(14)	O6^{i}–Nd1–O2^{i}	107.75(14)
O9–Nd1–O2W	77.16(16)	O5–Nd1–O2^{i}	67.99(13)
O1W–Nd1–O2W	73.60(15)	O9–Nd1–O2^{i}	72.62(14)

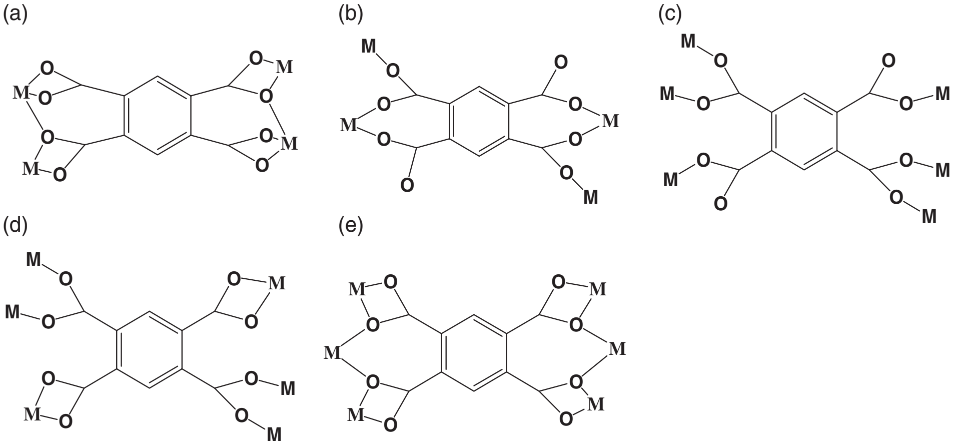
Symmetry codes: ${}^{i}-x+2,\ -y+1,\ -z+1$; ${}^{ii}-x+2,\ -y,\ -z$.

coordinate with 1,2,4,5-benzenetetracarboxylic acid. However, we cannot obtain crystals of **1** under the same conditions in the absence of $CoCl_2 \cdot 6H_2O$. Hence, it appears that $CoCl_2 \cdot 6H_2O$ plays a role in the crystallization of **1**. For both complexes, the pH was 4–5.



3.2. *Structural description*

As shown in scheme 1, five different types of coordination modes of btec^{4-} are presented in **1** and **2**. They are: (a) two *para*-carboxylates bidentate chelating, coordinating to one neodymium, whereas each of the other two *para*-carboxylates adopts a chelating-bridging mode; the whole ligand connects four neodymiums (^{a}btec, scheme 1a); (b) each of two *ortho*-carboxylates is bidentate chelating two



Scheme 1. Different types of coordination modes of btec^{4-}.

neodymiums. One *para*-carboxylate is monodentate, bridging two neodymiums (^{b}btec, scheme 1b); (c) each *para*-carboxylate is monodentate, coordinating to one metal, whereas each of the other two *para*-carboxylates is bidentate bridging, linking two metals (^{c}btec^{4-}, scheme 1c); (d) each of the two *para*-carboxylates bridges two metals, while each of the other two *para*-carboxylates chelates one metal (^{d}btec^{4-}, scheme 1d); and (e) each carboxylate adopts a chelating-bridging mode, and the whole ligand connects six metals (^{e}btec^{4-}, scheme 1e).

3.2.1. $[Nd(^{a}btec)_{2/4}(^{b}btec)_{2/4}(H_2O)]_n$ (1). Complex **1** is a 3-D porous polymer with the ladder structure, as shown in figure 1(b). Two coordination modes of btec^{4-} are presented in the structure, type (a) and (b). As shown in scheme 1(a) and (b), a neodymium(III) is coordinated by nine oxygens, common in the literature [18–20]. Complex **1** has a complex and interesting structure, as shown in figure 1. One oxygen is from coordinated water and the other eight are from benzenetetracarboxylic acid (figure 1a). The Nd–O bond distances range from 2.388 to 2.611 Å, compared to those reported for neodymium complexes [18–20]. Two coordination modes of btec^{4-} are shown in figure 1(c). Yellow represents the ^{a}btec^{4-} and blue the ^{b}btec^{4-}. Crystal data and structure refinement parameters are shown in table 1.

3.2.2. $[NdYb(^{c}btec)_{2/4}(^{d}btec)_{2/4}(^{e}btec)_{2/4}(H_2O)_4]_n$ (2). Complex **2** is a dinuclear species with a 3-D porous structure (as shown in figure 2b); it is hard to determine the heavy atoms in **2** because Nd and Yb have the same occupation possibility. According to the reactants we use, and common coordination numbers [21], we determine Nd and Yb. Similar to **1**, all carboxyl groups are deprotonated and three types of coordination modes of btec^{4-} exist [21]; type (c), (d), and (e) shown in scheme 1. Yb/Nd–O distances range from 2.202(5) to 2.658(4) Å, compared to those reported for Nd–O [18–20] that are from 2.313(4) to 2.771(4) Å and Yb–O [21] that are from 2.218(7) to 2.420(7) Å. In the structure of **2**, Yb was coordinated by eight oxygens, with two from the coordinated water. This coordination is similar

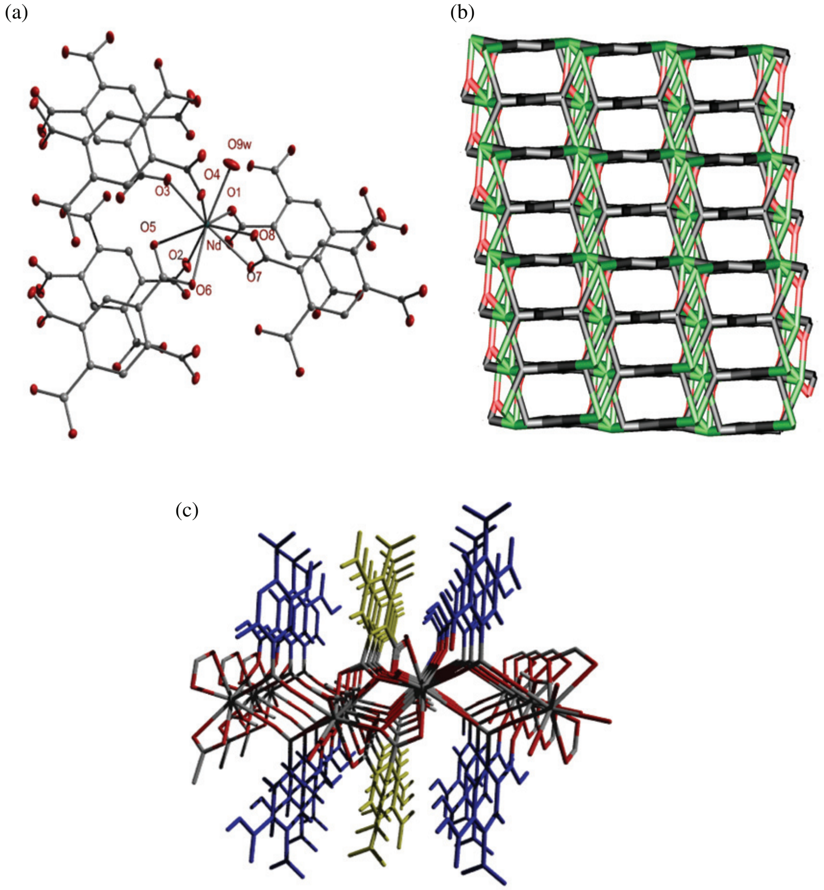


Figure 1. (a) Nine-coordinate Nd(III); (b) the ladder structure of **1**; and (c) the arrangement of different ligands in **1**.

to $[\{Yb(^{b}btec)_{1/4}(^{d}btec)_{3/6}(H_2O)_2\}_4 6H_2O]_n$ [21]. Nd was coordinated by nine oxygens, two from the coordinated water. The 3-D porous framework of **2** viewed along an *a*-axis (lattice water molecules are omitted for clarity) is shown in figure 2(c); space arrangement of three kinds of ligands (blue, green, and violet represent three different ligands) of **2** is shown in figure 2(d). Crystal data and structure refinement parameters are shown in table 1. The bimetallic Nd–Yb structures are rare in previous literature. In this kind of structure, Nd and Yb keep their common coordination number (nine for Nd and eight for Yb), which helped us to determine the metals of **2**.

3.3. *Solid-state photoluminescence spectra*

Both the acid and complexes show photoluminescence at room temperature (figure 3). As shown in figure 3(a), H_4btec exhibits fluorescent emission bands at 337 nm ($\lambda_{ex} = 280$ nm). Complexes **1** and **2** show the familiar multiple

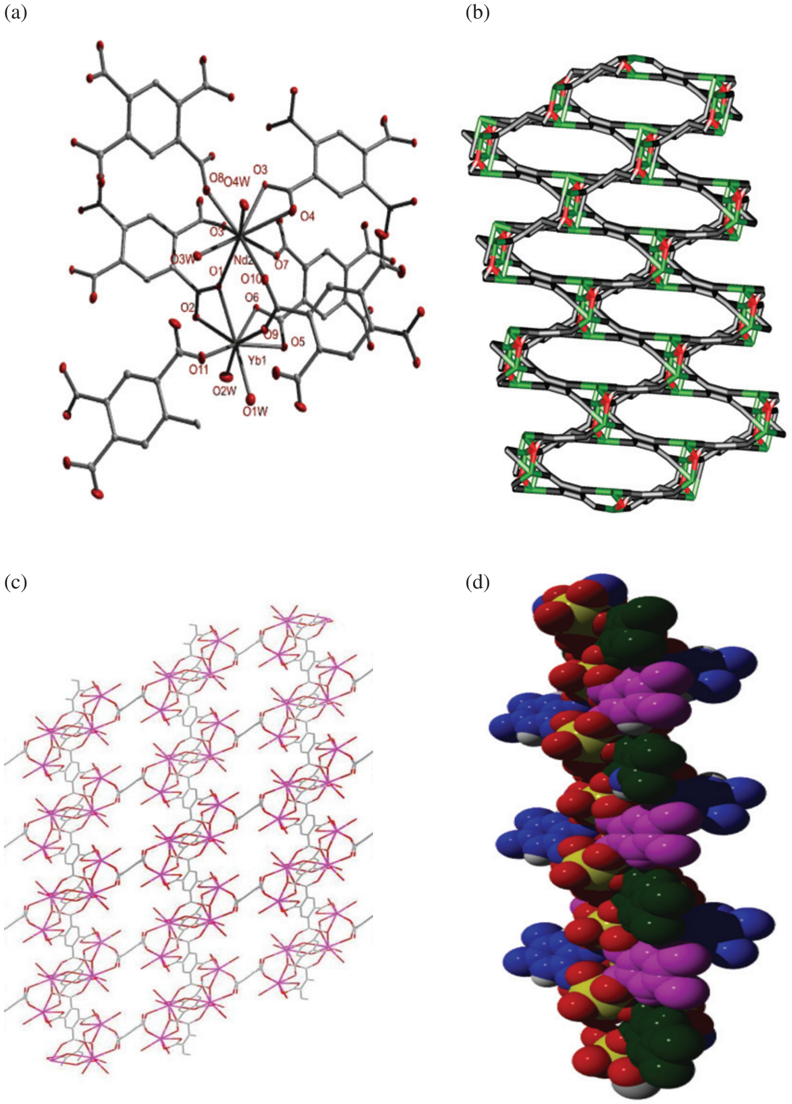


Figure 2. (a) Nine-coordinate Nd(III) and eight-coordinate Yb(III); (b) the porous structure of **2**; (c) the 3-D porous framework of **2** viewed along the *a*-axis (lattice water molecules are omitted for clarity); and (d) the arrangement of three kinds of ligands, blue, green, and violet, in **2**.

photoluminescence spectra which were monitored at the excitation wavelength of 280 and 300 nm, as shown in figure 3(b). Taking the emission bands of organic ligands into consideration, the emissions of **1** and **2** may be attributed to the ligand-to-metal charge transition (LMCT) [22–25]. The little difference between **1** and **2** may be attributed to their different 3-D structures.

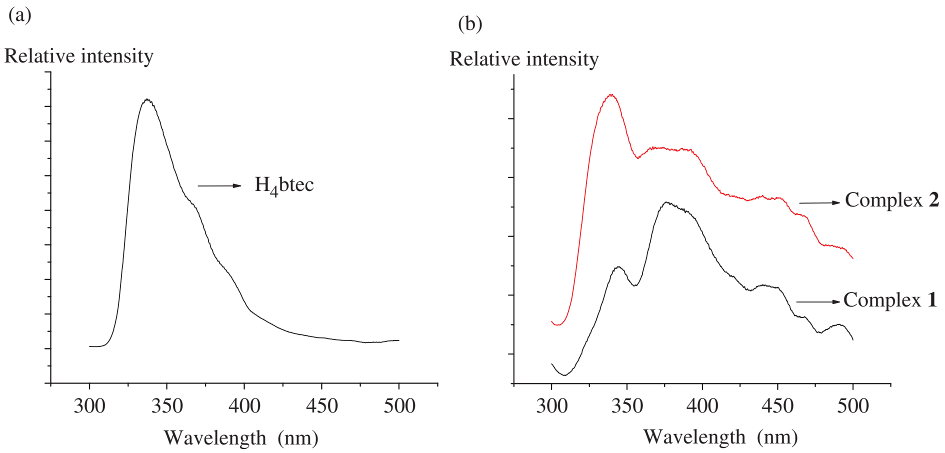


Figure 3. (a) Solid-state photoluminescence spectra of H_4btec ($\lambda_{ex} = 280$ nm); and (b) photoluminescence spectra of **1** ($\lambda_{ex} = 280$ nm) and **2** ($\lambda_{ex} = 300$ nm) at room temperature.

4. Conclusion

We have assembled 1,2,4,5-tetracarboxylate and Ln(III) into two 3-D porous polymeric complexes, $[Nd(^{a}btec)_{2/4}(^{b}btec)_{2/4}(H_2O)]_n$ (**1**) and $[NdYb(^{c}btec)_{2/4}(^{d}btec)_{2/4}(^{e}btec)_{2/4}(H_2O)_4]_n$ (**2**). The bimetal Nd–Yb structure in **2** has not been reported before. In the synthesis process, $CoCl_2 \cdot 6H_2O$ plays a crucial role in the formation of **1**, although Co(II) did not coordinate. We attribute this to $CoCl_2 \cdot 6H_2O$ playing a role in the synthesis of **1**. Both ligand and complexes show strong fluorescence at room temperature.

Supplementary material

Supplementary data are available from The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK, on request (Fax: +44 1223 336033; Email: deposit@ccdc.com.ac.uk or www: http://www.ccdc.cam.ac.uk) quoting the deposition numbers 664626 (**1**) and 706887 (**2**).

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