



Low pH hydrothermal syntheses, structural characterization and properties of several lanthanide complexes constructed with 1,2,3,5-benzenetetracarboxylic acid

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ABSTRACT

Fourteen new lanthanide coordination complexes based on tetracarboxyl tecton ligands, namely, $[\text{Ln}(\text{Hbtec})(\text{H}_2\text{O})_2]$ ($\text{Ln} = \text{La}$ (**1**) Ce (**2**) Pr (**3**) Nd (**4**) Sm (**5**) Gd (**6**) Dy (**7**) Ho (**8**) Er (**9**) Yb (**10**) Y (**11**)), $[\text{Yb}(\text{Hbtec})(\text{H}_2\text{O})_2]$ (**12**), $[\text{Na}_2\text{La}_2(\text{btec})_2(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$ (**13**), and $[\text{NaPr}(\text{btec})(\text{H}_2\text{O})_2]$ (**14**) ($\text{H}_4\text{btec} = 1,2,3,5$ -benzenetetracarboxylic acid) have been prepared and characterized by elemental analysis, IR spectra and X-ray diffraction. Complexes **1–11** are iso-structural, crystallizing in monoclinic $P2_1/c$ space group, the lanthanide atoms are nine coordinated, and the Hbtec^{3-} ligands bridge the Ln(III) metal oxide chain into a two-dimensional double layer structure with **SP 2-periodic** topology. As for complex **12**, it is an isomer of complex **10**. The Yb(III) atom is eight coordinated and leading a two-dimensional sheet with **kgd** topology in **12**. The tetracarboxyl ligands are fully deprotonated into btec^{4-} in complexes **13** and **14** with sodium atoms as counter cations. Different from the previous twelve complexes, the two complexes are **flu** topology three-dimensional framework with the lanthanide atoms ten coordinated. Representative thermal stabilities and photoluminescent properties were also studied.

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1. Introduction

During the past decades, extensive attention have been focused on the design and applications of the lanthanide coordination complexes due to their attractive photophysical properties, such as characteristic luminescent emissions, high fluorescence quantum yields, and long observed lifetimes [1–4]. Those properties enable them to be potential functional materials such as light-emitting devices, chemical sensors, biomedical and cell imaging, etc. [5–9]. On the other hand, different from the transition metal elements, the lanthanide elements possess partially filled 4f orbital, display high coordination number, sometimes lead coordination polymers that exhibit various coordination geometries even with the same ligand.

Similar to the transition metal complexes self-assembly, the choice of ligand is crucial in the formation of lanthanide functional coordination material. The aromatic polycarboxylic acids, such as 1,4-benzenedicarboxylic [10–13], 1,2,3- [14] or 1,3,5-benzenetricarboxylic [15–19], and 1,2,4,5-benzenetetracarboxylic acid [20–25], have been widely used to synthesize high dimensional lanthanide frameworks, various supramolecular structures with

fascinating properties displayed. In those widely developed aromatic poly-carboxylic acids, 1,2,4,5-benzenetetracarboxylic acid have been intensively studied by several groups, during self-assembly process, the four carboxyl groups could be completely or partially deprotonated under different circumstance, leading rich coordination modes. The carboxylate groups act as hydrogen-bond acceptor or hydrogen-bond donor with different deprotonation degree, thus do great influence on the final structure. Furthermore, even under same coordination mode, carboxyl groups could rotate with different angle between the phenyl ring and not being restricted to the same plane could meet the coordination hindrance requirement in different directions.

Despite numerous lanthanide coordination polymers with or without alkaline metal ion have been synthesized based on 1,2,4,5-benzenetetracarboxylic acid, little attention have been focused on its isomer 1,2,3,5-benzenetetracarboxylic acid. The 1,2,3,5-benzenetetracarboxylic acid is a derivative of 1,2,3-benzenetricarboxylic acid containing three adjacent carboxylate groups which prefer the formation of polynuclear coordination complexes [26]. In our previous work, we synthesized a series of transition metal complexes with or without N-donor coligands to construct new coordination polymers [27]. As part of our ongoing interests in exploring the coordination chemistry of 1,2,3,5- H_4btec , we synthesized lanthanide coordination complexes under low pH

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conditions. Herein, we report our research results on the preparation, crystal structures of fourteen Ln(III) complexes assembled from H₄btec and rare earth metal, namely [Ln(Hbtec)(H₂O)₂] (Ln = La (**1**) Ce (**2**) Pr (**3**) Nd (**4**) Sm (**5**) Gd (**6**) Dy (**7**) Ho (**8**) Er (**9**) Yb (**10**) Y (**11**)), [Yb(Hbtec)(H₂O)₂], (**12**), [Na₂La₂(btec)₂(H₂O)₄]-H₂O (**13**), and [NaPr(btec)(H₂O)₂] (**14**). The complexes could be divided into three different families, complexes **1–11** belong to family 1, feature a two-dimensional double layer structure. Complex **12** belongs to the family 2 and features a two-dimensional sheet. Despite different lattice water molecules in complexes **13** and **14**, the frameworks are same and belonging to family 3. Representative thermal stabilities and photoluminescent properties were also studied.

2. Experimental

2.1. Materials and instrumentation

All the solvents and reagents were purchased commercially available and used without further purification. Elemental analyses of C and H were measured with an Elementar Vario EL III analyzer and the IR spectra (KBr pellets) were recorded in the range of 400–4000 cm⁻¹ with a Nicolet Magna 750 FT IR spectrometer. The fluorescence measurements were performed on ground powder samples at room temperature using an Edinburgh Analytical Instrument FLS920. Thermal stability studies (TGA) were carried out on a NETSCH STA-499C thermoanalyzer at a heating rate of 10 °C·min⁻¹ in a nitrogen atmosphere (30–800 °C range). X-ray powder diffractions (XRPD) were collected at room temperature with a Bruker D8 Advanced diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$).

2.2. Preparation of the complexes

2.2.1. Synthesis of [Ln(Hbtec)(H₂O)₂] (Ln = La (**1**) Ce (**2**) Pr (**3**) Nd (**4**) Sm (**5**) Gd (**6**) Dy (**7**) Ho (**8**) Er (**9**) Yb (**10**) Y (**11**))

A mixture of Ln(NO₃)₃·6H₂O (45 mg, 0.1 mmol) and H₄btec (27.4 mg, 0.1 mmol) were added to 10 mL of HAC–H₂O (1:6) was sealed in Teflon-lined stainless steel vessel, heated at 160 °C for 3 days, and cooled to room temperature. Colorless crystals were obtained and dried in air, the yield based on H₄btec range from 55% to about 62%, which are very close.

[La(Hbtec)(H₂O)₂] (**1**). Elemental analysis (%): Calc. for C₁₀H₇O₁₀-La, C, 28.19; H, 1.66. Found: C, 28.14; H, 1.73. IR (KBr pellet): 3578w, 3451s, 3062w, 1716m, 1649w, 1629w, 1589m, 1543s, 1471m, 1414s, 1347w, 1214s, 1144s, 1044s, 810w, 786w, 632w.

[Ce(Hbtec)(H₂O)₂] (**2**). Elemental analysis (%): Calc. for C₁₀H₇O₁₀-Ce, C, 28.11; H, 1.65. Found: C, 28.10; H, 1.63. IR (KBr pellet): 3521w, 3406s, 3089w, 1714m, 1684s, 1617m, 1582m, 1535s, 1482s, 1427m, 1355s, 1223m, 1170s, 1088w, 941w, 854m, 819m, 796s, 724m, 692w, 654w, 599m.

[Pr(Hbtec)(H₂O)₂] (**3**). Elemental analysis (%): Calc. for C₁₀H₇O₁₀-Pr, C, 28.06; H, 1.65. Found: C, 28.13; H, 1.68. IR (KBr pellet): 3428w, 3085w, 1718m, 1679s, 1616m, 1581m, 1539s, 1490s, 1434m, 1356s, 1227m, 1174m, 1087w, 950w, 932m, 859m, 817m, 796w, 726m, 687w, 602m.

[Nd(Hbtec)(H₂O)₂] (**4**). Elemental analysis (%): Calc. for C₁₀H₇-O₁₀Nd, C, 27.84; H, 1.64. Found: C, 27.86; H, 1.69. IR (KBr pellet): 3580s, 3450s, 3065w, 1720m, 1652w, 1628w, 1579s, 1550s, 1472s, 1422s, 1350w, 1215s, 1150s, 1053s, 814w, 784w, 630w.

[Sm(Hbtec)(H₂O)₂] (**5**). Elemental analysis (%): Calc. for C₁₀H₇-O₁₀Sm, C, 27.45; H, 1.61. Found: C, 27.34; H, 1.72. IR (KBr pellet): 3585s, 3451s, 3067w, 1718m, 1650w, 1628w, 1588s, 1549vs, 1473s, 1421vs, 1348w, 1214s, 1151s, 1051s, 812w, 788w, 632w.

[Gd(Hbtec)(H₂O)₂] (**6**). Elemental analysis (%): Calc. for C₁₀H₇O₁₀Gd, C, 27.03; H, 1.59. Found: C, 27.48; H, 1.63. IR (KBr

pellet): 3585s, 3450s, 3067w, 1721m, 1653w, 1629w, 1588s, 1551vs, 1473s, 1423vs, 1349w, 1213s, 1152s, 1055s, 813w, 788w, 633w.

[Dy(Hbtec)(H₂O)₂] (**7**). Elemental analysis (%): Calc. for C₁₀H₇O₁₀Dy, C, 26.71; H, 1.57. Found: C, 26.74; H, 1.54. IR (KBr pellet): 3570s, 3459s, 3316s, 3119s, 1710m, 1638w, 1606s, 1574s, 1551s, 1511s, 1468s, 1402s, 1371s, 1163s, 1117s, 1064s, 832w, 780w, 627w.

[Ho(Hbtec)(H₂O)₂] (**8**). Elemental analysis (%): Calc. for C₁₀H₇O₁₀Ho, C, 26.57; H, 1.56. Found: C, 26.64; H, 1.65. IR (KBr pellet): 3570w, 3460s, 3120w, 1710m, 1630w, 1596s, 1571s, 1550s, 1470s, 1412s, 1370s, 1162s, 1118s, 1064s, 825w, 786w, 630w.

[Er(Hbtec)(H₂O)₂] (**9**). Elemental analysis (%): Calc. for C₁₀H₇O₁₀Er, C, 26.43; H, 1.55. Found: C, 26.44; H, 1.57. IR (KBr pellet): 3570w, 3458s, 3120w, 1712m, 1639w, 1608s, 1574s, 1554s, 1512s, 1470s, 1404vs, 1372s, 1161s, 1119s, 1064s, 833w, 780w, 629w.

[Yb(Hbtec)(H₂O)₂] (**10**). Elemental analysis (%): Calc. for C₁₀H₇O₁₀Yb, C, 26.10; H, 1.53. Found: C, 26.14; H, 1.58. IR (KBr pellet): 3566w, 3450s, 3090w, 1713m, 1681s, 1616w, 1584s, 1546s, 1500s, 1417m, 1409w, 1356s, 1239m, 1180m, 1092w, 956w, 867m, 825w, 791s, 729m, 694w, 609m.

[Y(Hbtec)(H₂O)₂] (**11**). Elemental analysis (%): Calc. for C₁₀H₇O₁₀Y, C, 31.94; H, 1.88. Found: C, 31.85; H, 1.83. IR (KBr pellet): 3486w, 3094w, 1710m, 1630w, 1600s, 1542s, 1463s, 1412s, 1387s, 1328s, 1156w, 1101w, 1037w, 929m, 848s, 806w, 733s, 634m.

2.2.2. Synthesis of [Yb(Hbtec)(H₂O)₂] (**12**)

The preparation of [Yb(Hbtec)(H₂O)₂] **12** was similar to that for complex **1–11**, except that 1 mmol HClO₄ was added to the reaction mixture of Yb(NO₃)₃·6H₂O (45 mg, 0.1 mmol), H₄btec (27 mg, 0.1 mmol) in 10 mL H₂O was sealed in Teflon-lined stainless steel vessel and heated to 160 °C for 72 h, then cooled to room temperature during 8 h. Colorless crystal was obtained and dried in air. The yield based on H₄btec is 35% with tiny complex **10** as byproduct. Elemental analysis (%): Calc. for C₁₀H₇O₁₀Yb, C, 26.10; H, 1.53. Found: C, 26.22; H, 1.56. IR (KBr pellet): 3584w, 3365s, 3082w, 1708m, 1637s, 1578s, 1540w, 1462s, 1408m, 1369s, 1250m, 1175w, 1154w, 1064m, 941m, 852s, 815w, 796s, 739w, 698m, 612s.

2.2.3. Synthesis of [Na₂La₂(btec)₂(H₂O)₄]-H₂O (**13**) and [NaPr(btec)(H₂O)₂] (**14**)

A mixture of Ln(NO₃)₃·6H₂O (45 mg, 0.1 mmol), H₄btec (27.4 mg, 0.1 mmol), and NaOH (40 mg, 1.0 mmol) were added to 10 mL of HAC–H₂O (1:6) was sealed in Teflon-lined stainless steel vessel, heated at 160 °C for 3 days, and cooled to room temperature. Colorless crystals were obtained and dried in air. The yield is 45% for complex **13** and 48% for complex **14**.

[Na₂La₂(btec)₂(H₂O)₄]-H₂O (**13**). Elemental analysis (%): Calc. for C₂₀H₁₄O₂₁La₂Na₂, C, 26.28; H, 1.54. Found: C, 26.04; H, 1.41. IR (KBr pellet): 3477w, 3232w, 1612s, 1567s, 1476m, 1420s, 1381s, 1349m, 1087w, 946m, 852m, 785m, 733s, 662w.

[NaPr(btec)(H₂O)₂] (**14**). Elemental analysis (%): Calc. for C₁₀H₆O₁₀PrNa, C, 26.69; H, 1.34. Found: C, 26.74; H, 1.49. IR (KBr pellet): 3470w, 3235w, 1614s, 1562s, 1468m, 1421s, 1372s, 1347m, 1084w, 951m, 851m, 786m, 730s, 660w.

2.3. Crystal structure determination

Suitable single crystals of complexes **1–14** were carefully selected under an optical microscope and glued to thin glass fibers. The diffraction data were collected on a siemens SMART CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 298 K. An empirical absorption correction was

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