

Template-assisted assembly of porous lanthanide coordination polymers with 2-aminoterephthalic acid

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Abstract

Porous lanthanide coordination polymers, $\{[\text{Ln}_2(\text{atpt})_3(\text{H}_2\text{O})_2] \cdot 0.5(4,4'\text{-bpy})(\text{H}_2\text{O})\}_n$ [Ln = Eu(1), Gd(2), Yb(3), H₂atpt = 2-aminoterephthalic acid, 4,4'-bpy = 4,4'-bipyridine] were obtained by hydro-solvothermal reaction, in which 4,4'-bpy acts as template. For the first time the nitrogen atom of an atpt ligand coordinates to metal ions in 1–3. The photophysical properties and thermal stability of 1 were investigated.

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Much attention has been focused on the assembly of porous networks for their potential applications in catalysis [1,2], adsorption and separation processes [3–6], and ion exchange [7,8]. In designing and synthesizing molecular-based porous materials constructed by coordination bonds, hydrogen bonds and π -stacks, the key factor is to preclude interpenetration. For example, in the compound $[\text{Yb}_2(\text{OH})(\text{atpt})_{2.5}(\text{phen})_2]_n \cdot 1.75\text{H}_2\text{O}$ (phen = 1,10-phenanthroline)[9] which was synthesized previously by us, the cavity in the 2-D structure is fairly large, but the channel in 3-D structure decreases due to the interpenetration of metal-organic frameworks (MOFs). Several tactics have been proven useful in precluding interpenetration: (1) applying branched chain or substituent group to avoid inserting [10]; (2) designing the crystal with specified structure, such as diamond network and NbO network [11]; (3) constructing a porous structure with appropriate guest or template [12–14].

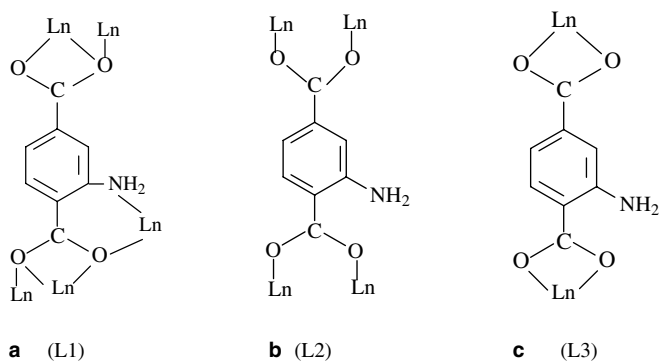
As is known, 4,4'-bpy belongs to soft base, while lanthanide ions belong to hard acid. Based on “soft–hard acid–

base theory”, it is much harder for lanthanide ions to coordinate with nitrogen atoms of 4,4'-bpy [15–17] than for transition metal ions [18–31]. But nitrogen atoms of 4,4'-bpy can form varieties of hydrogen bonds with other function groups, and π – π aromatic interactions can exist between 4,4'-bpy molecules or between 4,4'-bpy and other aromatic rings. Thus 4,4'-bpy can play a template role in porous lanthanide coordination polymers through non-covalent bonds. In the present case, the hydrothermal syntheses [32] and crystal structures [33] and properties of porous lanthanide coordination polymers with 2-aminoterephthalic acid are reported, in which 4,4'-bpy acts as template.

The crystallographic data of the three title complexes show that they are isostructural, so only the structure of 1 will be discussed in detail.

In the three title complexes atpt ligands adopt three coordination modes: (a) atpt ligand adopts an octadentate coordination mode, as shown in Scheme 1a. For convenience the octadentate ligand is named as L1, one L1 links five Ln(III) ions; (b) both of the carboxylate groups adopt a bridging bidentate mode, as shown in Scheme 1b, the tetradentate ligand is named as L2, one L2 ligand links four

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Scheme 1. Coordination modes of atpt ligands in the title complexes.

Ln(III) ions; (c) atpt ligand is coordinated to two Ln(III) ions in a bis-chelating coordination mode, as shown in Scheme 1c, which is named as L3. Carboxyl groups and amino groups of L1, L2 and L3 are in the same plane with the aromatic ring of L1, L2 and L3, respectively.

The asymmetric unit of **1** consists of two europium(III) ions, three atpt ligands, two coordinated and one uncoordinated water molecules, and half of an uncoordinated 4,4'-bpy molecule. In Fig. 1, Eu1 is coordinated with nine oxygen atoms, seven of them from two L1, two L2 and one L3 ligands, and two of them from two coordinated water molecules; Eu2 is coordinated by one nitrogen atom from amino group, eight carboxyl oxygen atoms from three L1, two L2 and one L3 ligands.

L1, L2 and L3 represent the three orientations of atpt ligands in **1**. The dihedral angles between L1 and L2, L1 and L3, L2 and L3 are 88.6(4)°, 161.3(4)° and 101.0(4)°, respectively. Eu(III) ions are joined to a 3-D metal-organic framework with microporous structure by the three orientational atpt ligands in three directions, as shown in Fig. 2.

In **1**, two aromatic rings of 4,4'-bpy are coplanar, the dihedral angles between 4,4'-bpy and L1, L2 and L3 are 160.1(4), 100.6(4)° and 1.6(4)°, respectively, thus 4,4'-bpy

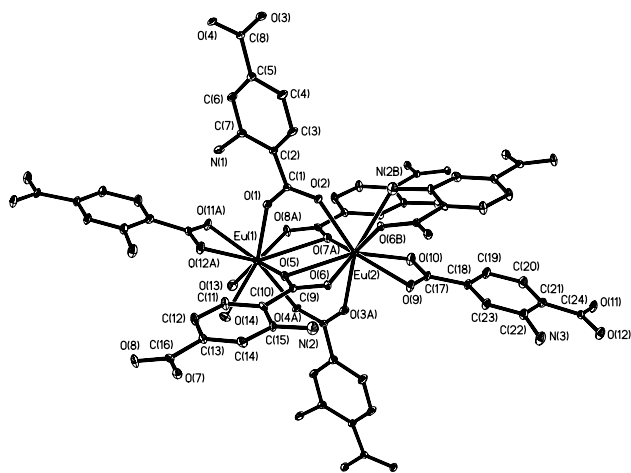


Fig. 1. Coordination environment of Eu(III) ions in **1**. Uncoordinated water and 4,4'-bpy molecules and all hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 20% probability.

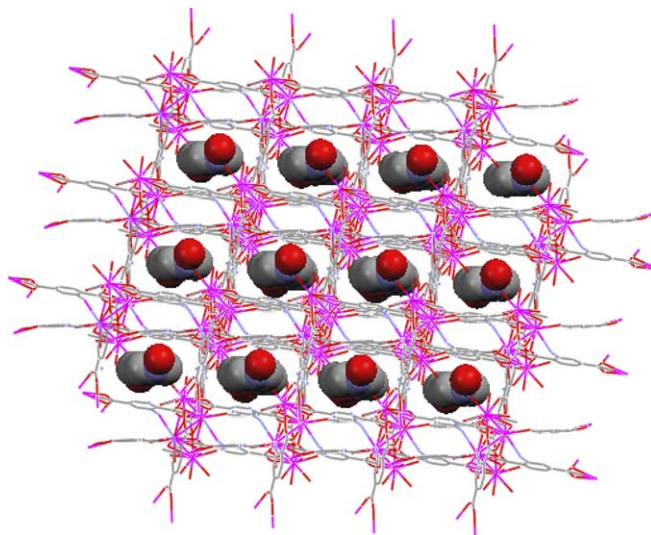


Fig. 2. 3-D structure of **1** viewed along [111] direction, 4,4'-bpy and uncoordinated water molecules in space filling model, all hydrogen atoms are omitted for clarity. (Grey: carbon atoms, Red: oxygen atoms, Blue: nitrogen atoms, Pink: Eu(III) ions). (For interpretation of the references in colour to this figure legend, the reader is referred to the web version of this article.)

molecules are almost parallel to L3 ligands. Two kinds of π - π stacks exist between 4,4'-bpy molecules and L3 ligands with the distance of 3.13(2) and 3.62(2) Å, as shown in Fig. 3a. There are two sorts of O-H...O hydrogen bonds between coordinated and uncoordinated water molecules. The distances of O...O are 2.65(2) and 2.82(2) Å, respectively, which forms a rhombus hydrogen bond network, four oxygen atoms occupy four apexes of the rhombus; uncoordinated water molecules and nitrogen atoms of 4,4'-bpy molecules form O-H...N hydrogen bond, the distance of O...N is 2.63(2) Å, as shown in Fig. 3b. Uncoordinated 4,4'-bpy and uncoordinated water molecules stay in the channels via weak non-covalent interactions (see Fig. 2).

In all the reported complexes with atpt ligands [9,34–41], the nitrogen atom of amino group does not coordinate to metal ions. It is the first time that it coordinates to Ln(III) ions in the title complexes. The average Ln–O bond lengths (2.458(3) Å for **1**, 2.450(6) Å for **2** and 2.386(3) Å for **3**) and Ln–N (2.688(5) Å for **1**, 2.683(8) Å for **2** and 2.599(5) Å for **3**) decrease with the increasing of lanthanide atomic number. But the coordination numbers of lanthanide ions and the coordination modes of atpt ligands in **1–3** are the same, they are not affected by lanthanide contraction, and complexes **1–3** are isostructural, which shows 4,4'-bpy as template plays an important role in the construction of title complexes.

Thermogravimetric analysis (TGA) of the crystalline complex **1** shows that after the loss of one uncoordinated and two coordinated water molecules (4.8%) from 82 to 124 °C (calculated: 5.5%), no weight loss occurred until 239 °C, which indicates the effect of 4,4'-bpy as template on the stability of [Ln₂(atpt)₃] framework. It continued to

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