

Short communication

## Crystal structures and luminescent properties modulated by auxiliary ligands for series of lanthanide coordination polymers with triazole-benzoic acid



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## ABSTRACT

Two series of lanthanide coordination polymers,  $\{[\text{Ln}_2(\text{tabc})_4(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_5] \cdot \text{H}_2\text{O}\}_n$  ( $\text{Ln} = \text{Nd}$  (**1**),  $\text{Sm}$  (**2**),  $\text{Eu}$  (**3**),  $\text{Htabc} = 4-(1-1,2,4\text{-triazolyl})\text{benzoic acid}$ ) and  $\{[\text{Sm}(\text{tabc})(1,2\text{-pdc})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$  (**4**), have been constructed via hydrothermal conditions through adding different auxiliary ligands. Compounds **1–3** are two dimensional coordination layer comprised of  $\{\text{Ln}1(\text{COO})_2\}$  chains and  $\{\text{Ln}2(\text{COO})_2\}$  dinuclear units which are connected by oxalate groups, whereas compound **4** is one dimensional chain containing  $\{\text{Sm}_2(\text{COO})_2\}$  dinuclear units. The IR spectra and thermal stabilities of all compounds have been studied in detail. Compound **3** shows characteristic emission of  $\text{Eu}^{3+}$  ions, and it is noteworthy that the luminescent properties for **2** shows no emission peaks whereas that for **4** exhibits characteristic absorption bands of  $\text{Sm}^{3+}$  ions.

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Lanthanide coordination polymers (LCPs), one of the most attractive research fields in recent years, have been applied in various products, such as sensors, magnetism, catalysts, gas adsorption and so on [1–6], because of their attractive physical properties resulting from the 4f electrons of lanthanide ions. In addition, based on our previous research [7,8], there are many factors affect the construction of LCPs such as the selection of ligands, molecule templates, solvents and so on. Maybe due to the high coordination numbers and different coordination affinities of lanthanide ions, the fabrication of LCPs with organic ligands to obtain precise target structures is relatively difficult.

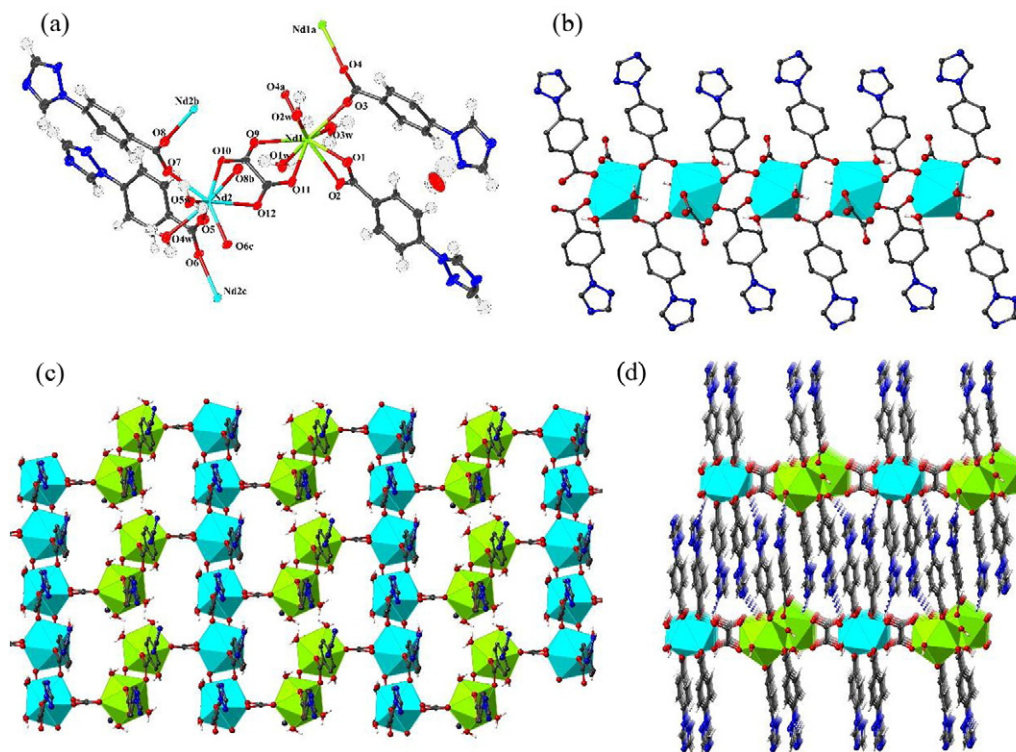
Multifunctional ligand, 4-(1-1,2,4-triazolyl)benzoic acid (Htabc), is a good candidate for constructing coordination polymers since it contains both carboxylate group and triazole group. To our best knowledge, Htabc ligand has been widely used to connect transition metal atoms [9–12], but only one report for lanthanide ions with Htabc [13]. Furthermore, as the introduction of auxiliary ligands can modulate the energy transfer process [14,15] and the interactions, oxalate and phthalate (1,2-pdc) ligands were added into the

systems and obtain two series of lanthanide coordination polymers,  $\{[\text{Ln}_2(\text{tabc})_4(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_5] \cdot \text{H}_2\text{O}\}_n$  ( $\text{Ln} = \text{Nd}$  (**1**),  $\text{Sm}$  (**2**),  $\text{Eu}$  (**3**)) and  $\{[\text{Sm}(\text{tabc})(1,2\text{-pdc})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$  (**4**). The structures, thermal stabilities, IR and luminescent properties of these compounds have been studied in detail.

Compounds **1–3** are isomorphous and synthesized in hydrothermal reaction via lanthanide nitrates and organic ligands. Hence, only the structure of **1** will be discussed in detail here. Single crystal X-ray crystallography reveals that compound **1** is a two-dimensional coordination layer structure. In the asymmetric unit of **1**, there are two  $\text{Nd}^{3+}$  atoms, four  $\text{tabc}^-$  ligands, one oxalate group, five coordination aqua molecules and one lattice water molecule (Fig. 1a). Nd1 atom is coordinated by nine oxygen atoms as a muffin geometry from three different  $\text{tabc}^-$  ligands which connect two Nd1 atoms into dinuclear unit  $\text{Nd}_2(\text{tabc})_2$ , a bridging ligand oxalate, and three coordinated aqua molecules respectively. Whereas Nd2 atom adopts a triangular dodecahedron geometry and is surrounded by eight atoms from four different  $\text{tabc}^-$  ligands, two coordinated aqua molecules, and the bridging ligand oxalate which also connects Nd1 atom in chelated form. The  $\text{tabc}^-$  ligands connect Nd2 atoms into infinite coordination chains (Fig. 1b) which are bridged by  $\text{Nd}_2(\text{tabc})_2$  dinuclear units through oxalate groups into two dimensional layer (Fig. 1c). It's interesting that all of the  $\text{tabc}^-$  ligands are located on the upper and lower of the layer, herein the

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**Fig. 1.** (a) Coordination environments of the Nd<sup>3+</sup> atoms and ligands with ellipsoids at the 50% probability level for **1**; polyhedral views of the 1D infinite chain (b), 2D coordination layer (c), and 3D supramolecular structure (d) for **1** (polyhedral color: green, Nd1; cyan, Nd2).

coordination layers are hydrogen bonded into 3D supramolecular structure (Fig. 1d).

As the oxalate groups play an important role in construction of compound **1** and introduction of different types of auxiliary ligands might be interesting (Fig. S1) [16]. A ligand with angle of 180° favored to form coordination layer while a 60° precursor with large steric group tended to a separator between the units [17, 18]. Herein phthalate ligand was used and compound **4** has been obtained in similar condition. Compound **4** is a 1D coordination chain and crystallizes in *P*<sub>2</sub><sub>1</sub>/*c* space group. The asymmetric unit consists of one Sm atom, one TABC ligand, one phthalate ligand, and four water molecules (Fig. 2a). Sm1 adopts a distorted tricapped trigonal prism geometry [19], coordinated by two oxygen atoms from tabc<sup>−</sup> ligand, five oxygen atoms from three different phthalate ligand and two aqua molecules. The tabc<sup>−</sup> ligands coordinate with Sm1 atoms in chelate mode (Fig. S2), whereas phthalate ligands are bridging two dinuclear units, Sm<sub>2</sub>O<sub>6</sub>, in which the coordination mode of one carboxylate group is μ<sub>2</sub>:η<sup>1</sup>,η<sup>2</sup> mode, into infinite coordination chains (Fig. 2b) that further are linked into 2D layers through hydrogen bonding interactions between free water molecules and tabc<sup>−</sup> ligands and π–π stacking interactions (3.31 Å). Finally 3D supramolecular structure is stabilized via weakly hydrogen bonding interactions (C–H⋯O = 2.65–2.71 Å, Fig. 2c).

The determination of powder X-ray diffraction (PXRD) which are in agreement with the simulated patterns for **1–4** have confirmed their phase purity (Fig. S3). Thermogravimetric analysis (TGA) is carried out to estimate the thermal stability of all compounds which are heated in nitrogen atmosphere to 700 °C (Fig. 3). Compounds **1–3** have similar TGA curves. For **1–3**, a weight loss of 8.9%, 9.0% and 8.9% respectively between 130 °C and 300 °C corresponds well to the loss of water molecules (calc. 8.7%, 8.6% and 8.6% for **1–3**

respectively). And then there is a big weight loss that indicates the decomposition of the organic ligands. For **4**, there is a weight loss of 6.1% before 130 °C and then another weight loss of 6.0% before 300 °C occurs which corresponds to the stepwise loss of four water molecules (calc. 12.5%), two free water molecules might be removed at first, and then the coordination water molecules are broken. Notably, the plateau occur before 130 °C in the TGA curves of **1–3** reveals that the free water molecule is very stable due to the strong hydrogen bonding interactions. The results of the different removal temperatures for the free water molecules in **1–4** might be ascribed to the different electron-donors that form hydrogen bonds with free water molecules.

As the unique electronic properties of lanthanide ions result in sharp emission bands, long luminescent lifetimes and large energy gap [20–23], the solid-state luminescent properties of compounds **1–4** have been investigated. Compounds **1** and **2** exhibit no emission peaks (Fig. S6) whereas compound **3** displays intense red luminescence and shows the characteristic emission of Eu<sup>3+</sup> ions at 561, 592, 616, 649 and 698 nm which correspond to the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>*J*</sub> (*J* = 0–4) transitions respectively (Fig. 4a). The peak at 561 nm attributed to <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>0</sub> is symmetric forbidden emission and reveals that Eu<sup>3+</sup> ions in **3** occupy sites with low symmetry and without inversion center [24–26]. Interestingly, compound **4** exhibits strong pink emission of Sm<sup>3+</sup> ions due to <sup>4</sup>G<sub>5/2</sub> → <sup>6</sup>H<sub>*J*</sub> (*J* = 5/2, 7/2, 9/2) transitions (Fig. 4b). The most intense peak is the hypersensitive transition <sup>4</sup>G<sub>5/2</sub> → <sup>6</sup>H<sub>9/2</sub> at 642 nm. There is a broad peak appearing before 550 nm that might be ascribed to the emission effect by tabc<sup>−</sup> ligands [10]. The different luminescent properties for Sm<sup>3+</sup> compounds **2** and **4** might be the result of introduction of different auxiliary ligands which can change the energy-transfer processes and light up the luminescent lanthanide ions [27,28].

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