

Short communication

## Three unprecedented high-connected 3D lanthanide–organic frameworks based on benzene-1,2,4,5-tetracarboxylic acid

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## ABSTRACT

Three unprecedented high-connected 3D lanthanide coordination polymers based on benzene-1,2,4,5-tetracarboxylic acid ( $H_4bta$ ),  $\{[Ln_2(bta)_{1.5}(H_2O)_4] \cdot 3H_2O\}_n$  ( $Ln = La$  (**1**) and  $Ce$  (**2**)) and  $[Pr(bta)_{0.5}(H_2bta)_{0.5}(H_2O)]_n$  (**3**), have been synthesized under hydrothermal conditions. Complexes **1** and **2** show trinodal (4,4,10)-connected 3D network structures consisting of tetranuclear metal clusters bridged by  $bta^{4-}$  ligands, and a chair conformation hexamer water cluster can be found within the cage enclosed by eight neighboring tetranuclear metal clusters in the two complexes. While **3** consists of 2D  $\{Pr(bta)_{0.5}\}_n$  layers linked by  $H_2bta^{2-}$  ligands, resulting in an unprecedented trinodal (4,6,10)-connected 3D topological network. The organic ligand exhibits five kinds of coordination modes, in which one of them is reported for the first time. Moreover, the luminescent properties of **1–3** have also been investigated.

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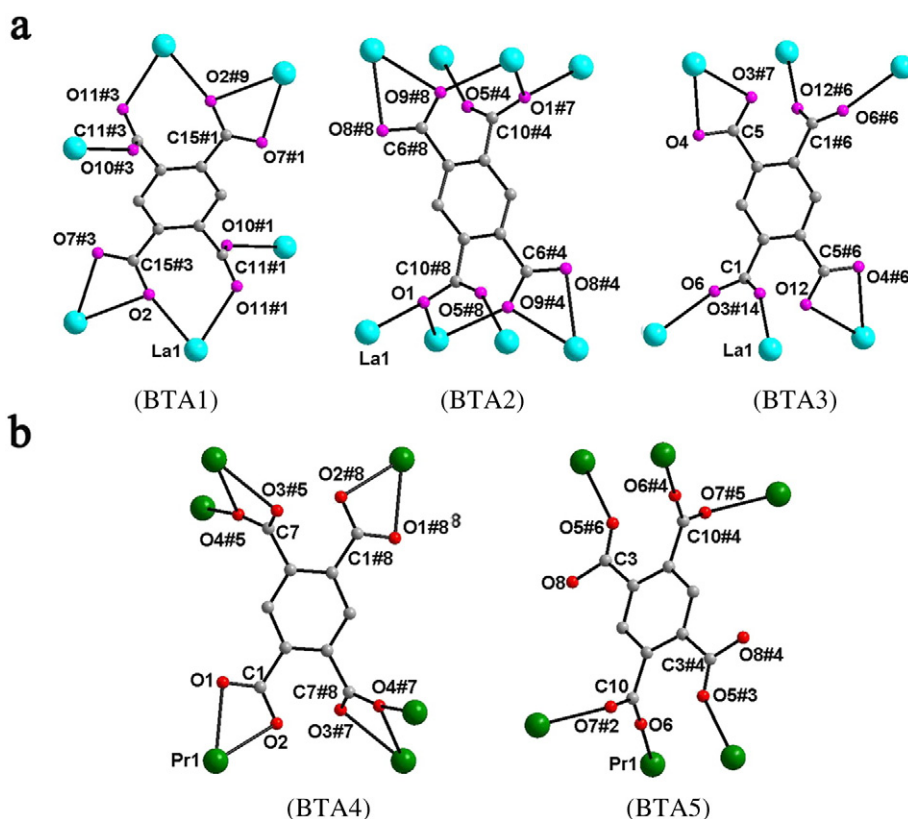
Investigations on the synthesis of metal–organic frameworks (MOFs) have attracted immense attention owing to the possibility to obtain various esthetically interesting structures and discover the new materials having potential applied value in many fields [1–8]. In comparison with transition metal ions, lanthanide ions not only have unusual coordination characteristics, but also display exceptional optical and magnetic properties arising from 4f electrons. However, it is still a continuing challenge to design and synthesis of lanthanide–organic frameworks because the higher coordination number of the lanthanide ions makes it more difficult to control the synthetic reactions. And the lanthanide–organic frameworks are still uncommon compared with those of transition metals [9]. The judicious design or selection of a suitable ligand is crucial in the building of MOFs. In particular, multicarboxylate ligands are usually used in the architectures of lanthanide complexes considering the strong affinities between lanthanide ions and carboxyl oxygen atoms. Benzene-1,2,4,5-tetracarboxylic acid ( $H_4bta$ ) has high symmetry and eminent  $\pi$ -conjugate system which contribute to the generation of regular structures, and its four carboxylic groups may chelate metal ions by various coordination modes [10–13] to form fascinating multidimensional compounds [10–35]. Additionally,  $H_4bta$  has been proven to be a good ligand in the construction of MOFs, and a few 3D MOFs involving high-

connected frameworks based on  $H_4bta$  have been obtained by other groups [14–20]. For example, Cui and co-workers prepared three high-connected MOFs,  $\{[Cd_3(bta)(btx)_{0.5}(\mu_3-OH)(H_2O)] \cdot H_2O\}_n$ ,  $[Cu_2(bta)(btx)_{1.5}]_n$  and  $\{[Co_5(bta)_2(btx)(\mu_3-OH)_2(H_2O)_2] \cdot 2H_2O\}_n$ , with  $H_4bta$  and 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene (btx) as mixed ligands [15,16]. Lanthanide–organic frameworks based on  $H_4bta$  exhibit fascinating topological structures and catch much more attentions [17–20]. Ln-MOFs based on  $H_4bta$  reported by predecessors could be mainly classified into four types as follows: (i) Ln- $bta$  [12, 17–19, 21–27], (ii) Ln- $bta$ -POM (POM = Polyoxometallates) [28], (iii) Ln- $bta$ -M (M = Na, K, Cu, Nb, U) [13, 29–32], (iv) Ln- $bta$ -L (L = oxalic acid, glutaric acid, 4,4'-bipyridine, etc.) [20, 33–35]. In view of the foregoing, we have utilized  $H_4bta$  to generate three high-connected Ln- $bta$  frameworks reported here,  $\{[Ln_2(bta)_{1.5}(H_2O)_4] \cdot 3H_2O\}_n$  ( $Ln = La$  (**1**) and  $Ce$  (**2**)) and  $[Pr(bta)_{0.5}(H_2bta)_{0.5}(H_2O)]_n$  (**3**). Notably, a new coordination mode of  $H_4bta$  and a sqc37 topology for a coordination network are first reported here. In addition, the thermal stabilities and luminescent properties of **1–3** have also been investigated.

X-ray single crystal diffraction [36] reveals that **1** and **2** are isostructural. Here, only the structure of **1** is discussed in detail as a representation. The asymmetric unit of **1** contains two crystallographically independent La(III) ions, three halves of  $bta^{4-}$  anions, four coordinated and three lattice water molecules. As shown in Fig. S1, La1 is nine-coordinated by nine oxygen atoms from four  $bta^{4-}$  ligands and three coordinated water molecules ( $La1-O_{bta} =$

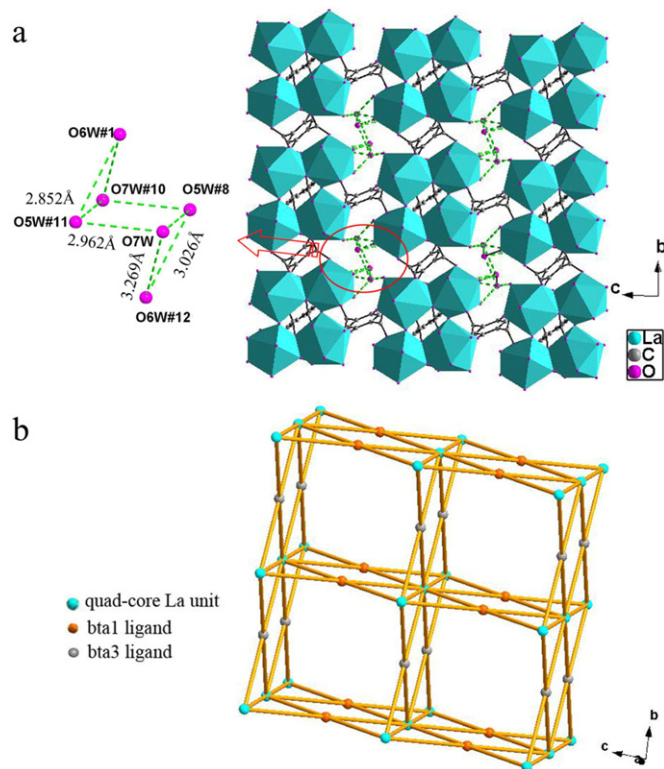
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**Fig. 1.** Five coordination modes of  $\text{bta}^{4-}$  ligands observed in **1** (a) and **3** (b). (Symmetry codes: **1**: #1, 1-x, 1-y, 1-z; #3, 1+x, y, z; #4, 1-x, 2-y, 1-z; #6, -x, 2-y, 2-z; #7, -x, 2-y, 1-z; #8, -1+x, y, z; #9, 2-x, 1-y, 1-z; #14, x, y, 1+z; **3**: #2, 1-x, 2-y, 2-z; #3, -1+x, y, z; #4, 1-x, 1-y, 2-z; #5, x, -1+y, z; #6, 2-x, 1-y, 2-z; #7, 1-x, 2-y, 1-z; #8, 1-x, 1-y, 1-z. All hydrogen atoms are omitted for clarity).

2.410(6)–2.615(5) Å and  $\text{La1-O}_w = 2.556(5)$ –2.588(6) Å). La2 is ten-coordinated by nine oxygen atoms from six  $\text{bta}^{4-}$  ligands and one coordinated water molecule ( $\text{La2-O}_{\text{bta}} = 2.503(6)$ –2.789(5) Å and  $\text{La2-O}_w = 2.598(5)$  Å). The La–O bond lengths fall in the range of those reported in other La(III) complexes with aromatic carboxylic acid ligands [27,40]. As shown in Fig. 1a, all carboxylic groups of  $\text{bta}^{4-}$  in **1** are deprotonated, and the  $\text{bta}^{4-}$  display three kinds of coordination modes ( $\mu_6\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^1$ , named BTA1;  $\mu_8\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1\text{:}\eta^2\text{:}\eta^1\text{:}\eta^2\text{:}\eta^1\text{:}\eta^2$ , named BTA2;  $\mu_6\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1$ , named BTA3). As far as we know, mode BTA2 is reported for the first time. In **1**, four La atoms are linked by six oxygen atoms (O1, O2, O3, O1#4, O2#4 and O9#4, symmetry code: #4, 1-x, 2-y, 1-z) from four different  $\text{bta}^{4-}$  ligands into a tetranuclear unit (Fig. S2a). Along the *a* axis, the tetranuclear units are connected by BTA2 ligands into a 1D chain (Fig. S2b). And the 1D chains are linked by BTA1 ligands into 2D layers along the *c* axis directions. Furthermore, the 2D layers are connected into 3D framework by BTA3 ligands along *b* axis directions (Fig. 2a). Thus each tetranuclear unit is connected with fourteen neighboring tetranuclear units in different directions by ten  $\text{bta}^{4-}$  ligands (four BTA1, two BTA2 and four BTA3 ligands). There are six guest water molecules in every cage enclosed by eight neighboring tetranuclear units. Interestingly, the six guest water molecules are further hydrogen bonded into a chair conformation hexamer water cluster (Fig. 2a). The  $\text{O}_w\text{-O}_w$  distances within the  $(\text{H}_2\text{O})_6$  cluster span the range of 2.70–3.27 Å (Table S3–S4), and the average distance (2.95 Å) is comparable to those found in liquid water [41] (i.e., 2.85 Å). These water molecules are interacted with the carboxyl groups on the surface of the cages through hydrogen bonding (Table S3). From the topological perspective, if the tetranuclear La units are viewed as ten-connected inorganic nodes, BTA1 and BTA3 ligands are considered as 4-connected organic nodes and BTA2 ligands as topological lines, the structure of **1** can be symbolized as a net with a  $(3^{24} \cdot 4^{63} \cdot 5^4)$  topology (Fig. 2b), which is



**Fig. 2.** (a) A hexamer water cluster consisting of lattice waters and the 3D framework of **1** containing 1D channels along the *a*-axis direction (Symmetry code: #10: -x, -y+1, -z+2; #11: 1-x, 1-y, 2-z; #12: -1+x, y, 1+z). (b) Perspective view of the 14-connected topology of **1**.

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