

A new (3,8)-connected pillared-layer lanthanide–organic framework with interconnected channel and mesoporous cage



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ABSTRACT

A novel non-interpenetrated lanthanide–organic framework constructed by dinuclear cerium cluster as pillar and trinuclear cerium cluster as layer with a uniform (3,8)-connected topology has been reported, which exhibits mesoporous cages between layers and 3D interconnected channels.

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The porosity of metal–organic frameworks (MOFs) plays an important role in the applications such as gas storage, gas separation and catalysis [1]. Although great efforts have been devoted to develop novel porous MOFs with desired topology and functionality, most of them are limited to microporous scale with the pore sizes less than 2 nm. Until now, the search of MOFs with mesopores of which the pore sizes range from 2 to 50 nm is still a big challenge. MOFs constructed with mesoporous cages are the most common among those examples of mesoporous MOFs [2], whereas MOFs with mesoporous channels are especially scarce [3].

A common strategy to construct mesoporous MOFs by expanding the length of organic ligand is often limited by interpenetration [4]. Employing highly-connected metal clusters is another way to assemble mesoporous MOFs, which might rigidify the structure and increase adsorption sites [5]. Recently, pillared-layer three-dimensional (3D) networks built with appropriate pillar moieties further linking well-defined two-dimensional (2D) layers have become attractive, due to their advantages such as tunable pore sizes and functional pillar module [6]. So far, bidentate organic ligands [7], simple inorganic ions [8], polyoxometalates [9], and coordinated homometallic cations [10] have been utilized as pillars in pillared-layer porous MOFs. Here we report a novel lanthanide–organic framework with pillared-layer structure and mesoporous cages, $[\text{Ce}_4(\text{OH})(\text{BTB})_3(\text{NO}_3)(\text{DMF})_2(\text{H}_2\text{O})_4](\text{NO}_3)_m(\text{H}_2\text{O})_n(\text{DMF})_n$ (**1**), where H_3BTB = 1,3,5-benzenetrisbenzoic acid and DMF = N,N-dimethylformamide. The novel non-interpenetrated framework has a uniform (3,8)-connected topology and exhibits mesopores between

layers and 3D interconnected channels. To the best of our knowledge, while three cases of mesoporous MOFs with lanthanide metals have been reported so far [2a,11], this is the first case of MOFs with dinuclear cluster as the vertex of pillar and trinuclear cluster as the vertex of 2D layer.

The single-crystal X-ray diffraction analysis exhibits that **1** crystallizes in the orthorhombic space group *Cmca*, and consists of cationic framework $[\text{Ce}_4(\text{OH})(\text{BTB})_3(\text{NO}_3)(\text{DMF})_2(\text{H}_2\text{O})_4]^+$, uncoordinated nitrate counter anion and DMF molecules. One BTB ligand lies in a crystallographic mirror with half occupancy of C35, C37, C38, C41, and C42 atoms in an asymmetric unit. Two different BTB ligands adopt three types of coordination modes, containing syn–syn bridging mode (mode A), η -O, O'- μ -O, O mode (mode B) and bidentate chelate mode (mode C), respectively (Fig. S1). Three crystallographically independent cerium ions in **1** compose two types of secondary building units (SBUs): cationic dinuclear cluster $[\text{Ce}_2(\text{OH})_2(\text{COO})_2(\text{H}_2\text{O})_4]^{2+}$ (Fig. 1a) and trinuclear cluster $\text{Ce}_3(\text{COO})_8(\text{NO}_3)(\text{DMF})_4$ (Fig. 1b). In trinuclear cluster, the Ce1 atom is coordinated to nine oxygen atoms from four separate carboxyl groups and two terminal DMF molecules. The central Ce2 atom resides at crystallographic two-fold axis with half occupancy in an asymmetric unit, which adopts a nine-coordinated mode to six separate carboxyl groups and a nitrate anion. The closest Ce1–Ce2 distance is 3.988 Å in the trinuclear cerium cluster. The carboxyl groups in the trinuclear cluster show a η -O, O'- μ -O, O (mode B) and bidentate chelate mode (mode C), respectively. In the dinuclear cerium cluster, the Ce3 atom is located in the symmetry plane with half occupancy in an asymmetric unit, and coordinated to eight oxygen atoms from two syn–syn bridging carboxyl groups (mode A), a μ_2 hydroxide and four terminal water molecules. It should be noted that the crystallographic

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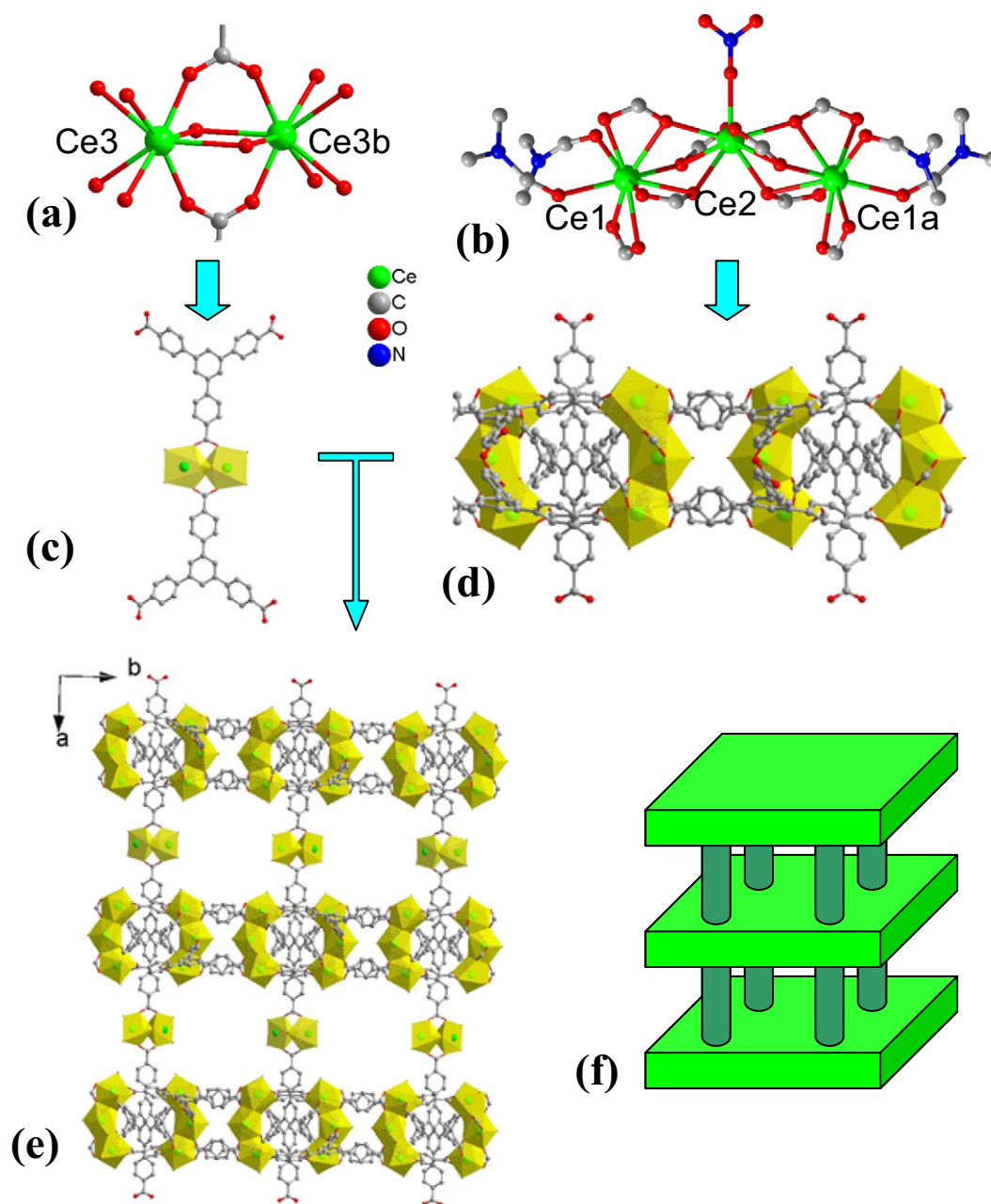


Fig. 1. Views of (a) dinuclear $\text{Ce}_2(\text{OH})_2(\text{COO})_2(\text{H}_2\text{O})_8$ cluster with the symmetric code of b: 1-x, -y, 1-z, (b) trinuclear $\text{Ce}_3(\text{COO})_8(\text{NO}_3)(\text{DMF})_4$ cluster with the symmetric code of a: 0.5-x, y, 0.5-z, (c) coordination pillar, (d) 2D layer, (e) 3D pillared-layer structure, and (f) schematic pillared-layer structure.

symmetric center is located in the middle of the two crystallographic symmetric Ce3 atoms with the separation of 4.291 Å in the dinuclear cluster. The lengths of Ce–O bonds fall into the range of 2.339–2.815 Å, which are comparable to the reported cerium coordination compounds [12].

The dinuclear SBU is connected by two BTB ligands in mode A to extend as pillars (Fig. 1c) in the structure. The BTB ligand keeps its original shape in the structure without distortion or π – π stacking effect. The trinuclear SBU contains zigzag array of three Ce(III) atoms through crystallographic *c* direction, connected by eight BTB ligands to form 2D layers (Fig. 1d). It is interesting to note that the 2D grid layers are linked by dinuclear clusters to finally form a cationic 3D pillared-layer open framework (Fig. 1e and f). Up to now, there are only one report of 3D pillared-layer porous framework, in which copper ions act as pillars that further link the lanthanide–organic layers into 3D framework [10]. In the case of **1**, only one single type of organic ligand (H_3BTB)

and Ce(III) ion are employed to construct 3D pillared-layer structure. To the best of our knowledge, this is the first example of cationic 3D pillared-layer LOF constructed from cationic pillars.

The layers in **1** are densified by the trinuclear SBUs (Fig. 2a), with ultramicropores in the size of $5 \times 4 \text{ \AA}^2$. Moreover, as illustrated in Fig. 2b, the thickness of one single layer of 12.03 Å is larger than the distance between adjacent layers of 11.01 Å, indicating that intertwining in **1** is impossible to happen. Because of the above factors, the structure of **1** is highly porous and non-interpenetrated.

1 exhibits interconnected channels between layers (Fig. 3). Generally, four types of 1D microporous channels can be found in **1** through different directions, as shown in Fig. 3. From the perspectives of the crystallographic *b* and *c* directions, the channels are $ca. 13 \times 14 \text{ \AA}^2$ and $16 \times 14 \text{ \AA}^2$, respectively. The other two types of channels along (0, 1, –1) and (0, –1, 1) directions are both of $18 \times 14 \text{ \AA}^2$ in size. It should be noted that **1** is quite different from our recently reported

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