

# Syntheses, structure, topological analysis and luminescent property of a new 3D Zn(II) coordination polymer based on a flexible tetracarboxylate ligand tecton



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## ABSTRACT

A new three-dimensional (3D) coordination polymer  $[Zn(L)_{0.5}(DMA)]_n$  (**1**), [ $H_4L = 5,5'-(p\text{-xylylenediamino})-1,1',3,3'-(\text{benzene-tetra-carboxylic acid})$ ], was constructed under hydrothermal condition. Single crystal X-ray diffraction indicates that compound **1** shows a (4,4)-connected *PtS* net with the point (Schläfli) symbol of  $\{4^2 \cdot 8^4\}$  which contains unusual *meso*-helical chains. Additionally, photoluminescence property and thermal stability of **1** were investigated.

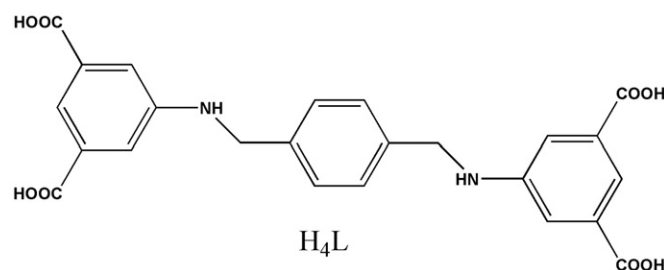
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Polycarboxylic acid ligands have attracted great interest for researchers to construct metal-organic frameworks (MOFs) due to their fascinating architectures and topological frameworks and promising applications as guest exchange, molecular adsorption, magnetism, catalysis and optic materials and so on [1–4]. Generally, the diversity in the framework architectures of such coordination polymers depends on many factors, such as the coordination geometry of metal centers, the coordination ability of organic ligand and the reaction conditions (pH value, temperature, metal-to-ligand ratio and so on) [5–9]. Among these factors, the selection of organic ligand with suitable binding groups is especially crucial. Polycarboxylic acids are widely used as bridging/chelating ligands for the building MOFs which have been described as one-, two- and three-dimensional structures of coordination polymers [10]. Additionally, the polycarboxylic acid as a multidentate bridging/chelating ligand, may lead to the formation of nanosized cages, honeycomb porous frameworks, metal-oxygen cluster and helical structure [11–14].

Based on the above, in this context, a polycarboxylic acid ligand, 5,5'-(*p*-xylylenediamino)-1,1',3,3'-(benzene-tetra-carboxylic acid) ( $H_4L$ , Scheme 1) is applied in the field of coordination chemistry [15a] according to the following considerations: (a)  $H_4L$ , as a flexible bridging multidentate tetracarboxylate ligand, have conformational and geometrical freedom because of flexible  $-\text{CH}_2\text{NH}-$  spacer and provide further insight into supramolecular isomerism, and may thus favor the formation

of helical and *meso*-helical structures [15b,c,f]. (b) It has a  $\pi$ -conjugated nonlinear structure with N, O donors that can offer additional hydrogen bonding and  $\pi$ - $\pi$  interactions to consolidate the whole network. (c) Much work is required to establish rational synthetic strategies to the desired architectures using flexible building blocks. While, the  $H_4L$  ligand can be very advantageous when designing interesting multidimensional architectures due to its various coordination modes to metal ions resulting from completely or partially deprotonated sites to allow for the large diversity in the topologies. Herein, we present the solvothermal synthesis and crystal structure of a 3D Zn(II) coordination polymer based on  $H_4L$ , namely  $[Zn(L)_{0.5}(DMA)]_n$  (**1**), as well as investigate its luminescent property and thermal stability.

$H_4L$  ligand was prepared according to previously reported method in our group [15a]. The purple block crystalline compound **1** was prepared by a mixture of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  with 5,5'-(*p*-xylylenediamino)-1,1',3,3'-



Scheme 1. Molecular structure of  $H_4L$  ligand.

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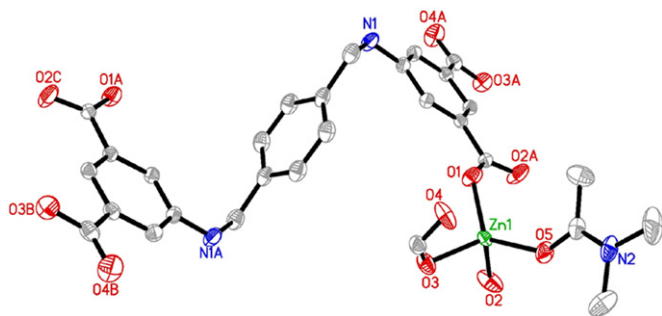


Fig. 1. The coordination environment of the Zn(II) atom in **1**.

(benzene-tetra-carboxylic acid) in the molar ratio of 1:1 in a solution of H<sub>2</sub>O and DMA under 120 °C for 24 h [16]. The phase purity of bull products was confirmed by power X-ray diffraction (Fig. S1).

X-ray single crystal structural analysis reveals [17] that the asymmetric unit of **1** contains one Zn(II) atom, half L<sup>4-</sup> anion ligand and one coordinated DMA molecule. As shown in Fig. 1, the Zn1 center is coordinated to three oxygen atoms (O1, O2, O3) from different L<sup>4-</sup> anion ligands, one oxygen atom (O5) from coordinated DMA molecule, respectively. The coordination geometry of Zn1 center can be described as a distorted tetrahedron, the O1, O3 and O5 atoms comprise the equatorial basal plane, and the O2 atom occupies the vertex position. The Zn–O bond lengths vary from 1.931(14) to 1.983(14) Å, which are similar to other Zn-based compounds [15a]. In compound **1**, the three phenyl rings of the H<sub>4</sub>L ligand are non-planar, two outer phenyl groups

are twisted with respect to the central one, the dihedral angles between the central and outer phenyl rings and the intersection angle between the central phenyl ring and its connected C–N group are the same (82.76°). Two outer phenyl rings are parallel and trans arrangement in the two sides of the central one with steady configuration. As a result, four carboxylate groups of one L<sup>4-</sup> anion show various coordination modes (monodentate-bridging and bidentate-bridging) to link four Zn(II) atoms in the self-assembly process of coordination polymers, as shown in Fig. S2.

Notably, two Zn(II) ions are combined by two carboxylate groups from two different L<sup>4-</sup> anions to form a dinuclear [Zn<sub>2</sub>C<sub>2</sub>O<sub>4</sub>] cluster that the Zn···Zn separation is 3.911 Å (Fig. S3). Each cluster is interlinked by L<sup>4-</sup> anion ligands to generate an unusual *meso*-helical chain structure with the pitch of 22.59 Å, which further connect L<sup>4-</sup> anions into a 2D layer (Fig. 2). These 2D layers are linked by Zn–O bonds of L<sup>4-</sup> anions ( $\mu_6-\eta^1:\eta^1:\eta^1:\eta^1:\eta^1$ ) to produce the final 3D framework (Fig. S4). Interestingly, two distinct channels (A and B) exist within the coordination framework of **1** (Fig. S4). The carboxylic groups and phenyl groups from L<sup>4-</sup> anion ligands protrude into the round channel A. Channel B is surrounded both by the L<sup>4-</sup> anion ligands and metal atoms, with the coordination DMA molecule located at the central position of the channel to further firm the whole backbone structure by the hydrogen bonding interactions. From the topological perspective, if the [Zn<sub>2</sub>C<sub>2</sub>O<sub>4</sub>] cluster can be regarded as a 4-connected node and the L<sup>4-</sup> anion ligand as 4-connected node, the complicated architecture of **1** is simplified to a (4,4)-connected 3D *Pts* topological network with the point (Schläfli) symbol of {4<sup>2</sup> · 8<sup>4</sup>} as shown in Fig. 3. Meanwhile, there are two different T sites and two unique tiles [8<sup>4</sup>] + [4<sup>2</sup> · 8<sup>2</sup>] in the three-periodic net (Fig. 4). To the best of our knowledge, only few MOFs with *Pts* network have been reported referenced to the Reticular Chemistry Structure

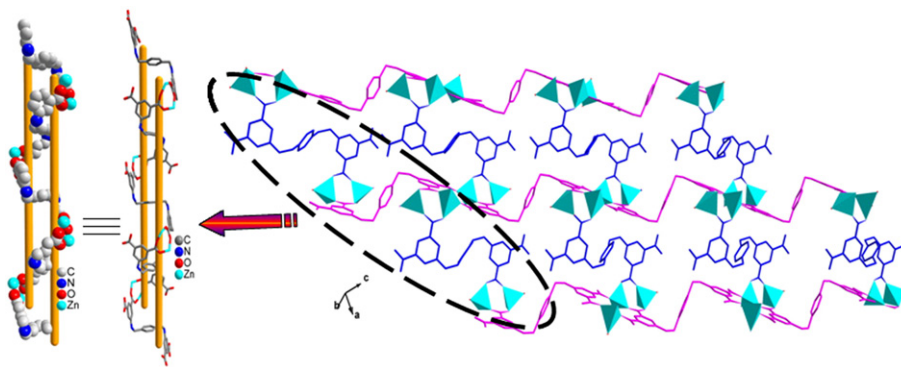


Fig. 2. The 1D *meso*-helical chain (left) and 2D layer (right) structure of **1**.

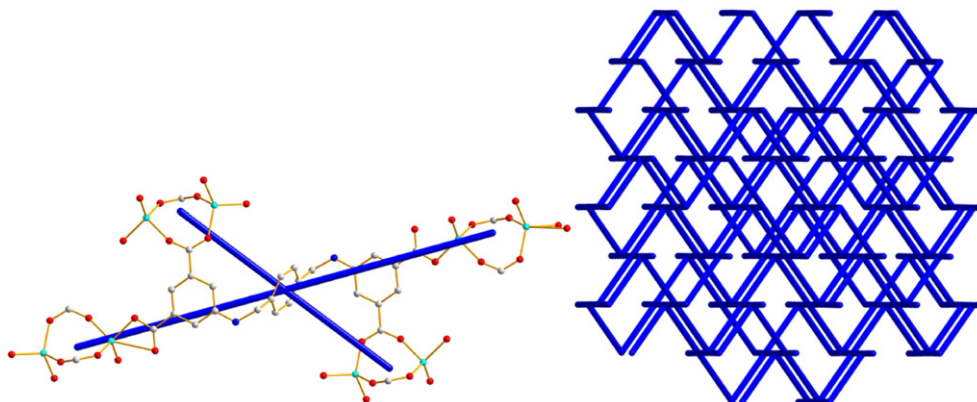


Fig. 3. The (4,4)-connected 3D *Pts* topological structure of **1**.

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