

A novel 3D homochiral helical coordination polymer based on a flexible tripodal ligand

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ABSTRACT

The reaction of the flexible tripodal ligand 1,3,5-tri(1,2,4-triazol-1-ylmethyl)-2,4,6-trimethylbenzene (ttmb) and Zn(II) with 3,3',4,4'-benzophenone tetracarboxylic dianhydride (3,3',4,4'-bptda) gives a novel 3D coordination polymer $\{[Zn_{1.5}(ttmb)(Hbptc)] \cdot H_2O\}_n$ (**1**) (H₄bptc = 3,3',4,4'-benzophenone tetracarboxylic acid). In **1**, the ancillary Hbptc³⁻ groups connect Zn(II) ions to form a 2D layered structure. The ttmb ligands further link the 2D structure to generate a fascinating tridimensional polymeric architecture containing infinite 1D single-stranded helical chains of the same *M* handedness.

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The design and construction of coordination polymers with a variety of intriguing architectures and topologies have attracted increasing attention in recent research activities [1–8]. Generally speaking, many factors affect the construction of the coordination polymers, such as the selection of metal centers, organic ligands and the presence of auxiliary ligands, etc. [9–12]. Among them, the design and selection of organic ligands with suitable binding groups are especially important [13,14]. In fact, flexible tripodal ligands have been proven to be a kind of most potential organic building blocks in construction of coordination polymers for their outstanding features of flexible coordination fashions [15–18].

1,3,5-tri(1,2,4-triazol-1-ylmethyl)-2,4,6-trimethylbenzene (ttmb) is one of the flexible tripodal ligands with a benzene ring and N-donors, which is a good bridging ligand for the construction of diverse structures [19–21]. On the one hand, the 1,2,4-triazole groups of ttmb ligands present strong and typical coordination capacity and can provide more potential coordination sites. On the other hand, 1,2,4-triazole groups can freely twist around the –CH₂– groups, so ttmb can adopt two different coordination conformations (*cis,trans*, *trans*- and *cis,cis,cis*-conformations) to prepare coordination polymers with charming structures. In addition, the application of mixed ligands is presently an effective approach for constructing compounds [22–24]. Thus, the employment of flexible tripodal N-donor ligands and aromatic polycarboxylate species may have great potential for the construction of a variety of fascinating structures. Taking all the above into account, we selected ttmb as a functional ligand and 3,3',4,4'-

benzophenone tetracarboxylic dianhydride (3,3',4,4'-bptda) as an ancillary group. Fortunately, a novel 3D homochiral helical Zn(II) coordination polymer $\{[Zn_{1.5}(ttmb)(Hbptc)] \cdot H_2O\}_n$ (**1**) were obtained under hydrothermal reaction. Here we report its synthesis, crystal structure, thermal property and photoluminescence properties.

1 was synthesized by the hydrothermal method in H₂O media [25]. The crystal structure of **1** [26] reveals that the complex crystallizes in the tetragonal chiral space group *P*₄₃₂₁₂ and exhibits a fascinating tridimensional polymeric architecture. As exhibited in Fig. 1, each Zn(II) is four-coordinated by two carboxylate oxygen atoms from two different Hbptc³⁻ groups and two nitrogen donors arising from two different ttmb ligands exhibiting a slightly distorted tetrahedral coordination geometry. The distances of Zn–O are in the range of 1.910–1.952 Å, and the Zn–N bond lengths vary from 2.005 to 2.062 Å, all of which are in the normal range of those observed in zinc complexes [27,28].

The incompletely deprotonated Hbptc³⁻ ligand, in which two carboxylate groups adopt the monodentate coordination modes and the third one adopts bidentate chelated coordination mode, acts as a μ₃-bridge linking three Zn(II) ions. The Zn₂ ions are bridged by carboxylate groups adopting the monodentate coordination mode to form 1D wave-like chains. The zigzag chains are further ligated by Zn1 and the carboxylate groups adopting the bidentate chelated mode to build the 2D Zn(II)/Hbptc³⁻ framework (Fig. 2).

The ttmb adopts a *cis,trans,trans*-conformation with the N_{donor}···N–C_{sp³}···C_{sp³} torsion angle of –96.938°, 145.159°, and 141.226° and coordinates with three Zn(II) ions as a tridentate ligand. ttmb ligands connect Zn ions to generate 1D infinite left-handed helices with the helical pitch of 14.2960 Å around the crystallographic 2₁ axis (Fig. 3b) along the *b* direction (Fig. 3a) [29]. Moreover, N4 and N8 atoms of triazole nitrogen atoms from ttmb ligands coordinate with Zn2 ions to form 1D infinite

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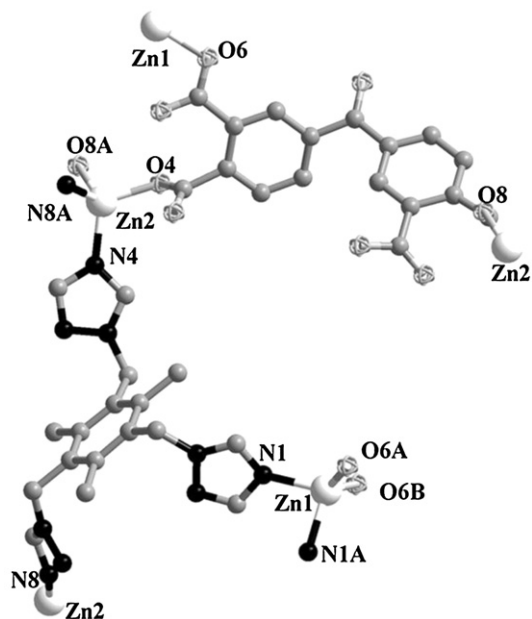


Fig. 1. The coordination environment around the Zn(II) centers in **1**. Hydrogen atoms and solvent molecule are omitted for clarity.

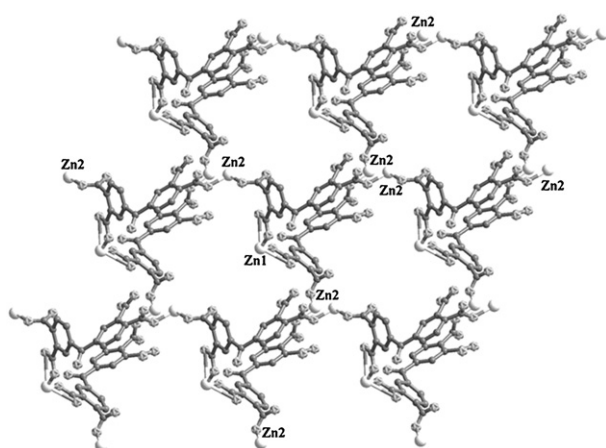


Fig. 2. Representation of the 2D layered structure built by Zn ions and Hbptc³⁻. All hydrogen atoms are omitted for clarity.

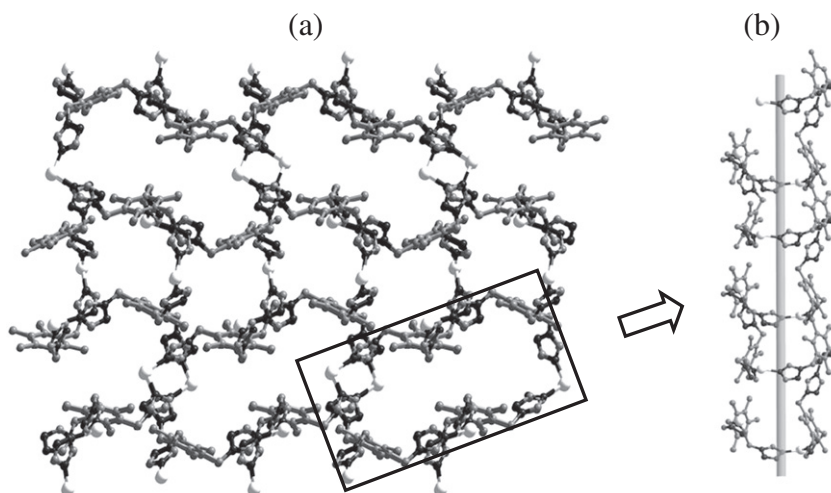


Fig. 3. (a) View of 3D network built by Zn ions and ttmb along the *b* direction. All hydrogen atoms are omitted for clarity; (b) View of the left-handed helical chain constructed by Zn centers and ttmb. All hydrogen atoms are omitted for clarity.

single-stranded helical chains of same *M* handedness (Fig. 4b). The long helical pitch is 33.755(7) Å corresponding to the length of *c*-axis. These 1D helical chains share Zn2 ions to generate a 3D porous structure along *c* direction (Fig. 4a). Finally, the 2D Zn(II)/Hbptc³⁻ structure is embedded in the 3D Zn-ttmb framework to generate a novel 3D extended network along the *c* direction (Fig. 5a).

From the topological point of view, if the Zn(II) ions are regarded as 4-connected nodes, and the ligands ttmb and Hbptc³⁻ are simplified as two kinds of 3-connected nodes, the whole framework of coordination polymer **1** can be described as a 3,4-connected topology with a Schläfli symbol of $(8^3)_2(8^5 \cdot 10)(7 \cdot 8^5)$ (Fig. 5b). The solvent-accessible volume from the crystal structure estimated by PLATON¹⁴ is 4.3% of the total volume.

The simulated and experimental XRPD patterns of **1** are shown in Fig. S1, indicating a pure phase of the bulky sample. The thermal stability of **1** was examined by thermogravimetric analysis (TGA) from 30 °C to 700 °C. For the compound, the first step weight loss, attributed to the lattice water molecule, is observed in the range of 29.9–237.5 °C (obsd, 2.14%; calcd, 2.16%). The second step weight loss from 237.5 to 567.5 °C corresponds to the decomposition of ttmb and Hbptc³⁻, leading to the formation of ZnO as the residue (obsd, 14.95%; calcd, 14.62%) (Fig. S2).

The solid state luminescence spectra of **1** and free ligands ttmb and 3,3',4,4'-bptda at room temperature are determined. **1** exhibits the weaker fluorescence emission at 487 nm upon excitation at 399 nm (Fig. S3). The emission can probably be assigned to the intra-ligand (π - π^*) fluorescent emission due to similar emission observed at 486 nm for the free 3,3',4,4'-bptda ligand [30].

In summary, a new coordination polymer has been synthesized with the mixed organic ligands ttmb and 3,3',4,4'-bptda under hydrothermal condition. This work shows that ttmb is a good candidate for the synthesis of coordination polymers with attractive motifs and has the potential to form homochiral helical compounds. Furthermore, the results highlight that aromatic polycarboxylate coligand can effectively tune the final structural features as well as build much more complicated and intriguing networks.

Acknowledgments

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