

# A highly twisting chiral qtz-d net built on a distorted tetrahedral node containing two types of helical substructure

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## ABSTRACT

Herein, we present one chiral metal-organic polymer, namely  $\text{Cd}_2(\mu\text{-H}_2\text{O})(\text{L})_2(4,4'\text{-bpy})(\mathbf{1})$ ,  $4,4'\text{-bpy} = 4,4'\text{-bipyridine}$ ,  $\text{H}_2\text{L} = 2\text{-(4-carboxyphenoxy)benzoic acid}$ ). The single crystal X-ray diffraction shows that polymer  $\mathbf{1}$  crystallizes in the chiral  $P6_522$  space group, and the overall structural feature is the intriguing topological building of twisting chiral qtz-d net built on a highly rare distorted tetrahedral node, containing two types of helical substructure.

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In the past decades, more and more researchers have been paying their efforts in the design and preparation of a newly developing matter, so-called ‘metal-organic framework’, due to not only their intriguing topology matrixes, but also their extensive applications in many fields. [1–3] From the structural point of view, recently the ‘slang’ such as MBB (molecule building block), MOP (metal-organic polyhedra), unitary node net, and binary node net has been developed and popularly utilized to analyze and design MOFs. [4–6] Among the topological antetype of MOFs, the four-connecting net is very common and often encountered. However, due to geometry of it and the connectivity fashions between them, in literature there have disclosed at least ten species of four-connecting nets, e.g. dia, NbO, qtz, sodalite, lonsdaleite,  $\text{CdSO}_4$ ,  $\text{CrBr}_4$ ,  $\text{SrAl}_2$ , moganite, PtS. [4–6] Moreover, another unusual four-connecting net, defined as dual qtz-d net with the  $7^59$  topological symbol, was firstly realized by Carlucci in 1998. [7] Further, Zhang and co-workers reported a twisting qtz-d net in 2005. [8] Herein, we present another twisting qtz-d net, which should present the first qtz-d net built on the four-coordinated tetrahedral node and composed of two kinds of helical substructure.

Polymer  $\mathbf{1}$  was synthesized by the hydro(solvo)thermal reaction of  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{H}_2\text{L}$ ,  $4,4'\text{-bipyridine}$ , and  $\text{Na}_2\text{CO}_3$  in the ratio of 1:1:1:1. [9] The yield of this compound is about 86% based on Cd. The phase purity of the bulk samples of  $\mathbf{1}$  is confirmed by XRD (see supporting information, Figure S1) and EA studies. The TG studies at 20–600 °C revealed the weight loss of coordinated water molecule is around 218 °C (calc. 2.0%, exp. 2.2%). Further there is no weight loss until the chemical decomposition of this compound around 306 °C (Fig. 1).

The single crystal X-ray diffraction shows that polymer  $\mathbf{1}$  crystallize in the chiral  $P6_522$  space group with the Flack factor of 0.14(18), indicating somewhat twin crystal observed here. [10] The asymmetrical unit of  $\mathbf{1}$  contains two crystallography-independent Cd(II) ions. The coordination surroundings of Cd1 and Cd2 ions are shown in Fig. 2. Both Cd1 and Cd2 located at the  $2_1$  axis own the position occupation of 0.5. Cd1 is seven-coordinated by four L oxygen, two  $4,4'\text{-bpy}$  nitrogen, and one terminal water molecule, resulted in the somewhat distorted pentagonal bipyramidal geometry, whilst Cd2 is six-coordinated by six L oxygen to afford the trigon-antiprismatic geometry. The Cd–O/N bond lengths

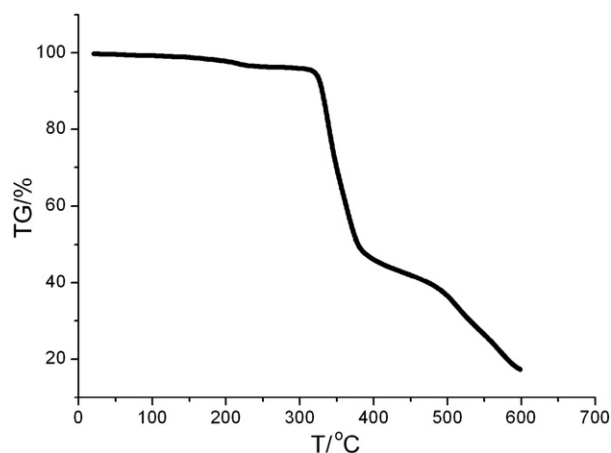
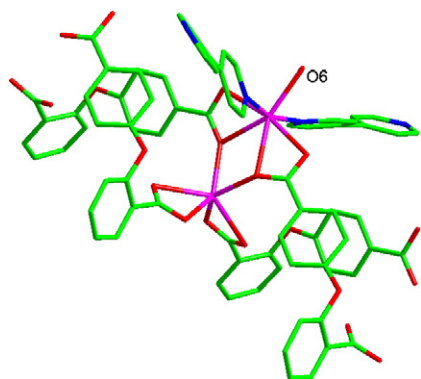


Fig. 1. View of the TG study of polymer  $\mathbf{1}$ .

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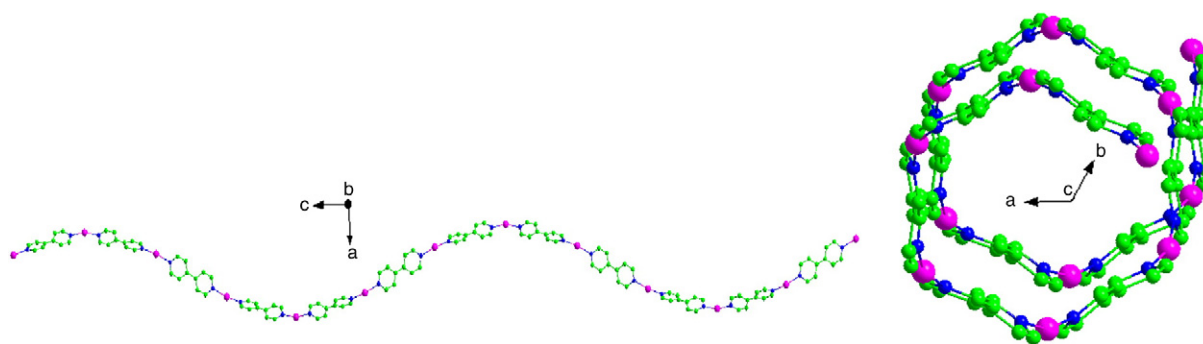
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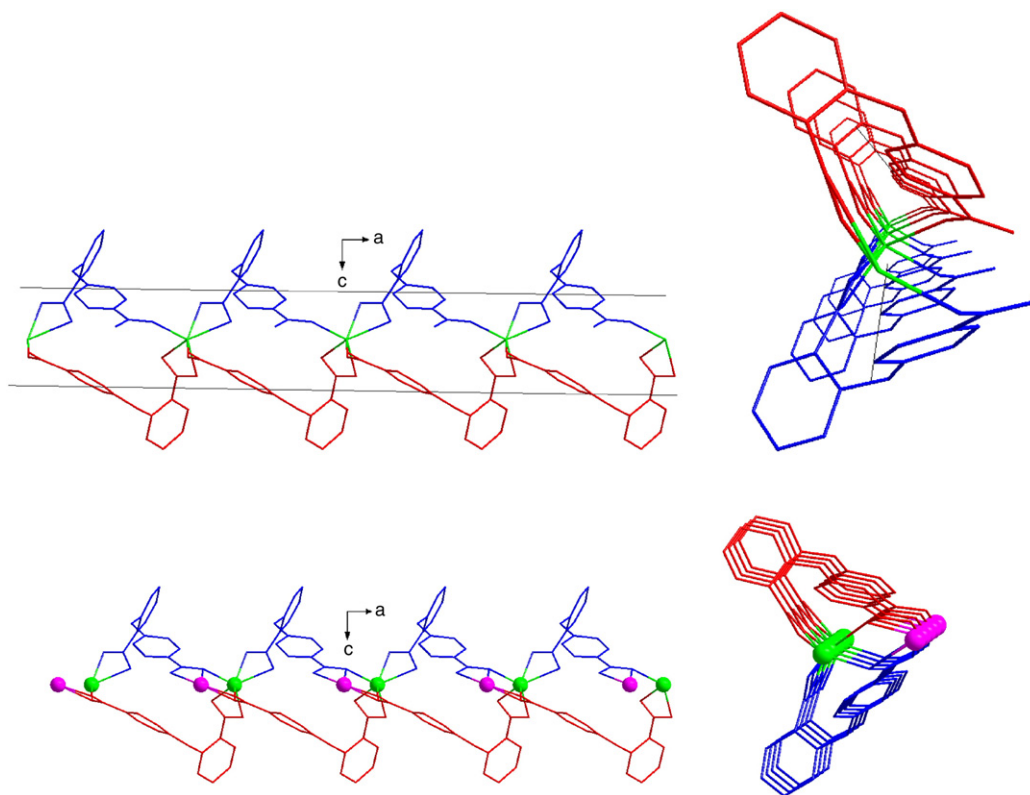
**Fig. 2.** View of the coordination surroundings of Cd(II) ions in **1**. The hydrogen atoms are omitted for clarity. The atoms are colored as follow: Cd – purple, C – green, N – blue, O – red. O6 is the coordinated water molecule.

range from 2.280(16) Å to 2.539(18) Å, comparable with other Cd(II)-containing coordination compounds [11].

As illustrated in Fig. 3, along *c* direction, the Cd1 ions are in-turn bridged by 4,4'-bpy ligand to give rise to the charge-positive helical substructure, namely  $\{\text{Cd}(4,4'\text{-bpy})\}_n$ . The two pyridine rings of 4,4'-bpy show the dihedral angle of ca. 21.9°. Within the helical substructure, the closest Cd–Cd distance is ca. 11.8 Å, the repeating period containing the  $\{\text{Cd}(4,4'\text{-bpy})\}_6$  fragment is ca. 63.9 Å, and the diameter of it is ca. 10.3 Å. On the other hand, in *ab* plane the Cd2 ions and L ligands are combined together to create another charge-negative helical substructure of  $\{\text{CdL}_2\}_n$ , where the two carboxyl groups of L ligand hold two coordinated modes, viz.  $\mu_1:\eta^1\eta^1$ ,  $\mu_2:\eta^1\eta^2$ , and the two benzene rings display the dihedral angle of ca. 79.1°. As illustrated in Fig. 4, the second helical substructure of  $\{\text{CdL}_2\}_n$  in fact is composed of two helical chains of  $\{\text{CdL}\}_n$ , but both of which share the Cd2 metal centre. Furthermore, the charge-positive helical substructures of  $\{\text{Cd}(4,4'\text{-bpy})\}_n$  and



**Fig. 3.** Along *c* direction, ball-stick description of the charge-positive helical substructure of  $\{\text{Cd}(4,4'\text{-bpy})\}_n$ .



**Fig. 4.** Along *a* direction, the above: wire-frame description of the charge-negative helical substructure of  $\{\text{CdL}_2\}_n$ ; the below: view of the charge-negative helical substructure of  $\{\text{CdL}_2\}_n$  connecting to the charge-positive helical substructure of  $\{\text{Cd}(4,4'\text{-bpy})\}_n$  via the coordination between L ligand and Cd1 marked in purple.

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