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Highly stable 3D homochiral coordination polymer with interweaving of double-stranded helices and extended metal-SO₄-metal chains

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ABSTRACT

Solvothermal synthesis of an achiral ligand N,N-bis(3-pyridyl) isophthalamide (bpip) with ZnSO₄ under 120 °C yield a novel compound, [Zn(bpip)SO₄]n, which displays chiral self-assembly into an infinite double-stranded helical coordination polymer consisting of two single-stranded helices with the same *P* handedness. These chiral infinite double-stranded helical chains are further interwoven by the 1D Zn–SO₄–Zn chains to form a novel 3D framework structure with a rare 6^{5} .10 topology. On the basis of the results of TG–DSC analyses, the structure is thermally stable up to ~467.4 °C.

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Since the discovery of the double-stranded helical structure of DNA, double-stranded helical structures constructed from metaldirected self-assembly have received much attention in coordination chemistry and materials chemistry because of the persistent interests in numerous enantioselective processes including asymmetric catalysis, chemical sensing, and selective guest inclusion [1-5]. These studies have usually been focused on the design and synthesis of dimeric helical assemblies mediated by metal-ligand coordination, in which the metal ions are helically wrapped by two helical bridging organic ligands. There are numerous reports on coordination polymers that exhibit infinite double-helical motifs based on stereoselective synthesis using chiral ligands or by spontaneous resolution upon crystallization without any chiral auxiliary [6–12]. Spontaneous resolution is a more economical and convenient approach, and has received much more attention, however, which is a relatively rare phenomenon and less predictable because the conglomeration processes are not yet fully understood [6,13–16].

Recently, some groups have made great contribution to the advance and comprehension of the elements that mediate the chirality of double-stranded helical metal complexes in the spontaneous resolution process [6,14,17]. In most cases, the metal-directed self-assembly and the hydrogen-bonding-driven self-assembly are common approaches to constructing supramolecular duplexes. Bu et al. have reported that

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hydrogen bonding interactions, which have definite directions that sometimes can efficiently transfer of stereochemical information between neighboring homochiral chains, are the driving force in the parallel packing to form double-stranded helical structure in the spontaneous resolution process [6]. Jung et al. also reported a supramolecular framework consisting of two kinds of channels via self assembly of a 1D double-stranded chain in a prismatic fashion. Weak C–H··π interaction may be the driving force in the assembly of the prismatic channel structure [17]. However, the precise prediction of chiral framework with double-stranded helical structure in the spontaneous resolution process is still a daunting task because the formation of such a framework is governed by many factors, and the control of framework chirality is particularly difficult.

It has been noted that the employment of rigid and V-shaped *exo*bidentate organic bridges can improve the helicity of the polymeric chains [15,18]. Recently, some groups including our group have introduced V-shaped symmetrical ligand of N,N-bis(3-pyridyl)isophthalamide (bpip) and N,N-bis(pyridine-3-yl)pyridine-3,5-dicarboxamide to acquire functional MOFs with helical structure [19–21]. Due to the distortion from the planarity of the two terminal pyridine rings and the freedom rotation of C–N bond between the amide and pyridyl moieties, the ligands may be locked in twisting configurations. If there are two strands with the same chirality and all parallel double helices are also the same chirality, the double-stranded polymer would be noncentrosymmetric and chiral even if it contains no chiral molecular unit in the helices.

Here, we report fascinating interwoven helices based on a Zn^{II} complex, namely $[Zn(bpip)SO_4]_n$ (1), which displays chiral self-

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Fig. 1. View of one layer of compound 1. C atoms (dark gray), O atoms (red), S atoms (yellow), Zn atoms (green). All hydrogen atoms are omitted for clarity.

assembly into an infinite double-stranded helical coordination polymer consisting of two single-stranded helices of the same handedness made from an achiral ligand bpip [22]. These chiral infinite doublestranded helical chains are further interwoven by the 1D Zn–SO₄–Zn chains to form a 3D architecture. Although some examples of double stranded helical coordination networks in the spontaneous resolution process have been reported, the double stranded helical coordination networks further interwoven with infinite linear M–SO₄–M chains have not been reported until now. Furthermore, the steady state fluorescence spectra and the thermal stability of the complex have been determined.

A single crystal X-ray diffraction study performed on **1** revealed that the complex crystallizes in the tetragonal chiral space group P4₁2₁2 and contains a fascinating tridimensional polymeric architecture consisting of three interwoven nets [23]. The symmetric unit of **1** consists of one Zn center, two SO_4^{2-} ions, and two bpip ligands (Fig. S1). Zn atom adopts a slightly distorted tetrahedral coordination geometry through bonding to two O atoms (O3 and O5) from SO_4^{2-} ions and two N atoms (N1 and N3) from two ligands. The Zn–O bond lengths (1.936(3)–2.387(2)) and the Zn–N bond lengths (2.024(3)–2.038(3)) are similar to those found in other related

structures [24]. Each SO_4^{2-} ion acts as a bidentate bridging linker to connect two Zn centers leading to the formation of a single-stranded with the O–Zn–O angle is 106.65(11)°.

As seen in Fig. 1, the unit of **1** consists of two bpip ligands with the dihedral angles being 45.4°, and each ligand exhibits two types of bridging modes (Mode a and b), which are important for the formation of the infinite double-helical structure. One kind of ligand (Mode a) bridges two Zn atoms along the 1D–S–O–Zn–O–S– chain. The other kind of ligand (Mode b) with two different bridging directions links two Zn atoms from two adjacent –S –O –Zn –O –S– chains.

The most fascinating topological feature in **1** is the ligands bridge the Zn atoms to form a chiral infinite double-helical chain with the *P* (right-hand) configuration (Fig. 2a). Each chain is rotated by 90° along the *c* axis on passing to each successive layer, in a 4₁ helical disposition, thus resulting in a chiral network. The helical pitch, given by the distance between equivalent atoms generated by one full rotation of the 4₁ screw axis, is 19.86 Å.

In general, the most important feature of the helix is its chirality. Right-handed (P) and left-handed (M) helices are nonidentical mirror images. The two single-stranded infinite helices in **1** are of the same P handedness and are intertwined to form a chiral infinite double-



Fig. 2. (a) View of the double-stranded helices showing the same chirality for the two chains of each double-stranded helix; (b) View of the double-stranded helical chains interwoven with the 1D S-O-Zn-O-S chains; (c) 3D framework of 1 showing its chiral layers and interwoven structure. All hydrogen atoms are omitted for clarity.

helical structure. The aromatic rings in the ligand at each side of the helix are arranged in a parallel fashion with an inner-ring distance of 9.47 Å; adjacent chiral helices are packed in a zipperlike, off-set fashion into 2D layers parallel to the *bc* plane (Fig. 2b). These chiral infinite double-stranded helical chains are further linked by the 1D S–O–Zn–O–S chains to form a 3D architecture (Fig. 2c). It is worth noting that all helicals are of the same chirality and are packed in a parallel manner, leading to a noncentrosymmetric and chiral solid. In such a case, this coordination polymer **1** is noncentrosymmetric and chiral even if it contains no chiral molecular unit. Though numerous infinite double helices have been structurally characterized to date, chiral 3D double helices of the same handedness based on achiral ligands are quite rare.

The driving force for the formation of the double helical arrangement is likely the definite directions of the ligand. The bpip group is a rigid and angular diptopic ligand which has two "arms" with 120° angle to act as an ideal half-cycle, and at the end of each "arm" there is a pyridyl donor group which is convenient for bridging metal centers to form an integrated macrocycle. Besides, the distortion from the planarity of the two terminal pyridine rings and the freedom rotation of the amido-N to 3-pyridyl-C bond could make the ligands may be locked in twisting configurations. In addition, the 1D S–O–Zn–O–S chains interwoven with the double-stranded helical chains further stabilize the double helical arrangement.

When the tetrahedral coordinated Zn(II) centers are regarded as nodes, and the organic ligands and SO_4^{2-} ions are regarded as connectors, the network of the complicated structure can be described topologically in a straight-forward way with node-and-connector approach. As shown in Fig. 3, the 1D S–O–Zn–O–S chains on the opposing ends of any given bpip ligands are disposed leading to the 3D framework structure which has a 6⁵.10 topology. The 6⁵.10 topology in **1** is a rare tetrahedrally four-connected net, related but different from the other nets for a 3D network of four-connected nets, such



Fig. 3. An unusual (6⁵, 10) net of compound **1** viewed along different directions (top) and a convenient view of the essential circuits of the vertex (bottom).

as diamond (6⁶), NbO (6⁴8²), PtS, CdSO₄ (6⁵8), dense (7⁵9), etc. [25–28].

To conform whether the crystal structure is truly representative of the bulk materials, the XRD powder patterns for compound **1** has been collected on a PANalytical X'prtPro diffractometer using graphite-monochromated Cu- $K\alpha$ radiation in the angular range $2\theta = 5-50^{\circ}$. The XRD of powder pattern was fully coincident with the compound **1** that calculated from its sing crystal structure data, so it exists as a single phase (Fig. S2).

The solid-state photo luminescent behaviors of the free ligand bpip and complex **1** have been investigated at room temperature. As shown in Fig. S3, excitation at 328 nm leads to broad fluorescence signals with the emission maxima at approximately 440 nm for the free ligand bpip, which is probably attributable to the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transitions. In comparison, complex **1** displays an emission band centered at about 390 nm when excited at 325 nm. Such fluorescence behaviors suggest the emissions of 1 are neither metal-toligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT), but they may be assigned to intraligand transition because Zn(II) is difficult to oxidize or reduce due to its d¹⁰ configuration. The partial quenching of fluorescence emission in **1** may be due to the fact that the introduction of the metal ions and sulfate anions reduce the rigidity of the polymer which causes a decrease in the conjugate degree of whole molecules. In addition, the weak interactions, especially the strong hydrogen-bonding interactions, also play an important role in weakening the fluorescence intensity of the supermolecules [29].

The thermal properties of the complex **1** were investigated. As shown in Fig. 4, TG curve of complex **1** exhibits that it is stable up to 467.4 °C. The surprising thermal stability of **1** is mainly due to the interwoven structure of double-stranded helices and extended metal-SO₄-metal chains. From 467.4 °C to 552.2 °C, it keeps losing weight because the structure collapsed resulting from the removing organic ligand. The curve observed from 552.2 °C to 676.9 °C is caused by the decomposition of SO₄²⁻ ions. Finally a white residue of ZnO (observed 18.26%, calculated 16.97%) remained.

We attempted to measure the CD spectrum of the sample to understand the P and M percentage distribution of the chiral crystals, which apparently needs further study.

In conclusion, the compound **1** reported here is an interesting example of a homochiral 3D chiral coordination polymer consisting of two single-stranded helices with the same handedness based on an achiral ligand bpip. The adjacent chiral double helices are of the same *P* handedness and are packed in a parallel fashion. These chiral infinite double-stranded helical chains are further interwoven with



Fig. 4. Thermogravimetric curve (TG and DSC) of compound 1.

the 1D S–O–Zn–O–S chains to form a 3D framework structure which has a rare 6^{5} .10 topology. On the basis of the results of TG/DSC analyses, the structure is thermally stable up to ~467.4 °C.

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Appendix A. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC reference number 640706 for complex **1**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223 336 033; or deposit@ccdc.cam.ac.uk). Details on the view of the building unit of structure **1**, powder X-ray diffractograms for **1**, solid-state emission spectra of bpip and **1**, selected bond lengths and bond angles are listed in the supplementary content.

Supplementary data to this article can be found online at doi:10. 1016/j.inoche.2012.01.021.

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