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Homochiral Coordination Polymer with Infinite Double-Stranded Helices

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Hydrothermal reaction of 4,4-trimethylenedipyridine (tmdp) with ZnI_2 under 175 °C yields a novel compound, $\{[Zn_2I_4(tmdp)_2]_n \cdot [Zn_2I_4(tmdp)_2]_n\}$, which has a chiral infinite double-stranded helical structure consisting of two single-stranded helices of the same handedness.

Since the discovery of the double-stranded helical structure of DNA,[1] chemists have devoted much attention to the synthetic design of artificial double helices.[2−6] In DNA, the driving force for the formation of the double-helical arrangement is hydrogen bonding between complementary nucleic acid bases, while in artificial analogues, the double helices can be formed through noncovalent interactions, such as hydrogen bonding, π stacking, electrostatic interactions, or coordination bonds.[7−10] Metal-directed self-assembly is widely used in constructing double-stranded helices. A special class of well-defined double-helical structures was termed double-stranded helicates by Lehn et al.[11] In addition, there are numerous reports on coordination polymers that exhibit infinite double-helical motifs in the solid state.[12−21] However, the chiral infinite double-stranded helical coordination polymers with only one handedness are rare. The synthesis of chiral materials is also of significance in studying the genesis of chirality in biological systems. A recent interesting example with controlled helicity is an infinite double-stranded helical coordination polymer consisting of two complementary strands that are intertwined through chiral amisinium carboxylate salt bridges.[22]

In general, most double-helical molecular assemblies in the crystalline phase reported to date are based on the use of achiral building blocks. How to design or make a chiral feature from extended helices without any chiral sources relies on the understanding of ligand effects and crystal packing.[23−26] The most important feature of the helix is its chirality. Right-handed (*P*) and left-handed (*M*) helices are nonidentical mirror images. Hence, for the double helix, if the two strands are of the same chirality and all parallel double helices are also of the same chirality, the polymer would be noncentrosymmetric and chiral even if it contains no chiral molecular unit in the helices. Here, we report an example that displays chiral self-assembly into an infinite double-stranded helical coordination polymer consisting of two single-stranded helices of the same handedness made from an achiral ligand.

One principle for constructing double helices is to select flexible exoditopic ligands and linear or cis-coordinated metal centers. In this report, we employed the 4,4-trimethylenedipyridine (tmdp) ligand because of its flexible structural configuration, which can adopt different conformations, such

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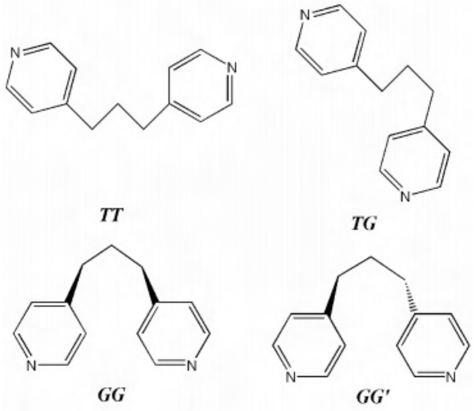
Chart 1. Schematic Representation of the Conformational Isomers of the tmdp Ligand



as *TT*, *TG*, *GG*, and *GG′* (Chart 1).[17,27,28] A flexible ligand such as tmdp with conformational freedom often shows a supramolecular isomerism by altering the geometry of the ligand. In addition, metal halides, as neutral blocks, have been widely used in the assembly of inorganic−organic hybrid materials. Consequently, the hydrothermal reaction of tmdp and ZnI_2 in a 1:1 ratio under 175 °C produced the title complex $\{[Zn_2I_4(tmdp)_2]_n{\cdot}[Zn_2I_4(tmdp)_2]_n\}$ in 73% yield.[29] The complex is stable in air and insoluble in water and common solvents. It is noteworthy that the hydrothermal method is crucial to the synthesis of the title complex because of the effect of temperature and pressure on crystallization. With the solution method at room temperature and under ambient conditions, the one-dimensional wave-shaped coordination polymer $[ZnI_2(tmdp)]_n$ was isolated.[30]

X-ray diffraction[31] on a pale-yellow single crystal revealed that the complex crystallizes in the orthorhombic chiral space group $P2_12_12_1$ and has a double-helical structure with the *M* (left-handed) configuration. The asymmetric unit consists of two independent and similar $[Zn_2I_4(tmdp)_2]$ sections. As shown in Figure 1, each Zn^{II} atom adopts a slightly distorted tetrahedral coordination geometry through bonding to two I atoms and two N donors from two tmdp ligands. The bond angles around the Zn^{II} center range from 102.2(4) to 120.99(6)°. The Zn−I bond distances range from 2.5244(15) to 2.5635(15) Å, and the Zn−N bond lengths range from 2.037(9) to 2.073(9) Å. Such angles and distances are similar to those found in other related structures.[30] Interestingly, the tmdp ligand displays two different conformations in each $[Zn_2I_4(tmdp)_2]_n$ section, which is important for the formation of the infinite double-helical structure. One is in a *TT* conformation (see Figure 1, left), of which the dihedral angles between two pyridine rings are 98.6° and 83.6°, respectively. The other is in a *TG* conformation (see Figure 1, right), of which the dihedral angles between two pyridine rings are 118.9° and 62.3°, respectively. The two different tmdp ligands bridge two Zn atoms, with the Zn···Zn separation being 13.406 and 13.402 Å, respectively.

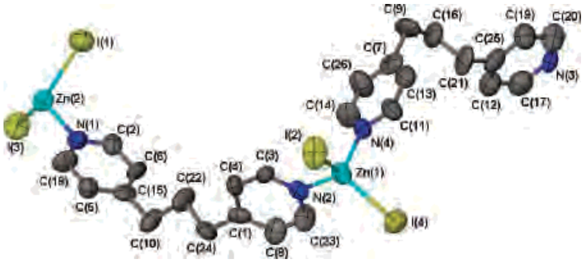


Figure 1. View of one independent $[Zn_2I_4(tmdp)_2]$ asymmetric unit section. Thermal ellipsoids were drawn at the 50% probability level.

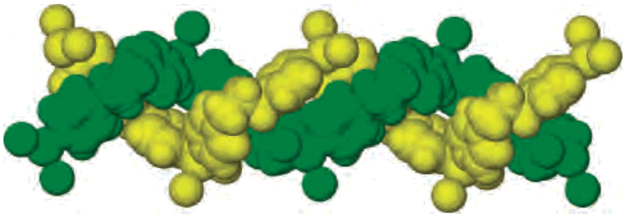


Figure 2. Space-filling representation of the intertwined infinite double-helical structure.

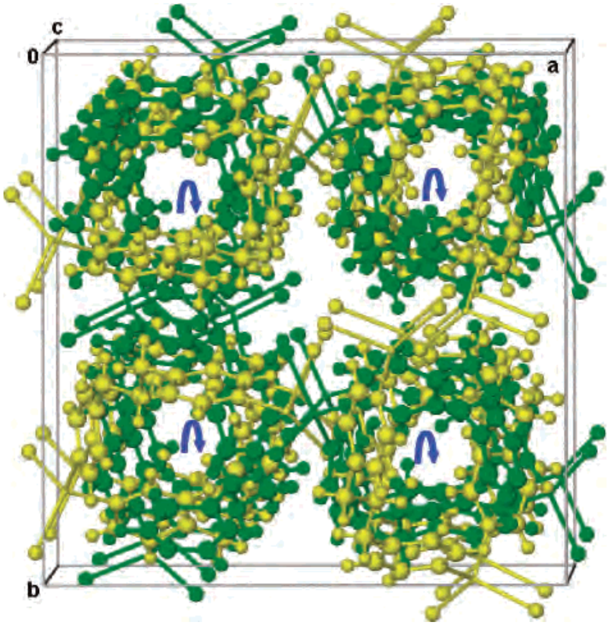


Figure 3. Parallel packing of adjacent double helices with the same chirality projected along the crystallographic *c* axis.

The helical pitch, given by the distance between equivalent atoms generated by one full rotation of the 2-fold screw axis, is 19.77 Å. The two single-stranded infinite helices are of the same *M* handedness and are intertwined to form a chiral infinite double-helical structure (Figure 2). Though numerous infinite double helices have been structurally characterized to date, chiral infinite double helices of the same handedness

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(29) Synthesis: A mixture of ZnI_2 (330 mg), tmdp (202 mg), and H_2O (5 mL) was placed in a 23-mL Teflon autoclave and then heated at 175 °C for 4 days. After cooling to room temperature, pale-yellow block crystals were obtained in 73% yield.

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(31) Crystal data for $C_{52}H_{56}I_8N_8Zn_4$: $M = 2069.73$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 18.0875(8)$ Å, $b = 18.3897(8)$ Å, $c = 19.7700(8)$ Å, $V = 6576.0(5)$ Å^3, $Z = 4$, $D_c = 2.091$ g/cm^3, $F_{000} = 3872$, Mo Kα radiation, $\lambda = 0.71073$ Å, $T = 293(2)$ K, $2\theta_{max} = 43.5°$, 36055 reflections collected, 7798 unique ($R_{int} = 0.0567$); final GOF = 1.006, R1 = 0.0339, wR2 = 0.0568, *R* indices based on 5334 reflections with $I > 2\theta(I)$ (refinement on F^2), 649 parameters, 0 restraints; absorption corrections applied, $\mu = 5.235$ mm^{-1}. Flack parameter = 0.02(3).

based on achiral ligands are quite rare. A detailed analysis shows that there are no obvious hydrogen-bonding and π-stacking interactions between the two strands. Therefore, the two strands of this double helix are connected through attractive intermolecular forces, van der Waals interactions. A double helix of two strands of poly(methyl methacrylate) was reported to form through van der Waals interactions in the solid state.[9]

It is of interest to note that all helices are of the same chirality (Figure 3) and are packed in a parallel manner, leading to a noncentrosymmetric and chiral solid. In such a case, this coordination polymer is noncentrosymmetric and chiral even if it contains no chiral molecular unit. The driving force in the parallel packing is likely C−H···I interactions, with the distances ranging from 3.136 to 3.216 Å.

In conclusion, the compound reported here is an interesting example of a homochiral infinite double-stranded helical coordination polymer consisting of two single-stranded helices of the same handedness based on an achiral ligand. The adjacent chiral double helices are of the same chirality and are packed in a parallel fashion, leading to a homochiral solid.

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Supporting Information Available: X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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