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Conversion from a Heterochiral [2 + 2] Coaxially Nested Double-Helical Column to a Cationic Spiral Staircase Stimulated by an Ionic Liquid Anion

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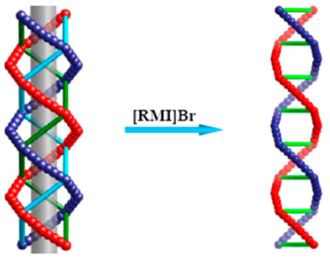
Supporting Information

ABSTRACT: The conversion from a [2 + 2] nested double-helical column, $\{[Mn_2(ptptp)(suc)(H_2O)_2]\cdot 1.5H_2O\}_n$ (**1**), to a cationic spiral staircase, $\{[Mn_2(ptptp)(suc)_{0.5}(H_2O)_3]\cdot Br\cdot 0.5H_2O\}_n$ (**2**), has been achieved through ionic liquid anion stimulations under solvothermal conditions. The conversion does not change the antiferromagnetic interactions.

Helicity is a highly attractive topological motif not only because of its fascinating structure but also for its realistic and potential applications in many fields.[1−4] To date, the self-assembly of a helical structure has been paid remarkable attention, and a large number of helical coordination polymers (CPs) have been reported since the pioneering work of Lehn.[5,6] However, several cases about [1 + 1]-,[5a] [2 + 1]-,[5b] [3 + 1]-,[5c,d] and [3 + 2]-type[5e] multihelical arrays, which contain two kinds of nested helices with the same helix axis, have been created. Among these coaxial nested helices, the rarest presents opposite orientation.[5e] Besides, the reported [*n* + *n*]-type multihelical arrays need to be extracted arduously from complicated three-dimensional (3D) frameworks. It is still a formidable challenging task for chemists to encapsulate different helical units into a one-dimensional (1D) [*n* + *n*] coaxially nested helical system. Herein, we report an unprecedented heterochiral 1D [2 + 2] coaxially nested double-helical column, $\{[Mn_2(ptptp)(suc)(H_2O)_2]\cdot 1.5H_2O\}_n$ (**1**), formed by using outer double helices $(Mn\text{-}ptptp)_n$ as a template to encapsulate inner double helices $(Mn\text{-}suc)_n$ in a hierarchical self-assembly process (H_2ptptp = 2-(5-{6-[5-(pyrazin-2-yl)-1*H*-1,2,4-triazol-3-yl]pyridin-2-yl}-1*H*-1,2,4-triazol-3-yl)pyrazine; H_2suc = succinic acid). To the best of our knowledge, **1** is the first example of a 1D CP that has [2 + 2] coaxially nested double-helical chains with reverse chirality.

Ionic liquids (ILs) have received increasing attention as the solvent of choice for the synthesis of crystalline materials such as zeolites and CPs.[7−10] Earlier reports showed that ILs could display several different types of behavior, such as templating by only the cation or by both the cation and anion simultaneously, and serve as a mineralizing agent or solvent only without being occluded in the final structure, which illustrates that ILs can play multiple functions even in the same systems.[7−10] These achievements inspire us to select ILs as anion sources to tune the configuration of the column in **1**. As expected, solvothermal reaction of **1** and 1 mL of [RMI]Br (RMI = 1-alkyl-3-methylimidazolium; R = ethyl, propyl, or butyl) in CH_3CN/H_2O led to $\{[Mn_2(ptptp)(suc)_{0.5}(H_2O)_3]\cdot Br\cdot 0.5H_2O\}_n$ (**2**), which resembles a 1D cationic spiral staircase (Scheme 1). The better dissolving capacity of ILs at high temperature and the more effective structure regulator of the IL Br^- anion are two crucial factors of the conversion from **1** to **2**. Besides, the large chiral channel formed by the outer double-helical chains in **1** may act as a "molecular container" or a "molecular reactor", where the inner double-helical chains were disturbed by the IL Br^- anions in the postsynthesis process.

Scheme 1. Conversion from 1 to 2



1

2

X-ray crystal structure analysis revealed that **1** crystallizes in the high-symmetry tetragonal space group $P4_2/n$. The asymmetric unit of **1** contains two crystallographically independent Mn^{2+} ions, one ptptp ligand, one suc ligand, two coordinated water molecules, and one and a half free water molecules (Figure S1 in the Supporting Information, SI). The apical Mn1 ion is coordinated by two terminal bidentate binding sites of two ptptp ligands and two carboxylate oxygen atoms of two suc ligands, resulting in a distorted octahedral $\{N_4O_2\}$ coordination geometry. The Mn2 ion is embedded in the central tridentate binding site of the ptptp ligand, along with one carboxylate oxygen atom from the suc ligand and two coordinated water molecules to complete a distorted octahedral $\{N_3O_3\}$ coordination geometry.

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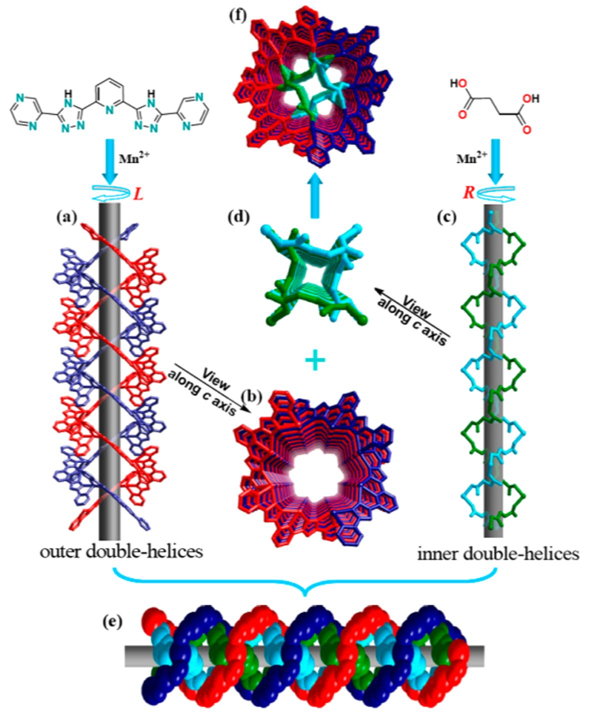

Figure 1. Hierarchical assembly of a [2 + 2] nested double-helical column constructed from outer and inner double helices with opposite orientation in **1**. Some atoms of the ptptp ligands are omitted for clarity in part e.

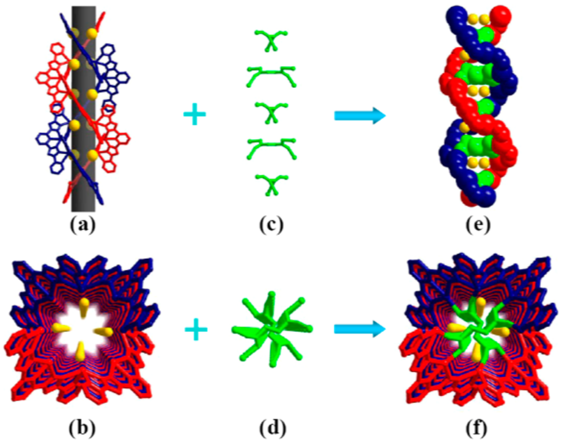

Figure 2. Hierarchical assembly of a cationic spiral staircase constructed from outer double helices and inner steps in **2**. Br^- anions are marked gold. Some atoms of the ptptp ligands are omitted for clarity in part e.

The most striking feature of **1** is that the linkages between the Mn^{2+} ions and ptptp and suc ligands form an unprecedented heterochiral [2 + 2] nested double-helical column constructed from two kinds of double-helical chains in opposite orientation with the coaxial 4_2 screw axis (Figure 1). Like a set of Russian nesting dolls, these [2 + 2] double-helical chains are deployed as beautiful double-wall square tubes viewed down the *c* axis (Figure 1f). On the basis of the distance from the screw axis, **1** can be distinguished as outer and inner walls. The Mn1 ions are wrapped by head-to-tail ptptp ligands, along with Mn2 ions inlayed in the central tridentate binding sites of the ptptp ligands, to form a distinct helical chain $(\text{Mn-ptptp})_n$ (Figure 1a). Two such $(\text{Mn-ptptp})_n$ chains wind around each other to form an outer wall, resulting in a large chiral channel with a diameter of 9.53 Å, which is restricted in order to ensure reasonable coordination geometries of Mn^{2+} ions and to ensure space enough to accommodate the suc ligands (Figure 1b). Combined with the Mn^{2+} ions, the suc ligands form other kinds of double-helical chains $(\text{Mn-suc})_n$ as the inner wall, which is encapsulated by the outer wall (Figure 1c,d). The arrangements of the outer wall provide an opportunity to develop the inner wall, which, in turn, should play an important role in the stability of the column. The outer and inner walls share the same Mn ions, which brings about the same separation (*c*) between adjacent chains of each type of double-helical chain and the same pitch (2*c*) (Figure 1e). Viewed along the *c* axis, the outer and inner walls exhibit pseudo-24-ring and pseudo-28-ring configurations, respectively.

More wonderfully, the outer wall transfers a reverse chirality to the inner wall and hence determines the orientation of the inner double-helical chains. In this sense, the outer wall, offering potential reverse helical coordinate-bonded identification sites, acts as a template for generation of the opposite helical chains inside. In fact, helical CPs containing [n + n] coaxially nested helices with opposite orientations are extremely rare. Interactions of face-to-face $\pi \cdots \pi$ stacking between these columns with reverse orientations extend the 3D racemic supramolecular network (Figure S5 in the SI).

The particular properties of ILs and the unique structural features of the [2 + 2] nested double-helical column provide the potential for conversion from **1** to **2**, which crystallizes in the space group $P4_2bc$. The asymmetric unit of **2** contains two crystallographically independent Mn^{2+} ions, one ptptp ligand, a half suc ligand, one IL Br^- anion, three coordinated water molecules, and a half free water molecule (Figure S2 in the SI). The distorted octahedral geometry $\{N_4O_2\}$ around the apical Mn1 ion is quite different from those in **1**, in which one suc ligand is substituted by a water molecule. The $\{N_3O_3\}$ coordination environment around the central Mn2 ion is the same as that observed in **1**.

Compared to **1**, the most remarkable change of **2** is the disappearance of inner double-helical chains $(\text{Mn-suc})_n$, although outer double-helical chains $(\text{Mn-ptptp})_n$ still exist (Figure 2a,b). Because of the stimulating effect of IL Br^- anions, the halved suc ligands have to change its screwed arrangement (Figure 2c,d) and act as steps to hold together outer double-helical chains to form a chiral cationic spiral staircase (Figure 2e,f). As can be seen in Figures 2 and S6 in the SI (see also Table S3 in the SI), the IL Br^- anions are accommodated in the helical groove of the cationic spiral staircase and interact with three coordinated water molecules through three O−H⋯Br hydrogen bonds with the following properties: O⋯Br distances 3.236(4)−3.401(4) Å; O−H⋯Br angles 148.6−172.7°. **2** may be regarded as an analogue of DNA in terms of topology, except that the hydrogen-bonding interaction between the two strands is substituted by suc ligands coordinating to Mn^{2+} ions. This arrangement has not been previously reported.

Furthermore, **2** could also be obtained solvothermally by the one-pot reaction, indicating that ILs play an important role in the hierarchical self-assembly process of **2**. The addition of small amounts of [RMI]Br can change the chemistry of the solvent, which can lead to great differences in the final structure compared to pure solvothermal conditions. Not only could the IL Br^- anion be occluded in the final structure as a template but also the IL cation could exert important effects on the formation of **2** despite the fact that they do not enter the final structure (see the SI). **2** is a rare example that clearly demonstrates the structure-directing function of IL anions for ultimate solid products under the combination of solvothermal and ionothermal conditions.[9e]

The molar magnetic susceptibilities for **1** and **2** in the 2−300 K range obey the Curie−Weiss law, giving Weiss constant $\theta = -3.90$ K and Curie constant $C = 8.85$ cm^3 K mol^{-1} for **1** and $\theta = -5.1$ K and $C = 8.7$ cm^3 K mol^{-1} for **2**. The magnetic behavior and negative θ value suggest that antiferromagnetic interactions are operative in **1** and **2**. Because of the very similar magnetic exchange pathways in both complexes, conversion from **1** to **2** does not change the antiferromagnetic interactions (Figure S11 in SI).

In conclusion, we have successfully synthesized the first examples of a [2 + 2] nested double-helical column (**1**) and a cationic spiral staircase (**2**) through hierarchical self-assembly. Conversion from **1** to **2** stimulated by the IL Br$^-$ anions could be achieved by introducing ILs into the solvothermal conditions. We are in the process of probing the multiple functional role of ILs in the synthesis of functional CPs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format and experimental details for the measurement. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Professor Xinquan Xin on the occasion of his 80th birthday.

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