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Construction of Two 3D Homochiral Frameworks with 1D Chiral Pores via Chiral Recognition

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S *Supporting Information*

ABSTRACT: The reactions of a pair of enantiomers of macrocyclic nickel(II) complexes with racemic penicillamine generated two 3D hydrogen-bonded homochiral frameworks of $\{[\mathrm{Ni}(f\text{-}(SS)\text{-L})]_2(l\text{-pends})(\mathrm{ClO_4})_2\}_n$ (Λ-**1**) and $\{[\mathrm{Ni}(f\text{-}(RR)\text{-L})]_2(d\text{-pends})(\mathrm{ClO_4})_2\}_n$ (Δ-**1**). The frameworks possess 1D tubular pores and opposite right/left-handed helical porous surfaces (L = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; pends^{2-} = penicillaminedisulfide anion).

During the past decade, the construction of homochiral metal–organic frameworks (HMOFs) has become increasingly attractive because of their utility in enantioselective separation and heterogeneous asymmetric catalysis.[1−3] Such HMOFs can be constructed using totally achiral components[4] or achiral components under chiral influence,[5] as well as chiral ligands as building blocks.[6] So far, numerous HMOFs have been reported,[1−6] but few have been assembled directly from racemic organic ligands.[7a−c] Generally, the reactions of racemic ligands with metal salts prefer to generate racemic products,[7d−g] whereas with enantiopure metal complexes, it may be easier to produce chiral compounds, indicative of a promising way to construct new HMOFs. This method requires easily obtained enantiopure metal complexes as building blocks. Our previous works have indicated that easily obtained enantiopure $[\mathrm{Ni}(\alpha\text{-}(SS)\text{-L})](\mathrm{ClO_4})_2$ and $[\mathrm{Ni}(\alpha\text{-}(RR)\text{-L})](\mathrm{ClO_4})_2$ are good building blocks for the construction of homochiral helical chains (L = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane).[8] Herein, we use them to react with racemic penicillamine for the construction of HMOFs. We have successfully obtained two novel 3D homochiral frameworks, $\{[\mathrm{Ni}(f\text{-}(SS)\text{-L})]_2(l\text{-pends})(\mathrm{ClO_4})_2\}_n$ (Λ-**1**) and $\{[\mathrm{Ni}(f\text{-}(RR)\text{-L})]_2(d\text{-pends})(\mathrm{ClO_4})_2\}_n$ (Δ-**1**), with 1D tubular chiral pores (pends^{2-} = penicillaminedisulfide anion).

The reactions of $[\mathrm{Ni}(\alpha\text{-}(SS)\text{-L})](\mathrm{ClO_4})_2$ and $[\mathrm{Ni}(\alpha\text{-}(RR)\text{-L})](\mathrm{ClO_4})_2$ with racemic penicillamine in the presence of NaOH in acetonitrile under ambient conditions gave two chiral compounds, Λ-**1** and Δ-**1**, respectively (see the Supporting Information). $[\mathrm{Ni}(\alpha\text{-}(SS)\text{-L})]^{2+}$/$[\mathrm{Ni}(\alpha\text{-}(RR)\text{-L})]^{2+}$ recognizes the *l*/*d* enantiomer from the racemic penicillamine to form $[\mathrm{Ni}(f\text{-}(SS)\text{-L})(l\text{-pen})]^+$/$[\mathrm{Ni}(f\text{-}(RR)\text{-L})(d\text{-pen})]^+$ (pen$^-$ = penicillamine anion). Two $[\mathrm{Ni}(f\text{-}(SS)\text{-L})(l\text{-pen})]^+$/$[\mathrm{Ni}(f\text{-}(RR)\text{-L})(d\text{-pen})]^+$ then dimerize to form $\{[\mathrm{Ni}(f\text{-}(SS)\text{-L})]_2(l\text{-pends})\}^{2+}$/$\{[\mathrm{Ni}(f\text{-}(RR)\text{-L})]_2(d\text{-pends})\}^{2+}$ through in situ oxidation of the SH group of penicillamine. Spontaneous resolution occurs during the reaction of racemic $[\mathrm{Ni}(\alpha\text{-}rac\text{-L})](\mathrm{ClO_4})_2$ with racemic penicillamine under the same conditions, and a conglomerate of Λ-**1** and Δ-**1** was generated in which each crystal is chiral. The pends^{2-} were formed by the oxidation of atmospheric oxygen in the presence of macrocyclic nickel(II) complexes. The disulfide was also found in the metabolites of *d*-penicillamine excreted in the urine formed by oxidation and exchange reactions.[9]

The results of X-ray crystallographic analysis (see the Supporting Information) reveal that Λ-**1** and Δ-**1** are enantiomers (Figure 1), with chiral space groups $P3_221$ and $P3_121$ and absolute structure (Flack) parameters of +0.01(6) and −0.04(7) for Λ-**1** and Δ-**1**, respectively. In Λ-**1**, two $[\mathrm{Ni}(f\text{-}(SS)\text{-L})]^{2+}$ are bridged by an *l*-pends^{2-} anion to form a crossbow-shaped dimer of $\{[\mathrm{Ni}(f\text{-}(SS)\text{-L})]_2(l\text{-pends})\}^{2+}$ (Figure 1), with a S−S distance and a C−S−S−C torsion angle of 2.047(5) Å and 85.68(8)°, respectively. These values are in good agreement with the ones reported.[10] Λ-**1** displays a distorted octahedral coordination geometry through the coordination of each Ni$^{\mathrm{II}}$ ion with four nitrogen atoms of *f*-(*SS*)-L in a folded configuration and one carboxylate oxygen atom and one nitrogen atom of *l*-pends^{2-} in the cis position. It is interesting to note that $\{[\mathrm{Ni}(f\text{-}(SS)\text{-L})]_2(l\text{-pends})\}^{2+}$ dimers are connected through intermolecular hydrogen bonding between the uncoordinated oxygen atoms of *l*-pends^{2-} in one dimer and two secondary amines of *f*-(*SS*)-L of an adjacent dimer (Figure S1 in the Supporting Information), resulting in a left-handed helical chain along the 3_2 axis (Figure 2a). Each helix contains three $\{[\mathrm{Ni}(f\text{-}(SS)\text{-L})]_2(l\text{-pends})\}^{2+}$ dimers with a pitch of 17.8 Å. Similar intermolecular hydrogen bonds of corresponding dimers of $\{[\mathrm{Ni}(f\text{-}(RR)\text{-L})]_2(d\text{-pends})\}^{2+}$ enantiomers lead to the formation of a 1D right-handed helical chain along the 3_1 axis in Δ-**1** (Figure 2b), demonstrating the existence of a correlation between the chirality of building blocks and the helicity of 1D helical chains constructed by these chiral building blocks.[8a]

In Λ-**1**, the outside $[\mathrm{Ni}(f\text{-}(SS)\text{-L})]^{2+}$ linked to the left-handed helical chains through the S−S bonds (Figure 2a) are also connected by intermolecular hydrogen bonds between the uncoordinated oxygen atoms of *l*-pends^{2-} and two secondary amines of *f*-(*SS*)-L of $\{[\mathrm{Ni}(f\text{-}(SS)\text{-L})]_2(l\text{-pends})\}^{2+}$ in adjacent chains. This leads to the formation of three additional left-handed helical chains surrounding the originally formed left-handed

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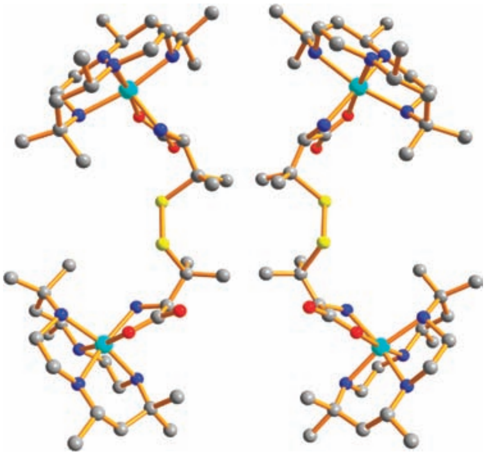

Figure 1. Pair of enantiomers of $\{[Ni(f\text{-}(SS)\text{-}L)]_2(l\text{-pends})\}^{2+}$ and $\{[Ni(f\text{-}(RR)\text{-}L)]_2(d\text{-pends})\}^{2+}$ in Λ-**1** and Δ-**1**, respectively. Color code: Ni, light blue; S, yellow; N, deep blue; O, red; C, gray.

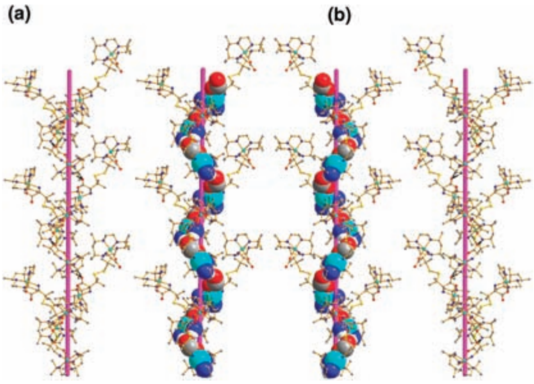

Figure 2. (a) 1D hydrogen-bonded left-handed helical chain in Λ-**1** and (b) 1D hydrogen-bonded right-handed helical chain in Δ-**1**.

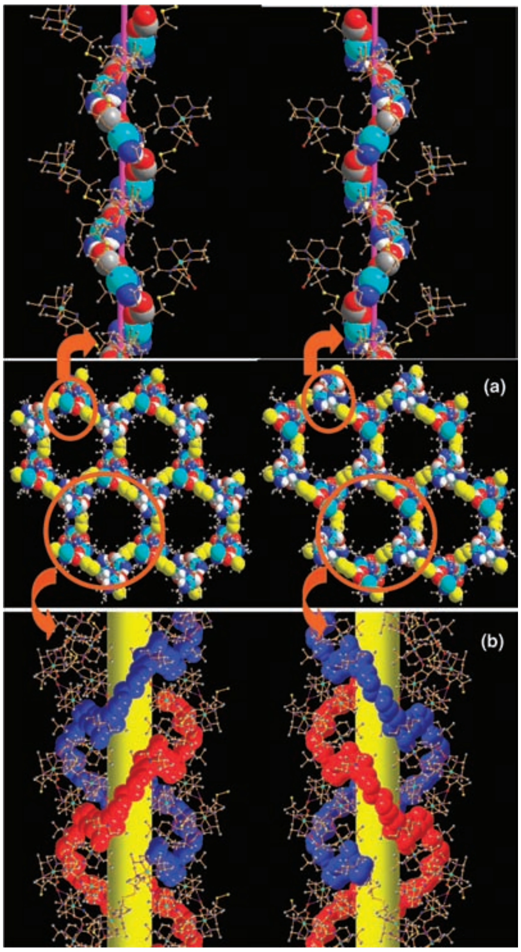

Figure 3. (a) Space-filling model of Λ-**1** (left) and Δ-**1** (right), showing honeycomb-like 3D homochiral frameworks with 1D tubular pores. (b) Side view of 1D right-handed (left) and left-handed (right) helical pores in Λ-**1** and Δ-**1**, respectively.

helical chains (Figure 3a, left). Thus, it can be considered that each left-handed helical chain is connected with three adjacent left-handed helical chains through the S—S bonds, resulting in a novel honeycomb-like 3D homochiral framework with 1D chiral tubular pores (Figure 3a, left), with a pore size of 7.5 Å × 7.5 Å. This leads to a very large solvent-accessible volume of 32.0%, calculated by *PLATON*.[11] The topology of the framework is similar to that of the reported $[Mn_3(HCOO)_4(DCam)]_n$ framework.[12] In Δ-**1**, the similar intermolecular hydrogen-bonding connections result in a 3D homochiral framework with 1D chiral tubular pores of opposite handedness (Figure 3a, right).

In Λ-**1**, there is also the existence of intermolecular hydrogen-bonding interactions between two uncoordinated oxygen atoms of *l*-pends^{2-} in one $\{[Ni(f\text{-}(SS)\text{-}L)]_2(l\text{-pends})\}^{2+}$ dimer and four secondary amines of two *f*-(*SS*)-L in an adjacent dimer (see Figure S2a in the Supporting Information). The $\{[Ni(f\text{-}(SS)\text{-}L)]_2(l\text{-pends})\}^{2+}$ dimers are connected through the above hydrogen-bonding interactions to generate 1D right-handed helical chains along the walls of the tubular pores (Figure 3b, left). Each pore contains double-stranded right-handed helical chains. Thus, the surface of the tubular pores in Λ-**1** is right-handed helical (Figure 3b, left). In contrast, the surface of the tubular pores in Δ-**1** is left-handed helical because of the opposite chirality of $\{[Ni(f\text{-}(RR)\text{-}L)]_2(d\text{-pends})\}^{2+}$ (Figure 3b, right). The pores are filled with disordered solvent molecules, which are easily lost at room temperature, because of the hydrophobic nature of the tubular pores (Figure S3 in the Supporting Information). The results of X-ray diffraction measurements indicate that all of the peaks displayed in the measured patterns closely match those in the simulated patterns generated from the single-crystal diffraction data (Figure S4 in the Supporting Information), demonstrating single phases of Λ-**1** and Δ-**1** formed.

The results of circular dichroism (CD) measurements confirm the chiral nature of Λ-**1** and Δ-**1**. As shown in Figure 4a, the bulk crystals of Λ-**1** in water show negative and positive Cotton effects at 220 and 243 nm, respectively, while the bulk crystals of Δ-**1** in water show opposite Cotton effects at the same wavelengths. Each crystal of the conglomerate, which was randomly picked from the bulk crystals, shows dichroic signals similar to those of Λ-**1** or Δ-**1** (Figure 4b), indicating spontaneous resolution occurring during the reaction of racemic $[Ni(\alpha\text{-}rac\text{-}L)](ClO_4)_2$ with racemic penicillamine. In addition, the results of solid-state CD spectral measurements also confirm their chirality in the crystalline state (Figure S5 in the Supporting Information).

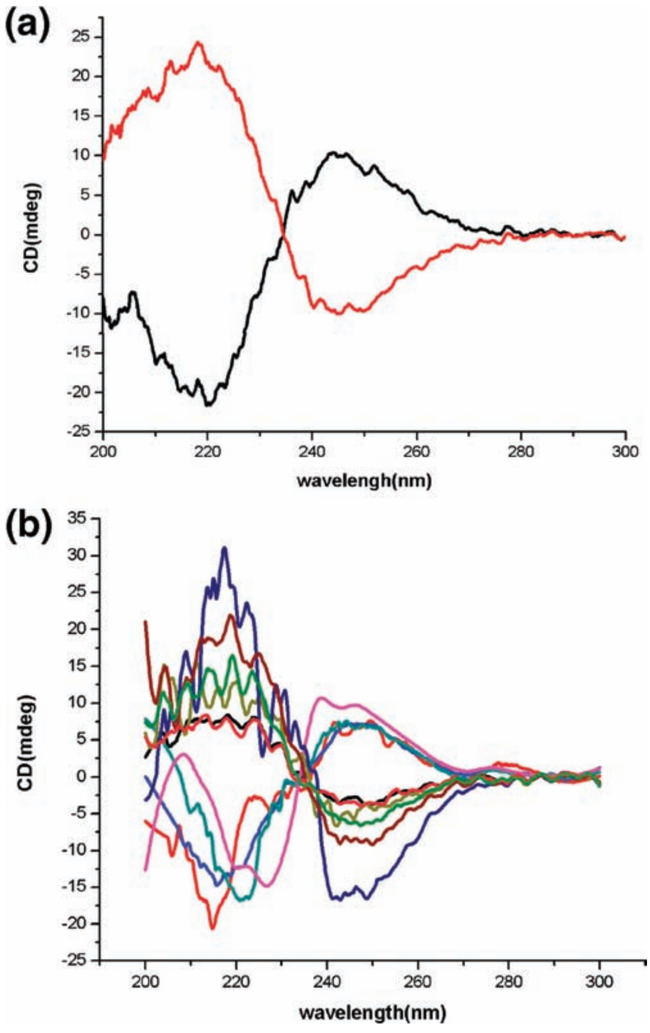

Figure 4. Aqueous CD spectra of (a) Λ-**1** (black) and Δ-**1** (red) and (b) 11 single crystals picked up randomly from the conglomerate, in which 6 are Δ-**1** and 4 are Λ-**1**.

In summary, two novel 3D homochiral frameworks of Λ-**1** and Δ-**1** with 1D tubular pores have been constructed by the reactions of chiral precursors [Ni(α-(*SS*)-L)]$(ClO_4)_2$ and [Ni(α-(*RR*)-L)]$(ClO_4)_2$ with racemic penicillamine. The porous surface is right- and left-handed helical in Λ-**1** and Δ-**1**, respectively. In addition, the chirality of the 1D tubular pores in 3D homochiral frameworks are controlled by the chirality of the precursors. The 1D hydrophobic chiral pores in Λ-**1** and Δ-**1** make it possible to recognize and separate racemic alcohols such as 2-butanol, which is an ongoing investigation in our laboratories.

■ ASSOCIATED CONTENT

S Supporting Information. Synthesis, crystallographic data, selected bond distances and angles, and structural figures of Δ-**1** and Λ-**1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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