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Synthesis and Chirality Control of Bulk Crystals and Nanocrystals: From a Right-Handed Nonpolar Chain to a Left-Handed Polar Chain

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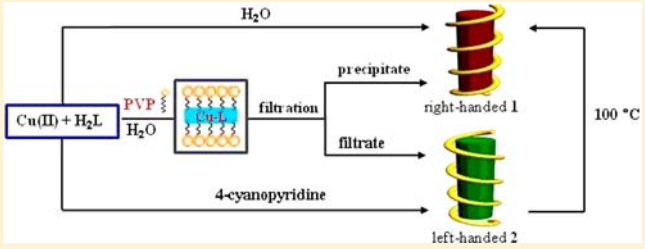
Supporting Information

ABSTRACT: Both bulk crystals and nanocrystals of two helical complexes, $[Cu(\mu_2\text{-}L)(H_2O)]_n$ (**1**) and $\{[Cu(\mu_2\text{-}L)(H_2O)]\cdot 2H_2O\}_n$ (**2**) (H_2L = thiazolidine-2,4-dicarboxylic acid), have been synthesized with the chiralities of right-handedness (**1**) and left-handedness (**2**), respectively. 4-Cyanopyridine and poly(vinylpyrrolidone) (PVP) have been applied to control the synthesis of complexes with different helicities in bulk-crystal and nanocrystal forms, respectively. **2** can be irreversibly transformed to **1** under heating. Associated with the conformation changing, the symmetry alters between nonpolar and polar space groups.



INTRODUCTION

Helicity has attracted much attention in biological and material chemistry as an essential element of life and an important structure in advanced materials.[1] Conformational control, which is a center feature in biopolymers, is of significant interest because polymorphism can lead to various physico-chemical properties.[2] Most previous studies focused on controlling the conformation of the helicity (left-handed or right-handed) by using isomeric chiral molecules as the primary linker supplementary.[3] However, the demands for starting materials and reaction conditions are quite critical. For example, the isomeric ligands used to synthesize complexes with different conformations have to be chirally pure and highly stable under corresponding synthesis conditions without racemization.[3,4] In order to overcome these inevitable limits, the development of new methods to control the conformations of helical complexes is urgent and important not only in gaining new materials but also in understanding the origin of life itself.[5,6] Recently, specific solutes and/or solvents were used to lead to new stereocenters or molecular-level chirality by self-assembly through hydrogen bonding, electrostatic effects, weak van der Waals force, and so on.[1,5]

Herein, we explore a simple strategy that allowed us to selectively design and synthesize helical structures with different handedness. 4-Cyanopyridine and poly(vinylpyrrolidone) (PVP) have been applied to control the synthesis of complexes with different helicities in bulk-crystal and nanocrystal forms, respectively, through adjustment of the number of water molecules in the crystal lattice. Conformational conversion behaviors have also been observed involving the change in symmetry between nonpolar and polar space groups.

RESULTS AND DISCUSSION

Synthesis and Structure of Complexes in Bulk-Crystal Form. Thiazolidine-2,4-dicarboxylic acid (H_2L; Scheme 1) was selected as the ligand, which has been reported to be efficient for the construction of chiral complexes.[7] The synthesis of H_2L is simple and in high yield from commercially available starting materials, but the product includes enantiomers (*R*,*R*) and (*R*,*S*), which are very difficult to separate. However, there is a reversible conversion of the isomers in the solution (Scheme 1).[7] Upon coordination to metal ions, the ligand H_2L or L^{2-} adopts the coordination mode via the nitrogen atom of the heterocycle and the oxygen atoms of the 2,5-dicarboxylate groups, forming two fused five-membered rings in order to achieve the most stable configuration. As a result, the optimal coordination mode and the reversible conversion of the isomers guarantee the enantiomerically pure products and avoid racemization of the 4 position in the ligand during the synthesis of complexes.[7] Equimolar amounts of $Cu(NO_3)_2\cdot 6H_2O$ and H_2L were mixed in water, leading to a blue solution, from which blue needlelike crystals of $[Cu(\mu_2\text{-}L)(H_2O)]_n$ (**1**) were obtained. Interestingly, when 4-cyanopyridine was involved in the reaction of H_2L with $Cu(NO_3)_2\cdot 3H_2O$ in water, cyan needlelike crystals of $\{[Cu(\mu_2\text{-}L)(H_2O)]\cdot 2H_2O\}_n$ (**2**) were crystallized out from the mixture.

The conformations and molecular structures of both **1** and **2** are illustrated by elemental analyses, IR, and single-crystal X-ray diffraction (XRD). The crystal structure of **1** is shown in Figure 1a,c. **1** crystallizes in the chiral space group $P2_12_12_1$ with one Cu^{II} ion, one L^{2-} anion, and one coordinated water molecule in a single asymmetric unit. Cu^{II} ions adopt distorted square-pyramidal geometries with the geometric parameter[8] τ = 0.08

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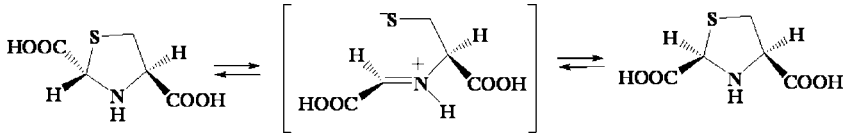
Scheme 1. Conformation Conversion of the Enantiomers (*R*,*S*) and (*R*,*R*) of H_2L in an Aqueous Solution



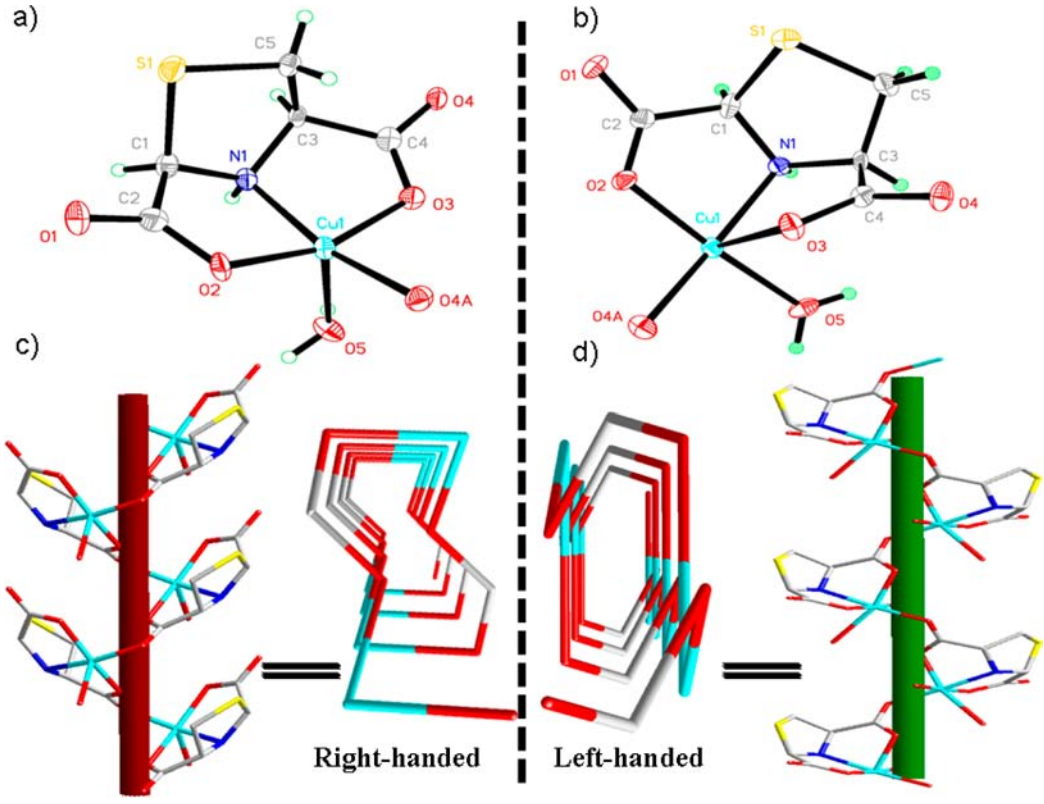


Figure 1. Coordination environments and helical structures of **1** (a and c) and **2** (b and d). Color code: Cu, cyan; N, blue; C, gray; S, yellow; O, red; H, green.

and coordinate with the ligands in a ratio of 1:1 to afford the helical chains. Each Cu^{II} ion is coordinated by one nitrogen atom (N1) and two oxygen atoms (O2 and O3) from one ligand and one oxygen atom (O4A) from the neighboring unit to complete the base of the distorted square pyramid as well as one water molecule (O5) at the vertex (Figure 1a). The adjacent Cu^{II} ions are connected by ligands L to form right-handed helical chains running along the *b* axis with a pitch of 5.76 Å (Figure 1c).

2 crystallizes in the chiral and polar space group $P2_1$ with the formula $\{[Cu(\mu_2\text{-}L)(H_2O)]\cdot 2H_2O\}_n$. As shown in Figure 1b, each Cu^{II} ion is five-coordinated by three oxygen atoms (O2, O4A, and O5) and one nitrogen atom (N1) at the equatorial plane as well as one oxygen atom (O3) at the vertex, forming distorted square pyramids with the geometric parameter[8] τ = 0.05. There are only one crystallographically independent L in a bidentate mode and only one kind of Cu^{II} ion coordinated by two ligands. As a result of this connectivity pattern, a one-dimensional (1D) chain is formed along the *b* axis (Figure 1b). Although both **1** and **2** contain a 1D chain structure and Cu^{II} ions in the geometry of distorted square pyramids, the coordination mode of **2** is different from that of **1** especially on both the rotation angle of the ligands and the atoms at the vertex. These differences lead the helixes in **1** and **2** to go along contrast helical modes (right-handedness in **1** and left-handedness in **2**), as shown in Figure 1c,d.

On the basis of crystal data analyses, the different conformations of **1** and **2** should be attributed to participation of the crystal lattice water molecules (Table 1). In both **1** and **2**, each Cu^{II} ion is coordinated to one nitrogen atom, three oxygen atoms from the ligand, and one oxygen atom from the water molecule. There is no crystal lattice water molecule in **1**, and the distance between O3 of the carboxylate group and the Cu^{II} ion in the adjacent unit (Cu1A) in complex **1** is relatively short (2.642 Å), indicating a strong interaction between them (Figure 2), which directs the right-handedness helical mode of **1**. Different from **1**, **2** contains two crystal lattice water molecules in each asymmetric unit, one (O6A) of which is involved in hydrogen-bonding interaction with O3 from the carboxylate group of the ligand (Figure 2). This hydrogen-bonding effect attracts O6A to locate quite near (2.501 Å) the copper atom (Cu1A) from the adjacent unit, which leads to a possible strong interaction between them. At the same time, the hydrogen bonding between O6A and O3 prolongs the distance of Cu1A−O3 to 3.009 Å and thus reduces the interactions of Cu1A and O3 in comparison with the situation in **1**. Consequently, introduction of the hydrogen-bonding effect and Cu1A−O6A interaction as well as reduction of Cu1A−O3 interaction determines the left-handedness mode of the 1D

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Table 1. Crystal Data and Structure Refinements of 1 and 2

	1	2
empirical formula	$C_5H_7CuNO_5S$	$C_5H_{11}CuNO_7S$
fw	256.74	292.75
T (K)	293(2)	293(2)
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1$
a (Å)	5.7404(10)	5.1721(10)
b (Å)	7.7327(14)	9.773(2)
c (Å)	17.870(3)	9.867(2)
β (deg)	90	102.08(2)
V (Å^3)	793.2(2)	487.73(17)
Z	4	2
ρ (mg cm^3)	2.150	1.993
μ (mm^{-1})	3.003	2.470
F(000)	516	298
θ (deg)	3.48−27.47	2.97−25.01
index ranges	$-7 \le h \le 7$	$-4 \le h \le 6$
	$-9 \le k \le 10$	$-11 \le k \le 11$
	$-20 \le l \le 22$	$-11 \le l \le 11$
Flack parameter	0.08(4)	0.08(6)
GOF on F^2	1.101	1.018
R1, R2 [$I > 2\sigma(I)$]	0.0732, 0.1276	0.0401, 0.0743
R1, R2 (all data)	0.0956, 0.1353	0.0476, 0.0763
largest diff peak and hole (e Å^{-3})	0.717 and −0.875	0.393 and −0.469

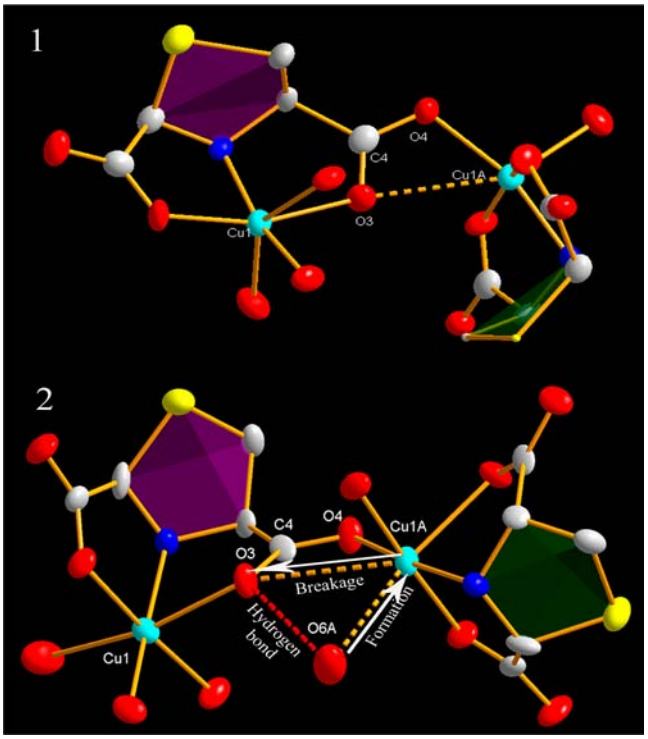

Figure 2. Comparison of interactions directing the helical modes in **1** and **2**.

helix in **2** instead of right-handedness helix in **1**. Moreover, the angle of C4−O4−Cu1A changes from 103.0° in **1** to 127.2° in **2** associated with the change of the interchain Cu···Cu distance from 4.5966 to 5.2943 Å.

Upon comparison of the synthesis procedures for bulk crystals of **1** and **2**, 4-cyanopyridine should play a crucial role for directing the formation of helixes in different chiralities. 4-Cyanopyridine and its derivates have been reported as effective reagents for the formation and enhancement of the hydrogen-bonding effect and proton transfer.[9] As a result, the addition of 4-cyanopyridine could lead to stronger hydrogen-bonding interaction between water molecules and L^{2-}, which subsequently allows the water molecules to be involved in the crystal lattice of **2** during the crystallization process as well as the interactions discussed in last paragraph to control the chirality of the helix.

Synthesis and Morphology of 1 and 2 in Nanocrystal Form. In an attempt to synthesize nanocrystals of chiral complexes **1** and **2**, PVP (K30; average M_w = 10000), which was proven to lead to rich hydrogen-bonding and electrostatic effects[10] and was used in our group for the preparation of nano- and microcrystals previously,[7c,d] was added to the reaction of H_2L and $Cu(NO_3)_2{\cdot}6H_2O$ in water, resulting in a cyan-blue solution. Curiously, after stirring for several hours, both light-blue solids of **1** and cyan supernatant of **2** were obtained from the final suspension (Figure 3). **1** can be filtered out as a precipitate at the bottom of the container; afterward, **2** can be subsided through the addition of acetone[11] to the filtrate and isolated by centrifugation. The morphology of **1** has been characterized by scanning electron microscopy (SEM) as hierarchical flowerlike microspheres with diameter of ca. 60 μm, which are assembled by nanobelts with thickness of ca. 800 nm (Figure 3b). SEM images show that **2** consists of uniform nanosheets with thickness of ca. 50 nm (Figure 3c,d). Powder XRD (PXRD) patterns of nanocrystals of **1** and **2** are consistent with the simulation patterns from single-crystal XRD data of their bulk crystals, respectively, as illustrated in Figure 3e. For comparison, the reactions without PVP gave only complex **1** in the bulk-crystal form both with and without the presence of acetone, as confirmed by PXRD.

PVP plays a double role in the synthesis procedure: (i) as a surfactant for the formation of nanocrystals and (ii) as a crucial element for affecting the conformations and chiralities of the products. It is well-known that PVP is amphiphilic and can form micelles in an aqueous solution (water−oil−water system).[12,13] When Cu^{II} ions and PVP were mixed in an aqueous solution, the formation of micelles could be proposed. This PVP-covered "water pool" offered an independent reaction microenvironment that is favorable for the formation of hydrogen-bonding interaction and for stabilization of the relatively thermally and kinetically unstable product **2**.[14] Consequently, different reaction environments were obtained inside and outside micelles,[13] leading to isolation of both kinds of products.

Transformation between 1 and 2. Further experiments were investigated to examine the transformation between **1** and **2**. When the cyan powder of **2** was heated at 100 °C for 3 h, a kind of light-blue powder was obtained and confirmed to be complex **1** by PXRD (Figure 4).

In the thermogravimetry measurement (Figure 5), **2** shows a weight loss of 12.3% in the range of 25−120 °C, which is consistent with the loss of two water molecules (one coordination and one crystal water, calcd 12.2%). The thermogravimetric analysis (TGA) curve of **2** above 120 °C is the same as that of **1**, indicating the formation of **1** by heating complex **2**. On the other hand, when **1** was exposed in a water-vapor atmosphere at room temperature for 3 days, PXRD proved that there was no hydration process or transformation occurring in **1**. These dehydration and hydration experiments indicate that **1** is both thermodynamically and kinetically favored compared with **2**. However, the addition of 4-

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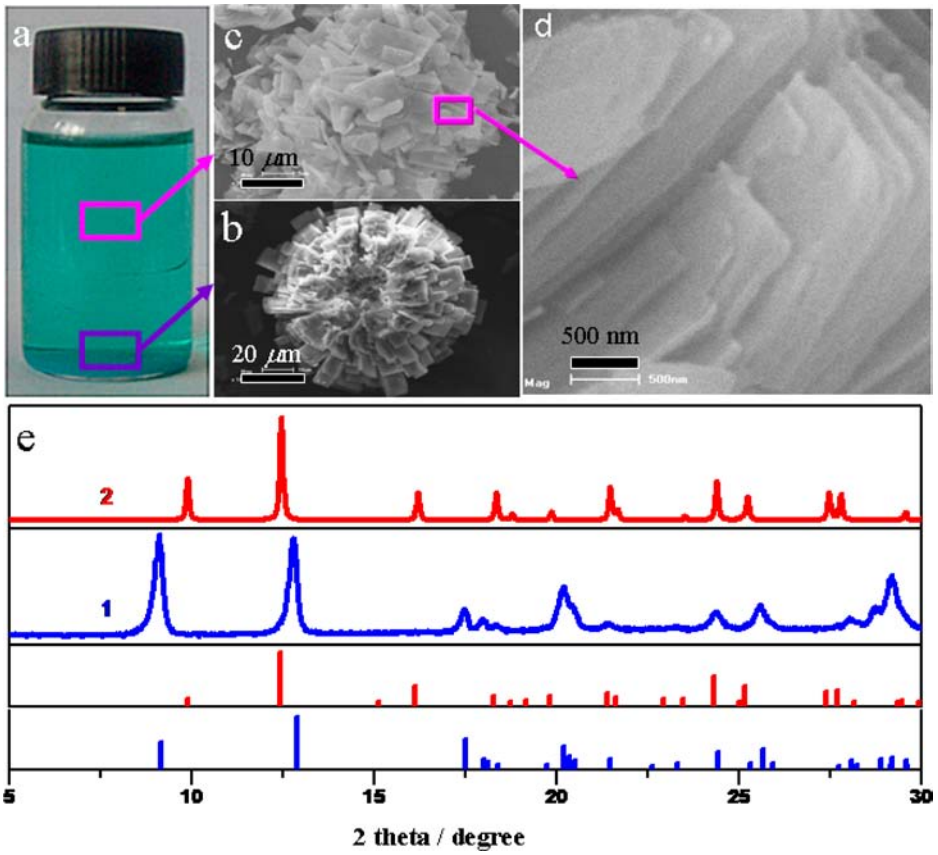

Figure 3. Solution of the reaction after the formation of nanocrystals (a). SEM images of **1** and **2** from the reaction solution with PVP (b–d). PXRD patterns of the as-obtained products and corresponding simulated patterns as columns from single-crystal XRD data (e).

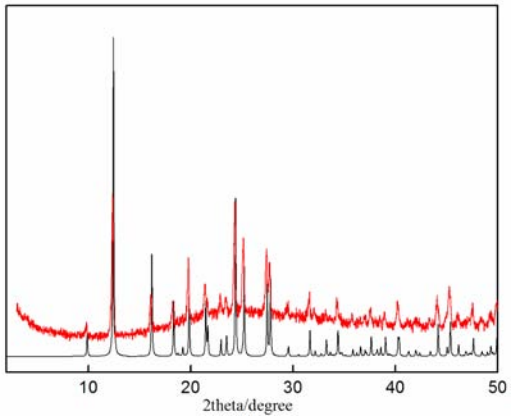

Figure 4. PXRD pattern of the powder obtained by heating **2** at 100 °C for 3 h (red) as well as the simulation PXRD pattern from single-crystal XRD data of **1** (black).

cyanopyridine or PVP leads to the formation and isolation of less thermally and kinetically stable product **2**. The whole synthesis and transformation procedure is summarized in Scheme 2.

It is worthwhile to compare **1** and **2** with the cobalt(II)[7c] and nickel(II)[7d] complexes reported previously in our group. For the Co^{II} ion, two different complexes can be synthesized with changing reaction temperature, the molecular structures of which exchange with each other together with conversion from bulk crystals to microcrystals upon the addition of PVP to the reaction systems. For the nickel(II) complexes, the molecular structures of both complexes obtained at different reaction temperatures are converted from discrete and 3D, respectively, to a totally new one with 1D structure during conversion under the effect of PVP. In this paper, when Cu^{II} was selected as the central metal ion, we exhibited new features of the H_2L-coordinated complexes: (i) besides temperature, the addition of 4-cyanopyridine can also be utilized to control the synthesis of complexes with different helicities; (ii) left-handed complex **2** can be transformed to right-handed complex **1** by heating; (iii) it is possible to synthesize and isolate both left-handed and right-handed complexes in nanocrystalline form at the same time with the addition of PVP.

Chiralities and Nonlinear Optical Behavior of 1 and 2. Resulting from the different symmetries (chiral space group $P2_12_12_1$ for **1** and chiral and polar space group $P2_1$ for **2**), significant changes in the properties could be expected between **1** and **2**. As shown in Figure 6, the circular dichroism (CD) spectrum of the chiral ligand H_2L gives rise to a positive band centered at λ = 250 nm, which can be attributed to $\pi \rightarrow \pi^*$ transitions. For the complexes, **1** features four Cotton effects consisting of two positive signals at λ = 240 and 320 nm as well as two negative peaks at λ = 275 and 350 nm. **2** displays one positive Cotton effect at 250 nm and broad positive peaks at λ = 345 nm. The peaks at λ = 240 and 275 nm for **1** as well as λ = 250 nm for **2** can be attributed to the ligand, while the peaks at λ = 325 and 350 nm for **1** and the broad positive peak at λ = 345 nm for **2** are due to the absolute conformation of the pyramidal ($CuNO_4$) geometries. As members of asymmetric point groups, both **1** and **2** display nonlinear optical behavior, which is evaluated by second-harmonic-generation (SHG)

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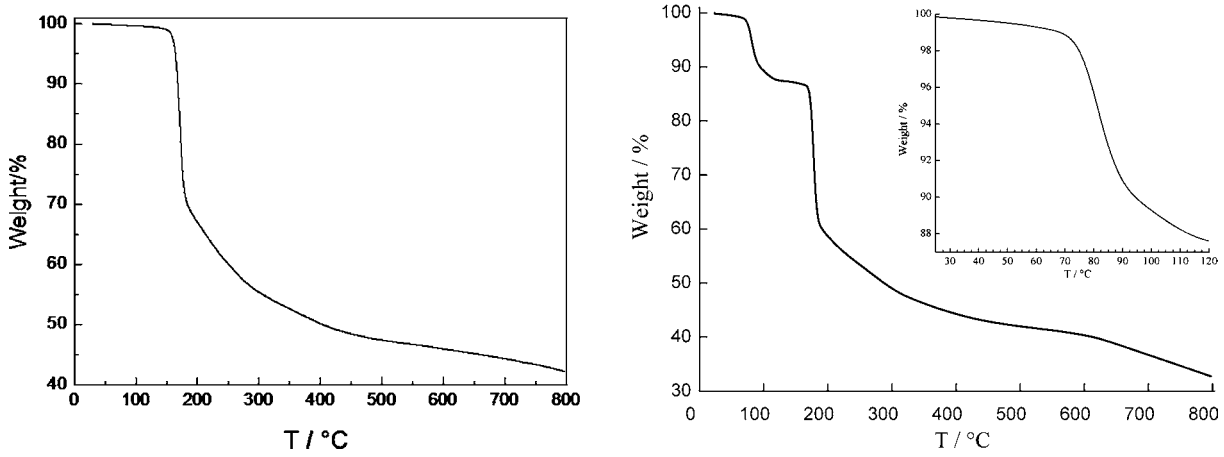
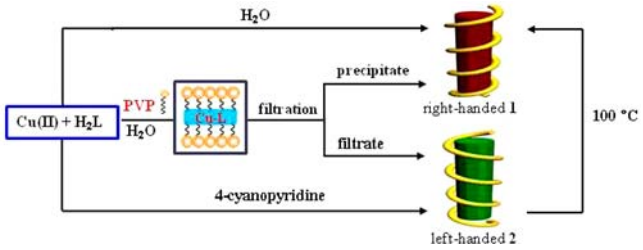


Figure 5. TGA of **1** (left) and **2** (right).

Scheme 2. Summary for the Synthesis and Transformation of 1 and 2



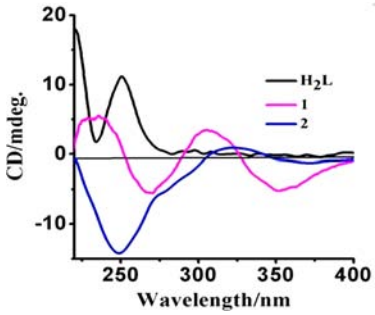


Figure 6. CD patterns of **1** and **2** as well as the free ligand (black line).

measurement. According to the principle proposed by Kurtz and Perry, SHG efficiencies of **1** and **2** are approximately 0.3 and 0.5 times that of urea, respectively.[15]

CONCLUSION

In summary, new chiral complexes have been prepared selectively in both bulk-crystal and nanocrystal forms. Water molecules located in the crystal lattice have been illustrated to be important for the construction manner of helixes through hydrogen-bonding interactions. 4-Cyanopyridine and PVP have been applied to synthesize thermodynamically and kinetically unfavored chiral products and to control the conformational polymorphism of helical structures by influencing the presence of lattice water molecules as well as the formation and strength of hydrogen-bonding effects in bulk-crystal and nanocrystal forms, respectively. The chirality of the complex can be converted from left- to right-handedness through the release of lattice water molecules by heating. The results shown here are valuable toward creating new helical complexes with controllable conformations and properties for the areas of nonlinear optics, chiral catalysis, and so on and are probably useful for understanding the natural selectivity of chiral components in the constitution of life (e.g., the helical direction of peptide chains, proteins, DNA, and RNA).

EXPERIMENTAL SECTION

General Methods. All reagents and solvents employed were commercially available and were used as received without further purification. IR spectra were obtained from KBr pellets on a Bio-Rad FTS 135 Plus spectrometer in the 400−4000 cm^{-1} region. Elemental analyses for carbon, hydrogen, and nitrogen were carried out by using a Perkin-Elmer analyzer. Thermal analyses (under a dinitrogen atmosphere with a heating rate of 10 °C min^{-1}) were carried out in a Labsys NETZSCH TG 209 Setaram apparatus. Single-crystal XRD data of **1** and **2** were collected with a Rigaku Saturn 007 CCD diffractometer and an Oxford SuperNova diffractometer, respectively, which were equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods using *SHELXS-97* and refined by least-squares procedures on F_o^2 with *SHELXL-97* by minimizing the function $\sum w(F_o^2 - F_c^2)^2$, where F_o and F_c are respectively the observed and calculated structure factors. The hydrogen atoms were located geometrically and refined isotropically. PXRD data were collected by using a D/Max-2500 X-ray diffractometer with Cu Kα radiation. The morphologies of the samples were inspected using a field-emission scanning electron microscope (Hitachi S-3500N). CD experiments were performed on a Jasco J-715 spectropolarimeter at room temperature. SHG measurements were carried out on a LAB130 Pulsed Nd:YAG laser (10 ns; 1064 nm).

Synthesis of Bulk Crystals of 1. In a typical experiment, an aqueous solution of $Cu(NO_3)_2{\cdot}3H_2O$ (5.0 mL, 0.5 mmol) was added to H_2L (0.5 mmol) in 10.0 mL of water. The solution was mixed under vigorous stirring for 2 h and then filtered. The filtrate was allowed to stand at room temperature (298 K). Blue needlelike crystals were obtained after 2 h at 298 K (**1**). Yield: 44% based on copper salt. Elem anal. Calcd for **1** ($C_5H_7CuNO_5S$): C, 23.39; H, 2.75; N, 5.46. Found: C, 23.55; H, 2.55; N, 5.83. IR (KBr, cm^{-1}): 3486, 3153, 1617, 1436, 1279−604.

Synthesis of Bulk Crystals of 2. A mixture of $Cu(NO_3)_2{\cdot}3H_2O$ (0.5 mmol) and 4-cyanopyridine (0.5 mmol) in distilled water (10 mL) was added to a solution of H_2L (0.5 mmol) in 10.0 mL of water. The solution was mixed under vigorous stirring for 2 h and then filtered. Cyan needlelike crystals were obtained from the filtrate after several days at 298 K (**2**). Yield: 28% based on copper salt. Elem anal. Calcd for **2** ($C_5H_{11}O_7SNCu$): C, 20.51; H, 3.79; N, 4.78. Found: C, 20.77; H, 3.53; N, 4.76. IR (KBr, cm^{-1}): 3421, 3287, 1617, 1552, 1428, 1384, 1278−524.

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Synthesis and Separation of 1 and 2 in Nanocrystal Form. $Cu(NO_3)_2{\cdot}3H_2O$ (0.48 g, 2.0 mmol) was dissolved in water (40.0 mL) with the presence of PVP (11.2 g), to which an aqueous solution of H_2L (0.34 g, 2.0 mmol, 20.0 mL) was added after stirring for a few minutes. The obtained solution was stirred vigorously for 2 h and kept overnight, from which light-blue solids of **1** and cyan supernatant were obtained at room temperature and separated by filtration. When 200.0 mL of acetone was added to the cyan supernatant, a light-cyan suspension was obtained, from which cyan powder of **2** was isolated by centrifugation at 4000 rpm for 15 min and washed with ethanol several times.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format. 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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