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A novel tubular coordination network [Zn(spcp)(OH)] (spcp = 4-sulfanylmethyl-4'-phenylcarboxylate pyridine) with a modest SHG activity based on two types of homo-chiral helices was synthesized and characterized.

Crystal engineering based on noncentrosymmetric metalorganic frameworks (MOFs) by using asymmetric bridging ligands as building blocks has attracted much attention owing to its potential applications as second-order nonlinear optical (NLO) materials.¹⁻⁴ The utilization of asymmetric bridging ligands can introduce electronic asymmetry (push-pull effect), which is essential for a second harmonic generation (SHG) response. At present, there are numerous examples with threedimensional interpenetrated diamondoid² or two-dimensional grid³ structural motifs assembled by combining unsymmetrical, rigid, and linear pyridinecarboxylate ligands and d10 metal ions (in particular Zn^{2+} and Cd^{2+}) for their favorable optical transparency. However, the helical and other recurring coordination networks used in NLO materials still remain few explored.⁴ Widely found in nature, helical structural motifs exhibit axial chirality, and can crystallize in noncentrosym-metric space groups.⁵ We believe that the introduction of chemical interaction sites in asymmetric bridging ligands is a challenging subject in developing new polar and chiral systems, and aesthetic structural motif with fascinating functions can be obtained.

Toward the goal of designing NLO materials with new noncentrosymmetric MOFs containing chemical interaction sites, we are currently taking an approach of self-assembly reaction between metal ions and sulfur-containing asymmetrical linking ligands,⁶ where sulfide moieties are well known as redox active functional groups that could enhance electronic asymmetry. Here we report a novel two-dimensional tubular coordination polymer, [Zn(spcp)(OH)] (spcp = 4-sulfanylme-thyl-4'-phenylcarboxylate pyridine), together with its SHG response, fluorescent property and thermal stability data. The structure of the polymer is an alternating assembly of two distinct homo-chiral helices with sulfide sites.



The Hspcp ligand in the Zn(II) complex was prepared by mixing 4-mercaptopyridine and α -bromo-*p*-toluic acid in water at refluxing temperature. After cooling down to room temperature, the resulting crystals were filtered out and were confirmed to be Hspcp.[†] Colorless crystals of the [Zn(spcp)(OH)] complex were obtained by diffusion of an aqueous solution of Hspcp into a methanol solution of Zn(NO₃)₂·6H₂O in the presence of triethylamine (yield 65%). The structure of the complex was identified by satisfactory elemental analysis, IR and X-ray diffraction.[‡] As shown in Fig. 1, each zinc atom locates at a distorted tetrahedral environment with two hydroxo oxygen atoms, a pyridine nitrogen atom, and a carboxylate oxygen atom. The bond angle (120.2(4)°) between the hydroxo oxygen (O(3A)) and the carboxylate oxygen (O(2)) is significantly larger than other bond angles $(104.7(3)^{\circ}-109.67(16)^{\circ})$. The bridging Zn–O–Zn angle is 137.6(4)°, similar to those found in other zinc complexes containing bridging hydroxo oxygen atoms.⁷ The Zn–N distance is 2.081(8) Å and the Zn–O distances range from 1.910(7) Å to 1.960(6) Å.

A striking structural feature of this polymer is the alternating assembly of the two distinct homo-chiral helices along the crystallographic b axis (Fig. 2). One helix is formed by hydroxo bridging Zn(II) atoms. The Zn…Zn distance bridged by a hydroxo anion is about 3.573 Å, and the pitch of the helix is about 5.824 Å. The other type of helix is constructed by spcp bridged between the Zn(II) centers, displaying an opposite helical orientation to the former helix. The Zn...Zn distance bridged by spcp is about 11.527 Å, and the pitch of the helix is identical with the former. The dimension of the [Zn-spcp] helical tube is about 1.0 \times 0.7 nm, which is close to those observed in others8 due to the large size of the spcp ligand. Furthermore, the formation of [Zn-spcp] helical tube is due to the sp³ configurations of C and S of the -CH₂S- spacer, forcing the spcp ligand to be nonlinear and generating the twisty helical conformation. The C-C-S (117.1(8)°) and Č-S-C (104.5(5)°) angles of spcp and the phenyl/pyridyl rings dihedral angle (79.7°) in the ligand clearly depict the nonlinear configuration of spcp in the complex. These two distinct homo-chiral helices are in an orderly arrangement with the zinc atoms functioning as hinges, and a novel two-dimensional layer in the bc plane stacks along crystallographic a axis in an interlocking fashion. For each tubular helix, only one helical orientation is involved in the crystal structure, which crystallizes in the asymmetric space group $P2_1$. One of two lone pair electrons of the sulfide group in spcp may locate parallel to the layer, while the other protrudes from the layer. As a result, the two lone pairs of electrons of the sulfide are stranded in an asymmetric environment, that is to say, the sulfide groups are located in the homo-chiral helices in each crystal. Although the bulk product is racemic because the complex was derived from spontaneous resolution from achiral components without any chiral sources, each crystal, however, has a chirality that could be applicable as functional materials.7

We have performed *quasi* Kurtz powder second harmonic generation measurements⁹ ($\lambda = 1064$ nm) on the complex to



Fig. 1 A view of the coordination arrangement of the zinc centers of the complex. Thermal ellipsoids for the nonhydrogen atoms were drawn at the 30% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)-O(2) 1.961(6), Zn(1)-O(3) 1.922(8), Zn(1)-N(1A) 2.081(8), O(3A)-Zn(1)-O(3) 109.67(16), O(3A)-Zn(1)-O(2) 120.2(4), O(3)-Zn(1)-O(2) 105.5(3), O(3A)-Zn(1)-N(1A) 108.2(3), O(3)-Zn(1)-N(1A) 107.9(4), O(2)-Zn(1)-N(1A) 104.7(3), Zn(1A)-O(3)-Zn(1) 137.6(4).







Fig. 2 A view of the two types of homo-chiral helices (top) and the twodimensional tubular network formed by the alternating assembly (middle), and a schematic showing the regular structure (bottom).

confirm its acentricity as well as to evaluate its potential as second-order NLO material. Preliminary experimental results show that the complex displays a modest powder SHG efficiency approximately 5 times higher than that of technologically useful potassium dihydrogen phosphate (KDP), and represents the first NLO-active bulk solid based on two-dimensional tubular coordination polymer alternating assembled by two types of homo-chiral helices with sulfide sites. The complex also exhibits remarkable thermal stability. TGA analyses show that it has an onset temperature for decomposition above 300 °C. The stability of the complex makes it potential candidates for practical applications.

The other interesting characteristic of this complex is its blue-green fluorescent property. Excitation of solid samples at $\lambda = 350$ nm produces an intense luminescence with peak maximum at 490 nm (Fig. 3), which probably originates from a ligand-centred $n-\pi^*$ or $\pi-\pi^*$ process including significant charge transfer character induced by the polar cation, mixed with hydroxo-zinc helix promoting the couplings of metal atoms through delocalized electron-rich systems. This luminescence is quite different from blue luminescence of the previously reported zinc polymers.²

In summary, we have developed a synthetic approach toward chiral solids based on 2D tubular coordination network using sulfur-containing asymmetrical linking ligands. This work will open the door for further exploration of other aesthetic structural motifs and NLO-active polymeric networks.



Fig. 3 Fluorescent emission spectrum of [Zn(spcp)(OH)] complex in solid state at room temperature.

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Notes and references

[†] Anal: Calc. for Hspcp: C, 63.65; H, 4.52; N, 5.71. Found: C, 63.58; H, 4.61; N, 5.57; ¹H NMR (500 MHz, DMSO-d⁶): δ 4.454 (s, 2H, −CH₂−), 7.31 (d, *J* = 4.5 Hz, 2H, −C₅H₄N), 8.34 (d, *J* = 4 Hz, 2H, −C₅H₄−), 7.56 (d, *J* = 8 Hz, 2H, −C₆H₄−), 7.88 (d, *J* = 8.5 Hz, 2H, −C₆H₄−); IR (KBr, cm^{−1}): 1630(s), 1590(vs), 1546(s), 1385(vs), 1110(m), 1091(m), 1018(m), 799(s), 746(s), 635(m), 536(w), 492(s).

Anal: Calc. for [Zn(spcp)(OH)]: C, 47.80; H, 3.39; N, 4.29. Found: C, 47.68; H, 3.15; N, 4.20; IR (KBr, cm⁻¹): 3371(vs), 2925(w), 2898(w), 1600(vs), 1560(vs), 1486(m), 1382(vs), 1226(m), 1066(m), 1025(m), 810(s), 761(s), 738(m), 598(m), 497(m).

‡ *Crystal data* for [Zn(spcp)(OH)]: C₁₃H₁₁NO₃SZn, M = 326.66, monoclinic, space group P_{21} , a = 10.9901(12), b = 5.8238(7), c = 12.5648(13)Å, $\beta = 112.091(3)^\circ$, V = 745.16(14)Å³, Z = 2, μ (Mo–K α) = 1.789 mm⁻¹, Dc = 1.456 g cm⁻³. The structure, refined on F^2 , converged for 1888 unique observed reflections with $I = 2\sigma(I)$ to give R1 = 0.0551 and $\omega R2 = 0.1668$ and S = 1.207. CCDC 214766. See http://www.rsc.org/suppdata/cc/b3/b308007b/ for crystallographic data in .cif or other electronic format.

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