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Novel Noncentrosymmetric Zinc Coordination Polymer Containing an Unusual Zinc Carboxylate−Sulfonate Substructure with a (10,3)-d Topology and Its Second-Harmonic-Generation Properties

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A novel 3D coordination polymer, $Zn_2(\mu_2\text{-OH})(SIP)(DPP)$ (**1**), with mixed ligands of 5-sulfoisophthalate (SIP) and 1,3-di-4-pyridylpropane (DPP), has been hydrothermally synthesized and characterized. **1** contains an unusual 3D subnet with distorted (10,3)-d topology and left/right-handed helical channels. Second-harmonic-generation (SHG) measurements revealed that the material has a strong SHG response (~2.5 times that of potassium dihydrogen phosphate (KDP)) and is phase-matchable. In addition, photoluminescent and thermogravimetric analysis were also performed on **1**.

The search for materials that possess crystallographic noncentrosymmetry (NCS) is of current interest and great importance because these materials can exhibit a variety of technologically important physical properties such as second-harmonic-generation (SHG), ferroelectricity, piezoelectricity, and pyroelectricity.[1,2] The most widely used such materials are inorganic oxide crystals based on octahedrally coordinated d^0 transition-metal ions such as Ti^{4+}, V^{5+}, Mo^{6+}, and W^{6+}, and lone-pair-containing Pb^{2+}, Sb^{3+}, Te^{4+}, Se^{4+}, and I^{5+} cations due to both of them are susceptible to second-order Jahn−Teller distortions.[3−6] The combination of d^0 transition-metal ions and lone-pair-containing cations in oxide materials can produce NCS structures with their inherent asymmetric coordination environments.[7] To date, much of the work on the synthesis of NCS materials has concentrated on the inorganic oxide solids. However, little attention has been paid to the NCS metal−organic coordination compounds that bear the advantages of the organic ligands and inorganic metal ions. Recently, Xiong et al. have done some pioneering work in this research field and demonstrated some useful strategies to assemble NCS coordination polymers through crystal engineering design.[2,8] The rational synthesis of crystallographic NCS materials, however, remains a great challenge. Of particular importance, the NCS coordination compounds commonly display no or small signals of related properties such as the SHG intensity and ferroelectricity. Herewith, we report on the synthesis and characterization of a novel three-dimensional (3D) zinc coordination polymer with a strong SHG response assembled from 5-sulfoisophthalic acid (H_3SIP) and 1,3-di-4-pyridylpropane (DPP) ligands. Accurate SHG, photoluminescent, thermogravimetric analysis (TGA), and IR measurements on **1** were performed.

The hydrothermal reaction of ZnO, NaH_2SIP, DPP, and H_2O at 160 °C for 3 days afforded colorless crystals of **1**, which is air-stable and insoluble in H_2O and most common used organic solvents. The TGA curve (Figure S1 in the Supporting Information) shows that the first weight loss occurs between 170 and 210 °C, which corresponds to the release of the coordinated H_2O molecule (weight loss: measured 2.77%; theoretical 2.96%). The sharp continual weight loss started at 370 °C, corresponding to decomposition of the organic ligands. Its Fourier transform IR spectrum exhibits a strong O−H stretching band centered at 3465 cm^{-1} due to the existence of a H_2O molecule and a hydroxyl group in the structure. Two sharp peaks that appear at 1618 and 1434 cm^{-1} are the expected absorptions for the asymmetric and symmetric stretching vibrations of the carboxylate groups, respectively. The sharp absorption at 631 cm^{-1} can be assigned to the C−S stretching vibration of the SIP ligand.

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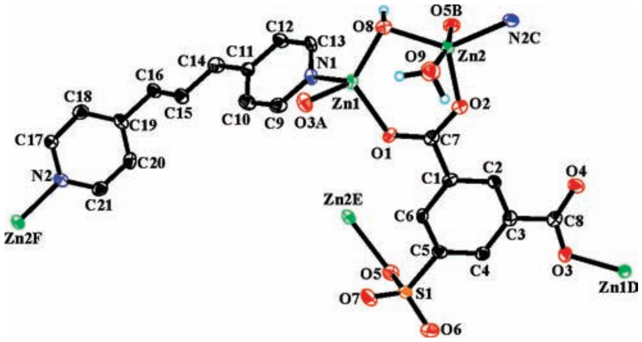

Figure 1. ORTEP drawing of the molecular structure of **1** with 30% probability thermal ellipsoids.

Single-crystal X-ray diffraction (XRD) of **1**[9] indicates that it crystallized in the noncentrosymmetric space group *Cc*. The asymmetric unit of **1** consists of two Zn^{II} ions, one SIP trianion, one DPP molecule, one coordination H_2O molecule, and one hydroxyl group. As depicted in Figure 1, the Zn1 atom is four-coordinated by two O atoms from two individual carboxylate groups and one hydroxyl group and one N atom from the DPP molecule in a distorted tetrahedral geometry. The Zn2 atom is five-coordinated by two O atoms from one carboxylate group and one hydroxyl group, one N atom from the DPP molecule in a trigonal-planar geometry, and two O atoms from the sulfonate group and H_2O molecule in the apical positions. The Zn1 and Zn2 ions are bridged by a carboxylate group and a μ_2-hydroxyl O atom to form a dinuclear zinc cluster unit with a Zn···Zn separation of 3.0584(11) Å, as illustrated in Figure.1. The SIP ligand adopts a tetradentate bridging coordination mode through its bidentate and monodentate carboxylate groups and monodentate sulfonate group (Figure 1). The dimeric $Zn_2(\mu_2\text{-OH})$ units are connected by the SIP and DPP ligands to form a complicated 3D network, as shown in Figure S2 in the Supporting Information.

A better insight into the nature of this intricate architecture can be achieved if one can imagine removing the DPP ligand from the structure. Elimination of the DPP ligand leaves a 3D Zn-SIP substructure (Figure 2a). The Zn-SIP subnet is formed by the bridging SIP ligands, which bridge the dimeric zinc cluster units into an unusual network. As depicted in Figure 2a, the dimeric zinc cluster units are connected by the tetradentate SIP ligands to form a 3D architecture with helical channels along the *b* axis. As illustrated in Figure 2b, the dimeric zinc cluster units are linked up via carboxylate and sulfonate groups of SIP to give rise to two types of helical chains with opposite chirality. The dimensions of the helical channel are about 7.6 × 9.1 Å^2. The carboxylate/sulfonate groups of the SIP ligand bind to the unsaturated site of the zinc centers of other helical chains, resulting in a 3D Zn-SIP subnetwork. In the Zn-SIP subnetwork, the dimeric zinc cluster is linked to three individual SIP ligands, and each SIP ligand links three dimeric zinc clusters. The network can thus be represented topologically by two types of three-coordinate nodes. It is interesting that the two three-connected nodes are topologically equivalent nodes representing either the dimeric zinc cluster center or an averaged SIP ligand position (Figure 3). Careful examination indicated that the network is an unusual decorated (10,3) net and has an extended Schläfli symbol of $10_2 \cdot 10_4 \cdot 10_4$, which is assigned to the (10,3)-d topology according to Wells' classification[10] or the utp net.[11] This net has a c10 number of 621. The c10 number allows for a distinction between nets with the same extended Schläfli symbol by describing the number of neighbors upon expansion of the net up to the 10th vertex.[12]

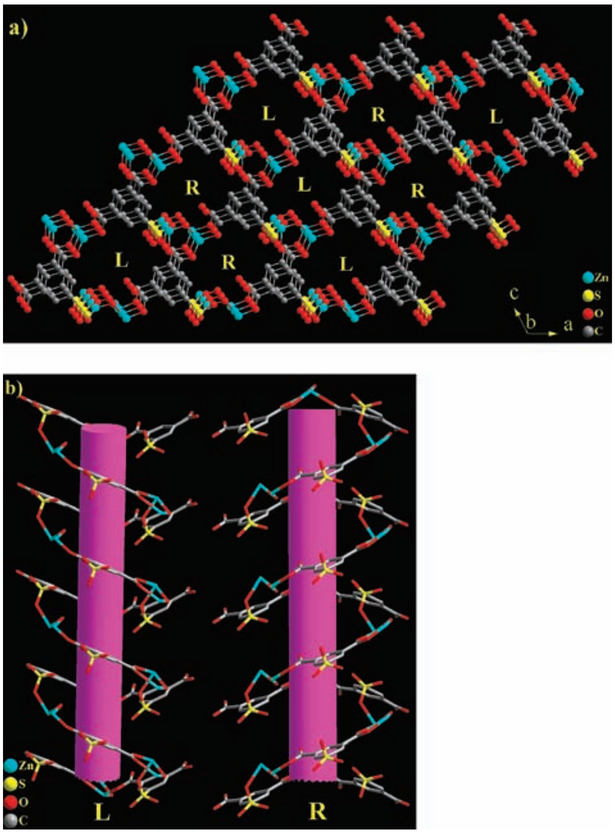

Figure 2. (a) 3D Zn-SIP framework viewed down the *b* direction, showing the left/right-handed (L/R) helical channels. (b) Left- and right-handed helical chains.

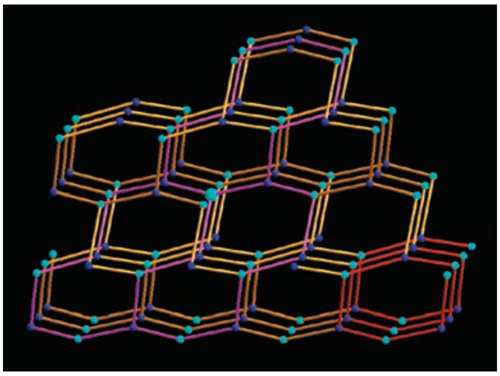

Figure 3. Schematic representation of the (10,3)-d net in **1** along the *b* axis (the cyan and dark-blue balls represent the dimeric zinc clusters and SIP ligands, respectively). Highlighted are the three 10-membered shortest circuits (pink) and a single helix (red).

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[9] Crystal data: $C_{21}H_{20}N_2O_9SZn_2$, M_r = 607.19, monoclinic, space group *Cc*, *a* = 20.907(8) Å, *b* = 7.810(3) Å, *c* = 15.367(6) Å, β = 117.4100(10)°, *V* = 2227.3(15) Å^3, *Z* = 4, ρ_{calc} = 1.811 mg/m^3, μ = 2.305 mm^{-1}, R1 = 0.0366, wR2 = 0.0690 [$I > 2\sigma(I)$], Flack parameter 0.033(14).

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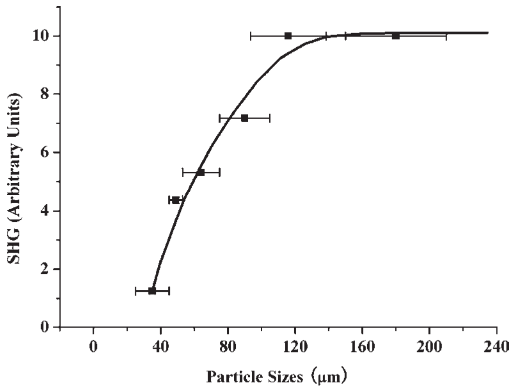

Figure 4. Phase-matching curve for **1**. The curve is to guide the eye and is not a fit to the data.

The most interesting feature of this (10,3)-d net is the presence of parallel left- and right-handed single helices, which in **1** alternate along the *a* axis (Figure 2a). Because the right- and left-handed helices are alternately arranged, the whole net, therefore, is racemic. The net is constructed by hexagonal helices along the *b* axis, as depicted in Figure 3. Each hexagonal helix connects to six adjacent helices by sharing a common edge, which projects as a (6,3) net (along the *ac* plane). This is the other interesting feature of the (10,3)-d net. To our knowledge, three interpenetrated[13−16] and two recently reported noninterpenetrated[17,18] (10,3)-d nets have been known to be present in coordination polymers, but such a (10,3)-d net as a subunit of a coordination polymer has not been reported previously. The DPP ligands further linked the dimeric zinc clusters of the Zn-SIP substructure to form the overall 3D network, as shown schematically in Figure S2 in the Supporting Information. This, therefore, defines a five-connected node based on the dimeric zinc cluster. It is a complicated mixture of three (SIP ligands) and five (dimeric zinc clusters) connectors, in a 1:1 ratio.

As described above, compound **1** crystallized in the noncentrosymmetric space group *Cc*, so we investigated its SHG properties. SHG measurements on powder samples using 1064 nm radiation[19] revealed that **1** exhibits a large SHG response, ~2.5 times that of KDP and ~120 times that of α-SiO_2, which confirms its acentricity as well as evaluates its potential as a second-order nonlinear optical material. Furthermore, by sieving of **1** into various particle sizes, ranging from 25 to 210 μm, and measurement of the SHG as a function of the particle size, the material was found to be phase-matchable (Figure 4).

In addition, we have also examined the photoluminescent properties of **1** in the solid state. Complex **1** exhibits a photoluminescent peak with a maximum at 333 nm upon excitation at 305 nm (Figure S3 in the Supporting Information). The emission peak is essentially the same as the photoluminescence signal of the free H_3SIP ligand at 320 nm. This indicates that the emission band of **1** is an intraligand transition.[20]

In summary, we demonstrate here a novel noncentrosymmetric 3D zinc coordination polymer containing a unprecedented subnet with a (10,3)-d net based on the dimeric zinc cluster and the SIP ligand. It exhibits a large SHG signal and is phase-matchable. Its photoluminescent properties are also investigated. All of these attributes make **1** an attractive candidate for future practical applications.

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Supporting Information Available: An X-ray crystallographic file in CIF format, experimental details, tables of a summary of crystal data and structural refinements and of bond lengths and angles, a 3D structure, schematic representation of the topological networks, photoluminescent spectra, TGA and DSC curves, dielectric constants, and XRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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