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New Semiconducting Coordination Polymers from Zinc Sulfide Clusters and Chains

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S Supporting Information

ABSTRACT: Two new semiconducting zinc coordination polymers, $Zn_8S(SPh)_{14}(bpy)$ (**1**) and $Zn_2(SPh)_4(bpy)$ (**2**), have been synthesized by a dual-ligand approach. Single-crystal structural analyses indicate that compound **1** has a helical-chain structure with P1 clusters bridging with bipyridyl (bpy) ligands and compound **2** possesses a layered structure with zinc sulfide chains cross-linked with bpy ligands. The diffuse-reflectance spectra reveal that the band gaps of the two compounds are 2.41 eV for **1** and 2.56 eV for **2**.

Functional coordination polymers have been extensively studied for their diverse structures and intriguing physical properties such as magnetism, photoluminescence, and electrical conductivity.[1] The frameworks of these compounds usually consist of metal ions linked by multifunctional organic ligands to form one-, two-, and three-dimensional structures that can be porous, indicating their potential applications in catalysis, separation, ion exchange, gas storage, and sensor technology.[2] One effective way to tune their framework structures and properties is to use different organic ligands with a wide variety of shapes.[3] For example, Yaghi and co-workers reported a series of microporous zinc imidazolates that had a high capacity for CO_2 storage.[4] Through functionalization of the imidazolate ligands, several zeolitic topologies, such as ANA, BCT, DFT, GIS, GME, LTA, MER, RHO, and SOD, have been achieved in this system.[5]

Recently, crystalline metal chalcogenide nanostructures are of particular interest for their size-dependent properties and potential applications as semiconductors, sensors, ion exchangers, and photocatalysts.[6] The integration of the semiconducting properties of chalcogenide materials with the flexibility of organic linkers in the same crystalline framework can produce a class of inorganic−organic hybrid solids with tunable structures and properties. For example, Huang and Li reported a number of II−VI quantum wells that exhibit different layer thicknesses, laminar distances, and optical absorption.[7] By using chalcogenide nanoclusters as nodes and pyridyl molecules as linkers, a number of cluster−organic frameworks have been successfully prepared and characterized.[8] A well-known example is provided by a nanoporous cadmium thiolate compound UCR-9, which has a three-dimensional open-framework structure with cubic cadmium thiolate clusters cross-linked by tetrapyridine ligands.[9]

Our interest is in the synthesis of new zinc coordination polymers containing benzenethiolate ligands. Such materials may have semiconducting properties because of the presence of Zn−S bonds in their framework structures. To enhance the structural diversity, the incorporation of an ancillary nitrogen-donor ligand into the zinc thiolate structure is highly desired. With this dual-ligand synthetic strategy, two new zinc coordination polymers, $Zn_8S(SPh)_{14}(bpy)$ (**1**) and $Zn_2(SPh)_4(bpy)$ (**2**), have been synthesized under hydro/solvothermal conditions, where SPh = benzenethiolate and bpy = 4,4′-bipyridine.

Compounds **1** and **2** were obtained as yellow crystals under autogenous pressure.[10] The agreement between the experimental and simulated powder X-ray diffraction (XRD) patterns indicates the phase purity of as-synthesized compounds. A single-crystal structural analysis reveals that compound **1** has a one-dimensional structure constructed from the building block shown in Figure 1.[11] The building unit containing eight zinc atoms is denoted as a pentasupertetrahedral P1 cluster in chalcogenide cluster chemistry.[12] A sulfur atom locates in the core of the cluster, which is connected to four zinc atoms to give a SZn_4 antitetrahedron. The four faces of the SZn_4 antitetrahedron are covered by two regular ZnS_4 tetrahedra and two ZnS_3N tetrahedra, resulting in the formation of a P1 cluster. All of the zinc atoms in the cluster are tetrahedrally coordinated. The Zn−S bond lengths are in the region 2.244(6)−2.419(5) Å, and the two Zn−N bond lengths are 2.031(11) and 2.059(14) Å, respectively.

In each tetrahedral P1 cluster, two corners are occupied by terminal SPh^- units and the remaining two corners are occupied by nitrogen donors from bpy ligands. Thus, the P1 clusters are linked by bpy ligands to form a one-dimensional structure. Careful analysis of the structure indicates that compound **1** crystallizes in the chiral space group $P2_1$ and the building units in the structure are organized along the 2_1 axis to produce a right-handed helical chain. All helical chains in the structure have the same chirality, and they are packed in a parallel manner. The pitch of the helix is 25.7135(6) Å, which is equal to the periodicity along the crystallographic *b* axis. Because all chemicals used in the hydrothermal synthesis are achiral, the bulk product of **1** is expected to be a 50:50 racemic mixture containing crystals with different handedness. To confirm this assumption, another crystal in the bulk product was selected for a second structure determination. Single-crystal structural analysis reveals that the structure of this compound consists of left-handed helical chains constructed from P1 clusters and bpy ligands.[11]

The presence of such a helical configuration in compound **1** is unprecedented in chalcogenide cluster chemistry and merits some attention. In previous literature, tetrahedral P*n* and C*n*

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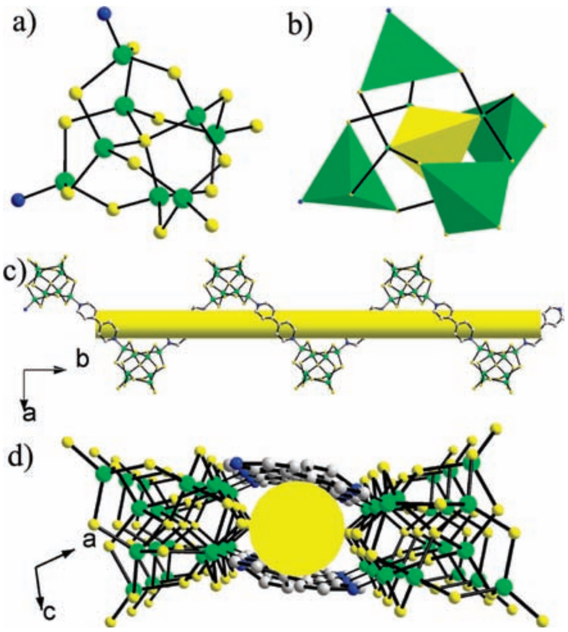

Figure 1. (a) Ball-and-stick and (b) polyhedral representations of the P1 cluster in **1**. One-dimensional structure of **1** viewed along (c) the [001] and (d) the [010] directions. The P1 clusters and bpy ligands are organized around the 2_1 axis to form the helical chain. Phenyl groups are omitted for clarity. Color code: Zn, green; S, yellow; N, blue; C, gray.

clusters can be organized by pyridine-based ligands to form various one-dimensional structures, such as straight-chain, zigzag-chain, and beltlike architectures.[13] Examples with a dimeric or layered structure are also known.[14] However, no example has a chiral or helical structure. Very recently, Feng and co-workers reported some chiral semiconducting frameworks constructed from corner-sharing cadmium sulfide clusters.[15] The chiral nature of these compounds comes from their intrinsically chiral network (i.e., quartz topology). In the present work, the chiral feature of compound **1** is endowed by its absolute helicity.

A single-crystal structural analysis indicates that compound **2** has a two-dimensional structure.[11] The asymmetric unit of **2** contains two zinc atoms, four benzenethiolate units, and one bpy ligand. Both of the zinc atoms are tetrahedrally coordinated by three sulfur atoms from different benzenethiolate ligands and one nitrogen atom from the bpy ligand. The Zn−S bond lengths are in the region of 2.2669(6)−2.4078(6) Å, and the Zn−N bond lengths are between 2.0573(16) and 2.0685(16) Å. Of the four benzenethiolate units, S(2)Ph and S(3)Ph each act as a bridging ligand to connect two adjacent zinc atoms, while S(1)Ph and S(4)Ph units each serve as a terminal ligand to fulfill the coordination sphere of the zinc atom. The bpy molecule possesses typical geometrical parameters, and it acts as a bidentate ligand to two adjacent zinc atoms. The bridged Zn···Zn distance along bpy is ca. 11.1 Å.

The connectivity between zinc atoms and benzenethiolate ligands creates a chainlike structure. Such chainlike structures are further cross-linked by bpy ligands to give rise to a layered structure parallel to the *ac* plane, as shown in Figure 2. It seems that the layered structure has a large pore with a diameter of 7.7 Å × 11.3 Å delimited by six ZnS_3N tetrahedra and two bpy molecules. In fact, two benzene rings that attach to the S(2) and S(3) atoms, respectively, point into the large window and occupy the "free" space. The inorganic−organic hybrid layers are stacked along the [010] direction in an ABAB sequence. The benzene rings that attach to the S(1) and S(4) atoms protrude into the interlayer region.

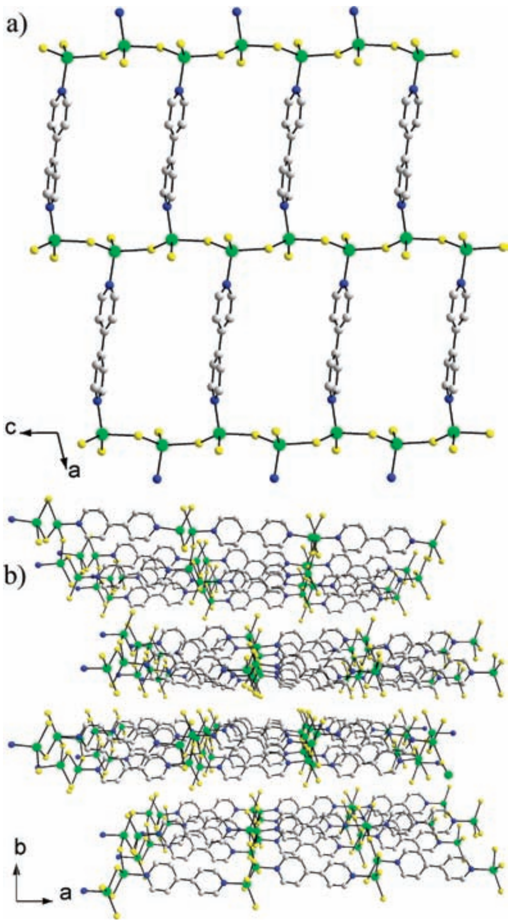

Figure 2. (a) View of the layered structure of **2** with zinc sulfide chains cross-linked by bpy ligands. (b) View of the packing of the layers along the [010] direction in an ABAB sequence. Phenyl groups are omitted for clarity. Color code: Zn, green; S, yellow; N, blue; C, gray.

It should be noted that dimer $[\{Zn(SPh)_2(bpy)\}_2(\mu\text{-}bpy)]$ and two forms of the zigzag one-dimensional coordination polymer $[\{Zn(SPh)_2(\mu\text{-}bpy)\}_n]$ have been reported in the Zn−SPh−bpy system.[16] The three zinc coordination compounds were synthesized under mild conditions by evaporation or diffusion techniques. In the three coordination polymers, SPh groups only act as terminal ligands to zinc atoms, whereas in compound **2**, SPh groups have dual functions: as terminal and bridging ligands. The presence of one-dimensional Zn−S−Zn connectivity in the structure of **2** is noteworthy.

Diffuse-reflectance spectra of compounds **1** and **2** were recorded at room temperature on a Shimadzu UV-3101PC double-beam, double-monochromator spectrophotometer in the wavelength range of 200−800 nm. As shown in Figure 3, the optical absorption data derived from the reflectance show an optical transition with a band gap of 2.41 eV for **1** and of 2.56 eV for **2**. Thermogravimetric analysis (TGA), carried out in a flow of nitrogen with a heating rate of 10 °C min^{-1}, showed that both compounds remained stable up to 220 °C. On further heating, weight losses of 68.46% for **1** and of 70.34% for **2** were observed, which was attributed to decomposition of organic species and the partial loss of sulfur atoms.

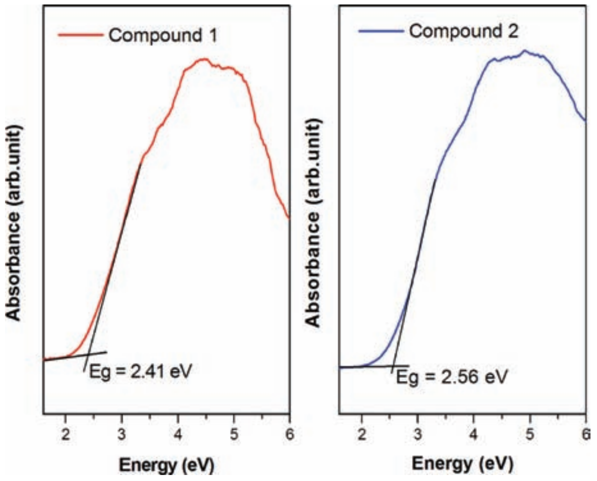

Figure 3. UV−vis absorption spectra of compounds **1** and **2**.

In summary, two new semiconducting zinc coordination polymers have been synthesized and structurally characterized. The synergetic effect of both inorganic and organic components endows the two compounds' unique structures and optical properties. The helical chain assembled by tetrahedral clusters and nitrogen-donor ligands is rare in chalcogenide chemistry. This work represents our first effort toward the construction of new chiral cluster−organic frameworks.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray data in CIF format, additional crystallographic figures, IR spectra, TGA curves, and powder XRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Synthesis of **1**: a mixture of $Zn(OAc)_2 \cdot 2H_2O$ (0.851 g), thiourea (0.042 g), bpy (0.101 g), thiophenol (0.75 mL), and H_2O (15 mL) was sealed in a Teflon-lined steel autoclave and heated at 170 °C for 5 days. After cooling to room temperature, yellow crystals of **1** were recovered by filtration, washed with *N*,*N*-dimethylformamide (DMF) and ethanol, and then dried in air (yield: 7.5% based on bpy). CHN elemental analysis confirmed its composition. Anal. Found: C, 48.83; H, 3.38; N, 1.21. Calcd: C, 50.41; H, 3.51; N, 1.25. Synthesis of **2**: a mixture of $Zn(OAc)_2 \cdot 2H_2O$ (1.301 g), thiourea (0.107 g), bpy (0.141 g), thiophenol (1.0 mL), DMF (4.015 g), and H_2O (2.012 g) was sealed in a Teflon-lined steel autoclave and heated at 80 °C for 7 days. After cooling to room temperature, yellow crystals of **2** were recovered by filtration, washed with DMF and ethanol, and then dried in air (yield: 38.4% based on bpy). CHN elemental analysis confirmed its composition. Anal. Found: C, 54.16; H, 3.82; N, 3.74. Calcd: C, 56.44; H, 3.90; N, 3.87.

(11) Crystal data for **1a**: $C_{94}H_{78}N_2S_{15}Zn_8$, $M = 2239.44$, monoclinic, space group $P2_1$ (No. 4), $a = 13.3740(4)$ Å, $b = 25.7135(6)$ Å, $c = 14.7678(5)$ Å, $\beta = 106.709(3)°$, $V = 4864.1(2)$ Å^3, $Z = 2$, $D_c = 1.529$ g cm^{-3}, $\mu = 2.304$ mm^{-1}, Flack parameter = −0.01(2), 20 601 reflections measured, 15 007 unique reflections ($R_{int} = 0.0328$). Final wR2 (all data) = 0.2107, final R1 = 0.0794. Crystal data for **1b**: $C_{94}H_{78}N_2S_{15}Zn_8$, $M = 2239.44$, monoclinic, space group $P2_1$ (No. 4), $a = 13.3685(4)$ Å, $b = 25.7159(6)$ Å, $c = 14.7774(6)$ Å, $\beta = 106.772(4)°$, $V = 4864.1(3)$ Å^3, $Z = 2$, $D_c = 1.529$ g cm^{-3}, $\mu = 2.304$ mm^{-1}, Flack parameter = −0.033(18), 20 909 reflections measured, 12 884 unique reflections ($R_{int} = 0.0423$). Final wR2 (all data) = 0.1582, final R1 = 0.0678. Crystal data for **2**: $C_{34}H_{28}N_2S_4Zn_2$, $M = 723.56$, monoclinic, space group $P2_1/c$ (No. 14), $a = 12.0867(2)$ Å, $b = 18.9621(3)$ Å, $c = 14.1751(3)$ Å, $\beta = 103.425(2)°$, $V = 3160.01(10)$ Å^3, $Z = 4$, $D_c = 1.521$ g cm^{-3}, $\mu = 1.810$ mm^{-1}, 12 171 reflections measured, 5557 unique reflections ($R_{int} = 0.0177$). Final wR2 (all data) = 0.0512, final R1 = 0.0243.

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