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Communications

Solvothermal Conversion of Discrete Cubic Cadmium Thiolate Cluster into Supertetrahedral Cluster Decorating Quartz-Type Chiral Superlattice

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The field of discrete CdS nanoclusters and their extended frameworks has attracted much attention as a result of the interest in their unique structures and potential applications in photocatalysis, photovoltaics, and sensing.[1–5] Of particular interest is the spatial organization of these clusters into semiconducting open-framework architectures because the unique collective phenomena, resulting from ordered covalently linked CdS nanoclusters, may find new applications in nanotechnology. Furthermore, crystalline chiral open-framework semiconductors represent a class of multifunctional materials that may lead to novel enantioselective applications.[6] However, so far little is known about chiral semiconductors.

This research, which is part of our systematic study on the synthesis of Cd−S−SAr clusters (SAr = phenylthiolate or substituted phenylthiolate such as 3-methylphenylthiolate, 4-methylphenylthiolate, 2,4-dimethylphenylthiolate, and 3-fluorophenylthiolate) and their superlattices, investigates how these semiconductor nanoclusters and their superlattices can be synthesized by controlling various synthetic parameters. One particular focus of this investigation is the effect of the surface-capping ligands on the cluster structure and their pattern of organization. In the earlier studies, the structure-directing effects of various alkyl-substituted thiophenols (R-PhSH) have been examined.[7,8] Here we are interested in surface ligands that contain highly electronegative elements. We demonstrate the use of fluorine-substituted surface ligand, 3-fluorophenylthiolate, for the synthesis of chalcogenide clusters. Another interesting aspect of this work is the use of presynthesized cubic (double four-rings in the zeolite terminology) clusters as the precursor for the synthesis of three-dimensional (3D) covalent chalcogenide superlattices.

Two types of clusters have been identified in this work, one as a discrete cluster ($[Cd_8(SPhF\text{-}3)_{14}(DMF)_6]^{2+}$) in an ionic crystal and the other $[Cd_8S(SC_6H_4F\text{-}3)_{12}(SC_6H_4F\text{-}3)_{4/2}]$ as the tetrahedral node in a neutral 3D covalent chiral framework

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(CMF-8) with α-quartz-type topology (CMF = capped metal−chalcogenide framework). As an important chiral mineral with a 4-connected net, α-quartz has been found not only to exhibit enantioselective adsorption of amino acids[6] but also to have technological applications related to its piezoelectric property. Therefore, the 3D chiral semiconducting chalcogenides with the quartz-type helical topology are of particular interest.

CMF-8 $[Cd_8S(SC_6H_4F\text{-}3)_{12}(SC_6H_4F\text{-}3)_{4/2}]$ was synthesized in a three-step process, in which an ionic compound CMM-5 (CMM = capped metal−chalcogenide molecule), $[Cd_8(SPhF\text{-}3)_{14}(DMF)_6(NO_3)](NO_3)$, was first prepared in two steps at room temperature.[9] Single crystals of CMF-8 were then obtained by reacting CMM-5 with thiourea in an acetone/H_2O solution at 85 °C.[10] Thiourea is essential for the conversion of the cubic cadmium thiolate cluster into the tetrahedral cluster because it provides the S^{2-} source that eventually forms the core of the tetrahedral cluster in CMF-8. The crystal structures[11] for CMM-5 and CMF-8 were determined from single-crystal X-ray diffraction data collected at 150 K on an APEX II CCD diffractometer, and the structures were solved by direct methods using the SHELX-TL program package.[12]

The cluster in CMM-5 is also known in a cadmium thiolate cluster with the unsubstituted −SPh group.[13] As shown in Figure 1, the cubic cluster $[Cd_8(SPhF\text{-}3)_{14}(DMF)_6]^{2+}$ has eight cadmium ions arranged at eight corners of a cube while 12 −SPhF-3 groups are distributed slightly off the center of each cubic edge as bridging ligands. Six corner cadmium sites are bonded to solvent DMF molecules and NO_3^- within the cage while the remaining two corners were occupied by mononegative −SPhF-3 groups. It is worth noting that, as a result of the lack of symmetry of the inversion center, nitrate groups are orientationally disordered in the CMM-5 (Figure S1, Supporting Information).

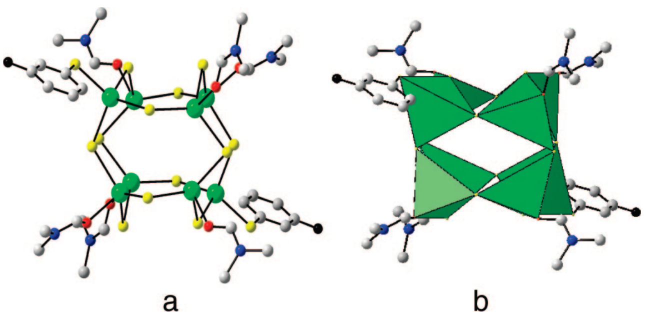

Figure 1. (a) Ball-and-stick and (b) polyhedral representation of the cubic cluster in CMM-5, $[Cd_8(SPhF\text{-}3)_{14}(DMF)_6(NO_3)](NO_3)$. Cd, green; S, yellow; O, red; N, blue; C, grey; F, black. Twelve organic ligands (PhF-3) bonded to the bridging sulfur sites at edge centers and two nitrate groups (one inside the cubic cage and the other outside the cage as charge-balance anion) are omitted for clarity.

The building unit in CMF-8 is a P1 cluster $[Cd_8S(SC_6H_4F\text{-}3)_{12}(SC_6H_4F\text{-}3)_{4/2}]$ that contains the same number of cadmium sites and −SPhF-3 sites as the starting cubic cluster (Figure 2a). One of the driving forces for the conversion of the cubic cluster into the tetrahedral cluster is the availability of the S^{2-} source during the hydrothermal treatment of CMM-5 with thiourea. The strong affinity between Cd^{2+} and S^{2-} leads to the formation of the SCd_4 core that forms the basis for the conversion of the cubic $[Cd_8(SPhF\text{-}3)_{14}(DMF)_6]^{2+}$ cluster into the tetrahedral $[Cd_8S(SC_6H_4F\text{-}3)_{12}(SC_6H_4F\text{-}3)_{4/2}]$ cluster.

The P1 cluster is the first member in a series of pentasupertetrahedral clusters (the P*n* series), which can be conceptually constructed by coupling four supertetrahedral clusters onto each face of an antisupertetrahedral cluster of the same order.[5d] An antisupertetrahedral cluster is defined as having the same geometrical feature as that of a supertetrahedral cluster (T*n*) with positions of cations and anions being exchanged. Thus the P1 cluster consists of four T1 clusters (MX_4) at corners and one anti-T1 cluster (XM_4) at the core, resulting in the composition of $(MX_4)_4(XM_4)$. The P1 clusters with other compositions are also known. Examples include $[SCd_8(SBu)_{12}(CN)_{4/2}]$,[14] $[Cd_8S(SPh)_{16}]^{2-}$,[14] $[Cd_8S(SPh)_{12}Cl_4]^{2-}$,[15] $M_8S(SPh)_{14}L_2$ (M = Cd, Zn),[16] $[Zn_8S(SCH_2C_6H_5)_{16}]^{2-}$,[17] $[M^{II}{}_4M_4S_{17}]^{10-}$ (M^{II} = Zn, Cd, Fe, Co; M = Sn, Ge),[18–20] $[Sn_4M^{II}{}_4Se_{17}]^{10-}$ (M^{II} = Co, Zn, Mn, Cd, Hg),[21–24] and $[In_8S_{17}]^{10-}$.[25] Unlike the 3D chiral structure

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[9] The detailed synthesis for CMM-5 is as follows: $Cd(NO_3)_2\cdot 4H_2O$ (3.08 g, 10 mmol) was dissolved in methanol (50 mL) to form a clear solution. This solution was then added to a methanol solution prepared by dissolving 3-fluorothiophenol (2.56 g, 20 mmol) and triethylamine (2.02 g, 20 mmol) in 50 mL of methanol. The mixture was stirred for 2 h at room temperature. The resulting white precipitate was filtered, washed with methanol, then dissolved in DMF, and layered by methanol. After 4−6 weeks, cubic crystals were harvested.

[10] The detailed synthesis for CMF-8 is as follows: 100 mg of CMM-5, 50 mg of thiourea, and 6 g of acetone/water (weight ratio = 2/1) were placed in a glass vial and stirred for 30 min. The vial was then sealed and heated at 85 °C for 3 weeks. After cooling to room temperature, the colorless crystals were collected and washed three times with methanol.

[11] Crystal data: CMM-5, $[Cd_8(SPhF\text{-}3)_{14}(DMF)_6(NO_3)](NO_3)$, triclinic, space group $P\bar{1}$, $a = 14.8591(2)$ Å, $b = 15.0112(2)$ Å, $c = 15.6142(2)$ Å, $\alpha = 93.2690(10)°$, $\beta = 114.2920(10)°$, $\gamma = 103.7010(10)°$, $V = 3036.82(7)$ Å^3, $Z = 1$, Mo Kα radiation, $\lambda = 0.71073$ Å, $2\theta_{max} = 50°$, 38561 reflections collected, 10670 unique ($R_{int} = 0.0185$); final GOF = 1.039, R1 = 0.0372, wR2 = 0.1042, *R* indices based on 9948 reflections with $I > 2\sigma(I)$ (refinement on F^2), 603 parameters; CMF-8, $Cd_8S(SC_6H_4F\text{-}3)_{14}$, trigonal, space group $P3_221$, $a = 18.3529(2)$ Å, $c = 24.0908(4)$ Å, $V = 7027.34(16)$ Å^3, $Z = 3$, Mo Kα radiation, $\lambda = 0.71073$ Å, $2\theta_{max} = 50°$, 81862 reflections collected, 8267 unique ($R_{int} = 0.0243$); final GOF = 1.088, R1 = 0.0162, wR2 = 0.0439, Flack parameter = −0.011(12), *R* indices based on 8149 reflections with $I > 2\sigma(I)$ (refinement on F^2), 573 parameters.

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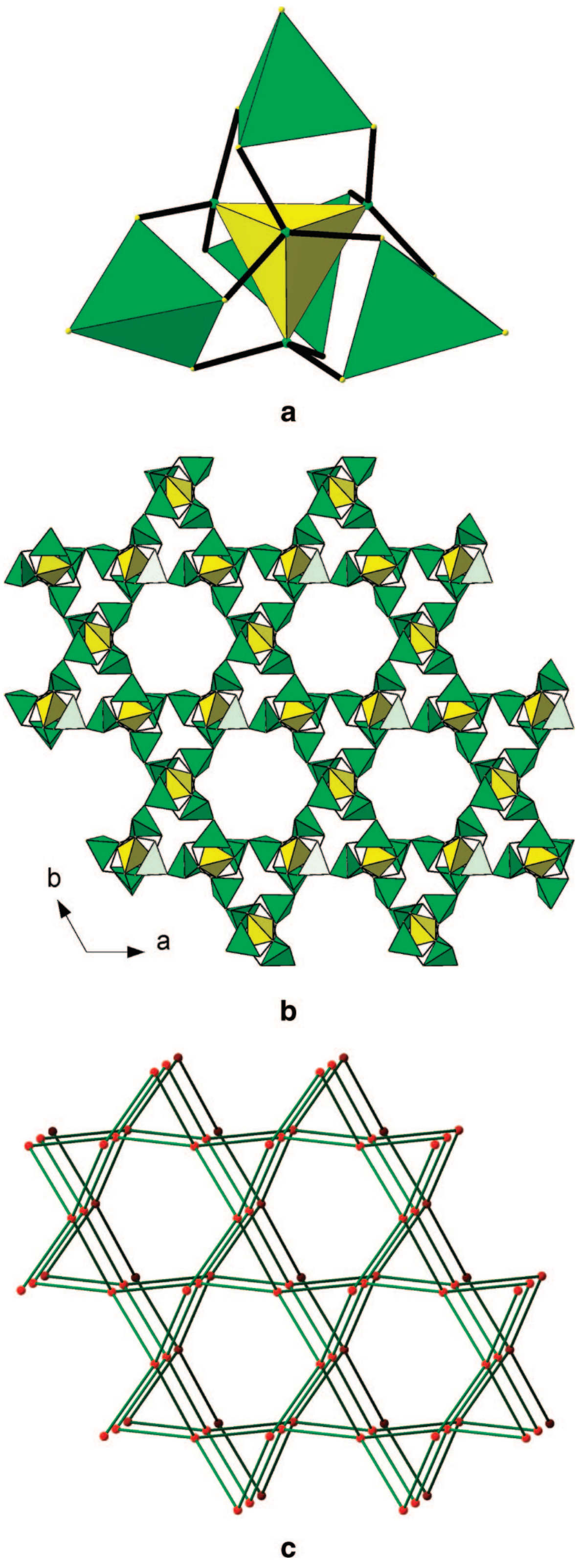

Figure 2. Crystal structure of CMF-8. (a) An individual P1 cluster. (b) The 3-D framework of CMF-8. (c) The α-quartz-type topology. In both a and b: CdS_4, green tetrahedra; SCd_4, yellow tetrahedra. The surface ligands are omitted for clarity.

reported here, the P1 clusters are found as isolated clusters in most cases.

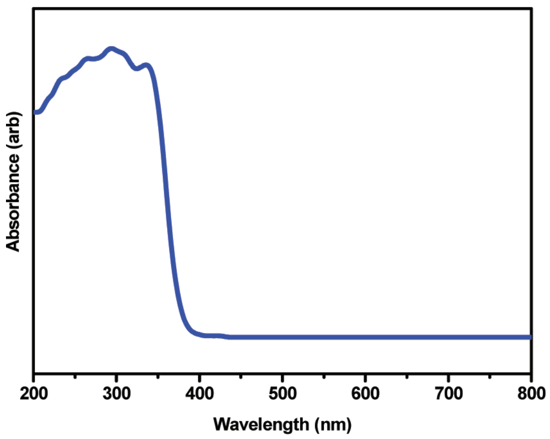

Figure 3. UV−vis absorption spectrum of CMF-8.

In CMF-8, each P1 cluster is linked to four surrounding clusters through four bridging $-SC_6H_4F\text{-}3$ groups. Figure 2b shows the linkage pattern of P1 clusters. The structure of CMF-8 $[Cd_8S(SC_6H_4F\text{-}3)_{12}(SC_6H_4F\text{-}3)_{4/2}]$ has a 3-fold screw axis along the *c*-direction. A simpler representation of the crystal structure can be obtained by considering each P1 cluster as a pseudotetrahedral atom. The resulting 3D noninterpenetrating network belongs to the 6^48^2-b net, characteristic of the α-quartz topology (Figure 2c).

The diffuse-reflectance spectrum of CMF-8 was studied on a Shimadzu UV-3101PC double-beam, double-monochromator spectrophotometer by using $BaSO_4$ powder as a 100% reflectance reference. As shown in Figure 3, CMF-8 has an absorption onset at 375 nm, indicating that CMF-8 is a wide-gap semiconductor with bandgap of 3.31 eV. The simultaneous TG-DSC analysis performed under the flowing N_2 atmosphere shows that CMF-5 is stable up to about 300 °C (Figure S2, Supporting Information).

In summary, two cluster-based structures, one having an ionic salt structure and one with the 3D chiral α-quartz-type topology, have been synthesized using a multistep synthetic procedure involving both solvothermal synthesis and room-temperature diffusion process. CMF-8 is a rare 3D covalent superlattice built from the direct assembly of the pentasupertetrahedral P1 cluster. Its synthesis by using a cluster precursor is unprecedented. The work represents a new method for the creation of 3D superlattices based on tetrahedral clusters.

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Supporting Information Available: Crystallographic data including positional parameters, thermal parameters, and bond distances and angles (CIF) and thermal analysis plot (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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