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# Chiral Semiconductor Frameworks from Cadmium Sulfide Clusters

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Chiral molecules are ubiquitous in nature, however, chiral solids with extended three-dimensional (3-D) framework are far less common. The α-quartz, a crystalline polymorph of silica, is an important chiral mineral with a 4-connected net. The topology of α-quartz or its high temperature form (β-quartz), is also found in some other $ABO_4$ oxides such as berlinite ($AlPO_4$). Despite the widespread occurrence of α-quartz, its topological type is rarely found in other 3-D frameworks even though recent studies in coordination polymers have resulted in some rare examples of the *interpenetrating* quartz-type framework such as $ZnAu_2(CN)_4$ with 6-fold interpenetration.[1]

Chiral framework solids such as quartz have attracted increasing attention because of their potential applications in enantioselective processes (catalysis, separation, sensing, etc.). Quartz is of particular interest because of its intriguing helical structure and its technological applications related to its unique piezoelectric property. Quartz has also been shown to exhibit enantioselective adsorption of amino acids, but its low surface area limits its application.[2] Therefore, the creation of other chiral 3-D framework materials with the helical quartz-type topology is of great interest.

Cadmium chalcogenide clusters are of current interest because of their significance in nanotechnology and metallothioneins-based biological processes.[3−5] The recent work on semiconductor frameworks constructed from Cd−S−SAr (or Cd−SAr) clusters tends to give nonchiral frameworks[6] or frameworks with clusters no larger than $Cd_4(SAr)_{10}^{2-}$.[7] We have now developed synthetic conditions that allow the helical self-assembly of different-sized chalcogenide clusters into intertwined helical chains characteristic of the quartz-type net. In addition, the moganite topology that is closely related to the quartz-type has also been synthesized in this work. Such helical self-assembly of chalcogenide clusters is unprecedented and represents a key advance in the development of novel framework materials from chalcogenide clusters.

This work is part of our systematic studies on the synthesis of Cd−S−SAr clusters and their superlattices. One focus of this research is to examine how key synthetic parameters such as temperature, solvent, surface ligand type (−Ar), and $S^{2-}$ sources affect the size and network topology of resulting chalcogenide materials. New helical superlattices denoted as CMF-*n* (CMF = capped metal-chalcogenide frameworks) were synthesized at room temperature or under solvothermal conditions at 85 °C.[8] CMF-1 was obtained as colorless crystals by slow diffusion of methanol into the yellowish solution (mass ratio, DMF:$CS_2$ = 2:1) containing $Cd(SC_6H_4Me\text{-}3)_2$ ($HSC_6H_4Me\text{-}3$ = 3-methylbenzenethiol) in 4−6 weeks. Here, $CS_2$ also serves as the $S^{2-}$ source. CMF-2, -3, and -5 were synthesized under solvothermal conditions with thiourea as the $S^{2-}$ source. The starting material is $Cd(SC_6H_4Me\text{-}4)_2$ ($HSC_6H_4\text{-}Me\text{-}4$ = 4-methylbenzenethiol) for CMF-2 and $Cd(SC_6H_4Me\text{-}3)_2$ for CMF-3 and CMF-5.

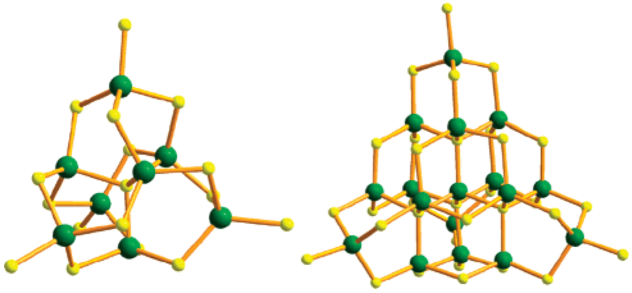

***Figure 1.*** (Left) The first member of pentasupertetrahedral clusters, P1; (right) the first member of capped supertetrahedral clusters, C1: green, $Cd^{2+}$; yellow, S. Organic surface ligands are not shown.

Three previously unknown clusters, $[Cd_8S(SC_6H_4Me\text{-}3)_{16}]^{2-}$, $[Cd_{17}S_4(SC_6H_4Me\text{-}4)_{28}]^{2-}$, and $[Cd_{17}S_4(SC_6H_4Me\text{-}3)_{28}]^{2-}$, are reported here. They differ in the type of surface ligand or the cluster size. The $[Cd_8S(SC_6H_4Me\text{-}3)_{16}]^{2-}$ cluster (denoted P1 cluster) found in CMF-1, -3, and -5 is the first member of a series of tetrahedral clusters termed pentasupertetrahedral clusters (the P*n* series).[9] One key structural feature of the P1 cluster is the presence of a core $Cd_4S$ anti-tetrahedron covered by four outer $CdS_4$ regular tetrahedra (Figure 1). P1 clusters are also known in other compositions, particularly II−IV (e.g., Zn−Sn) chalcogenides with no surface ligands.[10−11] The $[Cd_{17}S_4(SC_6H_4Me\text{-}4)_{28}]^{2-}$ in CMF-2 and $[Cd_{17}S_4(SC_6H_4\text{-}Me\text{-}3)_{28}]^{2-}$ in CMF-3 (both denoted C1 cluster) are the first member of a series of tetrahedral clusters termed capped supertetrahedral clusters (the C*n* series).[9] One key structural feature of the C1 cluster is the presence of a core $CdS_4$ tetrahedron sharing its S sites with four corner $Cd_4S_4$ barrelanoid cages (Figure 1).

Topologically, P1 and C1 clusters behave like large artificial atoms with tetrahedral coordination. They can occupy tetrahedral nodes in 4-connected nets, forming so-called decorated networks. Two adjacent clusters are covalently joined through the Cd−SAr−Cd linkage. CMF-1, -2, and -5 all have the β-quartz topology. CMF-1 and -5 contain P1 clusters, $[Cd_8S(SC_6H_4Me\text{-}3)_{16}]^{2-}$, while CMF-2 contains larger C1 clusters, $[Cd_{17}S_4(SC_6H_4Me\text{-}4)_{28}]^{2-}$. Prior to this work, P1 and C1 clusters formed either isolated clusters[12−13] or the diamond-type framework.[6a] In fact, the quartz-type topology has not been found in any chalcogenide with or without clusters. Thus the realization of the chiral quartz-type topology in chalcogenides as reported here is unprecedented.The main structural difference between CMF-1 and CMF-5 is that CMF-5 has a 6-fold supercell with ordered $S^{2-}$ sites between two adjacent clusters. The difference between CMF-1 and CMF-5 is further verified by multiple crystallographic refinements for CMF-1 and CMF-5 in various supercells and subcells, respectively.

One interesting feature in CMF-3 is the presence of both P1 and C1 clusters in the moganite-type net (Figure 2). So far there have been no prior examples of 3-D frameworks with mixed clusters from both P*n* and C*n* series. Moganite is a rare polymorph of silica that integrates both left- and right-handed features of the quartz

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***Table 1.*** A Summary of Crystallographic Data[a]

| name | cluster type | chemical composition | topology type | space group | *a* (Å) | *b* (Å) | *c* (Å) | *R*(*F*) | 2$\theta$ max |
|---|---|---|---|---|---|---|---|---|---|
| CMF-1 | P1 | $Cd_8S(SC_6H_4Me\text{-}3)_{14}$ | $\beta$-quartz | $P6_222$ | 19.7205(3) | 19.7205(3) | 22.9816(4) | 6.10 | 54.2° |
| CMF-2 | C1 | $Cd_{17}S_4(SC_6H_4Me\text{-}4)_{26}$ | $\beta$-quartz | $P6_222$ | 27.919(2) | 27.919(2) | 30.995(5) | 15.2[b] | 30.8° |
| CMF-3 | P1 and C1 | $[Cd_8S(SC_6H_4Me\text{-}3)_{14}]_2$<br>$[Cd_{17}S_4(SC_6H_4Me\text{-}3)_{26}]$ | moganite | $C2/c$ | 62.8179(7) | 20.1911(2) | 41.4214(5) | 7.41 | 41.8° |
| CMF-5 | P1 | $Cd_8S(SC_6H_4Me\text{-}3)_{14}$ | $\beta$-quartz | $P6_122$ | 34.1978(3) | 34.1978(3) | 45.9516(5) | 4.44 | 56.9° |

[a] X-ray data were collected on a Bruker APEX II diffactometer with Mo K$\alpha$ source at 150 K. The full-matrix refinements were against $F^2$. $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ with $F_o > 4.0\sigma(F_o)$. For CMF-3, $\beta$ =127.740(1)°. [b] The high $R(F)$ for CMF-2 is in part related to the extensive disorder of surface capping ligands, which limits the resolution of the diffraction data to 31° (data resolution = 1.3 Å) in 2$\theta$. However, such data resolution is adequate for resolving the Cd−S cluster structure with the Cd−S distance of about 2.4 Å.

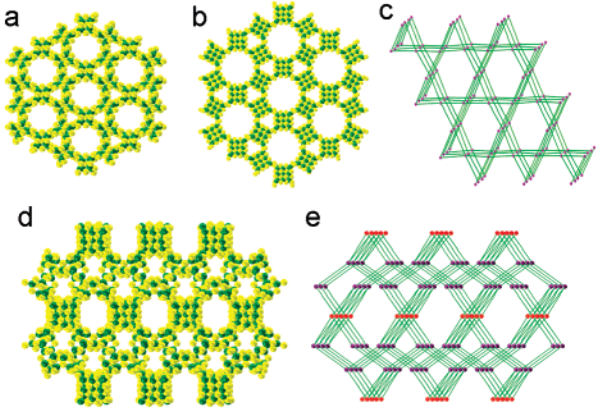

***Figure 2.*** 3-D Frameworks of CMF-1 (a), CMF-2 (b), and CMF-3 (d) showing P1 and C1 clusters at tetrahedral nodes of quartz and moganite nets. Panels c and e represent simplified net diagrams for quartz and moganite based on tetrahedral nodes. The open space shown in the diagrams is occupied by surface organic ligands not shown here: green, $Cd^{2+}$; yellow, S.

structure. Like the quartz-type, the moganite topology was not previously known in chalcogenides either. The observation of both P1 and C1 clusters in the same crystal offers a rare glimpse into the cluster solution chemistry that is likely to involve various equilibrium processes among clusters of different types or sizes.

The diffuse reflectance spectra show the absorption onset at about 370 nm (CMF-1), 415 nm (CMF-2), and 410 nm (CMF-3), indicating that CMF-1, -2, and -3 are wide-gap semiconductors with band gaps of 3.35 eV, 2.99 eV, and 3.02 eV, respectively (Figure S1). The simultaneous TG-DSC analysis performed under the flowing $N_2$ atmosphere, shows that CMF-1, -2, and -3 are stable up to 310, 330, and 300 °C, respectively (Figure S2).

In conclusion, four new chalcogenides reported here demonstrate a strong propensity for the formation of intertwined helical assemblies from large Cd−S−SAr clusters. Additionally, it is demonstrated here that it is possible to tune synthetic conditions so that helices of the same handedness or opposite handedness can cocrystallize into quartz-type or moganite-type topologies, respectively. If larger clusters such as $Cd_{32}S_{14}(SPh)_{40}^{4-}$ can be assembled into similar non-interpenetrating frameworks, there is a possibility to generate porosity in such framework structures. Therefore, this work raises hope for the synthesis of novel chiral semiconductors that may lead to new enantioselective processes such as sensing.

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**Supporting Information Available:** Detailed synthetic procedures, UV−vis spectra, TGA plots, experimental and simulated X-ray powder patterns, crystallographic data including positional parameters, thermal parameters, and bond distances and angles (CIF, PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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