

Nano-/Microporous Materials: Crystalline Metal-Chalcogenide Superlattices

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1 INTRODUCTION

Microporous materials including zeolite molecular sieves are porous solids with pore size below 20 Å.¹ These materials constitute an important area of materials science owing to their commercial applications in catalysis, separation, and ion exchange.^{2,3} Traditionally, zeolites refer to crystalline aluminosilicates constructed from TO₄ tetrahedra (T = Si and Al) to form three-dimensional structures with open channels or cages. In 1982, Flanigen *et al.* reported the synthesis of aluminophosphate molecular sieves that extended crystalline microporous materials to nonaluminosilicate compositions.⁴

Following this discovery, considerable efforts have been made in synthesizing open-framework materials by the replacement of framework cations (i.e., Al³⁺ or Si⁴⁺) in zeolites with other cations such as Ga³⁺, Ge⁴⁺, and P⁵⁺.⁵ This has led to the preparation of a large number of new porous materials, especially those containing extra-large pores, chiral frameworks, helical pores, and multidirectional intersecting channels. The structures of these materials are of great diversity in part because they can form extended structures with MO₅ trigonal bipyramids or square pyramids, MO₆ octahedra, as well as MO₄ tetrahedra. On the other hand, the use of structure-directing agents with various charges, sizes, and shapes is particularly effective in assisting

the formation of different frameworks. In general, open-framework materials are prepared with water as the main solvent under hydrothermal conditions in sealed autoclaves. The use of organic solvents, such as alcohols, pyridine, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), ionic liquids, etc., has also been studied.^{6,7}

The next advance in the synthesis of open-framework materials occurred in 1989,⁸ when Bedard *et al.* reported the synthesis of open-framework metal sulfides by the substitution of framework oxygen atoms with sulfur. Unlike oxide porous materials that are usually insulators, crystalline porous chalcogenides can have higher electrical conductivity, which in combination with uniform porosity and high surface area could lead to new applications in areas such as shape- and size-selective sensors and high-surface-area photocatalysts and photoelectrodes. The early attempts to prepare open-framework chalcogenides concentrated on germanium and tin sulfides; however, very few of these materials possess three-dimensional open structures.^{9,10} Frequently, oligomeric, one-dimensional, or layered structures are found in these compositions. A significant advance in chalcogenide synthesis occurred in late 1990s, when Parise, Yaghi, and their coworkers reported several three-dimensional open-framework indium sulfides.^{11,12} These materials contain the $\text{In}_{10}\text{S}_{20}^{10-}$ supertetrahedral clusters as their building blocks, which are then condensed to produce frameworks with different topologies. With the development of new synthetic strategies, many new metal chalcogenides incorporating a variety of main group and transition metal elements have been prepared during the past years.^{13–22}

From the viewpoint of structural chemistry, the choice of chalcogen atoms (e.g., S, Se) as building blocks will favor the creation of new zeolite-like structures because they will form structures with longer T–X bond distance and smaller T–X–T angles compared to oxides. The typical value for the T–S–T angle in metal sulfides is between 105 and 115°, much smaller than the typical T–O–T angle in zeolites that usually lies between 140 and 150°. This geometrical factor is desirable for the formation of three-membered ring, which could lead to highly open frameworks with low framework density. For example, the framework density of a metal sulfide (UCR-20) containing three-membered rings, measured by the number of tetrahedra per 1000 Å³, is 4.67,²³ much smaller than the value of 12.1 for SBT and TSC, which has the lowest framework density of 4-connected zeolite-type oxides.¹

Open-framework metal chalcogenides frequently consist of clusters as their structural building units. Among various clusters, tetrahedron-shaped clusters have attracted considerable attention partly because they can serve as artificial tetrahedral units to form zeolite-like nanocluster superlattices. The collective properties of nanocluster superlattices are dependent on individual clusters, cross-linking ligands if present, and their spatial organization. For example, in the case of noncovalent linkage, the activation

energy for electron transfer between nanoparticles has been found to depend on the cluster–cluster distance, while in the case of covalent linkage, the transport properties of the spacer play a vital role.²⁴

This article provides a review of the recent developments in the synthesis of open-framework metal chalcogenides based on tetrahedral clusters with the focus on the research between 2004 and till date. Other relevant reviews are available for the earlier work.^{25,26} The rich structural chemistry of open-framework chalcogenides is described along with their interesting properties such as ion exchange, photoluminescence, optical absorption, and ionic conductivity. Potential applications of these semiconducting materials, particularly in photocatalysis and ion exchange, are also discussed.

2 TETRAHEDRAL CHALCOGENIDE CLUSTERS AS BUILDING BLOCKS

Among the three series of tetrahedral clusters, the simplest series are called *supertetrahedral clusters* (denoted as T_n).^{12,25,26} T_n clusters are regular, tetrahedrally shaped fragments of the cubic ZnS-type lattice, as shown in Figure 1. One special case is T_1 and it simply refers to a tetrahedron with the composition of MX_4 (M = metal cation and $X = \text{S}^{2-}$, Se^{2-} , or Te^{2-}). For an isolated T_n cluster, the compositions of T_2 , T_3 , T_4 , and T_5 clusters are M_4X_{10} , $\text{M}_{10}\text{X}_{20}$, $\text{M}_{20}\text{X}_{35}$, and $\text{M}_{35}\text{X}_{56}$, respectively, where M is a metal cation and X is a chalcogen anion. In general, the number of cations in a T_n cluster follows a simple series: 4, 10, 20, ..., $[n(n+1)(n+2)]/6$ ($n \geq 2$), and the number of anions is equal to the number of cations in a $T(n+1)$ cluster (Table 1). Here, n is the number of metal layers in each cluster. For a network of covalently connected clusters, the overall stoichiometry of the framework varies depending on the pattern of connectivity. One common situation is that each of the four corners of a supertetrahedral cluster is shared with another supertetrahedron in an infinite three-dimensional framework. In this case, the total number of anions per supertetrahedral cluster will be reduced by 2.

The largest supertetrahedral cluster synthesized so far is the T_5 cluster with the composition of $[\text{Zn}_{13}\text{In}_{22}\text{S}_{56}]^{20-}$ or $[\text{Cu}_5\text{In}_{30}\text{S}_{56}]^{17-}$.^{27,28} These T_5 clusters occur in covalent two- and three-dimensional superlattices and are not yet known in the isolated form. For individual molecular supertetrahedral clusters, the largest one known so far is T_3 . Some examples are $[\text{Hdmp}]_2[\text{Ga}_{10}\text{S}_{16}(\text{dmp})_4]$ ($\text{dmp} = 3,5\text{-dimethylpyridine}$), $[\text{Na}_{10}(\text{H}_2\text{O})_{32}][\text{M}_5\text{Sn}(\mu_3\text{-S})_4(\text{SnS}_4)_4] \cdot 2\text{H}_2\text{O}$ ($M = \text{Zn}, \text{Co}$), and $[(\text{CH}_3)_4\text{N}]_4[\text{M}_{10}\text{E}_4(\text{SPh})_{16}]$ ($M = \text{Zn}, \text{Cd}$, $E = \text{S}, \text{Se}$, and Ph is a phenyl group).^{29–31}

The second series of tetrahedral clusters are called *pentasupertetrahedral clusters* (denoted as P_n).²⁵ As seen

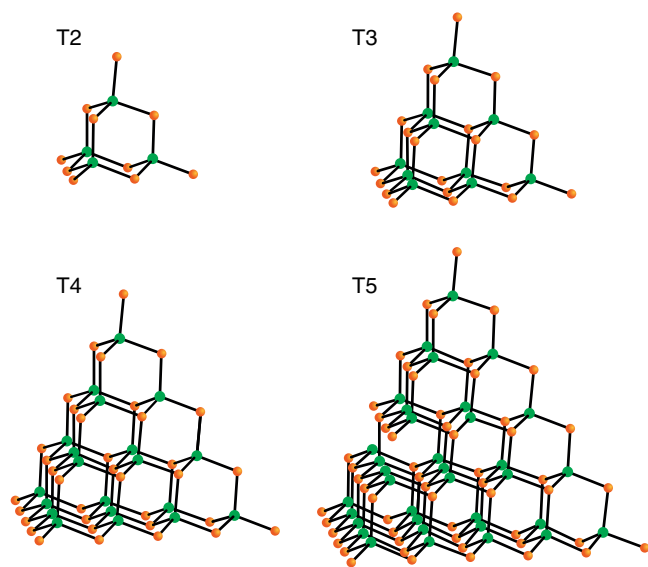


Figure 1 Ball-and-stick representation of T2, T3, T4, and T5 supertetrahedral clusters. Color code:cation sites, green; anion sites, orange

Table 1 A summary of supertetrahedral clusters

T_n	Stoichiometry	Examples
T2	M_4X_{10}	$Ge_4X_{10}^{4-}$ (E = S, Se), $Sn_4E_{10}^{4-}$ (E = Se, Te), $In_4X_{10}^{8-}$ (X = S, Se), $M_4(SPh)_{10}^{2-}$ (M = Fe, Co, Cd; X = S, Se)
T3	$M_{10}X_{20}$	$M_{10}X_{20}^{10-}$ (M = Ga, In; X = S, Se), $M_{10}X_4(SPh)_{16}^{4-}$ (M = Zn, Cd; X = S, Se), $Ga_{10}S_{16}L_4^{2-}$ (L = 3,5-dimethylpyridine)
T4	$M_{20}X_{35}$	$M_4In_{16}S_{35}^{14-}$ (M = Mn, Fe, Co, Zn, Cd), $Zn_4Ga_{16}Se_{35}^{14-}$
T5	$M_{35}X_{56}$	$Cu_5In_{30}S_{56}^{17-}$, $Zn_{13}In_{22}S_{56}^{20-}$
$\geq T6$	$M_pX_q^{(a)}$	None

^(a) $p = [n(n + 1)(n + 2)]/6$; $q = [(n + 1)(n + 2)(n + 3)]/6$.

in Figure 2, each P_n cluster can be conceptually constructed by coupling four T_n clusters onto each face of an anti- T_n cluster. Here, an anti- T_n cluster is defined as a tetrahedron-shaped cluster having the same geometrical feature as that of a T_n cluster; however, the positions of cations and anions are exchanged. Using this concept, a P1 cluster consists of one anti-T1 tetrahedron (XM_4) at the core and four T1 tetrahedra (MX_4) at corners, resulting in the composition of $(MX_4)_4(XM_4)$ (i.e., M_8X_{17}). Examples of P1 clusters include $[Cd_8E(E'Ph)_{16}]^{2-}$ (E, E' = S, Se, Te), $[K_{10}M_4Sn_4S_{17}]$ (M = Mn, Fe, Co, Zn) and $[Na_{10}(H_2O)_{34}][Mn_4(\mu_4-Se)(SnSe_4)_4]$.^{32–34} A P2 cluster has the composition of $(M_4X_{10})_4(X_4M_{10})$ (i.e., $M_{26}X_{44}$). There are only two examples of P2 clusters reported

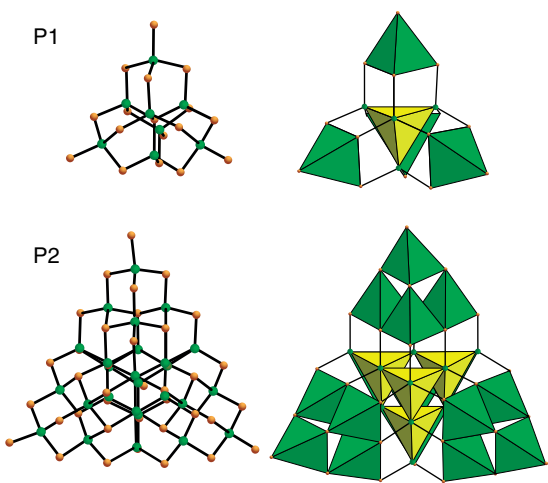


Figure 2 Ball-and-stick and polyhedral representation of P1 and P2 pentasupertetrahedral clusters. Color code:anti-supertetrahedral cluster, yellow; supertetrahedral cluster, green

so far. One is $[Li_4In_{22}S_{44}]^{18-}$ found in the three-dimensional framework of ICF-26,³⁵ and the other is present in an isolated form with the composition of $Cu_{11}In_{15}Se_{16}(SePh)_{24}(PPh_3)_4$.³⁶ Similarly, a P3 cluster has the composition of $(M_{10}X_{20})_4(X_{10}M_{20})$ (i.e., $M_{60}X_{90}$). The same procedure can be used to derive the composition of larger P_n clusters (Table 2). Clusters larger than P2 have not been synthesized yet.

The third series of tetrahedral clusters are termed as *capped supertetrahedral clusters* (denoted as C_n).²⁶ As seen in Figure 3, the C_n cluster consists of a regular supertetrahedral cluster (T_n) at the core. Each face of the T_n core unit is covered with a single sheet of atoms called the $T(n + 1)$ sheet and each corner of this cluster is covered with an MX group. Here, the $T(n + 1)$ sheet is defined as the bottom atomic sheet of a $T(n + 1)$ cluster, and the number of cations in each $T(n + 1)$ sheet is $[(n + 1)(n + 2)]/2$. As in T_n clusters, the number of anions in C_n clusters is equal to the number of cations in the next member (Table 3).

While the core of a C_n is a regular fragment of the cubic zinc-blende-type phase, its four corners are barrelanoid

Table 2 A summary of pentasupertetrahedral clusters

P_n	Stoichiometry	Examples
P1	M_8X_{17}	$M_4Sn_4S_{17}^{10-}$ (M = Mn, Fe, Co, Zn), $M_4Sn_4Se_{17}^{10-}$ (M = Mn, Zn), $ECd_8(E'Ph)_{16}^{2-}$ [E, E' = S, Se, Te], $In_8S_{16}(SH)^{9-}$
P2	$M_{26}X_{44}$	$Li_4In_{22}S_{44}^{18-}$, $Cu_{11}In_{15}Se_{16}(SePh)_{24}(PPh_3)_4$
$\geq P3$	$M_pX_q^{(a)}$	None

^(a) $p = [4n(n + 1)(n + 2)] + [(n + 1)(n + 2)(n + 3)]/6$; $q = [4(n + 1)(n + 2)(n + 3)]/6 + [n(n + 1)(n + 2)]/6$.

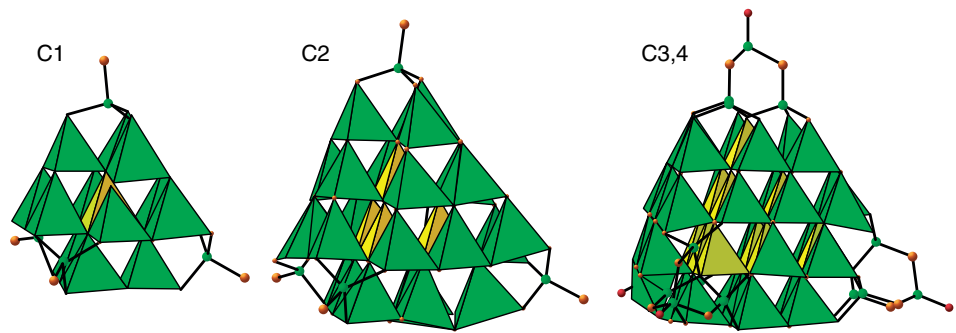


Figure 3 The structural diagrams of C1, C2, and C3, 4 capped supertetrahedral clusters. MX groups at the four corners of C_n clusters and the rotated barrelanoid cages in $C_{m,n}$ cluster are shown in the ball-and-stick form. T_n cluster core (yellow) and the surface capping sheets (green) are shown in the polyhedral style

Table 3 A summary of capped supertetrahedral clusters

C_n	Stoichiometry	Examples
C1	$M_{17}X_{32}$	$Cd_{17}S_4(SPh)_{28}^{2-}$, $Cd_{17}S_4(SC_6H_4Me-4)_{28}^{2-}$
C2	$M_{32}X_{54}$	$Cd_{32}Se_{14}(SePh)_{36}(PPh_3)_4$, $Cd_{32}S_{14}(SPh)_{40}^{4-}$
C3	$M_{54}X_{84}$	$Cd_{54}X_{32}(SPh)_{48}(H_2O)_4$ ($X = S, Se$) ⁴⁻
$\geq C4$	$M_pX_q^{(a)}$	None

^(a) $p = [n(n+1)(n+2)]/6 + [4(n+1)(n+2)]/2 + 4$;
 $q = [(n+1)(n+2)(n+3)]/6 + [4n(n+2)(n+3)]/2 + 4$.

cages possessing the characteristics of the hexagonal wurtzite-type phase. For C_n clusters, each M_4X_5 barrelanoid cage at one of four corners can be independently rotated (around the threefold axis of the tetrahedron) by 60° , which results in four additional series of tetrahedral clusters denoted as $C_{n,m}$ clusters (for $n = 1$, however, only one corner can be rotated). Here, m refers to the number of corners that have been rotated from their original position in parent C_n clusters. The largest capped supertetrahedral clusters synthesized so far are the C3,4 clusters with the composition of $Cd_{54}X_{32}(SPh)_{48}(H_2O)_4$ ($X = S, Se$), as shown in Figure 3.³⁷ These C3,4 clusters occur in the isolated form with the size of 20 Å (measured between corner metal sites).

By adding atoms into or removing atoms from regular tetrahedral clusters, other variations of clusters are possible. Notable examples include the coreless T5 clusters, in which the central metal site of a T5 cluster is not occupied,^{38–40} the stuffed T2 and T3 clusters in which there is an oxygen atom in each adamantane cage,¹⁰ and the truncated P1 cluster in which a surface T1 tetrahedron is removed.^{41–44}

To prepare crystalline porous chalcogenides, one promising approach is the directed assembly of these nanosized chalcogenide clusters into three-dimensional superlattices with framework topologies similar to those found in zeolites. By varying the cluster composition and size,

it should be possible to generate zeolitic frameworks with tailored pore sizes and topological features.

3 METAL CHALCOGENIDES CONSTRUCTED FROM SUPERTETRAHEDRAL CLUSTERS

Following the first discovery of open-framework metal sulfides by Bedard *et al.* in 1989,⁸ a wide range of metals, including groups 12–14 (e.g., Zn, Cd, Ga, In, Ge, and Sn) and first-row transition elements, such as Mn, Fe, Co, and Cu, have been incorporated into 4-connected chalcogenide frameworks. To investigate size-dependent properties of nanoclusters and to generate large pores, the synthetic efforts have focused on the creation of frameworks from large nanoclusters. By controlling the charge on metal cations, one can influence the size of T_n clusters. For example, in the Ge–S system, the largest supertetrahedral cluster is T2. Larger clusters have not been synthesized, because the charge at cationic sites is too high to satisfy the coordination environment of tri- or tetra-coordinate anionic sites in clusters larger than T2. One of the effective synthetic strategies in the preparation of open-framework chalcogenides containing T2 clusters is the use of mono- or divalent cations (e.g., Cu^+ , Mn^{2+}) as linking metals to join together adamantane-like T2 clusters (e.g., $Ge_4S_{10}^{4-}$). These low-valent cations help generate negative charges on the framework that are subsequently charge balanced by structure-directing agents. A notable example is the synthesis of a sulfide compound $[(CH_3)_4N]_2[MnGe_4S_{10}]$ by reacting discrete T2 cluster $[(CH_3)_4N]_4[Ge_4S_{10}]$ with metal salts.⁴⁵ This compound has a three-dimensional framework with single-diamond lattice, where tetrahedral nodes sites are alternately occupied by T1 and T2 clusters (i.e., T1–T2 superlattice). In addition to the single-diamond topology, other types of framework structures are also possible. For example, zeolitic ABW-type topology has been found in $MnGe_4S_{10} \cdot H_2DABCO \cdot 3H_2O$ (known as *DABCO-MnGS-SBI*).⁴⁶

In terms of chemical compositions, chalcogenides with tetravalent (M^{4+}) and trivalent (M^{3+}) metal cations are the closest analogs to aluminosilicate zeolites. However, the synthesis of microporous M^{4+}/M^{3+} chalcogenides by the use of trivalent cations (e.g., In^{3+}) to link T2 Ge_4S_{10} cluster has not been successful so far. Recently, it was found that the use of nonaqueous synthesis method could lead to the integration of M^{4+} and M^{3+} ions into the same crystalline frameworks.²³ A number of open-framework sulfides and selenides (denoted as UCR-20, UCR-21, UCR-22, and UCR-23) were made by combining tetravalent (i.e., Ge^{4+} , Sn^{4+}) and trivalent metal (i.e., Ga^{3+} , In^{3+}) ions in T2 clusters. The M^{4+} and M^{3+} ions are disordered in the T2 clusters and the M^{4+}/M^{3+} ratio varies from 0.2 to 1.2. The three-dimensional linkages of these T2 clusters give rise to four different framework topologies (i.e., sodalite (SOD), single diamond, double diamond, and CrB_4). It is interesting that the building unit of UCR-22 is a super-supertetrahedral cluster (denoted as T2,2 cluster), which could be generated by replacing each tetrahedron in a T2 cluster with a T2 cluster. The T2,2 cluster is also called as *coreless T4 cluster*, because it is similar to a regular T4 cluster without the anti-T1 core (SM_4), as seen in Figure 4. Another super-supertetrahedral cluster, denoted as T4,2 cluster, has also been observed in chalcogenide chemistry.⁴⁷

Compared to Ge^{4+} and Sn^{4+} , the lower charge on In^{3+} makes it possible to form tricoordinate sulfur sites needed for the formation of T3 clusters. In late 1990s, Parise, Yaghi, and coworkers reported several organically templated open-framework indium sulfides with double diamond, SOD, and CrB_4 topologies.^{11,12} By introducing monovalent (i.e., Cu^+) and divalent cations (e.g., Zn^{2+} , Mn^{2+} , Cd^{2+}) into the supertetrahedral clusters, the size of chalcogenide clusters could be further pushed up to T4 and T5. Unlike T2 and T3 clusters that have no core atoms, the T4 cluster contains a single chalcogen atom core and T5 cluster has a tetrahedral T1 core. The core atoms are all tetrahedrally coordinated. The three-dimensional connectivity of the large T4 and T5 clusters

usually leads to the formation of open frameworks with a double-diamond topology. In a few cases, the interpenetration of two identical lattices could be avoided. Examples include UCR-8 with a cubic C_3N_4 topology⁴⁸ and UCR-1 with a previously unknown zeolitic framework.^{49,50}

Despite the extensive research on open-framework chalcogenide materials, the progress with gallium chalcogenides is much slower. Recently, the synthesis of a series of three-dimensional gallium sulfide and selenide superlattices built from supertetrahedral T3 and T4 clusters was reported.^{50,51} Interestingly, all three gallium selenide phases are noncentrosymmetric, and none of them consists of interpenetrating lattices that are common for cluster-based superlattices. This structural feature is also in contrast with the corresponding Ga–S system, in which all four known structure types are interpenetrating and centrosymmetric. Synthetically, there is a major difference between gallium selenides and gallium sulfides. While the presence of water promotes the crystal growth of the gallium selenides, the synthesis of gallium sulfide superlattices is successful only in a nonaqueous system. This difference between gallium selenides and gallium sulfides might be related to the relative hydrothermal stability of Ga–S and Ga–Se bonds.

In addition to organically templated metal chalcogenides, inorganic cation templated chalcogenides with the zeolitic frameworks have also been prepared under hydrothermal conditions.²⁸ These inorganic chalcogenides share structural similarities with amine-directed chalcogenides. Three-dimensional structures containing T2, T4, and T5 clusters are produced in both synthetic systems. However, no T3 clusters have been found in purely inorganic chalcogenides so far even though T3 clusters are common in the organically templated system. It is noteworthy that there are no tetravalent cations present in the T2 clusters of ICF-21InSe–Na, ICF-22InS–Li, ICF-24, and ICF-25. This is apparently an effect of the host–guest charge density matching. The exclusion of M^{4+} cations in the purely inorganic phases results from the higher charge density of inorganic cations as compared to organic cations.

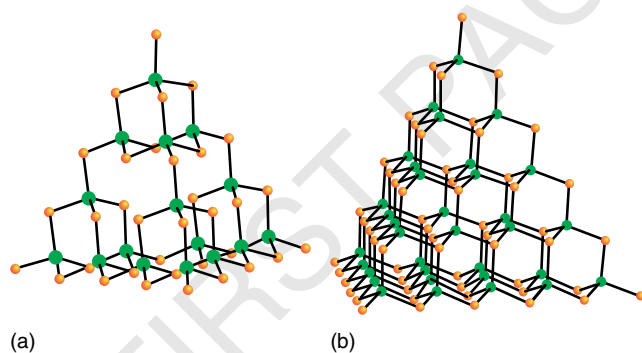


Figure 4 Ball-and-stick representation of (a) a coreless T4 cluster without the anti-T1 core (SM_4) and (b) a coreless T5 cluster without the central metal site

4 METAL CHALCOGENIDES CONSTRUCTED FROM PENTASUPERTETRAHEDRAL CLUSTERS

Open-framework metal chalcogenides are usually synthesized under hydro- or solvothermal conditions. The reactions take place in sealed autoclaves under autogenous pressure. The development of new synthetic concepts and techniques is very important for preparing novel microporous materials. For example, the use of alkali polychalcogenide flux method by Kanatzidis *et al.* in the synthesis of open-framework metal sulfides led to the formation of some new chalcogenide materials containing P1 clusters, $A_{5-x}K_{1+x}Sn[Zn_4Sn_4S_{17}]$ ($A = K^+$, Rb^+ , Cs^+ ;

$x = 0, 4, 5$).⁵² These materials have a robust open framework with a single-diamond topology. They are the first examples of compounds consisting of intact $[\text{Zn}_4\text{Sn}_4\text{S}_{17}]^{10-}$ clusters linked with Sn^{4+} centers (i.e., P1–T1 superlattice). It should be noted here that in aqueous or organic medium, $[\text{M}_4\text{Sn}_4\text{S}_{17}]^{10-}$ ($\text{M} = \text{Zn}, \text{Cd}, \text{Fe}, \text{Co}$) and $[\text{M}_4\text{Sn}_4\text{Se}_{17}]^{10-}$ ($\text{M} = \text{Co}, \text{Zn}, \text{Mn}, \text{Cd}, \text{Hg}$) clusters have only been obtained in isolated forms so far.^{33,34}

P1 clusters are also known in other compositions, particularly cadmium chalcogenides with surface ligands (e.g., phenyl groups). In an effort to examine how key synthetic parameters such as temperature, solvent, surface ligand type, and S^{2-} sources affect the network topologies of resulting chalcogenides, some novel three-dimensional cadmium sulfides were successfully synthesized.^{53,54} $[\text{Cd}_8\text{S}(\text{SC}_6\text{H}_4\text{Me-3})_{14}]$ (denoted as CMF-1) was obtained as colorless crystals by slow diffusion of methanol into the yellowish solution (mass ratio, DMF : $\text{CS}_2 = 2 : 1$) containing $\text{Cd}(\text{SC}_6\text{H}_4\text{Me-3})_2$ ($\text{HSC}_6\text{H}_4\text{Me-3} = 3\text{-methylbenzenethiol}$) in several weeks. It crystallizes in the hexagonal system with the space group $P6_222$. The structure contains P1 clusters with the composition of $[\text{Cd}_8\text{S}(\text{SC}_6\text{H}_4\text{Me-3})_{16}]^{2-}$ as its building units. Two adjacent P1 clusters are covalently joined through the $\text{Cd}(\text{SC}_6\text{H}_4\text{Me-3})\text{-Cd}$ linkage. Topologically, these P1 clusters behave like large artificial atoms with tetrahedral coordination. They can occupy tetrahedral nodes in the 4-connected net, adopting the β -quartz topology (Figure 5).

By using thiourea as the S^{2-} source, another chiral framework material CMF-5 could be prepared under solvothermal conditions at 85°C . This compound crystallizes in the hexagonal system with the space group $P6_122$, and it also has the β -quartz topology. The main structural difference between CMF-1 and CMF-5 is that CMF-5 has a sixfold supercell with ordered S^{2-} sites between two adjacent clusters.

Given that the nature of organic surface ligands may affect the formation of clusters and their assembly, it is of interest to investigate new semiconducting materials by using surface ligands containing electronegative elements, in addition to alkyl groups discussed above. By using 3-fluorophenylthiolate, a novel three-dimensional chiral framework $\text{Cd}_8\text{S}(\text{SPhF-3})_{14}$ (CMF-8) has been synthesized under hydrothermal condition at 85°C .⁵⁴ The solvent contains acetone and water in a mass ratio of $2 : 1$. This compound crystallized in the trigonal system with the space group $P3_221$. Each P1 cluster is linked to four surrounding clusters through corner $-\text{SC}_6\text{H}_4\text{F-3}$ groups. The three-dimensional noninterpenetrating network possesses the α -quartz-type framework topology.

The structures of above-mentioned compounds are based on regular P1 clusters. When one capping tetrahedron is removed from the P1 cluster, a truncated P1 cluster with the composition of $(\text{MX}_4)_3(\text{XM}_4)$ (i.e., M_7X_{13}) is formed. Such truncated P1 clusters are strongly polar with a threefold axis of symmetry and belong to the C_{3v} point group. They have been found in some 6-connected metal chalcogenides with open structures. For example, $\text{K}_6\text{Cd}_4\text{Sn}_3\text{Se}_{13}$ represents the first open-framework chalcogenide generated from the polymerization of truncated P1 clusters with the composition of $[\text{Cd}_4\text{Sn}_3\text{Se}_{13}]^{6-}$, which derives from a $[\text{Cd}_4\text{Sn}_4\text{Se}_{17}]^{10-}$ cluster via elimination of one $[\text{SnSe}_4]^{4-}$ anion.⁴¹ The connectivity of these truncated P1 clusters results in an open and polar structure with α -Po-type topology.

A pentasupertetrahedral cluster is considerably larger than a supertetrahedral cluster of the same order, and hence it is difficult to prepare open-framework chalcogenides with pentasupertetrahedral clusters larger than P1. Recently, in a procedure mimicking the preparation of natural zeolites by using alkali and alkaline earth metal cations as structure-directing agents, a three-dimensional open-framework material (denoted as ICF-26) was prepared from

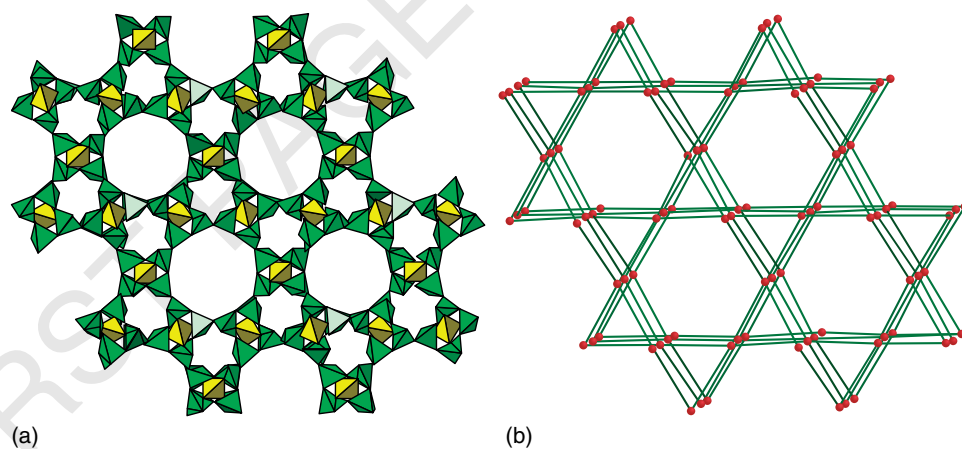


Figure 5 (a) Polyhedral representation of the three-dimensional structure of CMF-1 constructed from P1 clusters. Surface organic ligands are omitted for clarity. Color code: SCd_4 anti-tetrahedra, yellow; CdS_4 tetrahedra, green. (b) The structure has the β -quartz topology. The red balls represent P1 $\text{Cd}_8\text{S}(\text{SC}_6\text{H}_4\text{Me-3})_{16}$ clusters

the Ca–Li–In–S quaternary system.³⁵ This compound was built from P2 clusters with the composition of $\text{Li}_4\text{In}_{22}\text{S}_{44}^{18-}$. The connectivity of these P2 clusters by corner-sharing results in a three-dimensional framework with the double-diamond topology.

5 METAL CHALCOGENIDES CONSTRUCTED FROM CAPPED SUPERTETRAHEDRAL CLUSTERS

Since the first member of capped supertetrahedral clusters (i.e., $[\text{Cd}_{17}\text{S}_4(\text{SPh})_{28}]^{2-}$) was reported in 1988, the interest in metal chalcogenides containing C_n clusters has been steadily growing.^{55–57} Unlike colloidal nanoparticles, crystalline II–VI nanoclusters have unique advantages resulting from their precisely defined sizes and compositions. They allow the study of quantum confinement effects and collective properties at the lowest size limit of three-dimensionally confined quantum dot structures. In addition to their potential applications in nanotechnology, II–VI nanoclusters could serve as a model system and provide synthetic and structural insights into the formation, structure, and properties of larger colloidal nanoparticles and their superlattices that usually have less well defined structures.

Several useful synthetic approaches have been studied to prepare nanosized cadmium chalcogenide clusters and their superlattices. These approaches include the selection of different surface capping ligands to affect the topologies of spatially organized clusters, the use of large charge-balancing cations to increase the size of nanoclusters, and the use of organic linkers to assemble cadmium chalcogenide clusters into various structures. By careful control of the synthetic conditions, some three-dimensional cadmium chalcogenides that contain C1 or C2 clusters have been prepared.

5.1 Three-Dimensional Self-Assembly of C1 Clusters with Different Surface Capping Ligands

Metal-chalcogenide clusters with different thiolate surface ligands can adopt various nuclearities and great structural complexities. It has been reported that the topology of spatially organized clusters is strongly affected by surface ligands. For example, Dance *et al.* have shown that a change in the position of the methyl group on the thiophenyl ring gives different structures.^{58,59} Such structural diversities resulting from different organic surface ligands might open up a rich opportunity for the creation of a variety of metal chalcogenides with unprecedented structures, especially three-dimensional frameworks. In addition, because organic ligands on the surface of cadmium chalcogenide clusters may affect their optical properties, solubility, etc., it is desirable to study the formation of cadmium chalcogenide superlattices by using different surface ligands.

The first three-dimensional cadmium chalcogenide $\text{Cd}_{17}\text{S}_4(\text{SCH}_2\text{CH}_2\text{OH})_{26}$ containing C1 clusters was reported in 1995 with 2-mercaptoethanol as the surface ligand.⁶⁰ The connectivity of adjacent C1 clusters by sharing $\text{SCH}_2\text{CH}_2\text{OH}$ corners gives rise to a three-dimensional framework with a double-diamond topology. When 4-methylphenylthiolate was used as the surface ligand, $\text{Cd}_{17}\text{S}_4(\text{SPhMe-4})_{26}$ (CMF-2) was produced.⁵³ In this structure, each C1 cluster is connected to four other identical clusters through SPhMe-4 ligands to form the β -quartz network.

An interesting structure CMF-4 is generated when 3-methylphenylthiolate is used as the surface capping ligand.⁶¹ Unlike the two compounds mentioned above with 4-connected networks, CMF-4 possesses a unique (3,4)-connected framework, $(\text{NH}_4)_2[\text{Cd}_{17}\text{S}_4(\text{SPhMe-3})_{24}(\text{SPhMe-3})_{4/2}]_3[\text{Cd}_{17}\text{S}_4(\text{SPhMe-3})_{24}(\text{SPhMe-3})_{3/2}(\text{SPhMe-3})_4]$. Three -connected structural units, when present alone, tend to form low-dimensional structures. However, in combination with 4-connected clusters, they can form interesting three-dimensional open-framework architectures. Structural analysis reveals that CMF-4 has a framework topology similar to that of boracite. The C1 clusters in CMF-4 exhibit two different connectivities: 4-connected unit similar to $\{\text{B}\}\text{O}_4$ tetrahedra and 3-connected unit with one terminating corner similar to $\{\text{B}\}\text{O}_3$ triangles (Figure 6). The connectivity of the alternating 4-connected C1 clusters and 3-connected C1 clusters results in a three-dimensional framework. By considering C1 clusters as pseudo-tetrahedral atoms and ignoring the internal structures of C1 clusters, CMF-4 can be reduced to a simple structure type known as *boracite* (Figure 6).

5.2 Metal–Chelate Dye-Controlled Organization of $\text{Cd}_{32}\text{S}_{14}(\text{SPh})_{40}^{4-}$ Nanoclusters into Three-Dimensional Superlattices

It has been demonstrated that nanosized C1 clusters can be assembled into three-dimensional frameworks. However, no solvent accessible space is available from these superlattices, which is due to the presence of surface capping ligands and lattice interpenetration. If larger clusters such as C2 clusters (e.g., $\text{Cd}_{32}\text{S}_{14}(\text{SPh})_{40}^{4-}$) can be assembled into similar frameworks, it may be possible to generate more open architectures.

Because of the low charge density of C_n clusters, three-dimensional frameworks constructed from 4-connected $\text{Cd}_{32}\text{S}_{14}(\text{SPh})_{40}^{4-}$ nanoclusters have considerably lower charge density than those of T_n (e.g., $\text{T5 In}_{22}\text{Zn}_{13}\text{S}_{54}^{16-}$) or P_n (e.g., $\text{P2 In}_{22}\text{Li}_4\text{S}_{44}^{18-}$) clusters. According to the host–guest charge density matching, the use of bulky structure-directing agents with low charge density may favor the formation of C_n -cluster-based superlattices. Given that metal–chelate dye complexes generally have larger size and lower charge density than commonly used protonated amines or inorganic cations, metal–chelate dye complexes can be suitable candidates to

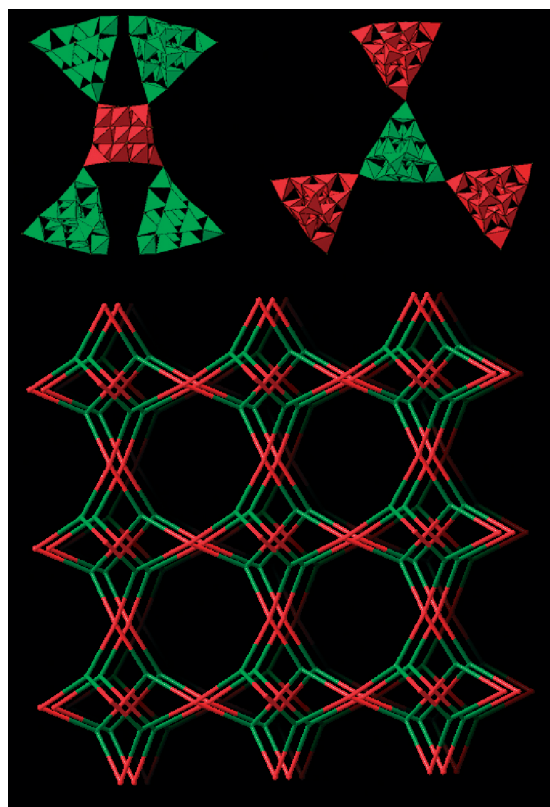


Figure 6 The connectivity of the alternating 4-connected C1 clusters (red color) and 3-connected C1 clusters (green color) results in a (3,4)-connected framework with the boracite topology in CMF-4

template the formation of II–VI superlattices. In addition, the matching of hydrophobic surfaces between metal–chelate dyes and organic ligand capped II–VI nanoclusters is also an important factor. From the viewpoint of materials chemistry, the coassembly of optically active metal–chelate dyes with covalent semiconductor superlattices of chalcogenide nanoclusters will open up new opportunities for the control of electronic or optical properties and help promote the potential applications of these hybrid semiconducting materials. For example, the integration of optically active metal–chelate dyes with crystalline cadmium sulfide frameworks can lead to more efficient absorption of solar energy.

By using optically active metal–chelate dyes (e.g., $[M(1,10\text{-phenanthroline})_3]^{2+}$, $M = \text{Fe}^{2+}$, Ru^{2+}) as templates, the assembly of C2 clusters ($\text{Cd}_{32}\text{S}_{14}(\text{SPh})_{40}^{4-}$) containing as many as 32 Cd^{2+} sites into three-dimensional open frameworks (denoted as COV-10, COV-11) has been achieved.⁶² Both materials adopt the twofold interpenetrating diamond-type lattice with C2 clusters at the tetrahedral nodes, as shown in Figure 7. The negatively charged framework is balanced by metal complex dye cations. Although the topology of these materials is common in the chalcogenide system, such large clusters as tetrahedral nodes are exceptional. As

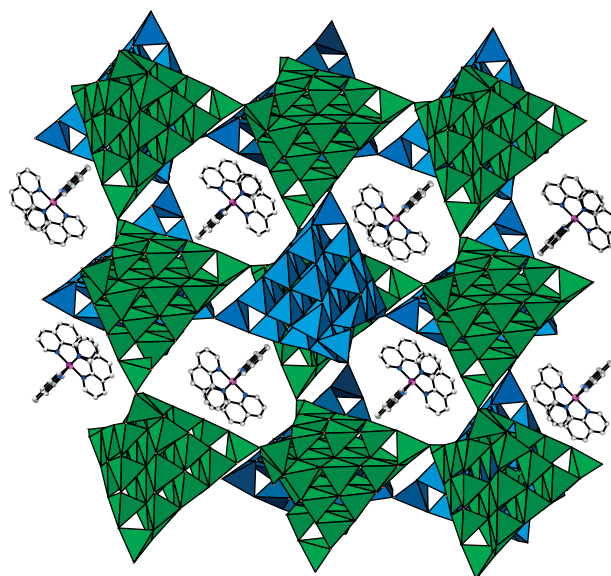


Figure 7 Three-dimensional open framework of COV-10 constructed from C2 nanoclusters. Two interpenetrating lattices are represented in green and blue tetrahedra, respectively. The extra-framework metal complex dye cations are shown in the ball-and-stick style

expected, the composite materials exhibit significant visible-light absorption that is quite sensitive to the nature of the metal–chelate dyes. The optical properties could be tuned by changing either metal centers or organic ligands within the metal complexes.

5.3 Inorganic–Organic Frameworks Built from Metal Chalcogenide Nanoclusters and Bifunctional Organic Ligands

Metal-chalcogenide nanoclusters are usually linked together to form extended structures through corner-sharing chalcogens (e.g., S^{2-} , SPh^- , and S_3^{2-}). One limitation with this approach comes from the inflexible $M-X-M$ angle (M = metal ions, X = chalcogens) that places a significant constraint on the number of topological types that can be achieved. To overcome this limitation and to expand topological diversity of nanocluster superlattices, one promising way is the utilization of organic ligands as the bridge to assemble semiconducting nanoclusters into crystallographically ordered superlattices. Compared with chalcogen atoms, organic ligands possess a wide variety of shapes and rich coordination chemistry, which may allow the creation of diverse nanocluster superlattices.

A key factor that controls the connectivity and assembly of chalcogenide clusters is the charge of the precursor cluster and organic ligand. For example, in the case of C_n clusters (e.g., $\text{Cd}_{17}\text{S}_4(\text{SPh})_{28}^{2-}$, $\text{Cd}_{32}\text{S}_{14}(\text{SPh})_{40}^{4-}$) connected by neutral organic ligands, in principle, up to four terminal corners in C_n clusters are available for

substitution by neutral bridging ligands. However, the consideration of the framework charge poses a limitation on the number of terminal—SPh groups that can be substituted. Under solvothermal conditions, neutral or negatively charged tetrahedral clusters are generally observed. Therefore, to avoid the formation of positively charged clusters and superlattices when neutral ligands are employed, only two corners of C1 clusters are usually available for cross-linking, whereas C2 clusters can use up to four corners for cross-linking. In addition to the charge of clusters and linkers, the number of donor atoms on each linker is also expected to influence the assembly and dimensionality of the resulting structures.

By employing linear neutral ligands, such as 4,4'-bipyridine (BPy), 1,3-trimethylenedipyridine (TMDPy), or 1,2-bis(4-pyridyl)ethane (BPEA), a series of cadmium chalcogenide clusters have been assembled into one- and two-dimensional structures, as shown in Figure 8.^{63,64} For simplicity, general terms such as Cd-17 and Cd-32 are used to refer to a nanocluster that contains the specified number of cadmium cations.

For the coassembly of Cd-32 clusters, two linking modes in which either four or two corners are used for cross-linking have been observed. Through the control of temperature, in combination with the optimization of other synthetic parameters such as solvents and molecular precursors, Cd-32 clusters have been coassembled into two-dimensional hybrid frameworks (COV-5 and COV-7) with TMDPy or BPEA linkers when four corners are used for cross-linking. The common structural pattern in the two-dimensional coassemblies is the presence of a dimeric unit formed by connecting two Cd-32 clusters through two organic ligands. Each dimer behaves like a pseudo-tetrahedral unit and is joined to four adjacent dimers through four cross-linking ligands to form two-dimensional arrays. Thus, the two-dimensional patterns are obtained through the combined use of single and double organic bridges between cadmium chalcogenide nanoclusters. For one-dimensional assemblies of Cd-32 clusters, two linking modes in which either four or two corners are used for cross-linking have been observed. In COV-1, adjacent Cd-32 clusters are joined together through

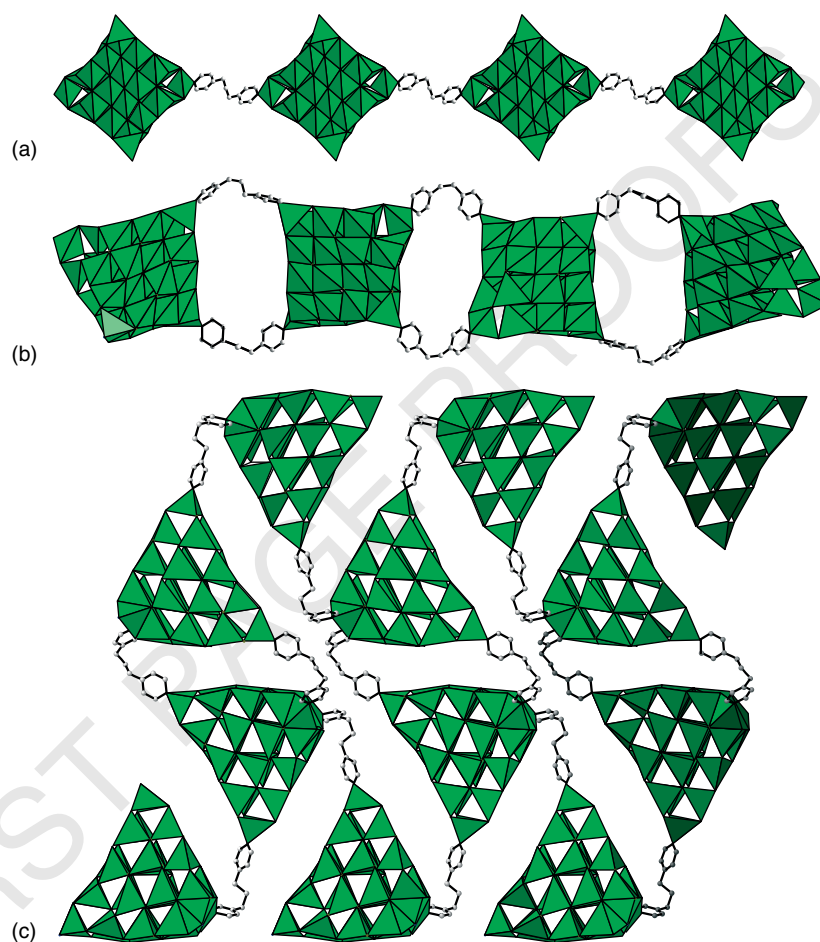


Figure 8 The coassembly of Cd-32 clusters with bidentate organic ligands to form (a, b) one- and (c) two-dimensional structures. In COV-2 (a), each CdS cluster alternates with one TMDPy ligand to form negatively charged chains. In COV-1 (b), adjacent CdS clusters are joined together through two TMDPy ligands into neutral chains

two TMDPy ligands into a doubly bridged chain. The replacement of all four corner–SPh groups by neutral ligands results in neutral chains (and clusters) that are aligned in the same direction. In comparison, adjacent Cd-32 clusters in COV-2 are joined together through only one TMDPy molecule into singly bridged chains. The replacement of two–SPh corners by neutral ligands decreases the charge on each Cd-32 cluster from -4 to -2 . The packing of these negatively charged chains therefore leaves void space to accommodate charge-balancing cations.

Similar to Cd-32 clusters, Cd-17 clusters can also be linked into one-dimensional arrays by neutral organic linkers. In COV-3, Cd-17 clusters form singly bridged chains with alternating neutral ligands and nanoclusters. Unlike -4 charged Cd-32 clusters that can use up to four corners for cross-linking, C1 clusters use only two corners because of their -2 charge, which explains their preference for the formation of one-dimensional configuration. One unique situation is the formation of an isolated dimeric structure (COV-8). In this structure, the two Cd-17 clusters are joined together through two organic ligands. For clusters smaller than Cd-17 nanoclusters, neutral organic ligands can also serve as bifunctional linkers to form different extended structures. For example, P1 clusters with eight metal centers, which could also be understood as C0 clusters, have been assembled by dipyriddy ligands to form different one-dimensional arrays.⁶⁵

If anionic organic ligands are involved in the synthesis of hybrid frameworks, three-dimensional structures can be realized even with Cd-17 clusters. The most common situation is the direct use of the mononegative thiolate surface capping ligand as the cross-linker.^{53,54,60} Another example is $\text{Cd}_{17}\text{S}_4(\text{SPh})_{24}(\text{CH}_3\text{OCS}_2)_2$.⁶⁶ In this case, all four corners of the Cd-17 cluster are occupied by $\text{CH}_3\text{OCS}_2^-$ groups, which are generated in situ from the reaction between CS_2 and methanol. These in situ generated $\text{CH}_3\text{OCS}_2^-$ species serve as bridging ligands to assemble Cd-17 clusters into a three-dimensional framework with a double-diamond topology.

6 METAL CHALCOGENIDES CONSTRUCTED FROM DIFFERENT TETRAHEDRAL CLUSTERS

In hydrothermal synthesis of open-framework chalcogenides, simple elemental forms (e.g., sulfur) and inorganic salts are often used. In this case, the initial process usually involves redox chemistry and formation of clusters. Clusters of various sizes and types could coexist in a solution. Equilibria between various clusters in solution would shift to favor one or more clusters when crystallization involving these clusters occurs. The final framework structure may consist of different-sized clusters from the same series of tetrahedral

clusters (e.g., T3 and T4) or from different series (e.g., P1 and C1 or P1 and T2).

One system that demonstrates the selective crystallization of different-sized clusters is the Zn–Ga–S mixture.⁵¹ The presence of both M^{2+} and M^{3+} ions in the synthetic system allows the formation of both T3 ($\text{Ga}_{10}\text{S}_{20}^{10-}$) and T4 ($\text{Zn}_4\text{Ga}_{16}\text{S}_{35}^{14-}$) clusters. By using different amine molecules as the structure-directing agents, one or both of them can be selectively crystallized into a superlattice. Three new phases denoted as UCR-7, UCR-5, and UCR-19 have been made in this system. All three phases have the same intercluster connectivity (i.e., double-diamond topology), and they only differ in the size of clusters at each tetrahedral node and the templating amine molecules. UCR-7 is made from T3 clusters only and UCR-5 is made from T4 clusters. UCR-19 has a hybrid framework and consists of alternating T3 and T4 clusters.

Another example of different-sized tetrahedral clusters in the same superlattice is provided by the synthesis of UCR-15, which consists of a double-diamond topology built from alternating T3 and coreless T5 clusters.³⁸ When both T3 and pseudo-T5 clusters are replaced with T4 clusters, CdInS-44 and UCR-5MInS ($\text{M} = \text{Zn, Mn, Co}$) are obtained.^{49,67} The formation of the alternating T3 and pseudo-T5 framework in UCR-15, however, significantly reduces the overall framework negative charge to -0.273 per metal site. In comparison, the charge per metal site in the T4–T4 framework is -0.5 , almost twice as negative as the T3–T5 framework. In the study of open-framework oxide materials, it was suggested that the host–guest charge density matching plays an important role in the formation of 4-connected zeolite-type materials. Here, the host–guest charge density matching may also be an important factor in the formation of the T3–T5 framework. In the simplest approximation, the charge density of a fully protonated amine molecule can be approximated by its C/N ratio. Thus, the more negatively charged T4–T4 framework is formed when 1,4-bis(3-aminopropyl)piperazine (the C/N ratio = 2.5) is used as the structure-directing agent, whereas the less negative T3–T5 framework is formed when dipiperidinomethane (the C/N ratio = 5.5) is used in the synthesis.

Hybrid chalcogenide frameworks are not limited to T_n clusters, but can be generalized to include all three series of tetrahedral clusters. For example, a new hybrid framework (denoted as CMF-3) based on P1 [$\text{Cd}_8\text{S}(\text{SC}_6\text{H}_4\text{Me-3})_{16}]^{2-}$ cluster and C1 [$\text{Cd}_{17}\text{S}_4(\text{SC}_6\text{H}_4\text{Me-3})_{28}]^{2-}$ cluster has been reported recently.⁵³ In CMF-3, every C1 cluster is surrounded by four P1 clusters and every P1 cluster is connected with two P1 clusters and two C1 clusters. The connectivity between these different clusters results in a three-dimensional framework with the moganite topology, as shown in Figure 9.

Another example of the hybrid framework is an indium sulfide (denoted as HCF-1) that consists of P1 [$\text{In}_8\text{S}_{16}(\text{SH})_9]^{9-}$ cluster and T2 [$\text{In}_4\text{S}_9(\text{SH})_7]^{7-}$ cluster.⁶⁸ The

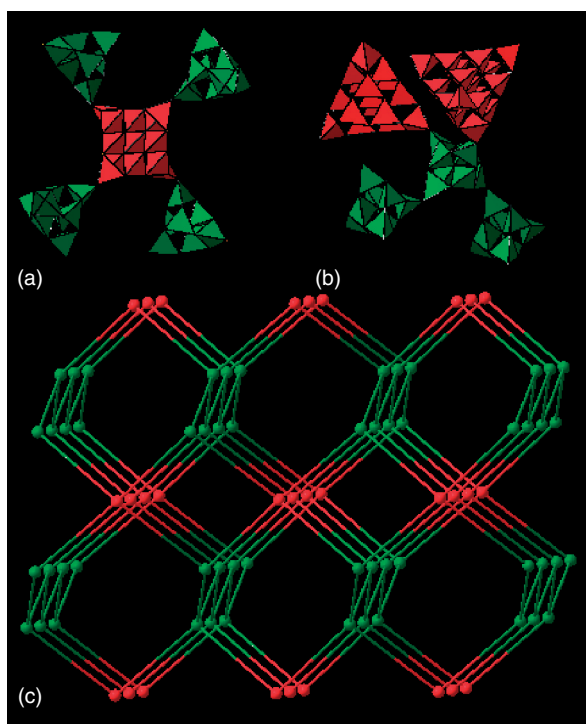


Figure 9 (a) Four P1 clusters are joined by a C1 cluster and (b) a P1 cluster is surrounded by two C1 clusters and two P1 clusters in CMF-3. P1 clusters, green; C1 clusters, red. Surface organic ligands are omitted for clarity. (c) The moganite-type topology is observed in CMF-3. The red balls represent C1 clusters and the green balls represent P1 clusters

structure is built from strictly alternating P1 and T2 clusters, forming a layered network with 15-membered ring windows. In contrast to previously known P1 clusters with divalent metal cations surrounding the core S^{2-} sites, the P1 $[In_8S_{16}(SH)]^{9-}$ clusters are made of trivalent metal cations (i.e., In^{3+}) with the core sulfur site bonded to four In^{3+} sites.

7 SELECTED PROPERTIES OF OPEN-FRAMEWORK CHALCOGENIDES

Ion exchange is among the most common properties of open-framework solids. Metal chalcogenides with open architectures could exhibit unique ion-exchange properties due to their diversity in pore and channel size and the specific affinity of the chalcogenide framework for certain cationic species. For example, an open-framework sulfide material, $K_6Sn[Zn_4Sn_4S_{17}]$, shows highly selective ion-exchange properties and exchange capacities for Cs^+ and NH_4^+ ions.⁶⁹ Interestingly, this material exhibits no selectivity for Li^+ and Na^+ ions because the large hydration sphere of these ions prevents them from entering the framework. By

replacing large organic cations with small inorganic cations through ion exchange, microporosity can be produced in organically templated chalcogenide frameworks. For example, organic cations in UCR-20GaGeS-TAEA could be almost completely ion exchanged by Cs^+ at room temperature.²³ The Cs^+ -exchanged material exhibits the type I isotherm characteristic of a microporous system. The material has a high Langmuir surface area of $807\text{ m}^2\text{ g}^{-1}$ and a total pore volume of $0.23\text{ cm}^3\text{ g}^{-1}$ despite the presence of much heavier elements (Cs–Ga–Ge–S) compared to those in zeolites.

Open-framework metal chalcogenides have been found to display photoluminescence with tunable emission wavelengths ranging almost continuously from 440 to 600 nm by varying their framework compositions and structures. For UCR-2InS-TMDP, a broad emission centered at 520 nm was observed when excited at 470 nm.⁷⁰ For UCR-2InSe-BAPP, the emission was centered at 563 nm when excited at 482 nm. The general trend is that materials with heavier elements are excited and luminesce at a longer wavelength. Compared to open-framework oxides such as phosphates and germanates with typical absorption and emission maxima at 360 nm and 410 nm, respectively, it is apparent that there is a systematic variation in the spectral characteristics of open-framework chalcogenide materials.

The electronic band gaps of open-framework chalcogenides are generally smaller than open-framework oxides and many of them are in the visible range. The optical properties of metal chalcogenides could be tuned by varying their framework compositions. Dehnen *et al.* have reported the optical absorption behaviors of a series of metal selenides and tellurides with ternary anions $[M_4X][(\text{Sn}X_4)_4]^{10-}$ ($M = \text{Zn}, \text{Cd}, \text{Mn}, \text{Hg}, X = \text{Se}, \text{Te}$).⁴⁴ The band gap decreases by 0.05–0.1 eV when going from $M = \text{Zn}$ through Cd and Mn to Hg for both series. Also, by changing the chalcogen atoms in the cluster from Se to Te, the band gap is decreased by 0.7–0.9 eV. In the case of open-framework metal chalcogenides, gallium selenides show optical transitions with band gaps between 1.4 and 1.7 eV. These band gaps are considerably smaller than those of corresponding gallium sulfides, which are about twice as large (2.6–2.8 eV). It appears that the framework anions generally have a more significant impact on the band gap than framework cations. The band gaps of metal chalcogenides can also be tuned by changing the extra-framework species. For example, the band gap of $[(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}_2]_5\text{In}_5\text{Sb}_6\text{S}_{19}$ is decreased from 2.62 to 2.38 eV after the organic cations is replaced by Cs^+ cation through ion exchange.⁷¹

It is of particular interest that the optical properties of cadmium sulfides are dependent on the size of C_n clusters. For example, the solution containing C3,4 clusters with 54 cadmium cations shows an absorption peak with the maximum at 353 nm.³⁷ In comparison, the absorption peak for the solution containing C2,2 clusters with 32 cadmium cations is blue shifted to 327 nm, as expected from the quantum size

effect. The solution containing C1 clusters with 17 cadmium cations shows a less well defined peak around 291 nm that may contain contributions from absorption by surface ligands.

Metal chalcogenides also exhibit photoelectronic effect upon photoexcitation. For example, when the $\text{SnO}_2(\text{F-doped})/\text{CMF-4}/\text{Nafion}$ electrode was subjected to excitation with visible light ($\lambda > 400 \text{ nm}$), a sharp photocurrent was generated.⁶¹ The photogenerated electrons in the CMF-4 are collected by SnO_2 to generate anodic current. Thus, a steady photocurrent can be observed in the CMF-4-based photoelectrochemical cells. The on–off cycles of illumination confirmed the reproducibility of the transient photocurrent response of the CMF-4 film. The I–V characteristics of the $\text{SnO}_2(\text{F-doped})/\text{CMF-4}/\text{Nafion}$ electrode shows an increased photocurrent generation with an increase in anodic potentials, suggesting that the CMF-4 film possesses *n*-type semiconductor behavior.

The electrical conductivity of chalcogenides may consist of contributions from both electronic and ionic conductions. The open-framework construction tends to lower the electronic conductivity while promoting the ionic contribution. For open-framework metal chalcogenides containing organic species as the structure-directing agents, relatively small electrical conductivity has been observed and the conductivity generally increases with increasing humidity. For example, alternating-current impedance measurements on a single crystal of OCF-6GaSe-TMDP show a humidity-dependent behavior of the electrical conductivity.⁵⁰ With increasing relative humidity, the specific conductivity increases by over 2 orders of magnitude and ranges from $1.32 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$ at 84.9% relative humidity to $5.37 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$ at 100% relative humidity. The direct synthesis of three-dimensional inorganic chalcogenides containing mobile alkali and alkaline earth metal cations has led to a new class of fast-ion conductors. These crystalline inorganic chalcogenides integrate zeolite-like architecture with high anionic framework polarizability and high concentrations of mobile cations. These structural features are particularly desirable for enhancing ionic conductivity. At room temperature and under relative humidity of 30% or higher, the specific conductivity of these materials is comparable to or exceeds previously known crystalline sodium or lithium conductors. For example, at 18 °C, the conductivity of ICF-5CuInS-Na ranges from $1.0 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$ under 0.2% relative humidity to $1.2 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$ under 100% relative humidity.²⁸ At about 26 °C, the conductivity of ICF-26 ranges from $0.011 \Omega^{-1} \text{ cm}^{-1}$ at 29.8% relative humidity to $0.15 \Omega^{-1} \text{ cm}^{-1}$ at 100% relative humidity, which is the highest specific conductivity achieved among crystalline open-framework chalcogenides.³⁵ In comparison, the ionic conductivity for ICF-29 containing highly ordered extra-framework Na^+ cations is quite low. At room temperature and under relative humidity less than 50%, its conductivity is smaller than $10^{-8} \Omega^{-1} \text{ cm}^{-1}$.⁷²

8 POTENTIAL APPLICATIONS

The use of crystalline porous semiconductors as photocatalysts possesses several unique advantages. First, the band structure, including band positions and band gaps, of open-framework semiconductors could be tuned within a given compositional domain by controlling framework architectures. Second, the open architecture may help to increase the number of active reaction sites because of the high surface area, and reduce the rate of charge recombination of the electron–hole pair because the electron or hole in open structures may not need to migrate all the way to the external surface of the catalyst particle for a reaction to occur. A comparative study of porous sulfides and compositionally related dense phases showed that porous sulfides have a significantly higher photocatalytic activity for hydrogen generation. For example, upon irradiation with visible light, about $18 \mu\text{mol h}^{-1} \text{ g}^{-1}$ of H_2 gas was produced from an aqueous solution of Na_2S (0.5 M) over the ICF-5CuInS-Na catalyst.⁷³ This activity was maintained for over 96 h and more than 890 mmol of H_2 gas evolved during this period. The quantum efficiency for ICF-5CuInS-Na was determined to be about 3.7% at 420 nm without the use of Pt cocatalyst. Even though the quantum yield of ICF-5CuInS-Na catalyst is lower ($\approx 35\%$) than that of the well-known Pt/CdS photocatalyst, the efficiency was considerably improved over two anhydrous dense phases with similar compositions: CuInS_2 with the cubic ZnS structure and CuIn_5S_8 with the spinel structure. The quantum yield of CuIn_5S_8 with the cocatalyst Ag_2S was reported to be smaller than 0.02% at 460 nm, while the efficiency of CuInS_2 was even lower.

Crystalline porous chalcogenides can also serve as hosts for the incorporation of metal complexes, organic dyes, or other optically active species into their cavities. The synergetic effects in such host–guest materials are often desirable for applications in solar cells, photocatalysis, and sensing. For example, the $[\text{Fe}(2,2'\text{-bipyridine})_3]^{2+}$ complex could be incorporated into UCR-20GaGeS through ion exchange.⁷³ X-ray powder diffraction (XRD) patterns before and after ion exchange were nearly identical; however, the absorption of the composite material was extended from the UV region to the visible-light region. This composite material showed photocatalytic activity for the generation of hydrogen under irradiation with visible light ($\lambda > 420 \text{ nm}$) for at least 24 h with SO_3^{2-} ions as the sacrificial agent. In comparison, the photocatalytic activity of both $[\text{Fe}(2,2'\text{-bipyridine})_3]^{2+}$ and UCR-20GaGeS-TAEA was also studied in the presence of the same sacrificial agent. They did not show observable activity in the visible-light region even though UCR-20GaGeS-TAEA was found to exhibit activity under the UV light. Only after ion exchange of $[\text{Fe}(2,2'\text{-bipyridine})_3]^{2+}$ into UCR-20 GaGeS-TAEA did the resulting hybrid material show activity in the visible-light region.

Crystalline metal chalcogenides have also been studied for heavy-metal remediation. Compared with oxide-based materials like zeolites, open-framework chalcogenides may be more suitable for removing heavy-metal ions from waste water because of their framework compositions (i.e., S, Se, Te). Kanatzidis *et al.* reported that an open-framework indium selenide, $(\text{NH}_4)_4\text{In}_{12}\text{Se}_{20}$, could undergo ion exchange with heavy-metal ions such as Hg^{2+} , Pb^{2+} , and Ag^+ .⁷⁴ The capacity of this material to remove heavy-metal ions from water solutions was found to be quite high. Specifically, it can remove 99.9% of Hg^{2+} , 99.8% of Ag^+ , and 94.9% of Pb^{2+} from aqueous solutions. Also interesting is the selectivity of some open-framework chalcogenides for Cs^+ in ion-exchange processes. Even when Cs^+ is in relatively low concentration and in the presence of several competitive cations (e.g., Li^+ , Na^+ , K^+ , Rb^+), the selectivity for Cs^+ is still high, suggesting possible application for the ^{137}Cs remediation in nuclear wastes.

9 ACKNOWLEDGMENTS

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10 RELATED ARTICLES

 Nano-/Microporous Materials: Hydrogen Storage
 Materials; Nano-/Microporous Materials: Hydrothermal Synthesis of Zeolites

11 ABBREVIATIONS AND ACRONYMS

BPEA = 1,2-bis(4-pyridyl)ethane; CMF-*m* = capped metal-chalcogenide framework, no. *m*; COV-*m* = covalent metal-chalcogenide framework, no. *m*; DABCO = 1,4-diazabicyclo[2,2,2]-octane; DMF = N,N-dimethylformamide; DMSO = dimethyl sulfoxide; HCF-1 = hybrid chalcogenide framework, no. 1; ICF-*m* = inorganic chalcogenide framework, no. *m*; OCF-*m* = organically directed chalcogenide framework, no. *m*; SPH = benzenethiolate; TAEA = tris-(2-aminoethyl)-amine; TMDP = 4,4'-trimethylenedipiperidine; TMDPy = 1,3-trimethylenedipyridine; UCR-*m* = University of California, Riverside, no. *m*, where *m* is an integer indicating a particular structure type. The *m* is followed by the composition of framework atoms and the name of extra-framework species (e.g., UCR-20GaGeS-TAEA).

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Abstract: This article describes the recent research progress in the field of crystalline metal-chalcogenide superlattices containing tetrahedron-shaped nanoclusters as building units. With the development of new synthetic strategies and structural concepts, new clusters that are members of three series of tetrahedral clusters (i.e., supertetrahedral clusters, pentasupertetrahedral clusters, and capped supertetrahedral clusters) have been prepared and organized into extended frameworks with a variety of topologies, such as single diamond, double diamond, ABW, CrB₄, SOD, cubic C₃N₄, UCR-1, ICF-24, ICF-25, α - and β -quartz, moganite, and boracite. These materials show rich compositional diversities with tunable optical properties, microporosity, and ion-exchange properties, suggesting their potential applications in photocatalysis, fast-ion conductors, solar cells, etc.

Keywords: nanostructured material; microporous material; open framework; metal chalcogenide; tetrahedral cluster; superlattice.

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