

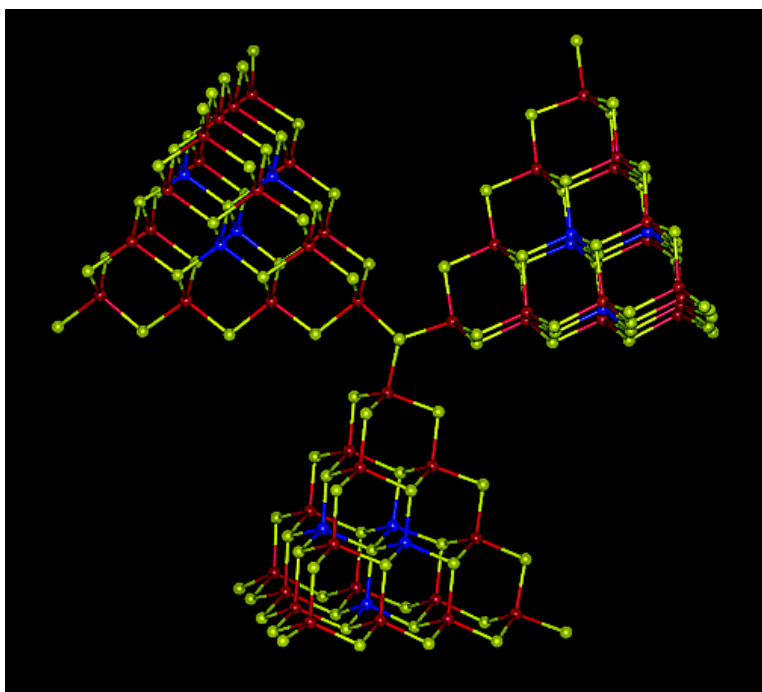
Communication

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Templated Assembly of Sulfide Nanoclusters into Cubic-C₃N₄ Type Framework

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Supertetrahedral clusters (denoted as T_n, n = 2, 3, 4 ...) are regular tetrahedrally shaped fragments of the cubic semiconducting ZnS type lattice.^{1–10} For isolated T_n clusters, the formulas for T_n (n = 2–5, n is the number of metal layers) are M₄X₁₀, M₁₀X₂₀, M₂₀X₃₅, and M₃₅X₅₆, respectively, where M is a metal ion and X is a chalcogen.^{2,3} Recently, supertetrahedral clusters have been found to be useful for the construction of porous covalent superlattices.^{2–11} By replacing regular tetrahedral atoms with T_n clusters in structures such as diamond, crystalline micro- and mesoporous solids with large pore size and high pore volume could be generated. This is because the ring size defined as the number of tetrahedral atoms is increased by n times. An increase in the ring size is important because crystalline porous materials with a ring size larger than 12 are rather scarce, but highly desirable for applications involving large molecules.

Two noticeable limitations exist in known superlattices built from supertetrahedral clusters. One is the inter-cluster linkage mode among supertetrahedral clusters. So far, supertetrahedral clusters are invariably joined together by bi-coordinated sulfur bridges. Another limitation is the tendency to form the interpenetrating, centrosymmetric diamond-type net.^{3,6,8} This is often undesirable because in addition to reducing the pore size and pore volume, the centrosymmetry resulting from the intergrowth of two nets hampers the efforts aimed at integrating electronic and optical functionality into these chalcogenide structures.

Here we report a series of compounds (collectively denoted as UCR-8) that possess a type of framework topology never previously observed in open framework solids. Because of the large cluster size and the elimination of the intergrowth of two nets, the volume fraction of the inorganic framework in UCR-8 is as low as 38%.

UCR-8 can be synthesized in more than one chemical composition from a nonaqueous solvent by employing different divalent cations such as Fe²⁺, Co²⁺, Zn²⁺, or Cd²⁺ (Table 1).¹² In UCR-8, the inter-cluster S²⁻ atom simultaneously bridges three supertetrahedral clusters to form a rare (3, 4)-connected three-dimensional framework with alternating 4-connected cornerless T₄ clusters (M₄In₁₆S₃₁, M = Fe, Co, Zn, and Cd) and 3-connected sulfur atoms (Figure 1). Prior to this work, a sulfur atom has not been known to bridge more than two supertetrahedral clusters. In a (3,4)-connected framework (Figure 2), the ratio of tetrahedral clusters to trigonal atoms is inversely proportional to their connectivity (i.e., 3:4). Therefore, the overall formula of the framework is (Zn₄In₁₆S₃₁)₃-(S)₄, which can also be written as (Zn₁₂In₄₈S₉₇)²⁶⁻.

UCR-8 has a framework topological type identical to that of the theoretically calculated cubic carbon nitride (cubic-C₃N₄) with S substituting for trigonally coordinated N atoms and Zn₄In₁₆S₃₁ substituting for tetrahedral carbon atoms (Figure 2).¹³ A number of carbon nitride polymorphs have been proposed (e.g., α-C₃N₄, β-C₃N₄, pseudocubic-C₃N₄, and graphite-C₃N₄). Among these

Table 1. A Summary of Crystallographic Data for UCR-8 Structures

name	framework formula	a (Å)	R(F)	2θ _{max}
UCR-8FeInS-DBA	(Fe ₁₂ In ₄₈ S ₉₇) ²⁶⁻	35.090(4)	6.41	40
UCR-8CoInS-DBA	(Co ₁₂ In ₄₈ S ₉₇) ²⁶⁻	35.002(3)	6.75	45
UCR-8ZnInS-DBA	(Zn ₁₂ In ₄₈ S ₉₇) ²⁶⁻	34.981(4)	6.11	45
UCR-8CdInS-DBA	(Cd ₁₂ In ₄₈ S ₉₇) ²⁶⁻	35.194(8)	8.79	32

^a Structures were solved from single-crystal data collected at 298 K on a SMART CCD diffractometer with Mo Kα. R(F) = Σ ||F_o| - |F_c|| / Σ |F_o| with F_o > 4.0σ(F). The space group is I-43d for all compounds.

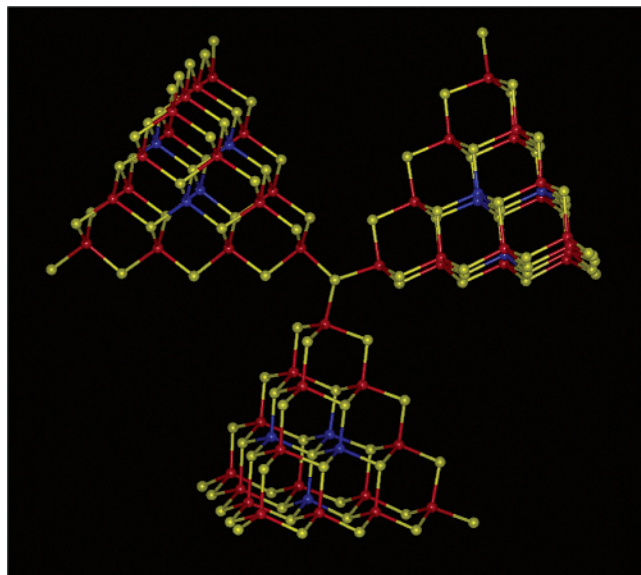


Figure 1. Three T₄ clusters, M₄In₁₆S₃₅ (M = Fe²⁺, Co²⁺, Zn²⁺, and Cd²⁺), are joined together by sharing a tri-coordinated sulfur: red, In³⁺; blue, M; yellow, S²⁻.

polymorphs, the cubic-C₃N₄ topology is of outstanding theoretical and technological interest because its bulk modulus is expected to exceed that of diamond. It has been suggested that the cubic-C₃N₄ may potentially be synthesized under high pressure and quenched to ambient pressure for use as a super-hard material.

The core of the M₄In₁₆S₃₁ cluster, a tetrahedrally coordinated sulfur atom, occupies the same position as the C atom in the cubic-C₃N₄. The coordination environment of the 3-connected vertex (i.e., S²⁻) is quite planar and has an In–S–In angle of 117.0°. The In–S–In angles in UCR-8 range from 104.1° to 117.0° and the formation of the cubic-C₃N₄ type framework in UCR-8 seems related to such flexibility of the In–S–In angle, particularly, the ability to form an angle near 120°.

If only the 4-connected vertex (the core tetrahedral sulfur site) and the 3-connected vertex (the bridging S²⁻ site) are considered, the angle surrounding the 3-connected vertex is even closer to the planarity (118.8°). The angle surrounding the 4-connected vertex

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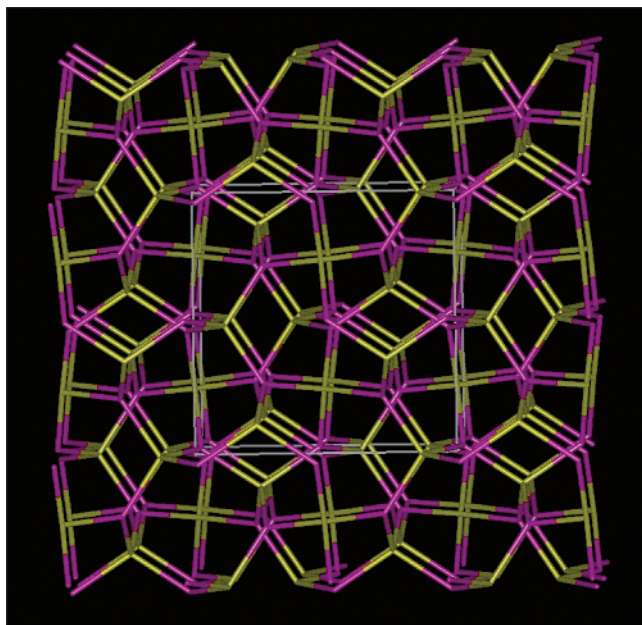


Figure 2. The mixed (3,4)-connected, non-centrosymmetric, non-interpenetrating three-dimensional cubic- C_3N_4 type framework projected down the unit cell axis. The purple sites represent the tri-coordinated S sites that are common corners of three T4 clusters. The yellow sites represent the center (i.e., the core tetrahedral S site) of T4 clusters.

is 107.5° and 113.4° . Therefore, ideal angles of 120° and 109.5° are not achieved at either vertex. The tetrahedral configuration around the 4-connected vertex highlights the difference between UCR-8 and another (3,4)-connected net (i.e., the Pt_3O_4 net) on which a recently reported metal-organic framework is based.^{14,15} In the Pt_3O_4 net, the 4-connected vertexes are in square planar coordination.

In comparison, in UCR-1 built from the same T4 clusters, the bridging sulfur site connects to two supertetrahedral clusters with the In–S–In angle of 106.5° . In UCR-8, the In–S–In angle expands by over 10° to 117.0° when a third supertetrahedron is added to the bridging sulfur atom. This is apparently because of the repulsion effect between supertetrahedral clusters.

The three-dimensional framework of UCR-8 consists of rings of four supertetrahedral clusters and four bridging sulfur atoms. In terms of the number of tetrahedral atoms, the ring size is 16. Compared to the C–N distance of 1.46 \AA in the cubic- C_3N_4 phase, the distance from the 3-connected vertex to the 4-connected vertex in UCR-8 is increased by over 6 times to 9.51 \AA (cubic unit cell lengths: 5.40 \AA for cubic- C_3N_4 and $\approx 35.0 \text{ \AA}$ for UCR-8, Table 1).¹³ The average dimension of six edges of the T4 cluster measured between corner metal atoms is 11.5 \AA . The large size of the T4 supertetrahedron leads to a large extra-framework space that is about 62% of the crystal volume as calculated with the program PLATON.¹⁶ This extra-framework space is occupied by highly disordered and charge-balancing organic guest molecules. Such a large extra-framework space is also related to the fact that UCR-8 has a non-interpenetrating framework.

The nitrogen adsorption measurements at 78K on Cs^+ exchanged samples of UCR-8 did not show the presence of the microporosity. In open framework sulfides templated with organic cations, it has

been found that the generation of microporosity depends on the nature of inorganic cations and it is possible to obtain microporosity if a suitable inorganic cation is found to help exchange out organic cations and stabilize the inorganic framework.¹¹

The incorporation of divalent cations into indium sulfide clusters is related to the valence sum requirement of the tetrahedrally coordinated sulfur atom at the core of the T4 cluster. To satisfy the Pauling's valence sum rule, divalent ions such as Zn are needed around the core tetrahedral S^{2-} site.^{3,8,10} Each of the four divalent cations contributes a bond valence of $2/4$ so that the valence sum around the tetrahedral S^{2-} is 2, consistent with the valence of the sulfur anion (Figure 1). The presence of divalent cations is supported by the structural refinement and the microprobe elemental analysis.

Despite the disorder of guest amine molecules, they exert an essential structure-directing role. Many different amines have been examined under similar conditions and only dibutylamine (DBA) is capable of directing the formation of the cubic- C_3N_4 type topology. UCR-8ZnInS-DBA has also been found to exhibit a strong photoluminescent emission (fwhm $\approx 100 \text{ nm}$) centered at 470 nm when excited at 410 nm .

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

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- (12) An example of a typical synthesis condition with the preparation of UCR-8ZnInS-DBA is as follows. Indium metal (123.6 mg), sulfur (121.6 mg), $Zn(NO_3)_2 \cdot 6H_2O$ (125.5 mg), di-*n*-butylamine (2.1036 g), and ethyleneglycol (4.2520 g) were mixed in a 23 mL Teflon-lined stainless steel autoclave and stirred for about 20 min. The vessel was then sealed and heated at $150^\circ C$ for 6 d. The autoclave was subsequently allowed to cool to room temperature. Clear tetrahedral crystals were obtained with an approximate yield of 36%.
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