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Three-Dimensional Covalent Co-Assembly between Inorganic Supertetrahedral Clusters and Imidazolates[**]

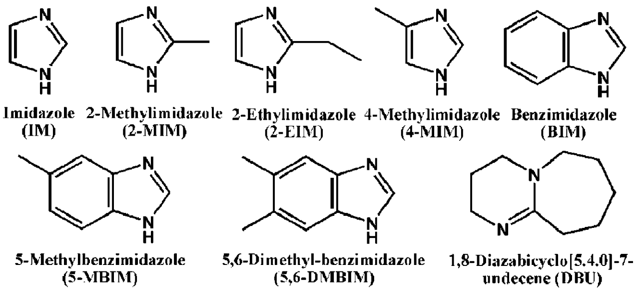
*Tao Wu, Ripsime Khazhakyan, Le Wang, Xianhui Bu, Shou-Tian Zheng, Victoria Chau, and Pingyun Feng**

Supertetrahedral chalcogenide clusters are of high current interest because their unique compositions and structures allow them to border several research areas including semiconductor nanoparticles, crystalline porous materials, and inorganic–organic hybrid framework materials.[1–8] While each of these research areas has undergone dramatic growth in recent decades, integration of synthetic and structural concepts from these different areas into a coherent synthetic methodology to develop new families of materials that combine functionalities of these individual material types is still at a nascent stage.[4] Composite materials in which chalcogenide clusters and organic functional molecules are covalently assembled into ordered 3D arrays belong to such new families of materials.

The assembly of chalcogenide clusters into extended frameworks generally occurs by sharing of anionic sulfur (or selenium) sites at four corners of each cluster, leading to extended frameworks with all linkages made through inorganic components.[9] For example, 3D inorganic frameworks made from T3 (e.g., $[In_{10}S_{20}]^{10-}$), T4 (e.g., $[In_{16}Cd_4S_{35}]^{14-}$), and T5 (e.g., $[Cu_5In_{30}S_{56}]^{17-}$) clusters are all known.[10] This type of intercluster linkage mode (i.e., M-X-M, X = S, Se) is common, in part because of the compatibility between inter- and intracluster M–X bonds. A more complex situation occurs when organic ligands are used to cross-link inorganic clusters, because of the need for matching the disparate intracluster (M–X) and intercluster (M–L, L = organic ligands) bond types. For example, the strong M–L interaction could lead to extraction of metal ions from chalcogenide clusters to form coordination polymers with monomeric metal sites.[11]

Integration of organic components into chalcogenide superlattices offers opportunities not only for new structures types, but also synergistic properties resulting from inorganic and organic components through their uniform integration at the molecular level. During the past decade, the covalent organization of Cd–S–SPh-based tetrahedral clusters into 1D chains and 2D layers has been achieved.[12] Recently, further progress has led to 1D and 2D assembly of inorganic Ga–S supertetrahedral clusters.[4,13] Despite these promising advances, a number of limitations still existed prior to this work, including: 1) only neutral organic ligands (usually bipyridine types) have been shown to function as cross-linkers between tetrahedral clusters; 2) only low-dimensional (0D, 1D, and 2D) superlattices have been made; and 3) for supertetrahedral clusters, the size of the cluster is limited to T3 with 10 metal sites.[4]

In this work, we seek to explore a new type of chemistry at the interface of two seemingly unrelated types of materials: 1) inorganic chalcogenide clusters and frameworks (e.g., CdInS-44-$[Cd_4In_{16}S_{33}]^{10-}$, UCR-17-$[Cu_5In_{30}S_{54}]^{13-}$), and 2) zeolitic imidazolate frameworks, commonly called ZIFs (e.g., [Zn(2-methylimidazolate)$_2$]).[14] We report here a new family of 3D four-connected superlattices (denoted supertetrahedral cluster imidazolate frameworks, SCIF) comprising supertetrahedral T3 and T4 clusters linked by imidazolate ligands (Scheme 1 and Table 1). The size and geometry of their pore space can be influenced by the size of the cluster and the type of substituents on the imidazolate. Their semiconducting properties (e.g., electronic band gaps) can also vary. One member of this family also displays permanent porosity with CO_2 uptake capacity comparable to those of some porous metal-organic framework materials.[15]



Scheme 1. Imidazole and derivatives and template amine.

Prior to this work, inorganic supertetrahedral frameworks were generally prepared by redox reactions between metal and nonmetal elements in the presence of different amines.[10] Under such conditions, we have found that addition of imidazole (or its derivatives) provides some control over the assembly processes, and leads to various 3D inorganic framework materials such as UCR-2,[16] UCR-7,[10b] ASU-31,[5c] ASU-32,[5c] ASU-34,[5b] and a previously unknown phase

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[*] T. Wu, R. Khazhakyan, L. Wang, V. Chau, Prof. P. Feng
Department of Chemistry, University of California
Riverside, CA 92521 (USA)
Fax: (+1) 951-827-4713
E-mail: pingyun.feng@ucr.edu
Prof. X. Bu, Dr. S.-T. Zheng
Department of Chemistry and Biochemistry
California State University, Long Beach
1250 Bellflower Boulevard, Long Beach, CA 90840 (USA)

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Table 1: Summary of crystal data and refinement results.[a]

Name	Framework composition	Space group	S.B.U.	*a* [Å]	*b* [Å]	*c* [Å]	*R*(*F*)	Net
SCIF-1	$[In_{10}S_{16}(IM)_2]^{4-}$	*Pbca*	T3 cluster $(In_{10}S_{16})^{2-}$	22.5121(6)	22.6610(6)	33.3409(10)	0.0521	D.D.
SCIF-2	$[In_{10}S_{16}(2\text{-}MIM)_2]^{4-}$	*C2/c*		49.9905(16)	68.2851(21)	25.5907(8)	0.0938	D.D.
SCIF-3	$[In_{10}S_{16}(2\text{-}EIM)_2]^{4-}$	$I\bar{4}2d$		25.0958(2)	25.0958(2)	36.6912(5)	0.0785	D.D.
SCIF-4	$[In_{10}S_{16}(4\text{-}MIM)_2]^{4-}$	*Pbca*		22.6617(3)	22.5629(4)	33.7015(4)	0.0710	D.D.
SCIF-5	$[In_{10}S_{16}(BIM)_2]^{4-}$	$P2_12_12_1$		21.2772(10)	21.4180(10)	36.0100(17)	0.0724	D.D.
SCIF-6	$[In_{10}S_{16}(MBIM)_2]^{4-}$	*Pbca*		22.4388(11)	22.4165(10)	33.9940(16)	0.0547	D.D.
SCIF-7	$[In_{10}S_{16}(DMBIM)_2]^{4-}$	*Pbca*		22.5220(3)	22.4835(4)	34.4841(5)	0.0571	D.D.
SCIF-8	$[In_{16}Cd_4S_{31}(2\text{-}EIM)_2]^{8-}$	$I\bar{4}2d$	T4 cluster $(In_{16}Cd_4S_{31})^{6-}$	30.8096(46)	30.8096(46)	16.6159(25)	0.0649	T.D.
SCIF-9	$[In_{16}Cd_4S_{31}(DMBIM)_2]^{8-}$	*Pbca*		25.7722(10)	25.6993(11)	48.340(2)	0.1459	D.D.
OCF-31	$[In_8S_{15}]^{6-}$	$P2_12_12_1$	P1 cluster	18.1936(24)	18.3672(25)	22.1072(28)	0.1018	S.D.

[a] $\beta = 91.159(2)°$ for SCIF-2. S.B.U. = secondary building unit, S.D. = single diamond, D.D. = double diamond, T.D. = triple diamond.

called OCF-31 (Scheme S1 and Figure S1, Supporting Information). Thus, when starting from elemental forms, clusters tend to self-assemble with themselves, instead of co-assembling with imidazolate.

By choosing both soluble metal and sulfide sources as precursor, a series of SCIF-*n* ($n = 1$–9) with T3 or T4 clusters have been made by using 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) as template and their structures determined by single-crystal X-ray diffraction. These SCIFs are constructed from T3 or T4 clusters interlinked by various imidazolate ligands (Figure 1 a and b), and their negatively charged frameworks are balanced by lithium cations and protonated DBU molecules ($HDBU^+$). These SCIFs adopt interpenetrating diamond-type topology (by treating an entire cluster as a single tetrahedral node, Figure 1 e, g, i, and k). The degree of interpenetration (i.e., 2-fold versus 3-fold) is related to the size of both clusters and imidazolate ligands. All SCIFs with T3 clusters exhibit twofold interpenetration (Figure 1 f, j and Figures S2 and S3 of the Supporting Information). With larger T4 clusters, threefold interpenetration, which has not been observed before in chalcogenide superlattices, can also be realized, as in SCIF-8 (Figure 1 h). However, twofold interpenetration can be restored with T4 clusters by using a more bulky imidazolate ligand, as in SCIF-9 (Figure 1 l). SCIF-8 and SCIF-9 are the first examples of covalent assembly of T4 clusters by an organic ligand. Prior to this work, T4 clusters had not been assembled into any dimension by any organic ligand. Even though these SCIFs exhibit the same diamond-type framework topology, they have quite different space-group symmetries and various channel geometries. The highest symmetry occurs when 2-ethylimidazolate is used.

The synthesis of SCIFs is a significant advance in several aspects. For the first time, supertetrahedral chalcogenide clusters have been cross-linked with anionic organic ligands (imidazolates in this case). The SCIFs are also the first 3D covalent inorganic–organic superlattices with chalcogenide tetrahedral clusters as one of the building blocks. While 3D frameworks comprising only supertetrahedral clusters are well known,[5,9,11] all previous efforts to cross-link tetrahedral chalcogenide clusters of any composition (e.g., organic-capped Cd–S–SPh system or inorganic Ga–S system) with organic ligands have only resulted in formation of low-dimensional structures (up to 2D).[13]

Formation of SCIFs depends on achieving a suitable balance among a number of factors. The complexity of the assembly can be seen from T4-containing SCIF-8 and SCIF-9 which require the assembly of a number of individual solution species (In^{3+}, Cd^{2+}, S^{2-}, IM^-, plus extra-framework charge-balancing and pore-filling species such as $HDBU^+$), each of which plays a unique role. From such initial solubilized species, a much higher structural hierarchy (i.e., large T4 clusters templated by cations and cross-linked by organic anions) is established. It is noteworthy that the chemistry of DBU is unique, because among many amines used for the synthesis, it is so far the

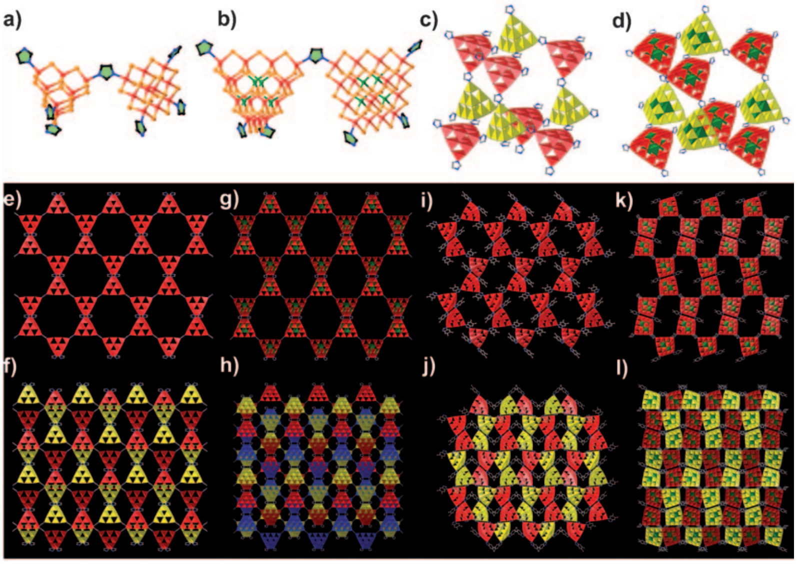

Figure 1. Connectivity of supertetrahedral chalcogenide T3 (a) and T4 (b) clusters cross-linked by imidazolates. Classical adamantane-like unit based on T3 cluster (c) and T4 cluster (d) in SCIFs. 3D single net and twofold-interpenetrated frameworks with diamond topology in SCIF-3 (e, f). Single net and threefold-interpenetrated frameworks with diamond topology in SCIF-8 (g, h) viewed down the *b* axis, with ethyl group omitted for clarity. 3D single and twofold-interpenetrated frameworks with diamond topology in SCIF-7 (i, j) and SCIF-9 (k, l), viewed down the *b* axis.

only one that has been found to template the formation of SCIFs.

Given the aforementioned complex multicomponent chemical system, it is not unreasonable to expect that multiple competing pathways for assembly into 3D (or lower dimensional) frameworks should exist. For example, T*n* clusters can self-assemble into purely inorganic frameworks, while Cd imidazolate can form ZIF-type porous MOFs.[17] Clearly the chemistry and bonding of the SCIF system lies at the interface between inorganic chalcogenide frameworks and ZIF materials. The benefit of co-assembly between chalcogenide clusters and imidazolates is the potential of such composite systems for incorporating new structural patterns and properties (e.g., semiconductivity).

Solid-state diffuse-reflectance UV/Vis spectra were recorded for SCIF-3, -7, -8, and -9 (Figure 2). The effect of the cluster size is obvious by comparing band gaps of T3-containing SCIF-3 (3.35 eV) and SCIF-7 (3.43 eV) with those of T4-containing SCIF-8 (3.12 eV) and SCIF-9 (3.22 eV). The difference in band gap between materials with the same cluster size is less prominent and can result from the effect of imidazolate ligands and the related change in lattice symmetry. The trend seems to be that the compound with higher symmetry (e.g., tetragonal SCIF-3 versus orthorhombic SCIF-7) has a smaller band gap. In fact, a similar trend is also observed in solid TiO_2 semiconductors (3.03 eV for rutile and 3.18 eV for anatase), in which the symmetry of TiO_6 pseudo-octahedra in rutile is higher than that in anatase.

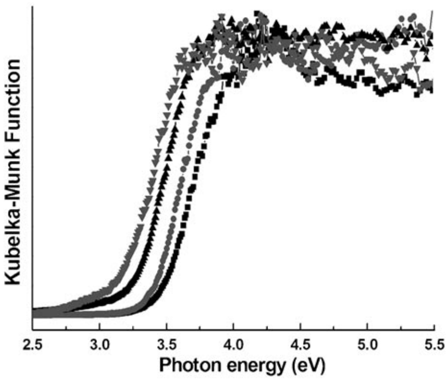

Figure 2. Normalized solid-state UV/Vis absorption spectra of SCIF-3, -7, -8, and -9. ■ SCIF-7 (5,6-DMBIM/T3); ● SCIF-3 (2-EIM/T3); ▲ SCIF-9 (5,6-DMBIM/T4); ▼ SCIF-8 (2-EIM/T4).

The above-observed variation of band gaps with crystal symmetry is likely determined by the p–π interactions between the sulfur atoms (near the corners of the supertetrahedra) and imidazolate π rings. Such interaction is strongly affected by the relative orientation of these two building blocks (i.e., cluster and imidazolate). A more parallel aligned p–π system gives a smaller band gap, and a more distorted alignment results in a wider band gap. To further support this, we performed quantum chemical calculations based on their crystal structures. Because of the relatively weak long-range interactions between clusters, we only focus on a molecular moiety, as shown in Figure S4 of the Supporting Information. The DFT calculations were performed with B3LYP functional and LANL2DZ basis set by using the G09 package.[18] The modeling systems were built to simulate two extreme cases involving perfectly aligned and most-distorted p–π systems. Figure S4 (Supporting Information) depicts the p–π conjugation in the T3–ethylimidazole–T3 moiety. The results show that in the perfectly aligned system, electrons are delocalized through the imidazolate ring onto both sides. However, such delocalization is dramatically decreased when distortion is introduced. While this preliminary simulation does not capture the whole picture of the crystal lattice, the results do help to better understand the experimental data and support the use of ligand–cluster interactions to control local orientations of framework building units as a means in band gap engineering.

The permanent porosity of SCIF-3 was confirmed by CO_2 gas sorption measurements on Micromeritics ASAP 2020 surface-area and pore-size analyzer. Compared to the bridging S^{2-} anions in T3 and T4 inorganic frameworks (such as UCR-5 and UCR-7), the longer and less negative (−1 vs. −2) imidazolate ligands contribute to the porosity, because fewer protonated template molecules are required to balance the less negative charge of the SCIF framework. However, framework distortion, bulky substituents on the imidazolate ring, and multifold interpenetration tend to reduce the porosity. Considering all these factors, SCIF-3 was chosen as a promising candidate for gas sorption analysis, because of its high symmetry, small substituent, and lower degree of interpenetration (Figure S5, Supporting Information). A sample of SCIF-3 was degassed at 100 °C prior to the measurement, and its stability on degassing was confirmed by PXRD (Figures S6 and S7, Supporting Information). While no obvious N_2 adsorption was observed, significant CO_2 uptake capacity (18.6 $cm^3 g^{-1}$ at 1 atm and 273.15 K, Figure 3) was found. This capacity is comparable to those of some quite porous metal–organic framework materials such as BIF-3.[19] The difference between N_2 and CO_2 adsorption is likely caused by the smaller dynamic diameter of CO_2 (0.33 nm vs. 0.36 nm for N_2) and the stronger interaction between CO_2 and charged porous environment.[20]

In conclusion, a family of 3D covalent arrays of supertetrahedral chalcogenide clusters and imidazolate ligands has been synthesized, and their unique structure, porosity, and

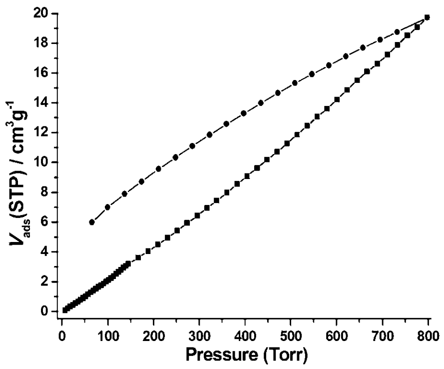

Figure 3. CO_2 gas sorption isotherms of SCIF-3 at 273.15 K. ■ adsorption; ● desorption.

semiconducting properties characterized. These are the first examples of supertetrahedral clusters being assembled with anionic ligands and are beautiful demonstration of integrative chemistry between metal chalcogenides and zeolitic imidazolates. Because of the wide availability of various anionic ligands including carboxylates, the use of negative ligands as a general strategy in co-assembly between chalcogenide clusters and organic ligands could lead to a new generation of hybrid multifunctional porous materials. The work also represents a significant step forward for metal chalcogenide chemistry because of the demonstrated feasibility of using organic ligands to covalently assemble larger supertetrahedral clusters into higher dimensions (3D).

Experimental Section

Typical synthesis of framework SCIF-1: Li_2S (76.3 mg, 1.66 mmol), $In(NO_3)_3\cdot x\,H_2O$ (98.1 mg, 0.326 mmol based on anhydrous indium nitrate), imidazole (72.5 mg, 1.07 mmol) were mixed with 2-amino-1-butanol (1.647 g, 18.5 mmol), acetonitrile (1.220 g, 29.7 mmol), and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU, 1.614 g, 10.6 mmol) in a 23 mL Teflon-lined stainless steel autoclave and stirred for 30 min. The autoclave was then sealed, heated at 150 °C for 12 d, and subsequently cooled to room temperature. Semi-transparent octahedral crystals (7.9 mg) are obtained after washing with ethanol and drying. Additional experimental details are given in the Supporting Information.

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