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Superbase Route to Supertetrahedral Chalcogenide Clusters

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Ⓢ *Supporting Information*

ABSTRACT: Supertetrahedral T*n* clusters are exact fragments of a cubic ZnS type lattice. Thus far, T*n* clusters up to T4 with 20 metal sites can be synthesized in a discrete molecular form. Yet, synthesis of larger discrete supertetrahedral clusters still remains a great challenge, likely due to the rapidly increasing negative charge on the cluster as the size goes up. By using organic superbases (DBN and DBU) to help stabilize the negative charge, a family of discrete supertetrahedral chalcogenide clusters with sizes spanning from T3 (10 metal sites) to T5 (35 metal sites) have been made. The T5 cluster represents the largest molecular supertetrahedral T*n* cluster known to date.

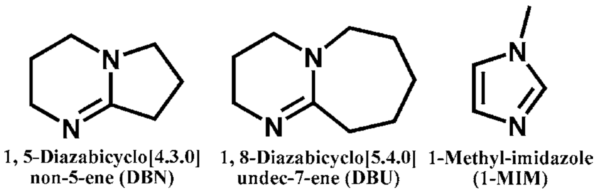
Inorganic nanoscale semiconducting materials, such as colloidal nanoparticles, have attracted great attention due to their diverse applications as a result of the quantum confinement effect.[1,2] Supertetrahedral chalcogenide clusters (T*n*, *n* indicates the number of metal sites along the edge of the tetrahedron), being structurally precise fragments of the well-known cubic ZnS-type semiconductors,[3] can be regarded as the smallest semiconductor nanoparticles and have also been found to exhibit size-dependent optical properties.[4,5] Unlike colloidal nanoparticles, supertetrahedral clusters can be crystallized and their structures analyzed with single crystal X-ray diffraction, which may provide insight into various structure−property relationships such as size-dependent band structures.

There has always been a strong interest in discrete molecular clusters, because they are directly related to both nanosized and nanoporous materials. In the area of open-framework metal chalcogenide materials, tetrahedral clusters can serve as pseudotetrahedral building blocks (artificial atoms with tunable "radii") to allow a rational construction of multidimensional inorganic frameworks or hybrid organic−inorganic frameworks through modular assembly processes,[6−9] in a way similar to the construction of coordination polymers.[10−12] Discrete clusters are also directly comparable to semiconductor nanoparticles in terms of properties such as quantum confinement effects. Furthermore, discrete soluble clusters are amenable for solution processing into various forms such as thin films or incorporated into functionalized semiconducting mesoporous structures or porous gels and aerogels, for potential applications in nanotechnology.[13−15]

One challenge with the synthesis of supertetrahedral clusters is their high negative charge that dramatically increases as the size of the cluster gets bigger. This is because the number of surface chalcogen anions (such as S^{2-}) which are underbonded to metal atoms (2 for edge anionic sites and 3 for facial anionic sites) increases significantly with the size of the cluster. The synthetic strategies developed so far to stabilize supertetrahedral clusters have been mainly focused on decreasing the negative charge on the clusters, for example, by introducing higher-valent metal ions (e.g., In^{3+}, Sn^{4+}) onto the surface,[16,17] by balancing the charge through metal complex cations,[18] or by terminating the cluster corners with neutral ligands.[19] The formation of 3-D frameworks is another way to trap supertetrahedral clusters in a particular size often determined by the host−guest charge density match.

In this work, we rely on two roles of organic species (charge reduction using neutral superbase or imidazole ligands and cluster stabilization using protonated superbases) to target the synthesis of chalcogenide clusters. Our reasoning is that while the lowering of the negative charge is beneficial, it should also be important to develop better ways to help generate and/or stabilize negative clusters. As a result of this thinking, we started to investigate the roles of organic superbases in the synthesis of chalcogenide clusters. Herein, we report a family of isolated hybrid supertetrahedral chalcogenide clusters (denoted as **ISC-*n***), which comprise supertetrahedral chalcogenide T*n* (*n* = 3, 4, 5) clusters with four corners terminated by 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) or 1-methylimidazole (1-MIM, Scheme 1). The negative charge of the clusters is balanced by protonated forms of organic superbase DBN or DBU (1,8-diazabicyclo[5.4.0]undec-7-ene).

Scheme 1. Template Amidines (Superbases) and Terminal Organic Ligand Used



Prior to the use of organic superbases DBN and DBU, we experimented with neutral pyridine and its derivatives (especially lutidine, the diverse dimethyl substituted derivatives of pyridine), first used by Vaqueiro et al. in the synthesis of Ga−S based T3 clusters.[19] While we were able to prepare two

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Table 1. Summary of Crystal Data and Refinement Results

Name[a]	Cluster Formula[b]	Template	S.G.[c]	C.T.[d]	a (Å)	b (Å)	c (Å)	β (deg)	R (F)
ISC-1	$[Ga_{10}S_{16}(SH)(3,5\text{-}DMP)_3]^{3-}$	H^+-3,5-DMP	$P\bar{1}$	T3	12.3629(1)	12.4197(1)	22.4555(3)	90.322(1)	0.0256
ISC-2	$[Ga_{10}S_{16}(SH)(3,4\text{-}DMP)_3]^{3-}$	H^+-3,4-DMP	R-3		21.7073(1)	21.7073(1)	28.5686(3)	90.0	0.0892
ISC-3	$[In_{10}S_{16}(DBN)_4]^{2-}$	H^+-DBN, Li^+	$P2_1/n$		15.2866(4)	30.0105(7)	20.3917(4)	110.852(1)	0.0828
ISC-4	$[In_{16}Cd_4S_{31}(DBN)_4]^{6-}$	H^+-DBN, Li^+	$P2_1/n$	T4	19.3156(4)	32.7633(8)	23.1691(5)	114.135(1)	0.0851
ISC-5	$[In_{16}Cd_4S_{31}(DBN)_4]^{6-}$	H^+-DBN, Li^+	$I4_1/a$		21.8413(2)	21.8413(2)	36.2785(7)	90.0	0.0714
ISC-6	$[In_{16}Mn_4S_{31}(DBN)_4]^{6-}$	H^+-DBN, Li^+	$I4_1/a$		21.751	21.751	36.119	90.0	/[e]
ISC-7	$[In_{16}Co_4S_{31}(DBN)_4]^{6-}$	H^+-DBN, Li^+	$P2_1/n$		19.61	33.29	24.05	115.87	/[e]
ISC-8	$[In_{16}Fe_4S_{31}(DBN)_4]^{6-}$	H^+-DBN, Li^+	$P2_1/n$		20.32	33.60	24.42	114.64	/[e]
ISC-9	$[In_{22}Cd_{13}S_{52}(1\text{-}MIM)_4]^{12-}$	H^+-DBU, Li^+	$I4_1/amd$	T5	28.0877(4)	28.0877(4)	26.7025(4)	90.0	0.1238[f]
SCIF-10	$[In_{16}Cd_4S_{31}(DMBIM)(DBN)_2]^{7-}$	H^+-DBN, Li^+	$P\bar{1}$	T4	17.5175(5)	17.6943(5)	23.4522(7)	99.634(2)	0.0973

[a] α = 96.0570(10)°, γ = 104.8850(10)° for ISC-1; α = 106.526(2)°, γ = 98.379(2)° for SCIF-10. [b] 3,5-DMP = 3,5-dimethylpyridine; 3,4-DMP = 3,4-dimethylpyridine; DBN = 1,5-diazabicyclo[4.3.0]non-5-ene; 1-MIM = 1-methylimidazole; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; DMBIM = 5,6-dimethylbenzimidazolate. [c] S.G. = space group. [d] C.T. = cluster type. [e] The quality of diffraction data is insufficient for obtaining satisfactory *R*-factors. [f] Before the application of the SQUEEZE routine of A. Spek, R_1 is 0.1946.

previously unknown isolated Ga−S T3 clusters (**ISC-1** and **ISC-2**, Table 1) with different terminal lutidines, our further efforts to expand the cluster size to T4 and T5 and to the indium−sulfide system have resulted in no targeted materials. In addition, DBN was used as the protonated template in the synthesis of an isolated chalcogenide cluster by Yaghi et al.[20]

It becomes clear that the choice of the organic base is crucial. As far as the charge reduction, charge stabilization, and charge balancing are concerned, two key factors with respect to ligands need to be considered: (1) the affinity of the base with the metal ion in the formation of M−N bond, which can reduce the cluster charge by terminating its corners, and (2) the basicity of the superbase which in the protonated form is needed for stabilizing the negative cluster. While a single base may meet both criteria under some special cases (e.g., lutidine in Ga−S T3 system), it is also advantageous to address these two factors separately to accomplish broader success. It is particularly worth noting that when only a single base (e.g., DBU) is used, it may not be able to fulfill both of the above two roles.

By extensive studies of organic superbases, we have determined that DBN can fulfill both the aforementioned roles by serving as the terminating ligand in the neutral form and simultaneously serving as charge-balancing species in the protonated form. This has led to the synthesis of discrete In−S T3 clusters (**ISC-3**) and T4 clusters (**ISC-4** to **ISC-8**). Interestingly, when DBN is supplemented with an imidazole ligand (5,6-dimethylbenzimidazole, DMBIM), two of the terminal DBN ligands can be replaced with deprotonated imidazole ligands), leading to one-dimensional cross-linked T4 chains (**SCIF-10**; see Table 1 and Figure S1). This shows that DBN and imidazolates have comparable affinities for indium and both can simultaneously terminate the cluster corners. Furthermore, the success in the synthesis of SCIF series[9b] of cluster-imidazolate frameworks indicates that 1-substituted imidazole (such as 1-methylimidazole) or its derivatives could also act as terminal ligands to form discrete supertetrahedral Tn clusters.

Indeed, when 1-methylimidazole is used as the terminating ligand, together with DBU for fulfilling the charge balancing and charge stabilization roles, **ISC-9** which contains the largest isolated supertetrahedral T5 nanocluster was obtained. Unlike DBN or imidazolate, DBU, a ligand larger than DBN, does not terminate the cluster corners (in the neutral form) and only serves to stabilize the anionic clusters in the cationic form.

The structures of **ISCs** and **SCIF** were studied by single-crystal X-ray diffraction. **ISC-1** consists of discrete supertetrahedral anionic units of $[Ga_{10}S_{16}(SH)(3,5\text{-}DMP)_3]^{3-}$ (3,5-DMP = 3,5-dimethylpyridine) and three ordered protonated 3,5-DMP cations ($[HNC_7H_9]^+$) (Figure S2). The Ga−N bond length ranges from 2.033(2) to 2.041(2) Å, significantly shorter than the Ga−S(H) bond length [2.2789(10) Å]. **ISC-2** is composed of an isolated T3 cluster $[Ga_{10}S_{16}(H_2O)(3,4\text{-}DMP)_3]^{2-}$ and highly disordered protonated 3,4-dimethylpyridine cations. Unlike **ISC-1**, one corner of the T3 cluster in **ISC-2** is occupied by H_2O with a distance of 2.195(2) Å. Compared with **ISC-1** and **ISC-2**, the discrete supertetrahedral cluster $[In_{10}S_{16}(DBN)_4]^{2-}$ in **ISC-3** is based on the In−S T3 cluster with four corners terminated by neutral DBN molecules with an In−N bond length of 2.208−2.297(2) Å (Figures 1a, S3).

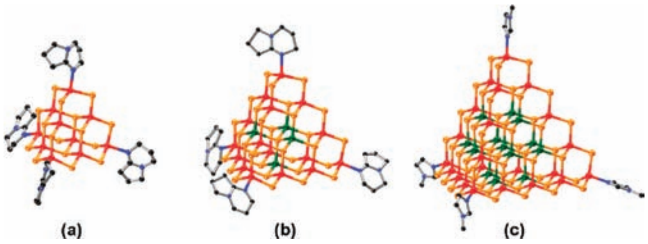

Figure 1. Isolated hybrid supertetrahedral T3 cluster in **ISC-3** (a), T4 cluster in **ISC-4** and **ISC-5** (b), and T5 cluster in **ISC-9** (c) (hydrogen atoms are omitted for clarity; orange balls = S, red = In, green = Cd, blue = N, and black = C).

Unlike the three above-mentioned discrete T3 clusters, **ISC-*n*** (***n*** = **4−8**) contain a larger discrete T4 cluster, $[In_{16}M_4S_{31}(DBN)_4]^{6-}$ (M = Cd^{2+}, Mn^{2+}, Co^{2+}, Fe^{2+}) (Figure 1b), all of which are terminated with four neutral molecules (DBN). The In−N bond length is around 2.245(2) Å, similar to that observed in **ISC-3**. Apparently, the crystallization is quite sensitive to the reaction conditions, as evidenced by the formation of two polymorphs **ISC-4** ($P2_1/n$) and **ISC-5** ($I4_1/a$), composed of similar clusters and protonated DBN (Figure S4).

One of the most important advances reported here is the synthesis of the largest isolated supertetrahedral nanoclusters so far. **ISC-9**, crystallizing in the tetragonal $I4_1/amd$ space group, is composed of a molecular supertetrahedral T5 cluster $[In_{22}Cd_{13}S_{52}(1\text{-MIM})_4]^{12-}$ (Figures 1c and S5) with four organic molecules as terminal ligands at the corners and highly disordered template molecules. This T5 cluster resembles the core−shell nanoparticles with the central core $\{Cd_{13}S_4\}$ being capped by an $\{In_{22}S_{48}\}$ shell, and then further capped by four neutral organic molecules through In−N coordination bonds at four corners. It is worth noting that T5 clusters were first reported almost 10 years ago.[21] But prior to this work, they only existed as a part of the covalent 2D and 3D frameworks. Isolated T5 clusters have not been made until the combined use of superbase DBU as the template and 1-MIM as the terminal ligand.

Although the positions of In and S in this T5 cluster were determined accurately, the guest atoms filling the cavities between the clusters, and even most of the C atoms (except N atoms bonded to terminal In^{3+} ions) in the terminal ligands, were not located due to the orientational disorder. Nevertheless, elemental microanalysis and ^1H NMR measurement confirmed the presence of 1-MIM and protonated DBU. As shown in Figure 2 (line e), signals from 1-MIM and protonated H^+-DBU are observed by comparison of line f with lines b and d.

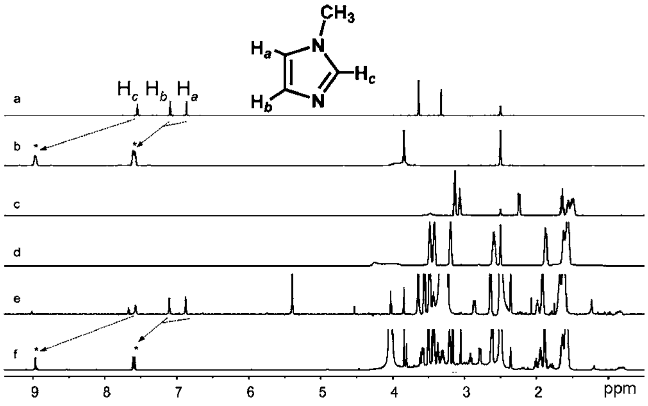

Figure 2. ^1H NMR spectra (500 MHz, DMSO-d_6, 298 K) of (a) 1-methyl-imidazole (1-MIM); (b) addition of 50 μL of DCl (1 M in D_2O) to (a); (c) 1,8-diazabicyclo[5,4,0]-7-undecene (DBU); (d) addition of 50 μL of DCl (1 M in D_2O) to (c); (e) solution part of **ISC-9** in DMSO-d_6; (f) addition of 50 μL of DCl (1 M in D_2O) to (e).

Further elemental analysis through atomic absorption spectroscopy (AAS) gives the Cd/In ratio as 1:1.81, close to the calculated value (1:1.69) in the formula. The purity of the as-synthesized sample was supported by PXRD, which matches well with its simulated diffraction pattern (Figure S6). The crystal shape, elongated square bipyramid, is also in agreement with the predicated crystal morphology (Figure S7).

Solid-state diffuse reflectance UV−vis spectra were studied by using crystalline samples of **ISC-3**, **-5**, and **-9** (Figure 3).

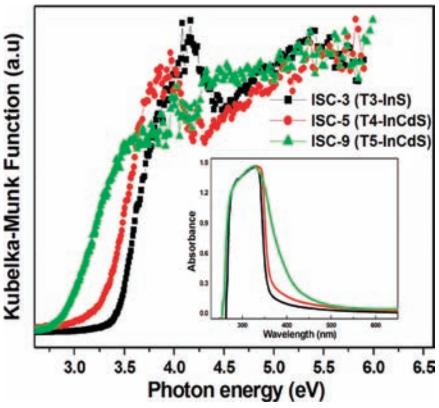

Figure 3. Normalized solid-state UV−vis absorption spectra of **ISC-3**, **ISC-5**, and **ISC-9** with different sizes of supertetrahedral clusters. The inset is UV−vis absorption spectra of these samples dissolved in organic solvents (**ISC-3** in DMF; **ISC-5** and **-9** in DMSO) at room temperature.

The band gaps of **ISC-3**, **ISC-5**, and **ISC-9** are 3.42, 3.27, and 2.87 eV, respectively, indicating a remarkable red shift. Such a wide variation of energy gap is a result of the roles of both compositional variations and quantum confinement effect. Due to their molecular nature, **ISC-*n*** materials are soluble in organic solvents, such as DMSO and DMF. The inset in Figure 3 gives the absorption spectra of the filtrates of crystalline **ISC-3**, **ISC-5**, and **ISC-9** in DMF or DMSO at room temperature. It is clear that the larger nanocluster exhibits a wider UV−vis absorption band. The photoluminescence properties of **ISC-*n*** (*n* = 3, 5, 9) have also been studied, which exhibit strong and broad emission at room temperature (Figure S8). The FWHMs for their emission peaks range from 70 to 100 nm. With the increasing size of clusters, both the maxima of excitation wavelengths (centered at 377, 392, and 437 nm, respectively) and emission wavelengths (centered at 460, 480, and 512 nm, respectively) show a gradual red shift. These emission maxima nicely lie between that of bulky In_2S_3 (~450 nm) and CdS (~520 nm).

In conclusion, by using organic superbases, either individually (in both neutral and protonated forms) or in combination with imidazoles, we have synthesized a series of isolated and one-dimensionally cross-linked supertetrahedral chalcogenide T*n* clusters. The synthetic success in creating the currently largest isolated T5 cluster demonstrates the feasibility for continued success in the quest for even larger supertetrahedral chalcogenide clusters that will seamlessly blend the size gap between small molecular clusters and larger colloidal nanoparticles. The use of organic superbases in the synthesis of chalcogenide materials opens a new route in the development of novel semiconducting clusters and frameworks.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental preparation, extra figures of description of structure, powder X-ray diffraction, SEM picture of crystals. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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