A photochemical route to discrete, ternary metal chalcogenide clusters†

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Ternary clusters $Cu_9In_{10}S_9(SEt)_{21}(PPh_3)_3$ and $Cu_{11}In_6S_7(S^tBu)_{15}$ were isolated from the UV-photolysis products of precursors $(PPh_3)_2CuIn(SEt)_4$ and $(PPh_3)_2CuIn(S^tBu)_4$, respectively, and structurally characterized.

Discrete, well-defined nanoscale clusters of semiconducting materials have been pursued for many years to model the growth and properties of bulk materials. These clusters have become more significant lately due to the explosion of interest in zero- and one-dimensional nanocrystalline materials and their special quantized properties.[1–3] In fact, clusters now serve as ideal models for nanocrystals, which are often non-uniform in size and structure and are ill-defined in their surface composition. Versatile methods for fabricating these clusters in a size- and shape-selective fashion and in a manner that will allow their surface chemistry to be manipulated will offer exquisite control over the optoelectronic properties and surface reactivity of these materials, and therefore benefit the various applications for which nanomaterials are currently being explored.

Metal chalcogenide clusters are typically prepared by metathesis reactions involving salt[4] or silane[5,6] elimination, the rearrangement of small clusters into larger ones,[7] or the condensation of small clusters with additional building blocks under solvothermal conditions.[3,8,9] Herein, we describe a new method for the fabrication of discrete, Cu–In–S ternary clusters *via* the photolytic decomposition of single source molecular precursors.

Complexes with the general formula $(R_3Pn)_2Cu(\mu\text{-}ER')_2\text{-}In(ER')_2$ (Pn = P, As; E = S, Se; R = alkyl, aryl), originally developed by Hirpo *et al.*,[10] have been used as single source precursors (SSPs) for the chemical vapor deposition of thin films of the photovoltaic materials $CuInE_2$[11–14] and also for the synthesis of $CuInE_2$ nanoparticles[15–18] *via* solvothermal and photochemical decomposition. We found that UV irradiation of solutions of $(R_3P)_2CuIn(SR')_4$ (R = Ph, octyl; R′ = propyl, *tert*-butyl) in organic solvents affords ultrafine nanoparticles of the ternary semiconductor $CuInS_2$ in the 1–2 nm size range.[18] Thioethers and phosphine sulfides are byproducts of the photolysis process. Since precursor decomposition was complete within five hours under UV irradiation from a mercury-arc lamp, we explored the possibility of isolating discrete clusters from the initial stages of the photolysis.

A toluene solution of $(Ph_3P)_2Cu(\mu\text{-}SEt)_2In(SEt)_2$[10] was photolysed for five hours, layered with methanol (normally used to precipitate nanoparticles), and left undisturbed in the dark for five days. Red polycrystalline spheres formed along with large yellow crystals. The latter crystals were suitable for a single crystal X-ray analysis. The molecular structure‡ of the resulting ternary cluster, **1**, is shown in Fig. 1.

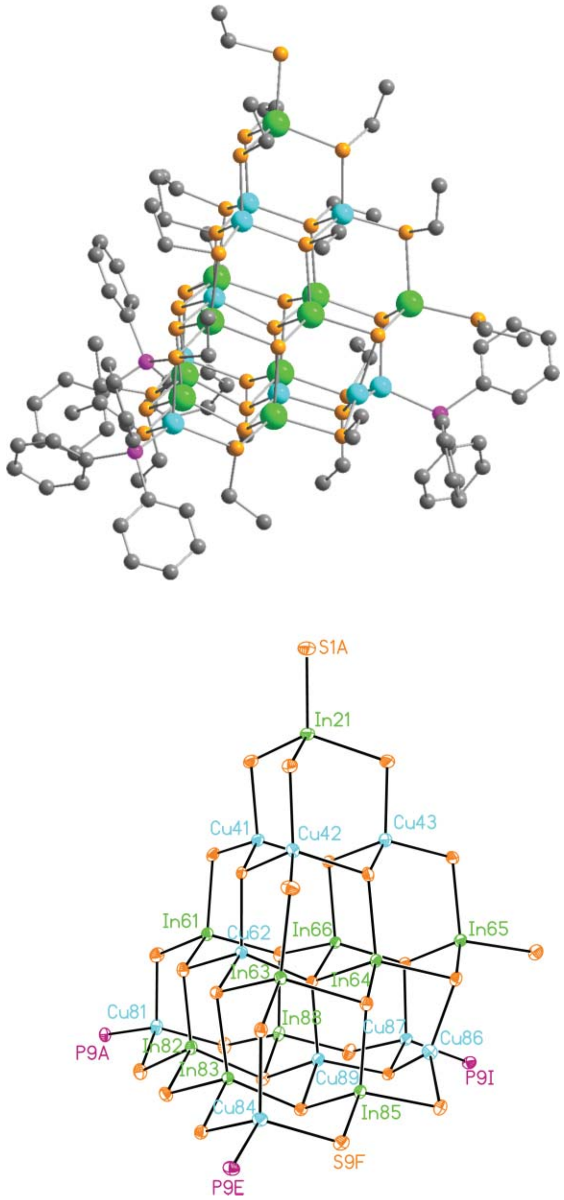

Fig. 1 Top: ball and stick drawing of cluster **1**. Hydrogen atoms are omitted for clarity. Bottom: thermal ellipsoid drawing (30%) of the inorganic core of cluster **1** with atom labeling scheme.

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The cluster contains a ternary $Cu_9In_{10}S_{30}$ inorganic core. Twenty one of the surface sulfurs are capped with ethyl groups, which are mostly disordered, and three copper atoms at the base of the cluster are capped with triphenylphosphine ligands. The inner core of **1** is an incomplete T4 supertetrahedral cluster[8] only missing a metal and two sulfur atoms to complete the corner. The cluster exhibits the adamantoid structure of bulk $CuInS_2$ with the exception of the copper/indium atom position swap between Cu42 and In64. The incomplete corner has one copper atom capped with a phosphine ligand and the other copper is three-coordinate. A smaller, structurally similar, copper-rich, anionic cluster $[PPh_4][Cu_6In_3(SEt)_{16}]$ was isolated by Hirpo *et al.* from the reaction of $[Cu(CH_3CN)_4][PF_6]$ with $[PPh_4][In(SEt)_4]$.[19] This partial T3 cluster was also missing a corner, leaving three uncapped trigonal planar copper atoms. It also differs from **1** by the absence of capping phosphine ligands and its negative charge. The Cu–S bond distances of the trigonal copper atoms in both **1** and $[PPh_4][Cu_6In_3(SEt)_{16}]$ are comparable (2.22–2.28 Å and 2.19–2.6 Å), however, the Cu–S bond distances of the tetrahedral atoms are significantly shorter in the latter cluster (2.29–2.39 Å compared to 2.44–2.49 Å). Thus, there is less variation in the Cu–S bond distances for different copper coordination geometries in the larger cluster, **1**. The longest dimension of the Cu–In–S core of **1** (*e.g.* from S1A to S9F) is 1.4 nm. Including the peripheral organic groups increases the size of the cluster to 2 nm. Significantly, the orange powder that was precipitated from the mother liquor using methanol following isolation of the crystals exhibited an X-ray powder pattern consistent with that of the single crystals (see ESI†).

The photolysis product of the SSP $(Ph_3P)_2CuIn(S^tBu)_4$ was studied to determine the effect of the alkylthiolate group on the size and composition of the cluster. Red crystalline needles were isolated from a toluene solution and the structure§ of cluster **2** is shown in Fig. 2. This cluster contains a copper rich core with the formula $Cu_{11}In_6S_{22}$. Fifteen *tert*-buyl groups cap the surface of the cluster. All eleven copper atoms in the cluster are three-coordinate. There is a high concentration of copper atoms at the center of the cluster, and the trigonal planar geometry causes a constriction resulting in short Cu–Cu distances ranging from 2.66 to 2.78 Å. This distorts the cluster from the adamantoid geometries of **1** and $[PPh_4][Cu_6In_3(SEt)_{16}]$. Although the possible existence of d^{10}–d^{10} cuprophilic interactions is still a matter of debate,[20,21] spectroscopic evidence of such an interaction has been reported for a dinuclear copper complex[22] and the electron density map of the simple oxide Cu_2O indicated covalent Cu–Cu interaction.[23] Theoretical calculations are under way to explore the bonding in **2** in greater detail.

We are exploring the photochemical decomposition of other new SSPs containing different functional groups on the alkylthiolate ligands. For example, photolysis of the new ester-containing precursor $(PPh_3)_2CuIn(SCH_2CH_2C(O)OMe)_4$ (**3**) affords a highly crystalline product that has, so far, eluded single-crystal X-ray structure characterization but exhibits an X-ray powder pattern that matches closely that of bulk $CuInS_2$ (roquesite) (see ESI†). Future work will be directed at understanding the mechanism of cluster formation and determining if this precursor photolysis method can be used to isolate discrete, uniformly sized clusters on a preparative scale.

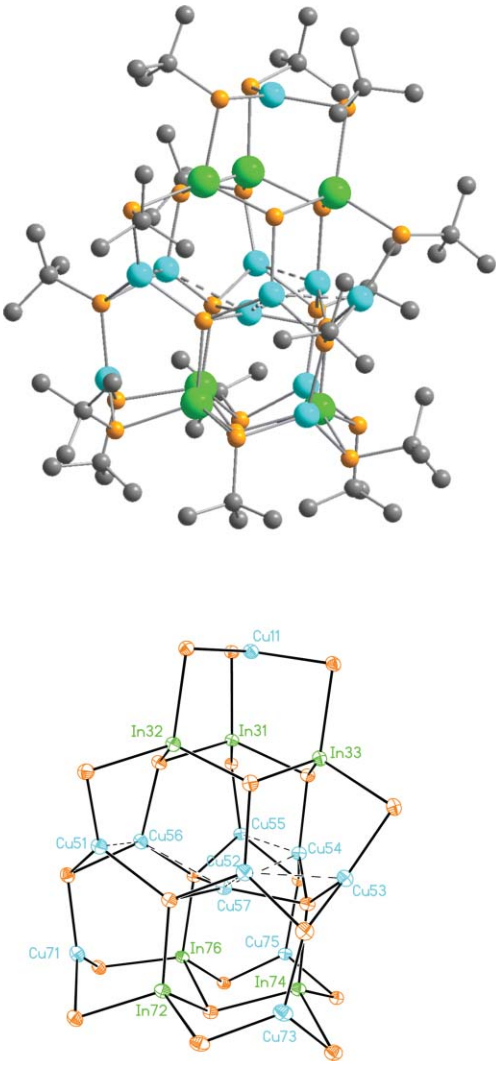

Fig. 2 Top: Ball and Stick drawing of cluster **2**. Hydrogen atoms are omitted for clarity. Bottom: Thermal ellipsoid plot (30%) of ternary core of **2** with atom labelling scheme.

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Notes and references

‡ *Crystal data*: **1** + C_7H_8: $C_{103}H_{158}Cu_9In_{10}P_3S_{30}$, M = 4171.06, triclinic, space group $P\bar{1}$ (#2), T = 89(2) K, a = 19.356(4), b = 19.767(4), c = 20.455(4) Å, α = 73.244(3), β = 89.939(4), γ = 74.387(3)°, V = 7193(3) Å^3, Z = 2, D_c = 1.926 g cm^{-3}, μ(Mo-Kα) = 33.8 cm^{-1}, F(000) = 4104. Yellow fragment, 0.22 × 0.11 × 0.06 mm^3. Collected reflns = 107092, data/restraints/parameters = 26046/43/1213, S = 1.043, R_1 = 0.0675, wR_2 = 0.1505 [$|F_o| > 2\sigma|F_o|$), 2θ = 25.25°]. CCDC 636541. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b702541f

§ *Crystal data*: **2** + 1.5 C_7H_8: $C_{70.50}H_{147}Cu_{11}In_6S_{22}$, M = 1049.66, monoclinic, space group $P2(1)/c$ (#14), T = 90(2) K, a = 25.295(5), b = 19.684(4), c = 23.290(5) Å, β = 100.149(4), V = 11415(4) Å^3, Z = 4, D_c = 1.797 g cm^{-3}, μ(Mo-Kα) = 36.2 cm^{-1}, F(000) = 6140. Orange truncated pyramid, 0.41 × 0.34 × 0.31 mm^3. Collected reflns = 156802, data/restraints/parameters = 20673/40/946, S = 1.014, R_1 = 0.0425, wR_2 = 0.0930 [$|F_o| > 2\sigma|F_o|$), 2θ = 25.25°]. CCDC 636542. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b702541f. More detailed crystallographic experimental information is given in the ESI.†

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