Supplementary material (ESI) for Chemical Communications

Supplementary Information for:

A photochemical route to discrete, ternary metal chalcogenide clusters

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General considerations:

All manipulations were performed using glove box and Schlenk/vacuum line techniques. Methanol and methylene chloride were dried over CaH_2 and distilled prior to use. Toluene and benzene were dried over Na and distilled prior to use. NMR spectra were acquired on a Bruker AMX 300 NMR spectrometer (300 MHz ^1H; 75.5 MHz ^{13}C; 121.5 MHz ^{31}P). ^1H and ^{13}C spectra were referenced to solvent signals. ^{31}P spectra were reference to an external H_3PO_4 standard ($\delta = 0$). UV-vis spectra were obtained on a Ocean Oprtics, Chem 2000-UV-VIS instrument. Photoluminescence spectra were obtained on a HoribaJobin Yvon FluoroMax-3 instrument. Micropowder analysis was preformed on a modified[1] Bruker SMART APEX system in Debye-Scherrer mode with exposures of 1200 x 2 seconds. Data was Collected using SMART[2] and interpreted and integrated using GADDS.[3]

Synthesis of $(Ph_3P)_2CuIn(S^tBu)_4$. Single source precursors were prepared according to a previously described procedure.[4] $Na[InS^tBu]_4$ was prepared by adding 0.48 ml (4.26 mmol) 2,2-dimethylpropanethiol to a methanol solution of $NaOCH_3$ formed by adding sodium (0.102 g, 4.45 mmol) to 15 mL methanol. After 30 min a methanol solution of $InCl_3$ (0.2308 g, 1.04 mmol) was added via cannula and the reaction mixture stirred for an

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[1] S. Guggenheim, University of Illinois at Chicago, Simulations of Debye-Scherrer and Gandolfi Patterns Using a Bruker SMART/APEX Diffractometer System, ACA, Chicago 2004; S. Guggenheim, Bruker Application Note 373.

[2] SMART v. 5.632, Bruker AXS, Madison, WI, 2005

[3] GADDS v. 4.1.16, Bruker AXS, Madison, WI, 2004

[4] Banger, K.K.; Jin, M.H.-C.; Harris, J.D.; Fanwich, P.E.; Hepp, A.F. Inorg. Chem. **2003**, *42*, 7713.

additional 1.5 hours. PPh_3 (0.574 g, 2.19 mmol) and CuCl (0.114 g, 1.15 mmol) were combined in 15 ml of CH_2Cl_2 and the mixture was added dropwise to the $Na[InStBu]_4$ solution. The reaction mixture was stirred overnight, affording a light yellow solution with a white precipitate. The white precipitate was collected by filtration and then redissolved in ca. 20 mL CH_2Cl_2 and filtered through celite to remove residual NaCl. The solvent was removed under reduced pressure, affording $(Ph_3P)_2CuIn(S^tBu)_4$ as a white solid (0.6079g, 55% yield) ^1H NMR (300 MHz, $CDCl_3$) δ 7.41-7.35 (br m, 30H, $P(C_6H_5)_3$), 1.47 (s, 36H, $SC(CH_3)_3$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.7 (d, J_{CP}=17 Hz, $P(C_6H_5)_3$), 130.43 (s, $P(C_6H_5)_3$), 129.55 (d, J=8.5Hz, $P(C_6H_5)_3$), 47.58 ($SC(CH_3)_3$), 37.86 ($SC(CH_3)_3$); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ -1.91; Anal. calcd for $C_{52}H_{66}CuInS_4P_2$: C, 58.94; H, 6.28; Found: C, 58.19; H, 6.46.

Synthesis of $(Ph_3P)_2CuIn(SCH_2CH_2CO_2Me)_4$ (3). The same procedure was used as described above for $(Ph_3P)_2CuIn(S^tBu)_4$**.** The reaction of Na[In(SCH2CH2CO2Me)4] (7.69 mmol) with CuCl (0.1976 g, 2.00 mmol) and PPh_3 (1.0323 g, 3.94 mmol) afforded **3**, which was precipitated as a white powder from a methanol/toluene solution cooled at 0ºC (1.5284 g; 69 % yield); ^1H NMR (300 MHz, $CDCl_3$) δ 7.34-7.27 (m, 30H, $P(C_6H_5)_3$), 3.59 (s, 12H, $SCH_2CH_2CO_2CH_3$), 2.84 (t, 8H, CH_2), 2.53 (t, 8H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.72 (d, J_{CP}=11Hz, C_6H_5), 129.66 (s, C_6H_5), 128.74 (d, J_{CP}=7.35, C_6H_5), 51.48 (CH_2), 38.96 (CH_2) ppm; ^{31}P NMR (121 MHz, $CDCl_3$) δ -1.55; Anal. calcd for $C_{52}H_{58}O_8CuInS_4P_2$: C, 52.95; H, 4.96; Found: C, 52.67; H, 4.83.

Isolation of $Cu_9In_{10}S_9(SEt)_{21}(PPh_3)_3$ (1). A quartz cuvette fitted with a glass/teflon needle valve was charged with 0.19g (0.23 mmol) $(Ph_3P)_2Cu(\mu\text{-}Et)_2In(Et)_2$ and in 6mL dry toluene. The vessel was sealed under nitrogen and the clear, colorless solution was irradiated with a medium pressure mercury arc lamp for 5 hrs, over which time the solution turned bright yellow. The toluene solution was layered with 20 mL methanol and stored in the dark, undisturbed for 5 days. Slow diffusion of the methanol into the toluene solution produced red polycrystalline spheres interspersed with yellow, needle-like crystals. Rapid mixing of the methanol and toluene phases caused precipitation of an orange-yellow powder. The yellow crystals were isolated for an X-ray crystal structure determination, yielding the structure of **1**. In a separate preparation, 0.16 g (0.16 mmol) of precursor was dissolved in 19 mL dry benzene. The solution was photolyzed in a sealable quartz cuvette for 5 hrs. with stirring. The benzene was removed from the photolysis product under reduced pressure and the residue was redissolved in CH2Cl2, and the solution was layered with acetone, affording 26 mg (6.3 μmol) of **1** as a microcrystalline powder after 1 day. A yield of 37% of **1** is calculated based on the requirement of 10 equivalents of precursor to obtain one equivalent of $Cu_9In_{10}S_9(SEt)_{21}(PPh_3)_3$. UV/vis (RT, $CHCl_3$): $\lambda_{max} = 265$ nm. Photoluminescence: (RT, $CHCl_3$): $\lambda_{max} = 498$ nm (fwhm = 98 nm; excitation at 372 nm).

Isolation of $Cu_{11}In_6S_7(S^tBu)_{15}$ (2). The modified quartz cuvette was charged with $(Ph_3P)_2CuIn(S^tBu)_4$ (0.15 g, 0.14 mmol) and 12 mL dry toluene. Irradiation of the colorless solution for 5.5 hours afforded a red-orange solution. The solution was concentrated to about 2 ml and layered with methanol and left undisturbed at room temperature for 14 days after which orange X-ray quality crystals of **2** had formed. In a separate preparation 0.10 g of $(Ph_3P)_2CuIn(S^tBu)_4$ μmol was dissolved in 17 mL benzene in a quartz cuvette sealed under a nitrogen atmosphere, and the solution was irradiated for 7 hrs. The solvent was removed under reduced pressure and the yellow solid residue was dissolved in $CHCl_3$ and purified on a silica gel column by eluting PPh_3 and Ph3P=S impurities with CH_3Cl and then eluting the product with acetone. The acetone solution was dried and the product was precipitated from a toluene solution treated with methanol, affording 7.6 mg of product. A 29% yield of **2** is calculated based on the requirement of at 11 equivalents of $(Ph_3P)_2CuIn(S^{t}Bu)_4$ to obtain one equivalent of $Cu_{11}In_6S_7(S^{t}Bu)_{15}$. UV/vis (RT, $CHCl_3$): λ_{max} = 262 nm. Photoluminescence: (RT, $CHCl_3$): λ_{max} = 494 nm (fwhm = 67 nm; excitation at 370 nm).

Crystallography Experimental. Crystals of compound **1** [**2**] were removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber and placed in the low-temperature nitrogen stream.[5],Data were collected at 89(2) [90(2)] K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans of 0.3 ° per frame for 30 [40] seconds, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.83 Å for both compounds. Cell parameters were retrieved using SMART[2] software and refined using SAINTPlus[6] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.[7] The structure was solved by direct methods and refined by least squares method on F^2 using the SHELXTL program package.[8] The structure was solved in the space group P-1 (#2) [P2(1)/c (# 14)] by analysis of systematic absences.

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[5] Hope, H. *Prog. Inorg. Chem.*, **1994**, *41*, 1.

[6] SAINTPlus: v. 7.23a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, **2004**.

[7] SADABS: v.2004/1, an empirical absorption correction program, Bruker AXS Inc., Madison, WI, **2004**.

[8] SHELXTL: v. 6.14, Structure Determination Software Suite, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, **2004**.

In cluster **2**, many of the ethyl groups were disordered (50% occupancy) and were held isotropic. Bond distance and thermal parameter restraints were used to stabilize these groups. The apical sulfur (S1a, S1a') was also disordered (50% occupancy) but was refined anisotropically.

In cluster **4**, three tBu groups were disordered and refined with partial occupancies, bond distance and thermal parameter restraints (C26a 66%, C31a 50%, C38a 30%). The solvent molecules were also disordered in 5 positions and were modeled as rigid groups. Their occupancies were allowed to refine, yielding 1.5 toluene molecules per cluster. All disordered groups were held isotropic.

All other non-hydrogen atoms in both clusters were refined anisotropically. No decomposition was observed during data collection for either compound.

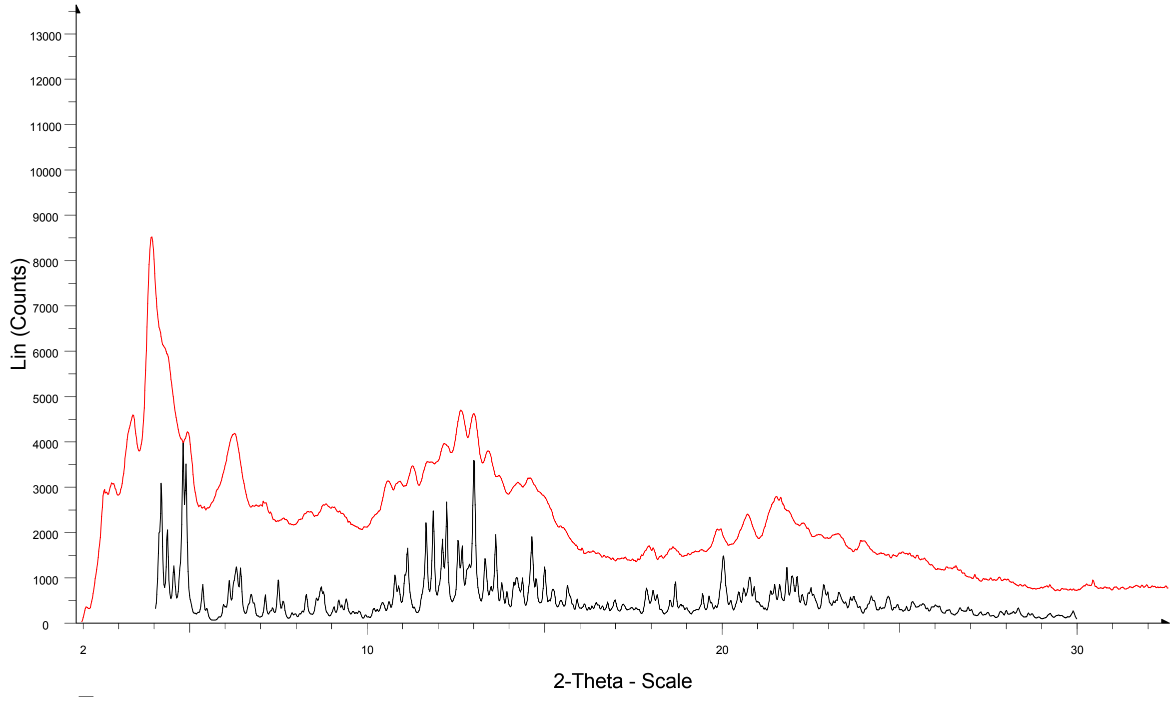

Figure 1. The black line spectrum is the powder pattern from the X-ray crystal structure of ***1****. The red line spectrum is the measured powder pattern of the orange-yellow powder precipitated from the toluene solution of the photolysis product of* $(PPh_3)_2CuIn(Et)_4$.

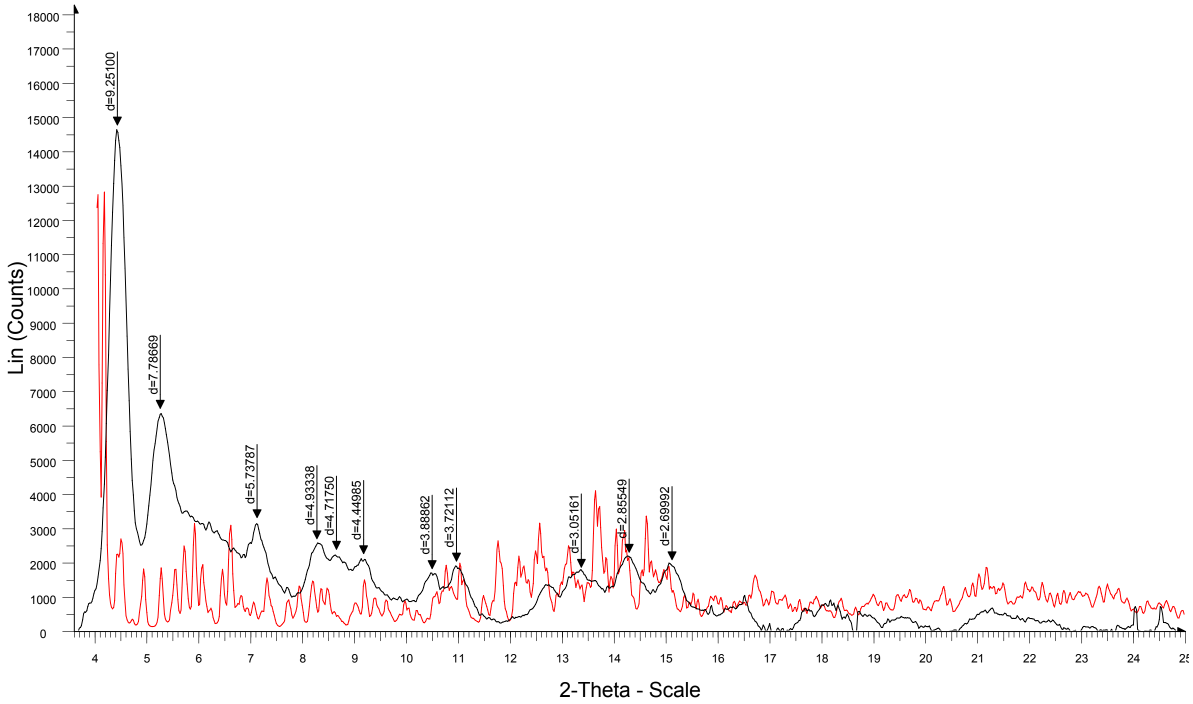

Figure 2. The red line spectrum is the powder pattern for the single crystal of ***2***. *The black line spectrum is the measured powder pattern of the yellow powder precipitated from the toluene solution of the photolysis product of* $(PPh_3)_2CuIn(^tBu)_4$.

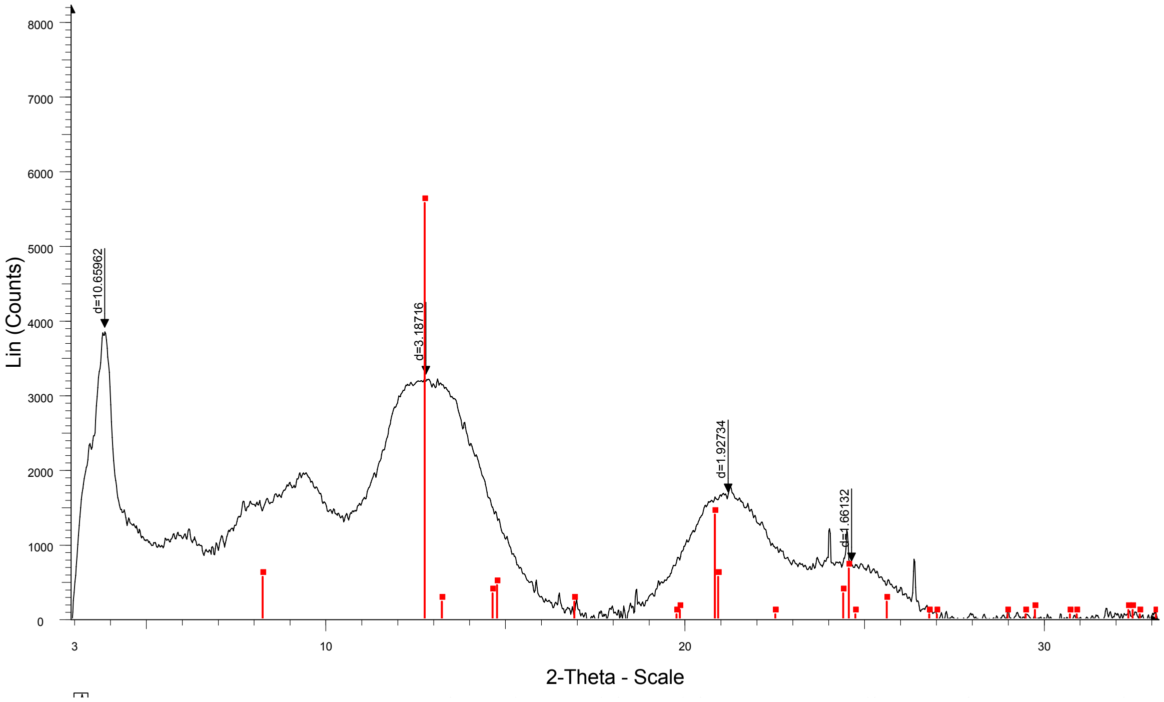

Figure 3. The black line spectrum is the measured powder pattern from the red crystals grown from the photolysis product of .. The red lines are a reference spectrum for bulk $CuInS_2$ (roquesite).