Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information for

Synthesis and molecular structure of a spheroidal binary nanoscale copper sulfide cluster

Sebastian Bestgen*, Olaf Fuhr, Peter W. Roesky, Dieter Fenske*

[*] Dr. S. Bestgen, Prof. Dr. P. W. Roesky,
Prof. Dr. D. Fenske
Institute of Inorganic Chemistry
Karlsruhe Institute of Technology (KIT)
Engesserstraße 15, 76131 Karlsruhe (Germany)
E-Mail: sebastian.bestgen@kit.edu
E-Mail: dieter.fenske@kit.edu

Dr. O. Fuhr, Prof. Dr. D. Fenske
Institute of Nanotechnology (INT)
and
Karlsruhe Nano Micro Facility (KNMF)
Karlsruhe Institute of Technology (KIT)
Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen,
Mailbox 3640, 76021 Karlsruhe (Germany)

Dr. O. Fuhr, Prof. Dr. D. Fenske
Lehn-Institute for Functional Materials, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou, People's Republic of China

Experimental Section

General procedures: All manipulations were performed under rigorous exclusion of moisture and oxygen in Schlenk-type glassware or in an argon-filled MBraun glovebox. Hydrocarbon solvents (toluene, *n*-pentane) were dried using an MBraun solvent purification system (SPS-800). Elemental analyses were carried out with an Elementar Micro Cube. [$CuSCH_2C_6H_4t$Bu] was synthesized following known procedures[1] for copper thiolates from $CuSO_4{\cdot}5H_2O$, $NH_2OH{\cdot}HCl$, NH_3 and (4-(tert-butyl)phenyl)methanethiol. Triphenylphosphine PPh_3 was obtained from TCI and used as received.

Synthesis of $[Cu_{52}S_{12}(SCH_2C_6H_4{}^t\mathrm{Bu})_{28}(PPh_3)_8]$ (1):

The copper(I) thiolate $[CuSCH_2C_6H_4{}^t\mathrm{Bu}]$ (450 mg, 1.85 mmol, 1.00 eq.) and triphenylphosphine (375 mg, 1.43 mmol, 0.77 eq.) are suspended in toluene (25 mL) and stirred for 5 minutes at room temperature. $S(SiMe_3)_2$ (0.08 mL, 68 mg, 0.38 mmol, 0.20 eq.) is added with a syringe. Within two hours, a color change from yellow to dark red is observed and a clear solution is obtained. After 24 hours of stirring, the solvent is removed under vacuum and *n*-heptane (35 mL) is added. A brownish precipitate forms, which is subsequently removed by filtration to afford a dark red solution, which is stored at room temperature for two days. Red crystals are formed at the wall of the Schlenk-tube. These are separated from the mother liquor by decantation. The crystals are washed with n-pentane (3 x 15 mL) and finally dried under high vacuum. Yield: 105 mg (32 % with respect to the limiting reagent $S(SiMe_3)_2$). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3051 (m), 2956 (vs), 2903 (m), 2866 (m), 1510 (m), 1475 (m), 1432 (m), 1361 (m), 1267 (vw), 1229 (m), 1199 (w), 1099 (m), 1020 (w), 876 (w), 828 (w), 742 (m), 692 (s), 551 (w), 515 (m), 429 (vw). Elemental analysis calcd. (%) for [$C_{452}H_{540}Cu_{52}P_8S_{40}$ x 3 C_7H_{14}] (10807.87): C 51.17, H 5.28, S 11.55; found C 51.74, H 5.06, S 11.51.

UV-Vis measurements

UV-Vis measurement of was performed with a LAMBDA 900 spectrometer (Perkin-Elmer) from a suspension of grinded crystals in mineral oil between two quartz plates under air at room temperature. The absorption wavelength of the HOMO-LUMO gap was calculated by laying the tangent line through the inflection point of the first increase of the curve. The intersection point of the tangent with the abscissa was considered as wavelength of the HOMO-LUMO gap.

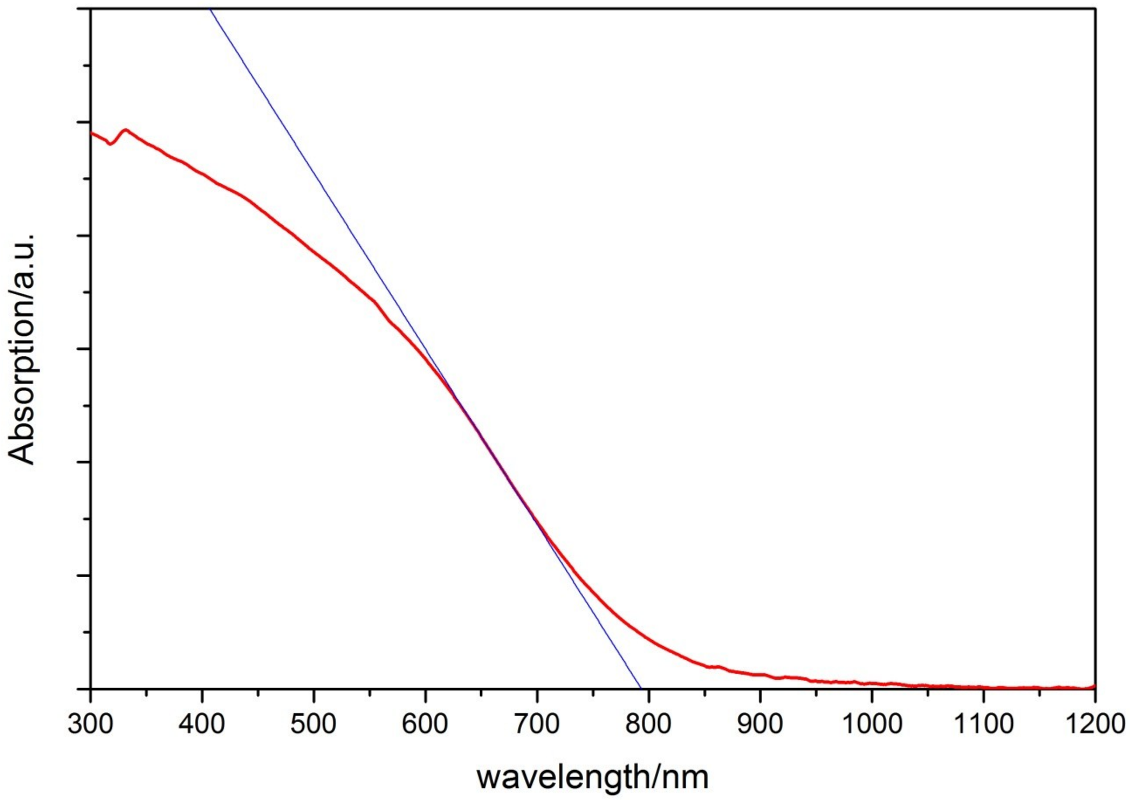

Figure S1: UV-Vis spectrum of **1** (red) and tangent line (blue) to determine the HOMO-LUMO gap (red).

IR-Spectra

IR spectrum was obtained on a Bruker Tensor 37.

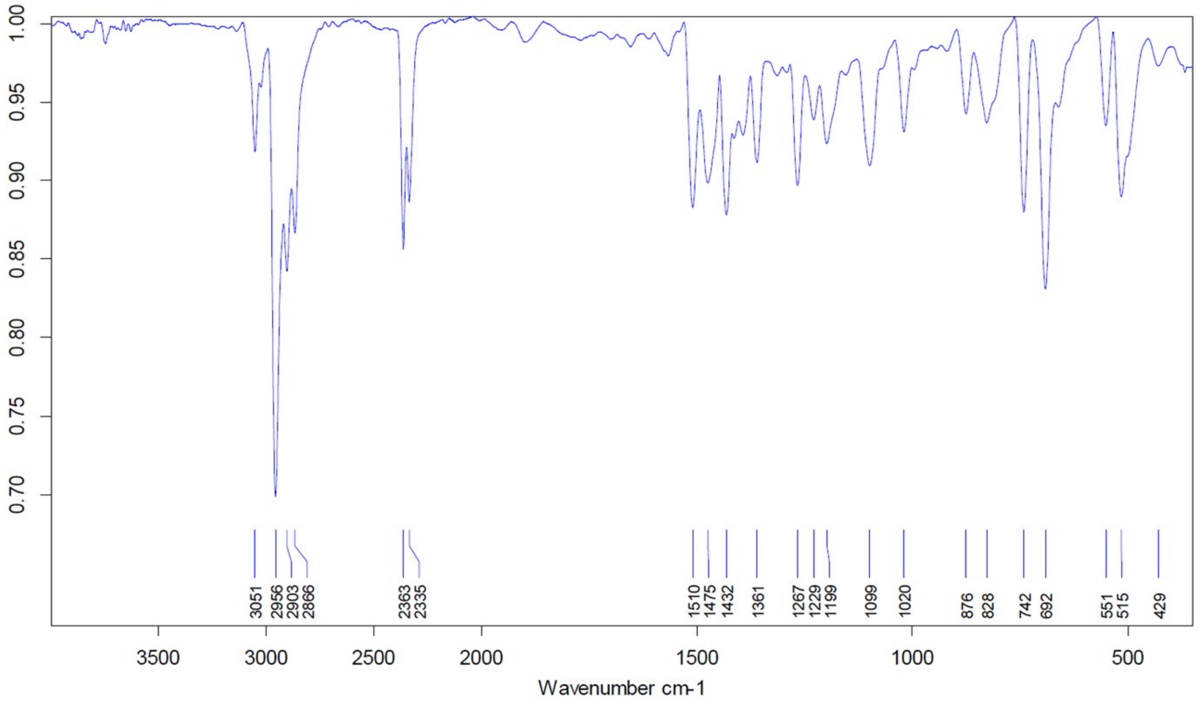

Figure S2: IR spectrum of **1** in the solid state.

Crystallographic information

Low temperature single crystal X-ray diffraction was performed on a STOE STADI VARI diffractometer using CuKα radiation (λ = 1.54186 Å) at 150.15 K. Using Olex2,[2] the structure was solved with the ShelXD structure solution program[3] using Dual Space method and refined with the ShelXL[4] refinement package using Least Squares minimization. For **1** refinement was performed with anisotropic temperature factors for all non-hydrogen atoms of the cluster molecule; *n*-heptane molecules were refined isotropically. Hydrogen atoms were calculated on idealized positions. Hydrogen atoms were calculated on idealized positions. CCDC 1499582 contain detailed crystallographic data of this article. The files can be obtained free of charge from the Cambridge Cristallographic Data Centre, www.ccdc.cam.ac.uk/datarequest/ cif.

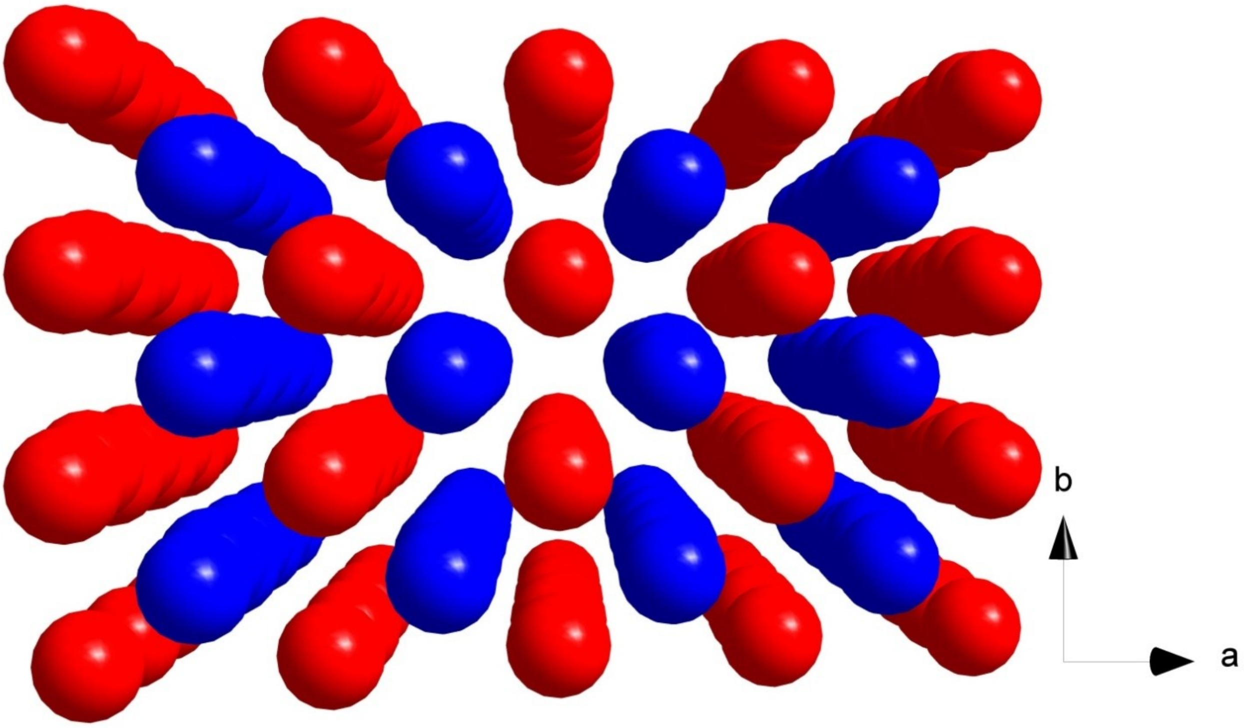

Figure S3: Extended solid state structure of **1**. The cluster molecules are illustrated as dummy atoms with r = 0.9 nm, which were positioned in the center of the original cluster. Their arrangement (shown along the c-axis) corresponds to a distorted *hcp* with ABAB… layers highlighted in red and blue.

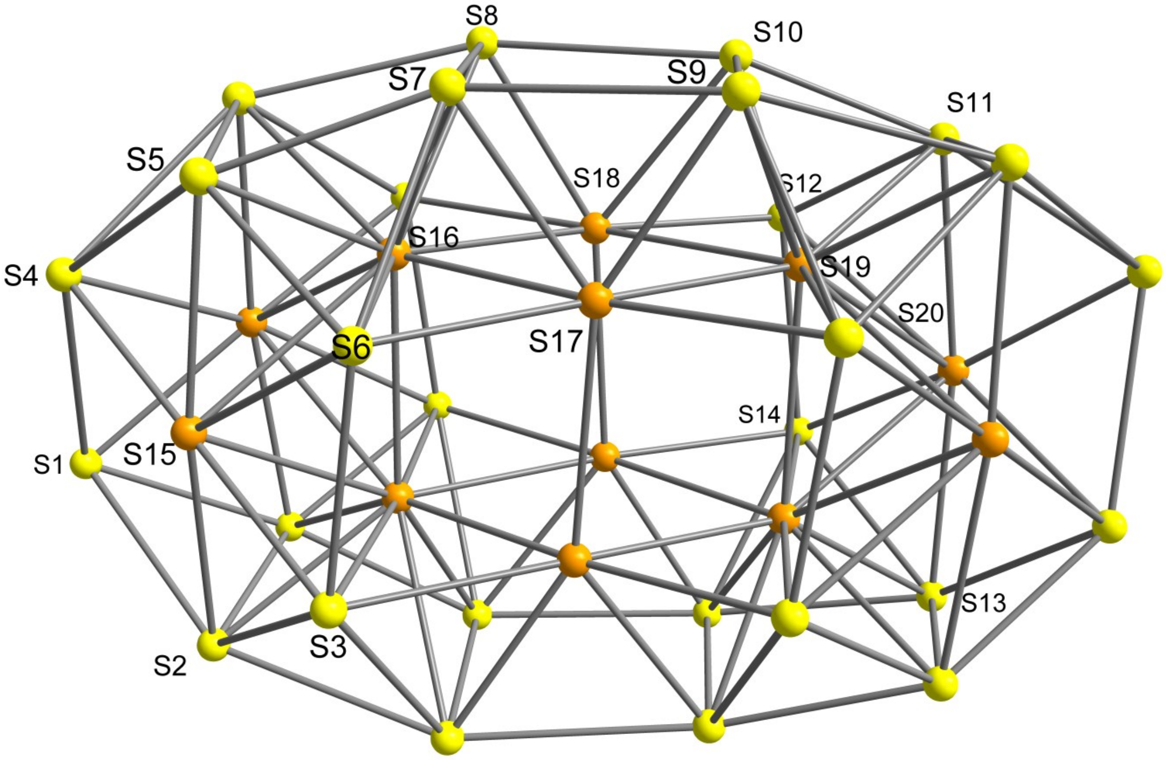

Figure S4: Sulfur-sublattice with RS^- (yellow) and S^{2-} (orange) in **1**. S-atoms of the asymmetric unit are labeled.

Table S1: Crystal data and structure refinement for $[Cu_{52}S_{12}(SCH_2C_6H_4{}^{t}Bu)_{28}(PPh_3)_8]$ (**1**)·10 *n*-heptane .

Empirical formula	$C_{522}H_{700}Cu_{52}P_8S_{40}$
Formula weight	11809.02
Temperature/K	150.15
Crystal system	monoclinic
Space group	*C*2/*c*
a/Å	41.0006(8)
b/Å	31.9188(4)
c/Å	45.9429(9)
β/°	113.674(1)
Volume/Å^3	55065.2(17)
Z	4
ρ_{calc}g/cm^3	1.424
μ/mm^{-1}	4.080
F(000)	24400.0
Crystal size/mm^3	0.22 × 0.17 × 0.12
Radiation	CuKα (λ = 1.54186)
2Θ range for data collection/°	4.89 to 120.606
Index ranges	$-45 \leq h \leq 45$, $-30 \leq k \leq 35$, $-50 \leq l \leq 31$
Reflections collected	147112
Independent reflections	39955 [R_{int} = 0.0884, R_σ = 0.1031]
Independent reflections [I≥2σ (I)]	20446
Data/restraints/parameters	39955/112/2657
Goodness-of-fit on F^2	0.804
Final R indexes [I≥2σ (I)]	R_1 = 0.0513, wR_2 = 0.1128
Final R indexes [all data]	R_1 = 0.0999, wR_2 = 0.1263
Largest diff. peak/hole / e Å^{-3}	1.02/-0.54

X-ray powder diffraction pattern of **1** (upper part of the Figure S5) was measured at room temperature on a STOE STADI P diffractometer (Cu-Kα1 radiation, Germanium monochromator, Debye-Scherrer geometry) as a suspension of grinded crystals in their mother liquor sealed in a glass capillary.

The simulated powder diffraction pattern (lower part of the Figure S5) was calculated on the basis of the atom coordinates obtained from low temperature single crystal X-ray diffraction by using the program package STOE WinXPOW.[5]

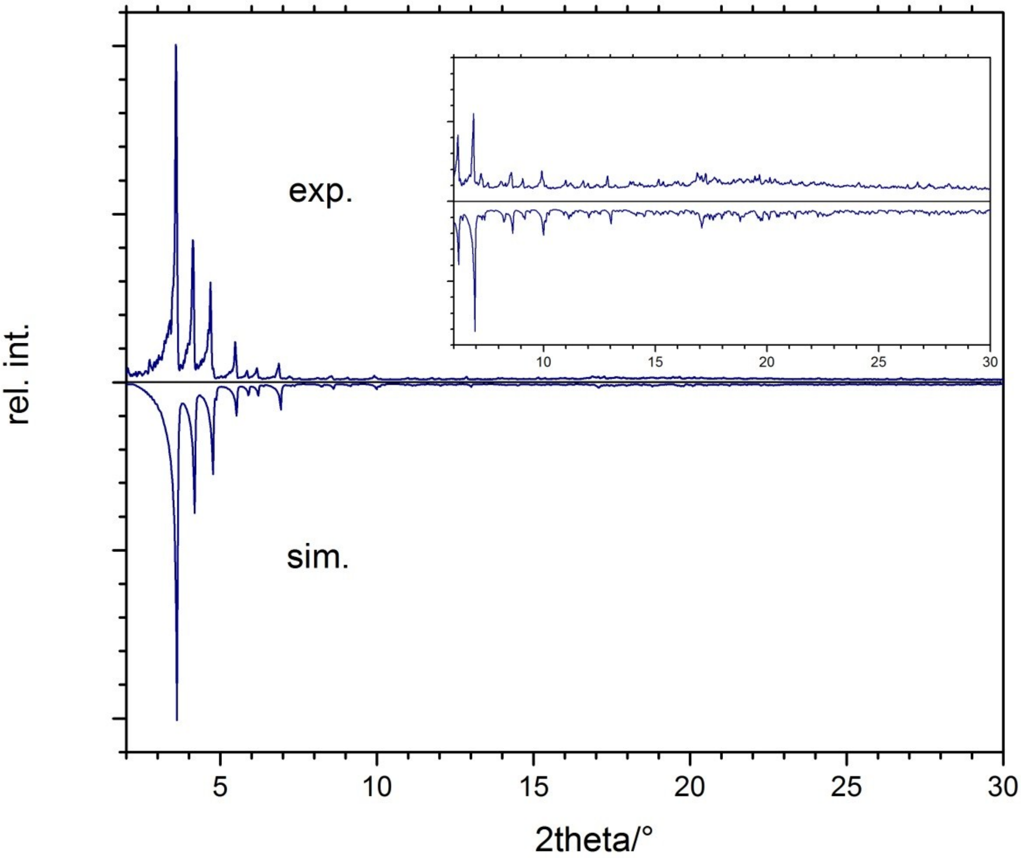

Figure S5: Experimental and simulated powder X-ray diffraction patterns of **1** (insertion: magnification of the patterns for higher 2θ).

References

1. L. M. Nguyen, M. E. Dellinger, J. T. Lee, R. A. Quinlan, A. L. Rheingold and R. D. Pike, *Inorg. Chim. Acta*, 2005, **358**, 1331-1336.
2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.
3. G. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112-122.
4. G. Sheldrick, *Acta Crystallogr. Sect. C*, 2015, **71**, 3-8.
5. STOE, WinXPOW, STOE & Cie GmbH, Darmstadt, 2000.