Supporting information

Ethynide-stabilized high-nuclearity silver(I) sulfido molecular clusters assembled with organic sulfide precursors

*Zi-Yi Chen, Dennis Y. S. Tam and Thomas C. W. Mak**

Department of Chemistry and Center of Novel Functional Molecules, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, People's Republic of China

Synthesis

All chemicals obtained from commercial sources were of analytically pure grade and used without further purification. Polymeric $[AgC{\equiv}C^tBu]_n$ and $[AgC{\equiv}CPh]_n$ were prepared according to the literature procedure.[1]

Synthesis namely $[Ag_9S_6@Ag_{36}(C{\equiv}C^tBu)_{32}(H_2O)_2]$ $[Ag(imidazole)(CH_3OH)(H_2O)](BF_4)_2 \cdot 8H_2O \cdot 2CH_3OH$ (**1**). A 0.095g suspension of polymeric $[AgC{\equiv}C^tBu]_n$ in 4 mL methanol was treated with dropwise addition of 0.1mL $AgBF_4$ aqueous solution (2 mol/L), and 0.014g 1,1'-thiocarbonyldiimidazole was added to the resulting clear solution in one portion under stirring. Then the mixture was stirred at room temperature for 12 hours in the dark. The

1 a) B. K. Teo, Y.-H. Xu, B.-Y. Zhong, Y.-K. He, H.-Y. Chen, W. Qian, Y.-J. Deng, Y. H. Zou, *Inorg. Chem.* 2001, **40,** 6794–6801; b) L. Zhao, X.-L. Zhao, T. C. W. Mak *Chem. Eur. J.* 2007, **13**, 5927–5936.

resulting yellow solution was collected by filtration. Yellow block-like crystals were obtained in 4~5 days by slowly evaporation of the solvent in the dark to furnish a yield of about 10% (based on Ag).

Synthesis of $[Ag_{120}S_{24}(PhC{\equiv}C)_{52}Cl_4(2\text{-pyridone})_{10}(H_2O)_8](H_3O)_4(SiF_6)_8(BF_4)_4 \cdot CH_3OH \cdot 22H_2O$ (**2**). A suspension of polymeric $[AgC{\equiv}CPh]_n$ (0.050g, 0.24mmol) and di(2-pyridyl) thionocarbonate (0.040g, 0.17mmol) in 5 mL methanol was treated with 0.3 mL $AgBF_4$ aqueous solution (2 mol/L) and 20 µL Ag_2SiF_6 aqueous solution (2 mol/L) dropwisely, whereupon the solid dissolved immediately to yield a dark brown solution. Then the solution was kept at 40 °C for fifteen minutes after addition of one drop of 0.1 mol/L HCl aqueous solution. A deep dark brown solution was then collected by filtration. Garnet block-like crystals were obtained in 3~4 days by slow evaporation of the solvent in the dark to give a yield of about 8% (based on Ag).

Elemental analysis (C, H, N) was performed on a Perkin Elmer 240 elemental analyzer. Results (%): for $Ag_{46}C_{197}O_4S_6N_2F_8H_{302}$ **1**, calcd C 29.32, H 3.77, N 0.35; found C 29.94, H 3.59, N under detection limit <0.50; for $C_{467}Ag_{120}B_4Cl_4F_{64}N_{10}O_{45}S_{24}Si_8H_{386}$ **2**: calcd C 25.27, H 1.75, N 0.63; found: C 24.38, H 1.66, N 0.60.

X-ray crystallography

Crystal data were collected on a Bruker Smart Apex II CCD diffractometer with Mo *K*α radiation (λ = 0.71073 Å) at 173(2) K. The intensities were corrected for Lorentz and polarization factors, as well as for absorption by the ω multi-scan method. The structure was solved by the direct method and refined by full-matrix least-squares fitting on F^2 with the ShelXS and ShelXL-97 [2] programs within the Olex2 suite[3]. All Ag, S and Si atoms were refined with anisotropic thermal parameters, whereas all other atoms were refined isotropically.

2 G. M. Sheldrick, *Acta Cryst. A* 2008, **64**, 112-122.

3 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339-341.

IR, UV-Vis and luminescent spectra

IR spectra were recorded on KBr pellets at room temperature on a Nicolet Impact 420 FT-IR spectrometer in the range of 4000−400 cm^{-1} at a resolution of 0.8 cm^{-1}. UV-Vis spectrum was recorded on Shimadzu UV-3600 UV-Vis-NIR absorption spectrophotometer in the range of 250−800 nm with scan speed 4500 nm/min. Luminescent spectrum was recorded on Hitachi-F-7000 spectrofluorometer.

Additional Figures

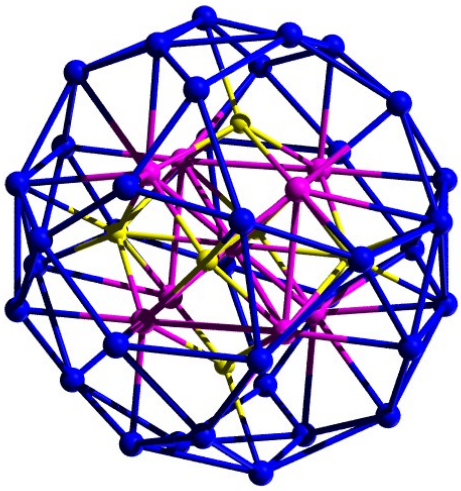

Figure S1. Ball-and-stick diagram of the $Ag_9S_6@Ag_{36}$ molecular skeleton of $[Ag_9S_6@Ag_{36}(C{\equiv}C^tBu)_{32}(H_2O)_2]$ $[Ag(imidazole)(CH_3OH)(H_2O)](BF_4)_2 \cdot 8H_2O \cdot 2CH_3OH$ (**1**). Color code: Ag(core) = pink; Ag(shell) = blue; S = yellow.

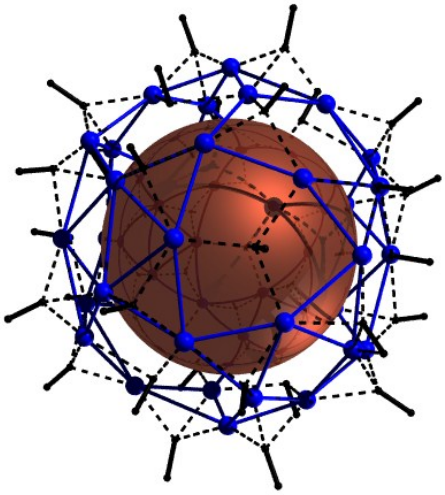

Figure S2. Ball-and-stick diagram of the Ag-C shell of compound **1;** the inner core is presented as a copper-colored ball. Color code: Ag = blue; C = black.

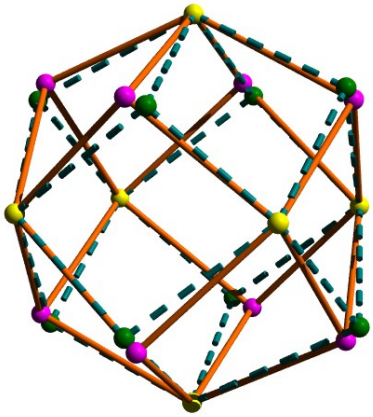

Figure S3. Diagram to illustrate the disorder of the Ag_9S_6 core of compound **1**. The pink balls represent the silver atoms with 2/3 occupancy and the green balls represent the silver atoms with 1/3 occupancy.

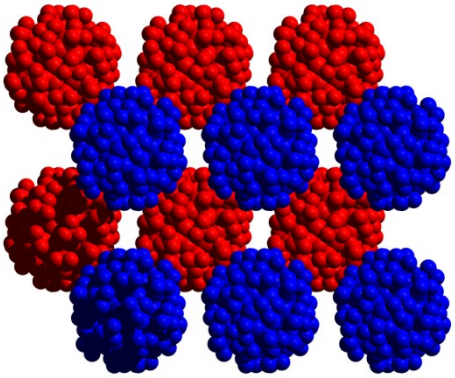

Figure S4. Space-filling diagram of ABAB packing of the clusters in **1**.

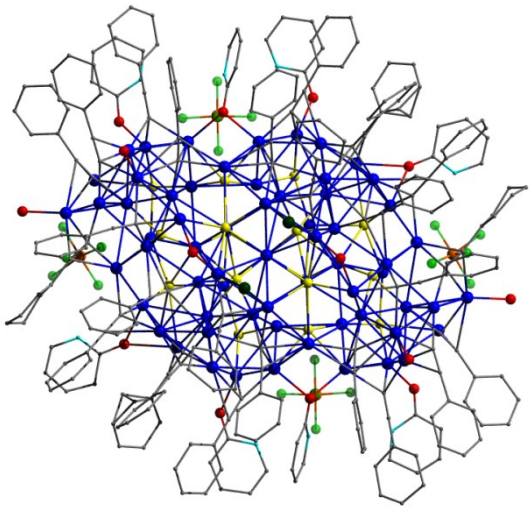

Figure S5. Ball-and-stick diagram of the molecular structure of $[Ag_{120}S_{24}(PhC{\equiv}C)_{52}Cl_4(2\text{-pyridone})_{10}(H_2O)_8](H_3O)_4(SiF_6)_8(BF_4)_4 \cdot CH_3OH \cdot 22H_2O$ (**2**) along the *b* axis, H atoms and some counter ions are omitted for clarity. Color code: Ag = blue; S = yellow; O = red; C = gray; Cl = dark green; F = light green; Si = orange.

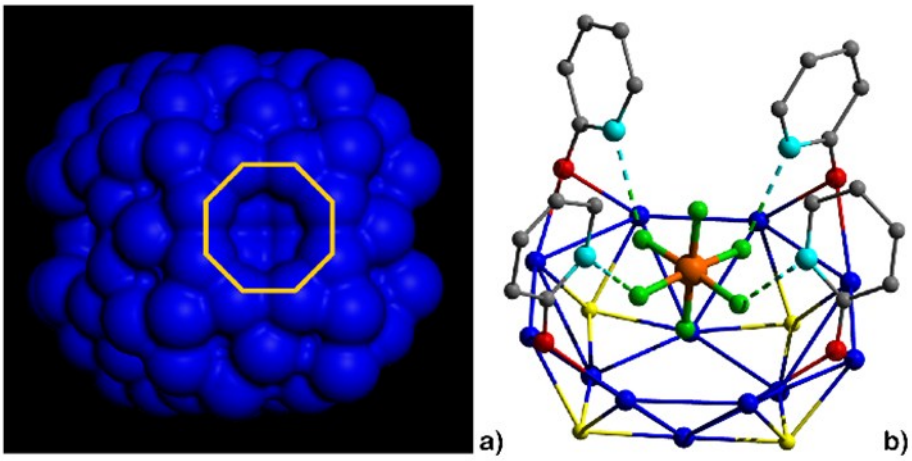

Figure S6. (a) Space-filling model showing Ag_{120} cluster in **2**; the octagon indicates the boundary of the hollow basket. (b) Ball-and-stick diagram of $Ag_{12}(2\text{-pyridone})_4S_4$ surface basket that accommodates the SiF_6^{2-} ion; Color code: $Ag_{(core)}$ = blue; S = yellow; Si = orange; F = light green, O = oxygen, C = gray.

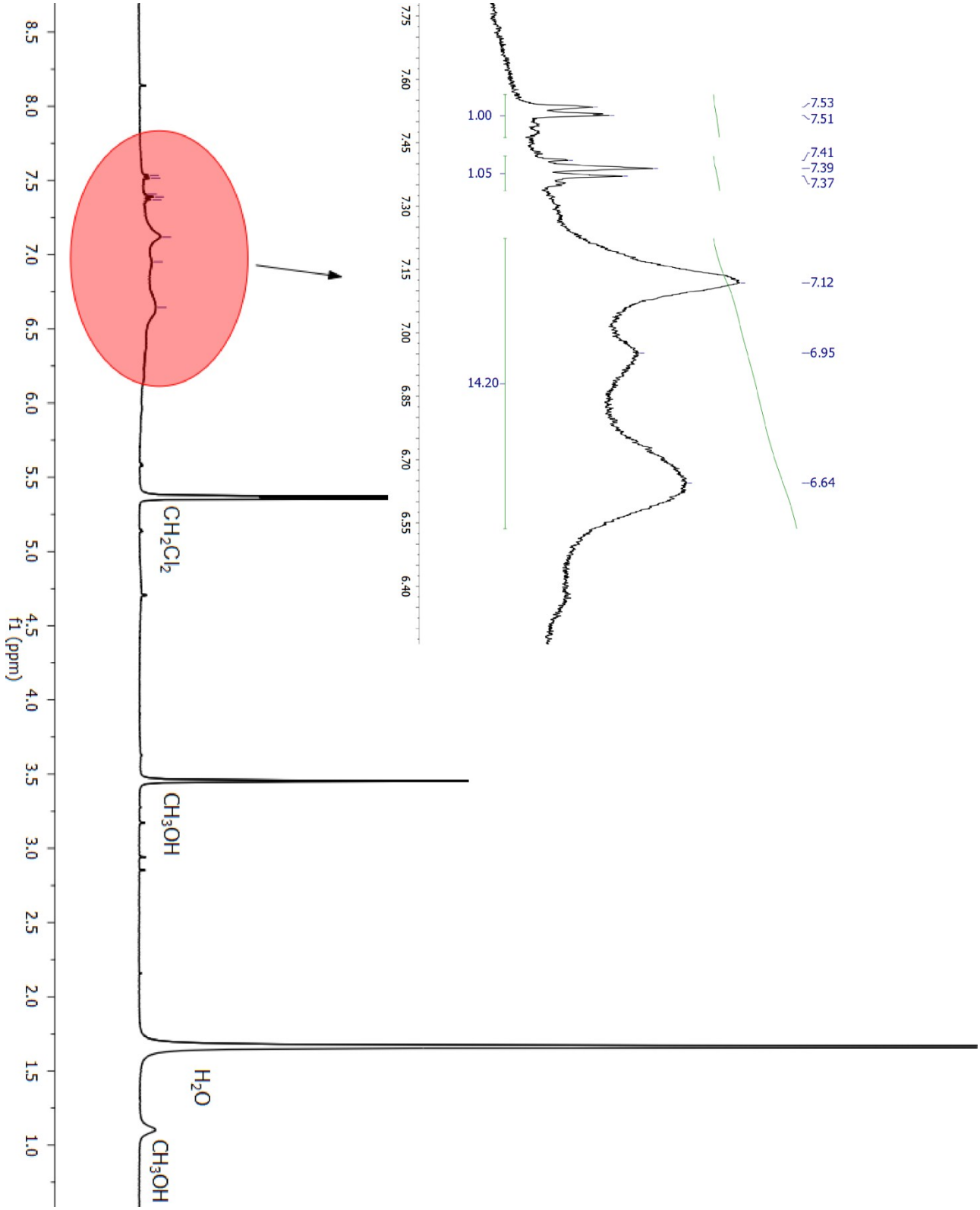

Figure S7. ^{1}H NMR spectrum of compound **2** in CH_2D_2.