Supporting information

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

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Synthesis

All chemicals obtained from commercial sources were of analytically pure grade and used without further purification. Polymeric [AgC≡CtBu]n and [AgC≡CPh]n were prepared according to the literature procedure.1

Synthesis namely [Ag69S6@Ag36(C≡CtBu)32(H2O)2] [Ag(imidazole)(CH3OH)(H2O)](BF4)2 · 8H2O · 2CH3OH (1). A 0.095g suspension of polymeric [AgC≡CtBu]n in 4 mL methanol was treated with dropwise addition of 0.1mL AgBF4 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

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** \([\text{Ag}_{120}\text{S}_{24}(\text{PhC≡C})(2\text{-pyridone})_{10}(\text{H}_2\text{O})_{8})(\text{H}_2\text{O})_4(\text{SiF}_6)_8(\text{BF}_4)_4 \cdot \text{CH}_3\text{OH} \cdot 22\text{H}_2\text{O} \)** (2). A suspension of polymeric \([\text{AgC≡CPh}]_n \) (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\(_2\)SiF\(_6\) 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 \(\text{Ag}_{46}\text{C}_{197}\text{O}_{56}\text{N}_{2}\text{F}_{8}\text{H}_{302} \) 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 \(\text{C}_{467}\text{Ag}_{120}\text{B}_{4}\text{Cl}_{4}\text{F}_{64}\text{N}_{10}\text{O}_{45}\text{S}_{24}\text{Si}_{8}\text{H}_{386} \) 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 Kα radiation (\(\lambda = 0.71073 \) Å) at 173(2) K. The intensities were corrected for Lorentz and polarization factors, as well as for absorption by the \(\omega\) 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.

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**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\(_9\)S\(_6\)@Ag\(_{36}\) molecular skeleton of 

\[ \text{Ag}_9\text{S}_6@\text{Ag}_{36}(\text{C}=\text{C}^\text{Bu})_3\text{c}(\text{H}_2\text{O})_2 \]  \[ \text{[Ag(imidazole)(CH}_3\text{OH)}(\text{H}_2\text{O})] \text{(BF}_4\text{)}_2 \cdot \text{8H}_2\text{O} \cdot \text{2CH}_3\text{OH} \; \text{(1). Color code: Ag(core) = pink; Ag(shell) = blue; S = yellow.} \]
**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$_{9}$S$_{6}$ 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 \([\text{Ag}_{120}\text{S}_{24}(\text{PhC}≡\text{C})_{52}\text{Cl}_{4}(2\text{-pyridone})_{10}(\text{H}_2\text{O})_8](\text{H}_3\text{O})_4(\text{SiF}_6)_8(\text{BF}_4)_4\cdot \text{CH}_3\text{OH} \cdot 22\text{H}_2\text{O}\) (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 \(\text{Ag}_{120}\) cluster in 2; the octagon indicates the boundary of the hollow basket. (b) Ball-and-stick diagram of \(\text{Ag}_{12}(2\text{-pyridone})_4\text{S}_4\) surface basket that accommodates the \(\text{SiF}_6^{2-}\) ion; Color code: \(\text{Ag}_{\text{core}}\) = blue; S = yellow; Si = orange; F = light green, O = oxygen, C = gray.
Figure S7. $^1\text{H}$ NMR spectrum of compound 2 in CH$_2$D$_2$. 