Supporting Information

Designed synthesis of size-tunable Ag₂S nanoclusters via distinguishable C-S bond cleavage reaction of alkyl- and aryl-thiolates

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General Consideration

All commercially available chemicals were used without further purification. Methylazacalix[6]pyridine (Py[6]) was synthesized according to the literature method by the [3+3] fragment coupling protocol between terminal dibrominated and dianimated linear trimers.[1] The solvents used in this study were processed by standard procedures. All reactions were carried out under a nitrogen atmosphere unless otherwise noted. ¹H NMR experiments were carried out on a JEOL ECX-400MHz instrument. [‘BuC₆H₄SAg]ₙ (1) and [‘BuSAg]ₙ (2) were prepared by a literature method.[2]

Synthesis of [Ag₃(BuC₆H₄S)(CF₃SO₃)(Py[6])]₂(CF₃SO₃)₂·2CH₃OH·CH₂Cl₂·2.5H₂O (3). In a 10 mL round-bottom flask, AgSO₃CF₃ (51.4 mg, 0.2 mmol) was dissolved in CH₃OH (2 ml) at room temperature. Then 4-‘BuPhSAg (27.3 mg, 0.1 mmol) solid was added to the solution under stirring. After 20 min, a CH₂Cl₂ solution (2 mL) of methylazacalix[6]pyridine (Py[6], 12.7 mg, 0.02 mmol) was added dropwisely. The mixture was further stirred for 4 hours at room-temperature. The suspension was filtered and the filtrate was diffused by diethyl ether in the dark. After several days, colorless crystals of 3 were obtained in 56% yield based on Py[6] ligand.

Synthesis of [Ag₄(BuS)(CF₃SO₃)₂(Py[6])](CF₃SO₃) (4). In a 10 mL round-bottom flask, AgSO₃CF₃ (51.4 mg, 0.2 mmol) was dissolved in CH₃OH (2 ml) at room temperature. Then t-BuSAg (19.7 mg, 0.1 mmol) solid was added to the solution under stirring. After 20 min, a CH₂Cl₂ solution (2 mL) of methylazacalix[6]pyridine (Py[6], 12.7 mg, 0.02 mmol) was added dropwisely. The mixture was further stirred for 4 hours at room-temperature. The suspension was filtered and the filtrate was diffused by diethyl ether in the dark. After several days, pale-yellow crystals of 4 were obtained in 75% yield based on Py[6] ligand.
X-ray Crystallographic Analysis

Data for complexes 3-4 were collected at 173K with Mo-Kα radiation (λ = 0.71073 Å) on a Rigaku Saturn 724+ CCD diffractometer with frames of oscillation range 0.5°. All structures were solved by direct methods, and non-hydrogen atoms were located from difference Fourier maps. All non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on $F^2$ by using the SHELXTL program unless otherwise noticed.[3]

Crystal data for \{[Ag₃(4-BuPhS)(Py[6])][(CF₃SO₃)₂]₂•(CH₂Cl₂)•(CH₃OH)•(H₂O)₂.5 \} (CCDC-1035674): C₉₉H₁₀₄Ag₆F₁₂N₂₄O₁₆.₅S₆, M = 3032.54, triclinic, space group P-1 (No. 2), a = 16.734(3) Å, b = 18.644(4) Å, c = 22.013(4) Å, α = 114.53(3)°, β = 92.62(3)°, γ = 99.60(3)°, V = 6109(2) Å³, Z = 2, T = 173 K, Dc = 1.649 g cm⁻³. The structure, refined on $F^2$, converged for 21447 unique reflections ($R_{int} = 0.0891$) and 18901 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.1132$ and $wR_2 = 0.3142$ and a goodness-of-fit = 1.064. Several solvent molecules could not be located in the difference map. As the structure model contained significant voids and the diffuse residual electron density could not be modeled adequately, the SQUEEZE procedure of PLATON was used.[4] The triflate group S5 was disordered at two positions with site occupancy ratios of 0.48:0.52. Solvent molecule (O3W) has a partial occupancy ratio of 0.5.

Crystal data for [Ag₄(t-BuS)(Py[6])][(CF₃SO₃)₃] (4) (CCDC-1035676): C₄₃H₄₅Ag₄F₉N₁₂O₉S₄, M = 1604.63, triclinic, space group P-1 (No. 2), a = 9.869(2) Å, b = 14.777(3) Å, c = 19.741(4) Å, α = 109.94(3)°, β = 91.21(3)°, γ = 99.21(3)°, V = 2662.4(9) Å³, Z = 2, T = 173 K, Dc = 2.002 cm⁻³. The structure, refined on $F^2$, converged for 12055 unique reflections ($R_{int} = 0.0358$) and 11269 observed reflections with $I > 2\sigma(I)$ to give $R_1 = 0.0479$ and $wR_2 = 0.1435$ and a goodness-of-fit = 1.122. Silver Ag1, Ag2, Ag3 and Ag4 were each disordered at two positions with the occupancy ratio of 0.87:0.13.

TEM Characterization

The morphology and size distribution of as-prepared Ag-S nanoclusters was determined on a Hitachi H-7650 transmission electron microscope. The SAED pattern, EDX and trials for searching lattice fringe of NP-1 were taken by a JEOL JEM-2011 high-resolution transmission electron microscope.

References

Supporting Figures

(a)

(b)

Fig. S1 Experimental (up) and theoretical (bottom) ESI-MS spectra corresponding to the charged species $[\text{Ag}_3(\text{BuC}_6\text{H}_4\text{S})(\text{CF}_3\text{SO}_3)(\text{Py}[6])]^+$ and $[\text{Ag}_3(\text{BuC}_6\text{H}_4\text{S})(\text{Py}[6])]^{2+}$ in complex 3.
**Fig. S2** $^1$H-NMR spectrum (400MHz, CD$_3$OD:CDCl$_3$ (v:v) = 1:1) of complex 3.

**Fig. S3** Powder X-ray diffraction of the black precipitate formed in the solution of complex 4.
**Fig. S4** $^1$H-NMR spectrum (400MHz, CD$_3$OD) of complex 4 collected right after the cluster formation reaction.

**Fig. S5** TEM images and particle size histogram (inset) of as-prepared NP-1.
**Fig. S6** FT-IR spectra of (1) NP-1 (2) complex 3 (3) Py[6] (4) Py[6] + 3AgOTf.

**Fig. S7** EDX of NP-1 (Ag-66.4%, S-33.6%; Ag/S elemental ratio equals 1.98 : 1).
Fig. S8 Lattice fringe spacing (0.23 nm) of $\alpha$-Ag$_2$S in NP-1.

Fig. S9 SAED pattern of NP-1 corresponding to (-103) and (232) facets of $\alpha$-Ag$_2$S.
**Fig. S10** TEM images and diagram (inset) of Ag$_2$S nanoclusters prepared by adding the CH$_2$Cl$_2$/MeOH solution of 3 (5×10$^{-4}$M, 1mL) into the acidified solution of 4 (5×10$^{-4}$M, 1mL) at different time intervals: (a) 0.5 h, (b) 1.0 h and (c) 1.5 h.

**Fig. S11** Excitation (left) and emission (right) spectra of Ag$_2$S nanoclusters with different mole ratio of complex 3 and 4 from 9:1, 7:3, 5:5, 3:7 to 1:9.