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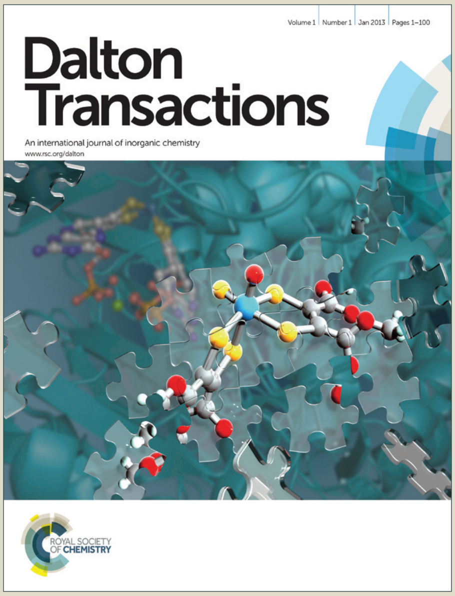

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Designed synthesis of size-tunable Ag_2S nanoclusters via distinguishable C-S bond cleavage reaction of alkyl- and aryl-thiolates

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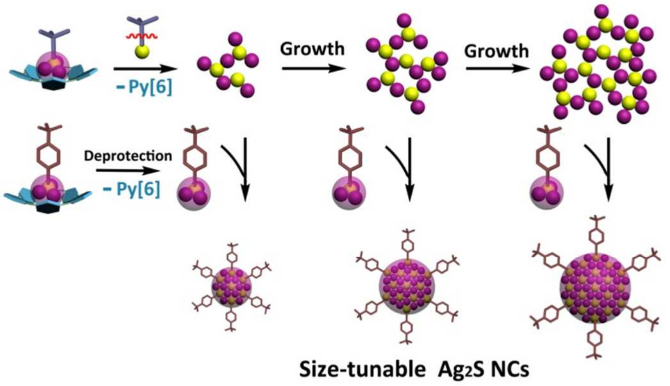
We report herein the synthesis of two different silver clusters of aryl- and alkyl-thiolates. These two cluster complexes exhibited biased C-S bond cleavage reaction rates upon removing protective hexamethylazacalix[6]pyridine (Py[6]) ligands, which was applied in the fabrication of silver sulfide nanoclusters with variable and controllable sizes.

Ag_2S nanoclusters have been of intensive recent interest due to their semiconductor properties,[1] intriguing near-infrared photoluminescent properties[2] and low toxicity to living tissues,[3] the latter two characteristics potentiating their possible application in biological imaging.[4] To date several different synthetic approaches[5] such as reverse-micelle, and single source precursor methods[2a] etc. have been developed for the synthesis of Ag_2S nanoclusters. However, the requirement of exotic ligand- or surfactant for stabilizing silver and sulfide ions or their precursors and the involved preparations at elevated temperature and high pressure in most cases made these methods arduous and inapplicable to biological imaging. It is still a challenging task to prepare Ag_2S nanoclusters with tunable sizes under mild conditions. Recently, a number of well defined, nanometer-sized metal chalcogen clusters (nanoclusters) that contain tens to hundreds of metal and chalcogen core atoms have been prepared and isolated as single crystals by Fenske and co-workers.[6] Chalcogenides (eg. S^{2-}, Se^{2-}) therein can be readily generated through carbon-sulfur (C-S) bond cleavage of thiolates or corresponding congeners in the presence of metal ions.[7] Inspired by this synthetic method, in this communication we describe a new methodology to achieve silver sulfide nanoclusters with controllable sizes by using distinguishable C-S bond cleavage reaction of alkyl- and aryl-thiolates in polynuclear silver thiolate clusters.

Previous studies have explored that the formation of thiolate-centered polynuclear metal cluster can induce the scission of the C-S bond in thiolates due to the electron withdrawal effect of metal cluster aggregate.[8] For example, the value for the homolytic bond dissociation energy of the C-S bond in C_6H_5SH is approximately 83 kcal/mol while this energy value decreases to 27 kcal/mol upon the phenylthiolate ($C_6H_5S^-$) attaching on a trinuclear $[Mo_2Co]$ cluster.[8a] This effect provides a viable means of transforming metal thiolate complexes to metal sulfide. On the other hand, we recently reported that azacalix[*n*]pyridines (**Py[*n*]**), a class of polypyridine macrocycles, are capable of facilitating the formation of polynuclear silver clusters of various acetylides due to their extraordinary positive allosteric effect in the process of metal binding.[9] We thus envision a new synthetic strategy toward the controllable synthesis of Ag_2S nanoclusters as illustrated in Scheme 1. Different silver thiolate clusters will be prepared inside the cavity of the **Py[*n*]** macrocyclic ligand. The cluster formation may expedite the C-S bond cleavage under appropriate reaction conditions to generate Ag_2S nucleate. Upon removing the polypyridine **Py[*n*]** ligands via protonation, the encapsulated silver thiolate clusters may be released and coalesce with the Ag_2S nucleate to finally produce stable thiolate-protected Ag_2S nanoclusters.



Scheme 1 Synthetic strategy for thiolate-protected Ag_2S nanoclusters.

We firstly synthesized polymeric silver thiolate compounds $[^t\mathrm{BuC_6H_4SAg}]_n$ (**1**) and $[^t\mathrm{BuSAg}]_n$ (**2**) by the reaction of corresponding thiophenol or thiol with silver nitrate. Subsequent treatment of the suspension of **1** or **2** and silver triflate with azacalix[6]pyridines (**Py[6]**) in a dichloromethane/methanol solution resulted in a pale-yellow solution after filtration. Diffusion of diethyl ether into the filtrate yielded pale-yellow crystals of two silver thiolate cluster complexes $[\mathrm{Ag_3(^tBuC_6H_4S)(CF_3SO_3)}(\mathbf{Py[6]})]_2(\mathrm{CF_3SO_3})_2\cdot 2\mathrm{CH_3OH}\cdot \mathrm{CH_2Cl_2}\cdot 2.5\mathrm{H_2O}$ (**3**) and $[\mathrm{Ag_4(^tBuS)(CF_3SO_3)_2}(\mathbf{Py[6]})](\mathrm{CF_3SO_3})$ (**4**).

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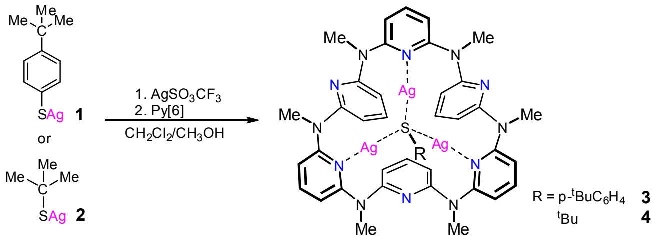
In contrast to previously reported synthetic methods for silver thiolate clusters by using silylated sulfide sources,[6b] the present approach features a direct transformation of highly insoluble bulk $[RSAg]_n$ into polynuclear silver-thiolate clusters. The crystal structures of **3** and **4** are very similar. As shown in Figure 1, the sulfur atom of each thiolate is bonded to three silver atoms by a μ_3-mode. Such Ag_3 aggregate is encircled by a **Py[6]** macrocycle through the coordination of three alternate pyridyl nitrogen atoms. The remaining three pyridine rings interact with the silver atoms by silver-aromatic π interaction of varying degrees. The Ag–S bonding distances in **3** (2.338(3)-2.403(3) Å) and **4** (2.339(3)-2.394(2) Å) were found to be 0.1~0.2 Å shorter than the values in a plethora of reported μ_3 silver-thiolate cluster complexes.[10] This indicates the strong size restriction effect of the peripheral coordinative **Py[6]** macrocycle. Noticeably, the C-S bond lengths in the arylthiolate of **3** (1.762(10) and 1.796(11) Å) are shorter than that (1.861(4) Å) of *tert*-butylthiolate in **4**. This observable difference due to the conjugation effect between the sulfur atom and the aromatic ring in the arylthiolate of **3** led to entirely different stability between **3** and **4** *vide infra*.

Formation of $[RSAg_3]$@**Py[6]** moiety as described in **3** was also confirmed by electrospray ionization (ESI) mass spectrometry and proton NMR (Fig. S1 and S2 in the Supporting Information). For example, ESI-MS displayed two isotopically resolved peaks at m/z = 1275.0559 and 563.0516 corresponding to $[Ag_3(^tBuC_6H_4S)(CF_3SO_3)(\textbf{Py[6]})]^+$ and $[Ag_3(^tBuC_6H_4S)(\textbf{Py[6]})]^{2+}$, respectively. In addition, the ^1H NMR spectroscopy of the solution of **3** revealed the 1:1 ratio of $^tBuC_6H_4S^-$ to **Py[6]**.



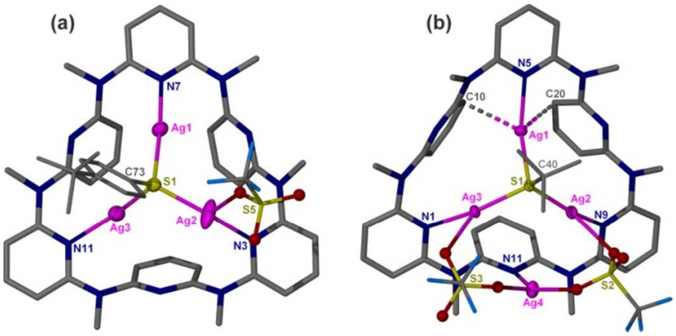


Fig. 1 (a) Crystal structure of complex $[Ag_3(^tBuC_6H_4S)(CF_3SO_3)(\textbf{Py[6]})]_2(CF_3SO_3)_2\cdot 2CH_3OH\cdot CH_2Cl_2\cdot 2.5H_2O$ (**3**). Hydrogen atoms, solvent molecules and another $[Ag_3(^tBuC_6H_4S)(CF_3SO_3)(\textbf{Py[6]})]$ unit were omitted for clarity. (b) Crystal structure of $[Ag_4(^tBuS)(CF_3SO_3)_2(\textbf{Py[6]})](CF_3SO_3)$ (**4**). All four silver atoms are disordered and only a set of position is shown here. Hydrogen atoms were omitted for clarity. Color scheme for atoms: Ag, purple; C, gray; N, blue; S, yellow; F, cyan.

Interestingly, the stability of the solution of **3** and **4** is quite different. The solution of **3** can keep its pale-yellow colour and solution homogeneity for several days while in sharp contrast the solution of **4** would generate black precipitate within a day. Powder X-ray diffraction substantiated that the black precipitate is Ag_2S of two crystalline phases (Fig. S3). In the NMR spectrum of **4** collected right after the cluster formation reaction (Fig. S4), the triplet and doublet peaks respectively corresponding to the pyridyl γ- and β-protons of **Py[6]** are in good resolution as similar as the NMR spectrum of **3**. However, after the formation of Ag_2S black precipitate the NMR spectrum of this solution sample exhibits broad peaks with poor resolution. In addition, adding (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO) into the solution of **4** can accelerate the decomposition process from the $[^tBuSAg_3]$ cluster to the Ag_2S black precipitate. This observation is consistent with a free radical mechism for C-S bond cleavage.[8a] Moreover, it is notable that removing the protective **Py[6]** of complex **4** by protonation to interrupt the coordination interactions between the central silver thiolate cluster and its surrounding **Py[6]** macrocycles can expedite the decomposition process to Ag_2S as well. Black precipitate of Ag_2S was acquired within an hour. This kind of C-S bond activation triggered by loss of the stabilizing coordinative ligand of metal-thiolate cluster has been reported previously.[11]

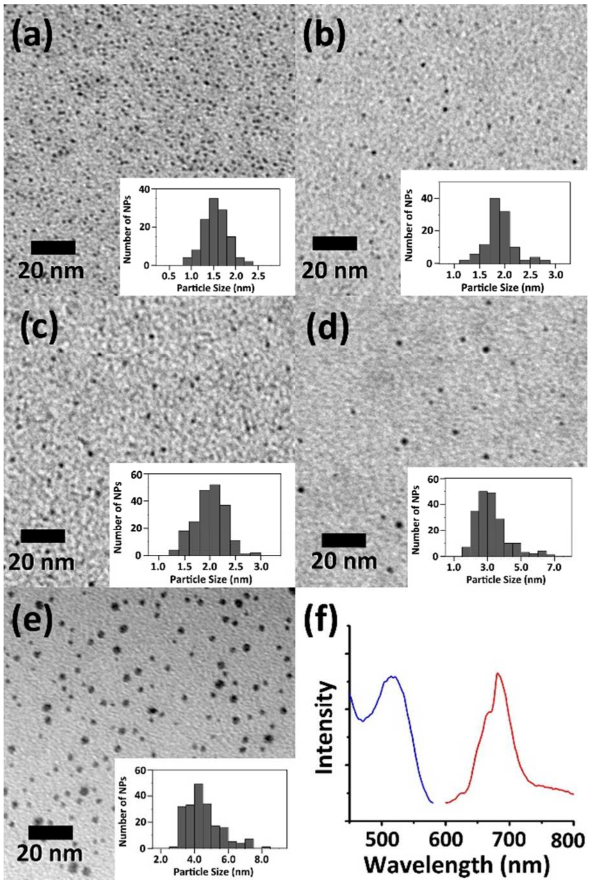


Fig. 2 TEM images of thiolate-protected silver sulfide nanoclusters generated by adding CF_3COOH into the mixed solution of **3** and **4** in different ratios: (a) 9:1, (b) 7:3, (c) 5:5, (d) 3:7 and (e) 1:9. (f) Excitation and emission spectrum of **NP-1** in cyclohexane at 298 K.

In contrast to the formation of Ag_2S precipitate in the protonation process of **4**, adding CF_3COOH into the solution of complex **3** led to a cloudy yellow solution. Separation by centrifugation resulted in a dark powder, which can be dissolved in cyclohexane to produce a yellow solution (denoted as **NP-1**). This yellow solution can retain its solution homogeneity for several days. TEM images of **NP-1** revealed the formation of nanoparticles with

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an average diameter of 1.0±0.3 nm (Fig. S5). FT-IR spectroscopy analysis of the solid sample of **NP-1** clearly showed the absence of **Py[6]** and the existence of ^{t}BuC$_6$H$_4$S (Fig. S6). This was evidenced by energy dispersive X-ray spectroscopy (EDX) of **NP-1**, which revealed no signals for the element N and offered the Ag/S atomic ratio equaling to approximately 1.98 (Fig. S7). Despite of small average size, high-resolution TEM (HR-TEM) of some selected large nanoparticles of **NP-1** showed a typical lattice fringe spacing (0.23 nm) of α-Ag$_2$S (Fig. S8). The selected area electron diffraction (SAED) also exhibited two feeble diffraction rings that could be indexed to the (-103) and (232) facets of monoclinic Ag$_2$S (JCPDS card 14-0072) (Fig. S9). We thus proposed a core-shell cluster model for **NP-1** as shown in Scheme 1, which is actually dominant in previously reported nanometer-sized metal chalcogen clusters.[6]

Above distinct reaction results of **3** and **4** upon protonation made us conceive a new synthetic method for Ag$_2$S nanoclusters with controllable sizes. The facile decomposition of silver *tert*-butylthiolate cluster may provide a means of generating Ag$_2$S nucleates (core) while [^{t}BuC$_6$H$_4$S-Ag] clusters can act as peripheral stabilizing units (shell). When the same concentrated solutions of **3** and **4** were mixed in a ratio of 9:1, 7:3, 5:5, 3:7 and 1:9 and were then subject to the protonation process by adding the same amount of trifluoroacetic acid, we can obtain a series of Ag$_2$S nanoclusters with variably increasing sizes from 1.5±0.4, 1.9±0.4, 2.0±0.5, 3.0±1.0, to 4.5±1.5 nm, respectively (Fig. 2). It must be admitted that the size polydispersity of these nanoclusters is barely satisfying. Furthermore, the size of the acquired nanoclusters can also be tuned by adding the CH$_2$Cl$_2$/MeOH solution of **3** into the acidified solution of **4** at different time intervals (Fig. S10).

Despite of variable sizes (1.0 to 4.5 nm) of the newly acquired Ag$_2$S nanocluster samples, we surprisingly found their excitation and emission spectra (Fig. S11) were the same and remarkably identical with the corresponding spectra of **NP-1** with λ_{ex} (max) = 522 nm and λ_{em} (max) = 684 nm (Fig. 2f). This result indicates that the photoluminescent property of these Ag$_2$S nanocluster samples is independent of their sizes. This unique feature could potentiate wide application of these nanoclusters in micro- and nanoelectronics since they may facilitate processing of devices on particular dimensions without introducing complicating quantum effects.[12]

Conclusions

In summary, we have developed a viable method of synthesizing Ag$_2$S nanoclusters by using the deprotection-driven biased C-S bond cleavage of alkyl- and aryl-thiolates in silver clusters. The sizes of acquired nanoclusters can be finely tuned by varying the stoichiometric ratio of two different thiolate clusters. The insights gained in this work are essential for extensive application of this method in the fabrication of other metal sulfide or mixed metal nanomaterials. This study also foresees great potential of conventional organic reactions in designed synthesis of new nanomaterials with novel properties.

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Notes and references

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Electronic Supplementary Information (ESI) available: Synthetic procedures and crystal structure determination details. Analytical data, spectra, and images. X-ray crystallographic data for **3-4** in CIF format. CCDC-1035674 (**3**) and 1035676 (**4**). See DOI: 10.1039/c000000x/

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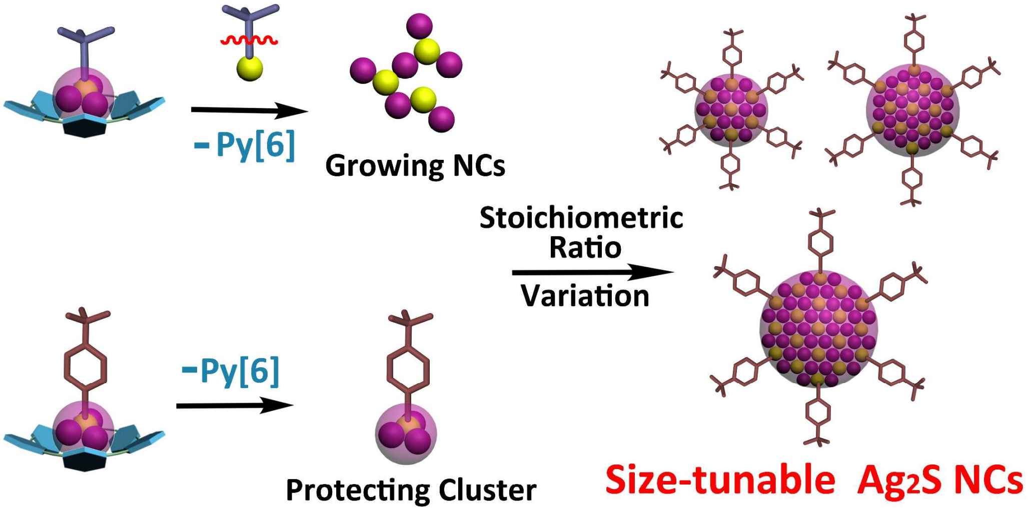

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