

New Protocols for the Synthesis of Stable Ag and Au Nanocluster Molecules

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ABSTRACT: “Catching” metals in the nonmetallic form in solution, as they grow to bulk, is one of the most exciting areas of contemporary materials research. A new kind of stabilization to catch the nonmetallic form of noble metals with small thiols has evolved as an exciting area of synthesis during the past decade. Gold clusters stay in the frontline of this research, yielding new “molecules” composed of a few to several hundreds of atoms. By taking guidelines from gold cluster research, various new protocols for silver nanoclusters were developed. In this Perspective, we highlight the recent advances on the synthesis of atomically precise silver, gold, and their alloy clusters with a special emphasis on silver. As a result of intense efforts of the recent past, clusters such as $\text{Ag}_{7,8}(\text{SR})_{7,8}$, $\text{Ag}_7(-\text{S}-\text{R}-\text{S}-)_4$, $\text{Ag}_9(\text{SR})_7$, $\text{Ag}_{32}(\text{SR})_{19}$, $\text{Ag}_{44}(\text{SR})_{30}$, $\text{Ag}_{140}(\text{SR})_{53}$, $\text{Ag}_{280}(\text{SR})_{140}$, and $\text{Ag}_{152}(\text{SR})_{60}$ (SR and S–R–S refer to thiolate and dithiolate ligands, respectively) were added to the literature. Moreover, “silver-covered” and “gold-covered” alloy clusters have also been synthesized. Early reports of the crystallization of such clusters are available. Several of these clusters are shown to act as sensors, catalysts, and pesticide degradation agents, which suggests that these materials may find applications in daily life in the foreseeable future.



Creation of new materials has always been fascinating to researchers as it provides immense opportunities to study the emergence of novel physical and chemical properties. Often, newly identified materials open up ways to discover novel phenomena. One such example, which changed the directions of noble metal research, is the colloidal gold synthesized by Faraday.¹ Although several methods for the synthesis of colloidal gold were known even earlier, as reviewed previously, the method of Faraday was the first example in which unusual properties of this form of matter were attributed to the divided state of the metal. This has been the seed material for understanding several phenomena experimentally² and theoretically.³ Since then, decades disappeared without significant growth in experimental research in this area. However, theoretical³ and technological⁴ developments have taken place. The synthesis method⁵ pioneered by Turkevich et al. showed a convenient method for obtaining gold nanoparticles, 15–30 nm in diameter, formed by the chemical reduction of Au^{3+} using sodium citrate. Here, citrate acts as a capping agent too, and the system is referred to as $\text{Au}@citrate$. A similar method is used to make silver nanoparticles ($\text{Ag}@citrate$) using silver nitrate and sodium citrate.⁵ Followed by this, a variety of alkyl chains possessing O, P, N, and S linkers in their head group have been used as protective agents for Ag and Au nanoparticles.² Surface plasmon resonance is one of the essential features of these particles of size >2 –100 nm.² Among several capped nanoparticles, thiolate-protected ones are of greater attention in view of their higher stability⁶ and applicability in biology. However, decades spent on thiolate-protected plasmonic systems have now culminated in the discovery of a new form of matter

composed of a few atoms, which exhibit molecular behavior.⁷ Such particles are called quantum clusters (QCs) or subnanoclusters. They are also referred to as clusters, monolayer-protected clusters, nanocluster molecules, as well as super atoms. They are composed of a few tens to a few hundreds of atoms, having a core with size in the nanometer regime, possessing a discontinuous density of states.⁷ Because of their discrete electronic energy levels, they show molecule-like optical transitions in their optical absorption and emission spectra. Although they are composed of a metal core and a ligand shell, the optical properties are dominated by the core-derived states, composed of the metal atoms and the metal–ligand binding shell.^{8–10} They are often considered to bridge the gap between atomic/molecular (exhibiting distinct optical properties) and nanoparticle (exhibiting plasmons) behaviors. In this Perspective, clusters and nanoparticles are treated as two distinct regimes of matter.

Unlike the plasmonic systems, TEM investigations have not been hugely successful for these clusters. Mainly two drawbacks, namely, (1) size of these clusters being too small to be observed in standard TEM¹¹ and (2) electron-beam-induced growth of clusters during microscopic examination, have thwarted TEM investigations. Clusters in the size regime of 1 nm undergo electron-beam-induced coalescence, leading to bigger particles.¹² The tendency of cluster collapse upon irradiation is prominent for Ag clusters. The experimental techniques, used

Received: February 14, 2013

Accepted: April 11, 2013

Creating metal systems in “nonmetallic” form has been a subject of intense research for several decades. Efforts in this area lead to the development of gas-phase and template-assisted clusters of various kinds. Many silver clusters were observed in templates due to the facile photoreduction of silver ions.

especially for characterizing organic and inorganic molecules, such as elemental analysis, UV/vis, mass spectrometry (ESI and MALDI MS), IR, ^1H NMR, and so forth, can be used eminently for characterizing these clusters. In recent years, crystallographic data of $\text{Au}_{102}\text{SR}_{44}$,¹³ $\text{Au}_{25}\text{SR}_{18}$,¹⁴ $\text{Au}_{38}\text{SR}_{24}$,¹⁵ $\text{Au}_{36}\text{SR}_{24}$,¹⁶ and $[\text{Au}_{24}(\text{PPh}_3)_{10}(\text{SR})_5\text{Cl}_2]^+$ (SR = thiolate)¹⁷ have helped in acquiring more knowledge about these systems. Irrespective of whether they are crystalline or not, ESI and MALDI MS studies reveal precise compositions of these clusters.^{18,19} In the following, we briefly discuss how research on gold and silver clusters has progressed, principally focusing on the synthesis aspects.

Evolution of Synthetic Efforts. (a) Using Charged Particles and Photons. Both silver and gold in the cluster form have been investigated since the 1980s.²⁰ In the early period, sputtered M (M = Ag or Au) atoms were obtained from a target of M by impinging inert gas ions or pulsed lasers, which subsequently underwent nucleation to form clusters upon gas-phase coalescence. Inert gases were used for cooling clusters by gas-phase collisions, leading to deactivation and removal of excess internal energy as kinetic energy. During the same time, Ag_n clusters were synthesized in templates such as zeolites.²¹ Later, inorganic glasses were also used as solid matrixes to stabilize these clusters. In a general synthesis process, Ag^+ -doped zeolites/glasses were prepared initially by well-known techniques.²¹ Irradiation of suitable light then makes Ag_n clusters inside of the cavities of these templates. Formation of silver clusters in zeolites was achieved by taking advantage of the photoreducibility of silver ions.²¹ Au_n clusters in zeolites appeared only lately, starting with the report of Boudart and Meitzner in the 1980s as quoted in ref 22. Only a few investigations of Au_n clusters in zeolites were available, unlike for Ag_n . Au_n clusters, in comparison to Ag_n , were unstable due to the migration of Au_n clusters to the outer surface of the inorganic templates. The affinity of zeolites toward silver, as opposed to that against gold, is due to the fact that Ag^+ is the only noble monovalent cation that forms a mononuclear species with appreciable stability in water. Among the noble metals, only Ag^+ forms aqueous solutions, which can easily be exchanged in zeolites. Also in contrast to Ag^+ , Au^{3+} does not have photoinduced reducibility in the typical photon energies used.²² Generally, Au^{3+} requires chemical reduction. However, recently, Zhang et al. have achieved red-luminescent Au and Cu clusters through a photoreduction process.²³

(b) Using Templates. During the same time, another attractive way of creating Ag_n in polymer templates was demonstrated.²⁴ It is known that bare, small silver clusters are generally short-lived and undergo aggregation, being transformed into plasmonic systems in aqueous solutions, at ambient temperatures.²⁴ Henglein succeeded in stabilizing such intermediate clusters

using sodium polyacrylate. Here, the synthesis involves radiolytic reduction of Ag^+ ions in the presence of sodium polyacrylate. The very first product in the reduction of Ag^+ by the hydrated electron is the silver atom. Atomic Ag, formed rapidly, reacts with Ag^+ to produce a diatomic cluster, Ag_2^+ , which then grows into a stable polyatomic cluster on the polymer chains. The Coulombic repulsion between the chains prevents the clusters from coming closer. A similar scenario to obtain gold clusters is not favorable due to the fact that Au^{3+} is not photoreduced, unlike Ag^+ . After the synthesis of red-luminescent silver clusters by Kumecheva and co-workers²⁵ in the interior cavities of microgels by UV irradiation, several fluorescent silver clusters were synthesized.²⁶ Ras and co-workers have synthesized PMAA–AgQCs [PMAA = poly(methacrylic acid)] through reduction of Ag^+ , which was initiated by visible light. For the first time, they demonstrated strong solvatochromic and solvatofluorochromic properties along with the novel electroluminescence property of these clusters.²⁶ New methods such as sonochemical²⁷ and microwave-assisted²⁸ approaches were used to synthesize polymer-templated AgQCs. Most of the synthetic reports are limited to clusters in water. However, there are reports where clusters, first obtained in water, were subsequently transferred to other solvents. Recently, Diez et al. have succeeded in direct synthesis of blue-, green-, and red-emissive silver clusters in polar and nonpolar solvents (toluene, dichloroethane, THF, DMF, etc).²⁹ Nevertheless, there have been many polymer-templated, highly luminescent AuQCs but not to the extent of AgQCs.³⁰ Dendrimer encapsulation is also one of the efficient ways to control the size of the clusters.³¹ In recent years, dendrimers are engineered in such a way that they can hold a specific number of atoms.³²

DNA-hosted luminescent silver clusters have been one of the hot areas of research since the oligonucleotide-encapsulated AgQCs synthesized by Dickson and co-workers.³³ Synthesis and applications of such luminescent silver³⁴ and gold³⁰ clusters were thoroughly reviewed. AgQCs of different sizes with blue/green-, yellow-, red-, and NIR-emitting properties were synthesized. Several studies were also carried out to know the importance of bases and base sequences on the formation of oligonucleotide-stabilized luminescent AgQCs. However, in the case of DNA-template gold clusters, there are not many synthetic and optical tunability reports in the literature. Recently, DNA-templated, blue-³⁵ and red-³⁶ emitting gold nanoclusters were synthesized using mild reducing agents. Also, DNA-hosted, sequence-dependent formation of gold clusters was also reported.³⁷

Protein-encapsulated Ag or Au clusters are a subject of current research. This subject is extensively reviewed by Xavier et al.³⁸ The research activity of BSA-protected Ag_n clusters (BSA = bovine serum albumin) intensified following the report of $\text{Au}_{25}@\text{BSA}$ by Xie et al.³⁹ MALDI MS is the most important tool to characterize these clusters. Although ESI MS is successfully used to characterize proteins and protein–metal ion complexes, it is not very useful in characterizing their clusters. The number of metal atoms in a given protein-encapsulated cluster can be found from the difference between the mass values of free protein and protein-encapsulated clusters observed in MALDI MS. $\text{Au}_{25}@\text{BSA}$ is the first system that was observed by MALDI MS. Subsequently, MALDI MS provided the composition of several silver and gold clusters in protein templates. It is worth noting that through mass spectral studies, it was possible to understand the growth of metal

clusters in a given protein.⁴⁰ Intense research activities are currently undertaken on both Au⁴¹ and Ag⁴² @protein systems.

(c) Thiolate-Protected Clusters. Since the Brust–Schiffrin two-phase method for gold nanoparticles reported in 1994, studies of thiolate-protected gold clusters have become a fascinating area of research.⁴³ Molecular clusters of gold, distinctly different from nanoparticles, were noticed in 1997.⁴⁴ Evolution of research on thiol-protected gold clusters has contributed to newer excitement in cluster research.^{45,46} Correlation between theoretical and experimental results contributed to understanding these systems in detail. Different aspects of these clusters have been extensively reviewed by Jin,¹¹ Lu and Chen,⁴⁷ and our group.³⁸ Theoretical studies of these clusters were reviewed by Hakkinen.⁴⁸ In the following, we discuss recent developments in terms of synthetic protocols and also our own contributions to the development of new clusters.

Several types of synthetic routes exist that can produce clusters with desired characteristics in the final product. Besides the studies of the effect of thiol and of solvent on the nature of the products, not much information is available on other aspects, for example, on the effect of reducing agents. New protocols showed that the reduction potential of the reducing agent has a tremendous effect on the clusters.^{49–51} Ghosh et al. reported⁴⁹ a one-step route for the synthesis of an atomically precise cluster, Au₁₈SG₁₄ (SG, thiolate of glutathione). It is known that the reduction of Au³⁺ with a strong reducing agent, NaBH₄, in the presence of GSH resulted in a mixture of “magic” clusters (Au₁₀(SG)₁₀, Au₁₅(SG)₁₃, Au₁₈(SG)₁₄, Au₂₂(SG)₁₆, Au₂₂(SG)₁₇, Au₂₅(SG)₁₈, Au₂₉(SG)₂₀, Au₃₃(SG)₂₂, and Au₃₉(SG)₂₄),¹⁸ whereas using a slow reducing agent, NaBH₃CN, produces one cluster alone, namely, Au₁₈SG₁₄. Figure 1a shows the distinct absorption bands of Au₁₈(SG)₁₄ clusters, one centered at 590 nm (2.1 eV), a broad band at 515 nm, (2.4 eV) and another in the UV region at 290 nm (4.2 eV). It exhibits red luminescence at room temperature upon illumination with UV light. The quantum yield is ~5%, nearly 25-fold higher than that of Au₂₅SG₁₈. ESI MS shows a series of multiply charged peaks due to Au₁₈SG₁₄ (Figure 1b).

The success of the synthesis of Au₁₈(SG)₁₄ is attributed to the use of a mild reducing agent. This demonstrates that as in the case of organic synthesis, here too, controlled reactions are indeed possible. For example, in organic synthesis, sodium cyanoborohydride (NaBH₃CN) is used as a mild and selective reducing agent, which gives selective products, whereas the typical strong reducing reagent, NaBH₄, is less selective. A mild and selective reducing agent can help in slowing down the nucleation and retard the growth of the nuclei, which may result in the direct formation of smaller Au–SG QCs. A report⁵⁰ by Jin et al. presented the synthesis of Au₁₉(SPh)₁₃ (PET = phenylethane thiolate) QCs by the combination of both kinetic and thermodynamic control of the reaction. In this case, clusters of different sizes were formed initially, which then underwent size convergence into a monodisperse product by means of a prolonged aging process. For slow reduction, a weaker reducing agent, borane-*tert*-butylamine complex, was used. We note that upon using NaBH₄ as the reducing agent, another cluster, Au₂₅SR₁₈, is produced.⁵² In addition to these reports, a simple method to produce various gold clusters is to use CO as the reducing agent.⁵¹ These results demonstrate that variation in reactions could make single-step methods feasible for Au_n(SG)_m (*n* = 10, 15, 18, 19, 25, 29, 33) clusters.

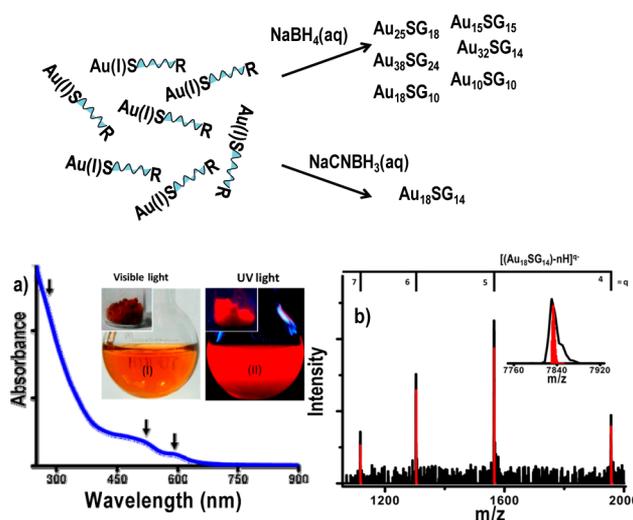


Figure 1. Schematic representation of two reduction processes, one using NaBH₄ and the other using NaCNBH₃. (a) UV/vis absorption profile of Au₁₈SG₁₄ clusters in water. Insets show the photographs of clusters in water upon illuminating with visible and UV light. (b) ESI MS spectrum of Au₁₈SG₁₄ in the negative mode, in the region of *m/z* 1000–2000. The peaks observed are due to Au₁₈SG₁₄. Red lines represent the calculated values for the charge states. The inset shows a deconvoluted spectrum based on the multiply charged species observed. Besides the molecular ion feature at *m/z* 7830, it shows higher mass number shoulders due to sodium addition. Here, the red spectrum gives the expected isotope distribution. Reprinted with permission from ref 49.

The similarity of organic reactions and cluster syntheses is demonstrated by these experiments.

From now onward, we shall describe recent developments of thiolate-protected silver clusters. Application of several traditional routes has resulted in the formation of plasmonic Ag systems and silver thiolates. Synthesis of silver clusters has learned significantly from the gold literature.

Variation in reduction methods produces clusters of different sizes. One such change is varying the strength of the reducing agent in a given reaction. This variation resulted in atomically precise Au₁₈SG₁₄ and Au₁₉SPh₁₃ nanoclusters.

Silver Clusters. Among a vast amount of research on thiolate-protected noble metal clusters, a major portion has been on gold, and very little has been on silver. This is due to the lack of suitable synthetic methods to produce the latter and also due to their reduced stability. The main difficulty in synthesizing silver clusters is the higher susceptibility of silver to oxidation. It makes conversion of the Ag_n core to Ag_nO_x, resulting the loss of characteristic optical features.⁵³ More focused research is needed to produce atomically precise Ag analogues of AuQCs. Detailed spectroscopic characterization is another challenge. Obviously, theoretical analyses are also needed.

After the successful synthesis of thiolated AuQCs,⁷ immediate attention was drawn to produce the Ag analogues. Most of the thiols, which stabilize effectively Au clusters, do not do so for Ag. For the latter, instead of stabilizing at the molecular level, they undergo further growth, forming plasmonic silver nanoparticles. Excellent studies in various areas, especially understanding the electronic band structure in comparison to metals, have appeared on these plasmonic systems.⁵⁴ Continuous improvement in this area produced new kinds of thiolated AgQCs, which possess discrete energy levels due to strong quantum confinement. Murray et al. had demonstrated quantized one-electron double-layer charging (QDL) for the first time in silver clusters.⁵³ Kimura et al. have synthesized mixtures of silver clusters protected with various hydrophilic thiols and separated them by gel electrophoresis.⁵⁵ Molecular behavior is seen in their optical properties. Lack of stability, which thwarts analysis by mass spectrometry, also restricted the initial efforts to characterize their photophysical and chiroptical properties.

(a) Synthetic Diversity. Some successful methods to achieve a handful of silver clusters are interfacial,⁵⁶ solid-state,⁵⁷ gel-mediated,⁵⁸ and reversible phase transfer;⁵⁹ ripening,⁶⁰ core etching,⁶¹ and high-temperature⁶² routes were added to the literature in the recent past. In addition, some traditional routes with minor changes^{63–66} were also used for their synthesis. Recently, interfacial synthesis is gaining attention as one of the promising methods for the synthesis of nanomaterials and their assemblies. Various metal nanocrystals and semiconducting materials have been synthesized using the interfacial route.⁶⁷ Interfacial properties, such as surface tension and interfacial potential, offer new synthetic variables to make nanomaterials. The interfacial etching route was initially used to synthesize 7 kDa silver QCs.⁶⁸ It was reported that clusters were formed only at the interphase. Later, using the same method, gram-scale syntheses of two luminescent silver clusters protected by mercaptosuccinic acid (H_2MSA), having well-defined molecular formulas ($Ag_8(H_2MSA)_8$ and $Ag_7(H_2MSA)_7$), were performed. Here, nanoparticles of different sizes, taken as starting materials, ultimately converged to a mixture of the above two clusters. This reaction was performed in an aqueous–organic biphasic system. During the reaction, the optical absorption spectra of the aqueous phase showed gradual disappearance of the surface plasmon resonance of metallic silver nanoparticles at 400 nm, indicating that nanoparticles were being converted to smaller cluster molecules. The mixture of two clusters, namely, Ag_7 and Ag_8 , was separated using gel electrophoresis. Ag_8 exhibits a peak at 520 nm in its optical absorption spectrum (Figure 2) and an emission in the red region. It shows strong temperature-dependent emission. A layer of toluene on top of the aqueous phase might have minimized the direct contact of silver with air during the etching process. Bigger nanoparticles (i.e., initially taken unetched nanoparticles) form a 2-D assembly at the water–toluene interphase in the course of this reaction.

The solid-state method is an interesting and novel route to make diverse silver clusters. Here, the time required to produce the desired cluster is substantially less. High yield of clusters and easy handling of reaction make this route novel. It is expected that this protocol opens up a new way to make a variety of cluster materials. It is in contrast to the general solid-state synthetic routes to make ceramics where most of the reactions take place at high temperatures in order to allow diffusion and nucleation between two or more reagents.

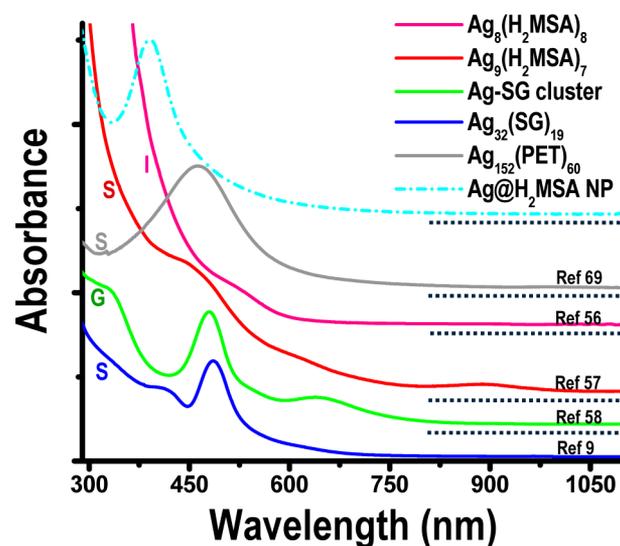


Figure 2. Optical absorption profiles of clusters obtained by different methods. Labels I, S, and G on the traces indicate interfacial, solid-state, and gel-mediated routes, respectively. The dashed trace at the top corresponds to $Ag@H_2MSA$ nanoparticles of 5–10 nm prepared by the traditional method.

Clusters were obtained by grinding metal precursor(s) and ligand (solid or liquid) followed by reduction with solid $NaBH_4$. In this process, initially, silver thiolate is formed due to the reaction between the silver salt such as $AgNO_3$ and thiol ($RSH = H_2MSA, GSH, phenylethanethiol (PETH), etc.$). High affinity of sulfur toward noble metal ions is the reason for thiolate formation. Upon addition of $NaBH_4$ in the solid form, the ground mixture turns to a brownish-black powder that shows high affinity to water. This situation is different from the synthesis in the solution phase. The essential steps of cluster formation, such as nucleation and growth, are controlled due to the lack of protic solvent as they are mixed in the solid state. Three main contributions have been made using the solid-state route;^{9,57,69} these are 9-, 32-, and 152-atom silver clusters protected by thiols of $H_2MSA, GSH,$ and $PETH,$ respectively. Some more clusters are yet to be characterized fully.⁷⁰ $Ag_9(H_2MSA)_7$ was obtained by grinding a mixture of $AgNO_3$ and H_2MSA in a 1:5 molar ratio with $NaBH_4$. Here, all of the precursors are taken in the solid form. The cluster shows a step-like feature in its UV/vis absorption spectrum, similar to the Au_{25} clusters. $Ag_{32}(SG)_{19}$ was also synthesized through the solid-state route, where $AgNO_3, GSH,$ and $NaBH_4$ were taken as precursors. Optical absorption spectra of this cluster possess a sharp peak at 480 nm and shoulder peaks at 420 and 610 nm (Figure 2).⁹

Recently, the synthesized Ag_{152} cluster opened the way to fundamental studies and potential applications in this area.⁶⁹ It was obtained by a solid-state route in which solid $AgNO_3$ was ground with $PETH$ (oily liquid) in a 1:5.3 molar ratio in a mortar and pestle. Adding 25 mg of $NaBH_4$ (solid) with continued grinding completes the reaction. Immediate extraction of excess thiol in the reaction mixture using ethanol and subsequent dissolution of the residue in either toluene or tetrahydrofuran (THF) gives a solution of the cluster. The crucial aspect of this procedure is the limited supply of water needed for the reduction, which becomes available from the laboratory atmosphere as well as from ethanol used for subsequent washings. The clusters were monodisperse, as confirmed by

the HPLC studies. The composition of the cluster Ag_{152} was detected by MALDI MS analyses (Figure 3). The spectra

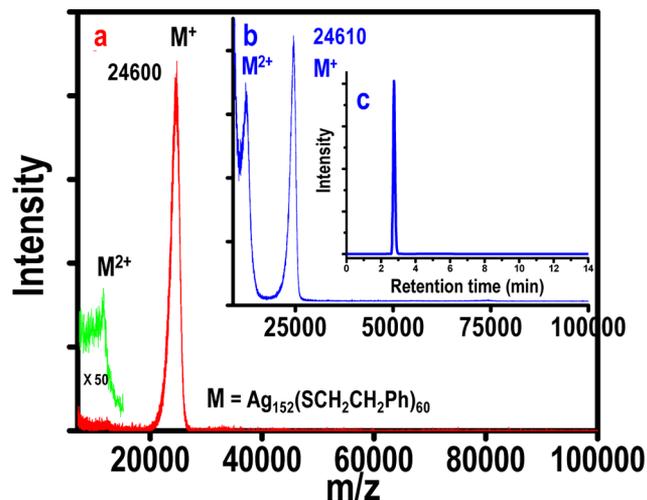


Figure 3. (a) MALDI MS spectrum of an as-synthesized 25 kDa cluster collected in the positive mode. It gives a sharp (fwhm, 1.5 k) molecular peak centered at m/z 24 600 \pm 100. A minor peak, at m/z 12 300 \pm 30, is seen, which corresponds to the doubly charged species. For clarity, this is expanded 50 times in the vertical axis. (b) Same as (a) but for the HPLC-purified sample, extracted in THF. It shows a narrower peak (fwhm of 1.3 k) at m/z 24 610 \pm 80 and a pronounced dication peak at m/z 12 320 \pm 30. (c) Chromatogram of the Ag_{152} cluster extracted in THF. Reprinted with permission from ref 69.

shown in Figure 3 are at the lowest laser power needed to observe ion signals. Mass spectra for the purified and unpurified samples show the same features with a single peak centered at m/z 24 600 [full width at half-maximum (fwhm) of 1.5 k] and the doubly charged cluster at m/z 12 300 \pm 30. However, HPLC-subjected samples show sharper peaks compared to the as-synthesized samples. Recent results from our lab have also shown the formation of gold and copper clusters by this route. This synthetic approach may make the synthesis of clusters of other elements feasible, as evidenced by the synthesis of iridium nanoparticles.⁹⁰ It is important to point out that because all products are in the solid/pasty state during synthesis, it is possible to collect samples at intermediate steps of reaction in order to get information about the progress of the reaction.

(b) Clusters to Superlattices (SLs). Another interesting report from Sugi et al.⁷⁰ described the systematic size evolution of organic-soluble, atomically precise Ag clusters monitored by various techniques. The same protocol as that above was used in this experiment to make clusters. In MALDI MS investigations, the initial product during the synthesis was a 13 kDa cluster (Figure 4a). These clusters transform gradually to more stable plasmonic nanoparticles with molecular masses of 70 and 80 kDa (Figure 4b). Again, a suspension of these nanoparticles upon constant heating at 100 °C leads to the formation of self-organized nanoparticles of higher molecular mass (148 kDa) (Figure 4c). These clusters of 13, 70, 80, and 148 kDa are tentatively assigned as $\text{Ag}_{\sim 75}(\text{PET})_{\sim 40}$, $\text{Ag}_{\sim 530}(\text{PET})_{\sim 100}$, $\text{Ag}_{\sim 561}(\text{PET})_{\sim 150}$, and $\text{Ag}_{\sim 923}(\text{PET})_{\sim 351}$, respectively (as the mass peaks are broad, the atomic composition is approximated). Accompanying this gradual mass evolution, systematic changes in optical absorption spectra are also observed. Those results show

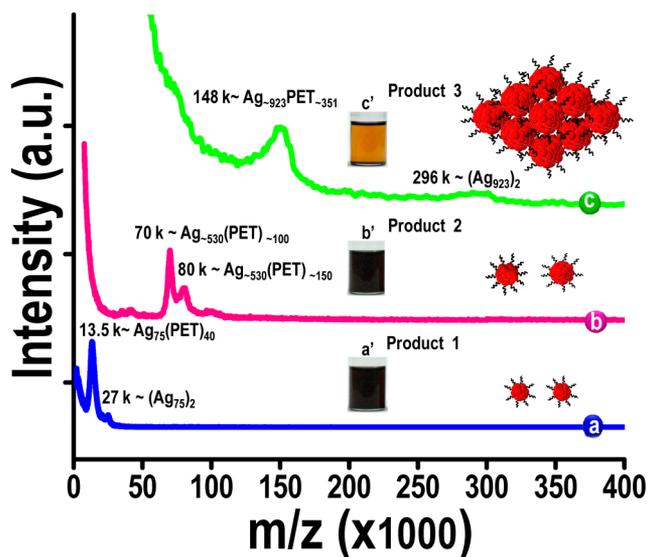


Figure 4. MALDI mass spectra showing the systematic size evolution of a cluster, labeled as product 1, to particle crystals. A sharp peak centered at m/z 13 k (a) obtained by operating at the threshold laser fluence is assigned as $\sim \text{Ag}_{75}(\text{PET})_{40}$ (product 1), with a hump at m/z of 27 k probably due to the dimer. Product 1 converts to product 2 (b), exhibiting plasmonic absorption, with a mass of 70 k and a weaker feature at 80 k tentatively assigned as $\text{Ag}_{\sim 530}(\text{PET})_{\sim 100}$ and $\text{Ag}_{\sim 561}(\text{PET})_{\sim 150}$ respectively). Gradual heating allows assembly of plasmonic product 2 to self-organized nanoparticles with definite periodicity (c) composed of ~ 923 Ag atoms ($\text{Ag}_{\sim 923}(\text{PET})_{\sim 351}$). Its dimer at 296 k has also been observed (c). Insets of mass spectra show the corresponding photographs and cartoon representations of the size evolution. In photograph (c'), a black precipitate can be seen at the bottom of the sample vial, corresponding to the SL. Reprinted with permission from ref 70, copyright 2013, Wiley-VCH.

the possibility of synthesis of nanomaterials with tunable properties in a one-pot method. Tunability arises as nanoparticle sizes can be controlled as they are formed starting from atomically precise clusters.

(c) Use of Gels. An important issue of concern of synthesis of any desired cluster is related to mass transfer, leading to controlled nucleation. Gels are composed of molecular cages that may be used to control mass transfer and to nucleate the preferred clusters. Cage dimensions and kinetic parameters may be controlled to yield desired results. Molecular cages of polyacrylamide gel were used for the direct synthesis of monodisperse silver–SG clusters in a single step and within 30 min. These clusters show prominent features at 350, 470, and 650 nm in their UV/vis absorption spectrum (sample G of Figure 2). The method involves reductive decomposition of $\text{Ag}(\text{I})\text{SG}$ thiolates in polyacrylamide gel cavities of sub-micrometer size. In this method, an acrylamide/bisacrylamide solution containing $\text{Ag}(\text{I})\text{SG}$ thiolates was allowed to polymerize in a beaker to form a gel. On top of this gel, aqueous NaBH_4 was added. The color of the gel changed from light yellow to dark brown within 0.5 h, indicating the formation of clusters inside of the cavities. Free clusters were extracted into water and precipitated using excess ethanol. Dry powder was obtained after the removal of solvent using a rotary evaporator. These clusters can selectively detect $\text{Hg}(\text{II})$ ions down to the ppb level.⁵⁸ Kitaev et al. also reported on the synthesis of similar clusters by two routes, (1) creating new kinds of reaction environments (cyclic reduction under oxidative conditions, where

NaBH₄ was used for reduction and H₂O₂ was used for oxidation) for Ag(I)SR, leading to the formation of AgQCs,⁶⁵ and (2) a direct process that involves the reduction of Ag(I)SG thiolates using NaBH₄ in H₂O/MeOH mixtures at basic conditions.⁶³

Addition of new protocols (interfacial, solid-state, and gel-mediated) and the resulting clusters expose enormous opportunities to study silver at the cluster level.

(d) Other Strategies. Bigioni et al.⁸¹ have synthesized crude Ag_nSG_m clusters by the reduction of Ag(I)SG thiolates with NaBH₄ in water. A series of clusters were isolated using gel electrophoresis, and their optical properties were studied. Compositions of these clusters were explored using electrophoresis by comparing their relative mobilities with the known gold QCs. Later, Guo et al.⁸² studied the composition of one of the clusters isolated from the sixth band of the gel. The optical properties of the cluster are given in Table 1. Figure 5a shows the ESI MS of the cluster at optimized conditions, a series of multiply charged peaks corresponding to [Ag₃₂(SG)₁₉]^{q-} are labeled on the spectrum, where *q* = 4, 5, 6, 7, and 8. This assignment was further confirmed by the agreement between the experimental and calculated isotope distributions of [Ag₃₂(SG)₁₉-4H]⁴⁻ (inset of Figure 5a).

Silver clusters of size ~2.1 nm were synthesized by incubating as-synthesized polydisperse Ag@SBB (SBB = thiolate of 4-*tert*-butylbenzyl mercaptan (BBSH)) clusters in the presence of clean BBSH at 60 °C.⁶⁰ Multiple characterization studies revealed that their chemical composition is Ag₂₈₀(SBB)₁₂₀. An interesting method reported by Yuan et al. is also added to this list for synthesizing fluorescent metal nanoclusters (Au, Ag, Pt, Cu).⁵⁹ It involves the phase transfer of water-soluble non-fluorescent metal nanoclusters (which were synthesized by a common chemical reduction method) to the organic medium by a phase-transfer agent. This method is mainly applicable to the clusters whose surfaces are passivated by ligands that are readily phase-transferable with cetyltrimethylammonium bromide (CTAB). As-synthesized clusters in the aqueous phase are nonfluorescent. In the toluene phase, after phase transfer, mild etching takes place, and the resulting nanoclusters exhibit strong fluorescence. Moreover, the fluorescent clusters can be easily transferred back to the aqueous phase upon adding a salt to remove the hydrophobic cation, CTA⁺.

Chemical reduction with minor changes in conditions such as solvent, pH, the ligand, and so forth are able to make molecular silver clusters. Among the well-characterized systems are Ag₇(DMSA)₄, Ag₄₄(4FTP)₃₀, Ag₃₂(SG)₁₉, and Ag₂₈₀(SSB)₁₂₀. More are waiting to be characterized fully.

Dhanalakshmi et al. showed the synthesis of red-luminescent silver clusters protected by H₂MSA, in milligram quantities by the direct core reduction of Ag@citrate.⁶¹ This route provides nearly pure clusters. On the basis of TG and elemental analysis, the composition of the cluster was tentatively assigned to Ag₃₈SG₂₄. An interesting protocol was reported⁶² by Indranath et al. for the synthesis of highly stable red-luminescent ~Ag₇₅ clusters. It involves formic-acid-mediated reduction of silver glutathionates in an aqueous medium at higher temperatures (70 °C). Absorption peaks evolved with time at constant temperature of 70 °C (Figure 5b). Here, Ag⁺ to reduction was initiated by electrons, which were produced by the decomposition of formic acid. A well-defined spectrum with prominent peaks appeared at the third hour of the reaction. Note that at these temperatures, AgQCs usually undergo decomposition, resulting in the formation of Ag₂S nanoparticles.⁸⁴ The optical properties of these clusters remain the same for several months at both room and higher temperatures. So far, this is the first example of the successful synthesis of Ag clusters in solution at higher temperatures.

Silver clusters, namely, intensely and broadly absorbing nanoparticles (IBANs), with high molar extinction coefficients were reported by Bakr et al.⁶⁴ The synthetic method belongs to the category of traditional routes but with major alterations. Briefly, IBANs were prepared through the reduction of a silver salt solution in the presence of the capping ligand 4-fluorothiophenol (4FTP) in the usual, one-phase nanoparticle synthesis (4FTP/Ag = 2:1). Initially, 4FTP was stirred with a silver salt in *N,N*-dimethylformamide (DMF) for 15 min, followed by the addition of 4 molar excess of NaBH₄ in DMF. This resulted in a darkened nanoparticle solution with a UV/vis absorption peak at 450 nm. Transparent yellow solution was formed upon further stirring (4 h), indicating the disassociation of nanoparticles to silver ions or silver thiolates. Remnant NaBH₄ in the resultant solution was activated upon the addition of a small amount of water. Again, the solution turned dark and showed a broad peak centered at around 490 nm in its UV/vis spectra. By leaving the reaction at freezer temperatures (-4 °C) over several days (~less than 1 week), it transferred to IBANs. These IBANs show eight distinct absorption bands with huge extinction cross sections of 2.59 × 10⁵ L mol⁻¹ cm⁻¹ (Figure 5c). Another report presented the ESI mass spectrum of 4-FTP-protected IBANs with high isotopic separation.⁸⁰ It revealed that the compositions of these IBANs are [Ag₄₄(4FTP)₃₀]⁴⁻ (Figure 5d). These clusters tend to be magic clusters because of their closed electronic shell (44e⁻ - 30e⁻ + 4e⁻ = 18e⁻).

Interestingly, a few clusters, protected by dithiols, were synthesized with slight changes in the common chemical reduction method. Dimercaptosuccinic acid (DMSA),⁷¹ lipoic acid (LA),⁸⁸ and polyethylene glycol (PEG)-appended LA⁸⁹ are some of the dithiols that can effectively passivate Ag clusters. Among these, Ag₇(DMSA)₄ has been studied in some detail in the literature. Electrochemical,⁷² theoretical,⁷³ and mass spectral⁷⁴ studies have been done on this system. LA and related dithiol-protected clusters are highly red-luminescent. The quantum yield can be increased to ~12%.⁸⁹ Compositions of LA-protected clusters are yet to be explored.

Among the Ag clusters described in the previous paragraphs, some, such as Ag₇,⁷¹ Ag₈,⁵⁶ and Ag₉,⁵⁷ could be categorized as small clusters, and others, such as Ag₃₂,⁸² Ag₄₄,⁸⁰ ~Ag₁₄₀,⁵³ Ag₁₅₂,⁶⁹ and Ag₂₈₀,⁶⁰ can be categorized as bigger clusters. Several of them have optimized protocols for their synthesis. Optical absorption profiles of each of the above-mentioned

Table 1. List of Silver Clusters Synthesized and Their Essential Properties^a

formula	synthetic method	cluster analysis	absorption peaks (in nm)	luminescence		other studies
				λ_{ex}	λ_{em}	
Ag ₄₀ (SBB) ₅₃ ⁵³	modified Brust protocol	MALDI MS/EA	475 (b)			electrochemistry
Ag ₃₈₀ (SBB) ₁₂₀ ⁶⁰	ripening process	ESI MS/TG	700 (w) and 800 (w)			
Ag ₇ (DMSA) ₄ ⁷¹	reduction of Ag(I)DMSA in EtOH	ESI MS/MS	500 (s), 415 (w) and 625 (w)	550	650	electrochemical, ⁷² theoretical, ⁷³ and mass spectral ⁷⁴ studies
Ag ₈ (H ₂ MSA) ₈ ⁵⁶	interfacial etching	ESI, MALDI MS/EA	550 (w)			catalysis, ⁷⁵ investigations on Hg(II) ion interaction, ⁷⁶ theoretical studies, ⁷⁷ and electron-transfer properties ⁷⁸
Ag ₉ (H ₂ MSA) ₇ ⁵⁷	through solid grinding of AgNO ₃ , H ₂ MSA, and NaBH ₄	ESI MS/EA	886 (w), 625 (w), 450 (w), 479 (w), and 315 (w)	620	720	pesticide degradation ⁷⁹
Ag ₄₄ (FTP) ₃₀ ⁸⁰	controlled reductive conditions	ESI MS	multi bands	independent	1345	
Ag ₃₂ (SG) ₁₉ ^{9,81,82}	isolated from crude Ag clusters ^{81,82}	ESI MS	486 (s), 415 (w) and 330 (w)			
Ag ₁₅₁ (PET) ₆₀ ⁶⁹	through solid grinding ⁹ of AgNO ₃ , SG, and NaBH ₄	ESI, MALDI MS/EA	486 (s), 415 (w), and 330 (w)	420, 500	680	
7 kDa cluster ⁶⁸	grinding of AgNO ₃ , PET, and NaBH ₄	MALDI MS/theoretical studies	460 (s, broad)	375	800	
ref 65	interfacial etching	PAGE	550 (w)	550	700	Hg(II) sensor
ref 63	cyclic oxidation and reduction of Ag(I)SR		490 (s), 660 (w), and 335 (w)	430, 450	625	chiroptical studies ⁶⁵
ref 58	reduction of Ag(I)SR at basic conditions		490 (s), 660 (w), and 335 (w)	495	595	chiroptical studies ⁶³
ref 66	reduction of Ag(I)SG inside gels		480 (s), 640 (w), and 330 (w)	480	630	Hg(II) sensor, ⁸³ graphene-based composite, ⁸³ and thermal studies ⁸⁴
ref 67	chemical reduction route	TG	469 (s)			chiroptical studies
ref 59/Ag ₅₉ (SG) ₂₂	Ag@PET		395 (w) and 462 (s)			cysteine detection ⁸⁵
ref 86	Ag@FTP		478 (s)			Hg(II) sensor ⁸⁶
ref 87	Ag@SG		490 (b)	508	620	
ref 88 and 89	cyclic phase transfer	TG/EA	500 (b)			Pb(II) sensor ⁸⁷
Ag ₇₅ cluster ⁶²	reduction of Ag(I)SG using N ₂ H ₄ ·2H ₂ O at basic conditions similar to ref 86		435 (s), 335 (w), and 500 (w)	325, 500	650	Hg(II) sensor ⁸⁸
ref 61 (~Ag ₃₈)	reduction of Ag(I)LA in H ₂ O high-temperature synthesis	MALDI MS	480 (s), 420 (s), and 320 (w)	360, 400, 430	670	
	core etching reaction	EA	520 (w)			

^aAbbreviations: EA = elemental analysis; TG = thermogravimetric analysis; b = broad; w = weak; s = strong.

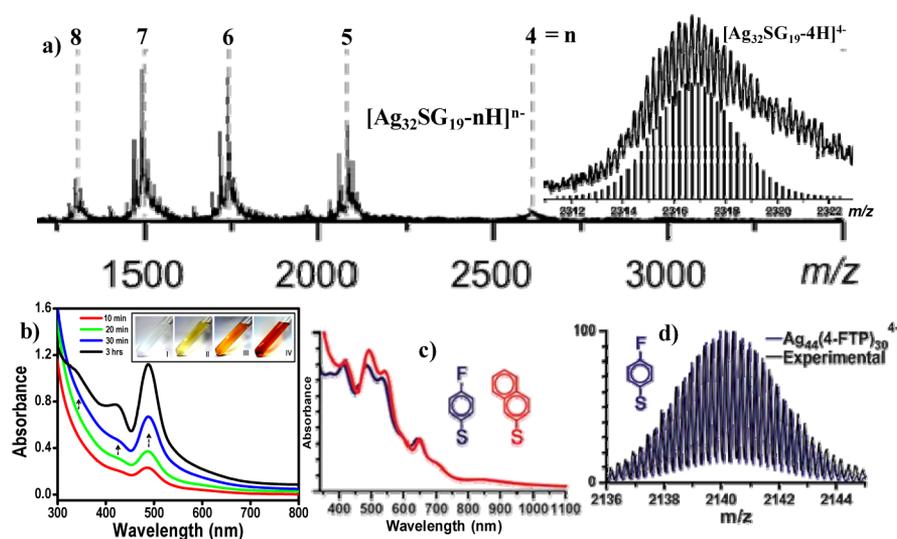


Figure 5. (a) ESI MS of $\text{Ag}_{32}(\text{SG})_{19}$. Multiply charged peaks are marked on the spectrum. The inset shows the comparison of the experimental (black trace) and simulated (bars) isotopic distributions for $[\text{Ag}_{32}(\text{SG})_{19-4\text{H}}]^{4-}$. (b) UV/vis absorption spectra of the growth of Ag_{75} clusters with time. (Insets) Photographs of the reaction mixture during synthesis at 0 (I), 10 (II), and 20 min (III) and 3 h (IV). (c) UV/vis absorption of $\text{Ag}_{44}(\text{4FTP})_{30}^{4-}$ and $\text{Ag}_{44}(\text{2NPT})_{30}^{4-}$. (d) ESI MS of $\text{Ag}_{44}(\text{4FTP})_{30}^{4-}$. The mass spectrum matches well with the calculated spectrum (blue and black, respectively). (a) Reprinted with permission from ref 82; (b) reprinted with permission from ref 62, copyright 2012, RSC; (c,d) Reprinted with permission from ref 80, copyright 2012, RSC.

clusters is different. The origin of optical transitions in silver nanoclusters is yet to be understood. Some of these clusters were used for applications in several fields. For example, alumina-loaded $\text{Ag}_{7,8}$ shows enhanced catalytic activity,⁷⁵ and $\text{Ag}_{7,8}$ shows sensing of Hg^{2+} .⁷⁶ A report by Bootharaju et al.⁷⁹ showed that Ag_9 could be used for the removal of pesticides for water purification. Silver clusters protected with $-\text{SG}$ with unknown compositions were obtained through hydrazine ($\text{N}_2\text{H}_4 \cdot 2\text{H}_2\text{O}$) reduction. They were used for selective sensing of metal ions such as $\text{Hg}(\text{II})$ ⁸⁶ and $\text{Pb}(\text{II})$.⁸⁷ Protein-protected Ag_{15} clusters, in combination with mesoporous gold nanostars, could be used in the visible detection of TNT down to zeptomolar concentrations.⁹¹ It indicates that application possibilities of these systems are bright. List of various silver clusters reported and their essential properties are listed in Table 1.

Obtaining a desired AgQC depends on a synthetic protocol. Once these are synthesized, they show huge applications in the areas of sensors, catalysts, water purification, and so forth.

Stability of Silver Clusters. From the developments in gold cluster research, it is evident that the effectiveness of the staple motif, super atom electronic count, core stability against dissociation, and a large HOMO–LUMO gap are the factors that decide the stability of these systems.⁹² However, chemical interactions too play their part in determining the above factors. Stronger strength of metal–metal and metal–ligand bonds helps to build a stable atomic structure and an effective protection of the core by the staple motif. The connection between bond strength and stability was demonstrated experimentally and theoretically.^{93,94} Clusters in the category of super atom (systems satisfying the jellium model) also exhibit higher stability than others. In the case of silver clusters, the Ag–Ag

and Ag–S interactions are weaker in comparison to Au–Au and Au–S interactions ($\text{Au–Au} > \text{Ag–Ag}$; $\text{Au–S} > \text{Ag–S}$). In addition, gold systems possess aurophilic attractions, and the corresponding interactions are less in the case of Ag. These advantages of Au in comparison to Ag help to span the gold cluster research to a broad range of systems.

Practical difficulties to stabilize the silver clusters were overcome by encapsulating them in polymer templates.⁶³ The degradation rates can be minimized by storing the cluster samples in suitable solvent mixtures⁵⁷ and at an optimized pH⁵⁷ and, more importantly, keeping the cluster solution at lower temperatures.^{64,71} Powder samples are more stable in comparison to their solutions. Some of these clusters are highly stable even at ambient conditions ($\text{Ag}_{32}(\text{SG})_{19}$). The stability of the clusters can be easily understood by monitoring the UV/vis of cluster solutions. Characteristic optical properties of a given AgQC are very sensitive to pH, temperature, and solvents.^{56,82} In the case of less stable clusters, optical absorption spectra undergo changes with time. We speculate that this happens either by a change in the net charge of the cluster or by the interconversion of isomers or due to the transformation of cluster cores. Some absorption peaks in a particular sample are sensitive, and they disappear rapidly. For example, we have observed the disappearance of the 650 and 350 nm peaks with time in sample G of Figure 2, leaving only an intense peak at 480 nm. It has to be noted that all of the peaks are arising from the same sample, confirmed from gel electrophoresis. In the first case, AgQCs may carry excess negative charge (evident in the case of $[\text{Ag}_{44}(\text{4FTP})_{30}]^{4-}$). It is possible to observe a variety of absorption profiles for the same cluster by varying the charge ($4^-, 3^-, 2^-, 1^-, 0, 1^+$). It is known that minor changes were seen in the case of $[\text{Au}_{25}(\text{SG}_{18})^0]$ to $[\text{Au}_{25}(\text{SG}_{18})^-]$. However, crystallographic studies on these clusters are waiting for a better understanding. Recently, there has been some progress in this area due to the single-crystal analysis of AgQCs protected by thiolate and phosphine ligands.^{95,96} These studies reveal the different atomic structure of thiolated AgQCs in comparison to

AuQCs, suggesting that new structural models may be needed to understand AgQCs.

Alloy Quantum Clusters. Alloy nanoparticles (3–100 nm) made up of Ag and Au were well-studied materials in the recent past.⁹⁷ However, efforts to obtain quantum alloy clusters of these elements are very few. Reports include phosphine-protected Au₁₈Ag₂₀⁹⁸ and Au₁₃Ag₁₂⁹⁹ clusters. Another kind of material emerging in this area are the Au_nSR_m analogues. There are several successful reports for the synthesis of monodisperse clusters of the type, Ag_nAu_{25-n}(SR)₁₈,¹⁰⁰ (AuAg)₁₄₀(SR)₆₀,¹⁰¹ and Au_{38-n}Ag_n(SR)₂₄.¹⁰² These were obtained by the simultaneous reduction of appreciable concentrations of silver and gold salts in suitable conditions. Motivated by these reports, theoreticians have predicted their structural details based on DFT calculations.¹⁰³ An important outcome from such calculations is the preferential occupancy of silver on the surface of a gold core. Both experiments and calculations have shown that an increase in the number of silver atoms in Au₁₄₀(SR)₆₀ slightly decreases the optical band gap^{104,105} and alters the electronic shell structure, which results in changes in the optical transitions present in the high-energy region (interband transitions). In the case of protein template AgAu alloy clusters, only a few reports are available.^{106,107} Among the alloy clusters, Au_{38-n}Ag_n@BSA was well-characterized using MALDI MS.¹⁰⁷ Synthesis and studies of alloy clusters in protein templates are awaited.

Another way to produce alloy clusters is to use the advantage of the galvanic exchange process at the atomic level. By the addition of Au(I)SR to silver clusters at suitable conditions, one can produce alloy clusters. Direct addition of Au³⁺ may collapse the clusters. Murray et al. had reported the creation of luminescent alloy clusters through this process.¹⁰⁸ As compared to the parent silver clusters, noticeable changes were observed in the optical properties of alloy clusters. The same methodology was applied on still smaller silver clusters, Ag_{7,8}(H₂MSA)₈, which eventually resulted in the formation of a 13-atom alloy cluster.¹⁰⁹ Its chemical composition, Ag₇Au₆(H₂MSA)₁₀, was found from ESI MS along with elemental analysis. A galvanic reaction between Au(I) thiolate and crude silver clusters (Ag_{7,8}(H₂MSA)_{7,8}) made this alloy cluster. Optical absorption (350 and 692 nm) and luminescence (λ_{ex} 390 and λ_{em} 650 nm) were changed drastically as compared to the parent clusters. Theoretical results suggested that the cluster possessed a distorted icosahedral core. The simulated absorption spectrum of this structure is in agreement with the experimentally obtained spectrum. It is proposed that the clusters obtained in the galvanic exchange process may carry gold on the surface with silver in the core. It is in contrast to the clusters obtained in earlier cases (simultaneous reduction of both metal salts). If this is proven by future theoretical and experimental studies, there is a possibility to have both “silver-covered” and “gold-covered” alloy clusters with tunable electronic, optical, and catalytic properties.

MS/MS Analysis. Most of the compositions of clusters were determined by mass spectrometry. While soft ionization mass spectrometry is an invaluable tool in determining the molecular formulas of clusters, profound structural insights are derived from MS/MS analysis (tandem mass spectrometry). As expected, these kinds of studies were done initially on the well-known cluster Au₂₅SR₁₈.¹¹⁰ MS/MS studies on other magic gold clusters are awaited. Recently, tandem mass spectrometry of Au₁₈SG₁₄ by Ghosh et al. showed the possibility of monolayer-protected “super atoms” in the gas phase. Note that so far, we know only

about naked (unligated) gas-phase super atoms. Mass spectral peaks of [Au₁₈(SG)_{14-n}H]^{q-} at m/z 1956.2, 1565.2, 1304.3, and 1117.4 for $q = 4, 5, 6,$ and 7 were subjected to MS/MS analyses. Upon subjecting these peaks to MS/MS, we got several fragments, which were all 8e⁻ entities, that is, $m - n + q = 8$, where m is the number of gold atoms, n is the number of thiolate ligands, and q is the charge on the ligand. For example, [Au₁₈SG₁₄]⁵⁻ underwent various types of dissociations and produced peaks of 4⁻ charge during MS/MS at various collision energies. MS/MS for other charged anions also ended with cluster ions carrying 4⁻ charge. All of them satisfy the condition, $m - n + q = 8$. Here, the electron count includes the charges on the ligands as well. At all collision energies, super atom formation was observed.

Signatures of two kinds of alloy materials, namely, “Au-centered/silver-covered” and “Ag-centered/gold-covered”, are seen.

MS/MS studies on Ag₇(DMSA)₄ show Ag_nS₄⁻ ($1 \leq n \leq 7$) species at various collision energies.⁷⁴ The ions Ag₇S₄⁻, Ag₆S₄⁻, Ag₅S₄⁻, Ag₄S₄⁻, Ag₃S₄⁻, Ag₂S₄⁻, and AgS₄⁻ were formed sequentially from [Ag₇(DMSA)₄]²⁻ with an increase in collision energy (25, 40, 50, 70, 80, 90, and 100 eV, respectively). A DFT-based global-minimum search further confirms that the formed species are stable.

Perspectives. The science of quantum-confined cluster cores of silver with ligand protection possessing well-defined molecular formulas has attracted intense interest in the recent past. Although a uniform synthetic strategy is not available to make clusters of all kinds, available methods can produce a number of cluster cores with several ligands. The most important property of these clusters is their luminescence in the visible region and the sensitivity of this luminescence to various analytes. The composition of clusters can be varied by making alloys, and a few of these are now available. The chemistry of the cluster systems is beginning to evolve, and their specific reactivity is a subject of attention. Noble metal clusters are now made in the confinement of proteins, and applications of these systems are evolving fast. The most immediate need in the chemistry of such systems is crystallization and understanding the properties in a size-dependent fashion. Early signs of expansion of the science of silver clusters are evident from the recent reports. Utilization of their properties in areas such as sensing, environmental remediation, water purification, imaging, and diagnostics will be important areas of exploration.

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ACKNOWLEDGMENTS

We thank the Department of Science and Technology, Government of India for constantly supporting our research program on nanomaterials.

REFERENCES

- (1) Faraday, M. *Philos. Trans. R. Soc., London* **1857**, *147*, 145–181.
- (2) Daniel, M.-C.; Astruc, D. Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-Size-Related Properties, and Applications toward Biology, Catalysis, and Nanotechnology. *Chem. Rev.* **2003**, *104*, 293–346.
- (3) Mie, G. *Ann. Phys.* **1908**, *25*, 377.
- (4) Knoll, M. K.; Subjective Light, J. Pattern Spectroscopy in the Electroencephalic Range. *Nature (London)* **1959**, *184*, 1823–1824.
- (5) Turkevich, J.; Stevenson, P. C.; Hillier, J. A Study of the Nucleation and Growth Processes in the Synthesis of Colloidal Gold. *Discuss. Faraday Soc.* **1951**, *11*, 55–75.
- (6) Link, S.; El-Sayed, M. A. *Int. Rev. Phys. Chem.* **2000**, *19*, 409–453.
- (7) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. Monolayer-Protected Cluster Molecules. *Acc. Chem. Res.* **1999**, *33*, 27–36.
- (8) Zhu, M.; Aikens, C. M.; Hollander, F. J.; Schatz, G. C.; Jin, R. Correlating the Crystal Structure of a Thiol-Protected Au₂₅ Cluster and Optical Properties. *J. Am. Chem. Soc.* **2008**, *130*, 5883–5885.
- (9) Udayabhaskararao, T.; Bootharaju, M. S.; Pradeep, T. Thiolate-Protected Ag₃₂ Clusters: Mass Spectral Studies of Composition and Insights into the Thiolate Structure from NMR. *Nanoscale* **2013**, submitted.
- (10) Walter, M.; Akola, J.; Lopez-Acevedo, O.; Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Whetten, R. L.; Grönbeck, H.; Häkkinen, H. A Unified View of Ligand-Protected Gold Clusters As Superatom Complexes. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 9157–9162.
- (11) Jin, R. Quantum Sized, Thiolate-Protected Gold Nanoclusters. *Nanoscale* **2010**, *2*, 343–362.
- (12) Ramasamy, P.; Guha, S.; Shibu, E. S.; Sreeprasad, T. S.; Bag, S.; Banerjee, A.; Pradeep, T. Size Tuning of Au Nanoparticles Formed by Electron Beam Irradiation of Au₂₅ Quantum Clusters Anchored within and Outside of Dipeptide Nanotubes. *J. Mater. Chem.* **2009**, *19*, 8456–8462.
- (13) Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Bushnell, D. A.; Kornberg, R. D. Structure of a Thiol Monolayer-Protected Gold Nanoparticle at 1.1 Å Resolution. *Science* **2007**, *318*, 430–433.
- (14) Heaven, M. W.; Dass, A.; White, P. S.; Holt, K. M.; Murray, R. W. Crystal Structure of the Gold Nanoparticle [N(C₈H₁₇)₄]-[Au₂₅(SCH₂CH₂Ph)₁₈]. *J. Am. Chem. Soc.* **2008**, *130*, 3754–3755.
- (15) Qian, H.; Eckenhoff, W. T.; Zhu, Y.; Pintauer, T.; Jin, R. Total Structure Determination of Thiolate-Protected Au₃₈ Nanoparticles. *J. Am. Chem. Soc.* **2010**, *132*, 8280–8281.
- (16) Zeng, C.; Qian, H.; Li, T.; Li, G.; Rosi, N. L.; Yoon, B.; Barnett, R. N.; Whetten, R. L.; Landman, U.; Jin, R. Total Structure and Electronic Properties of the Gold Nanocrystal Au₃₆(SR)₂₄. *Angew. Chem., Int. Ed.* **2012**, *51*, 13114–13118.
- (17) Das, A.; Li, T.; Nobusada, K.; Zeng, Q.; Rosi, N. L.; Jin, R. Total Structure and Optical Properties of a Phosphine/Thiolate-Protected Au₂₄ Nanocluster. *J. Am. Chem. Soc.* **2012**, *134*, 20286–20289.
- (18) Negishi, Y.; Nobusada, K.; Tsukuda, T. Glutathione-Protected Gold Clusters Revisited: Bridging the Gap between Gold(I)–Thiolate Complexes and Thiolate-Protected Gold Nanocrystals. *J. Am. Chem. Soc.* **2005**, *127*, 5261–5270.
- (19) Harkness, K. M.; Cliffel, D. E.; McLean, J. A. Characterization of Thiolate-Protected Gold Nanoparticles by Mass Spectrometry. *Analyst* **2010**, *135*, 868–874.
- (20) Wurth, W. M. M. Atomic Clusters: From Gas Phase to Deposited. In Woodruff, D. P., Ed.; *The Chemical Physics of Solid Surfaces*; Elsevier: Oxford, U.K., 2007.
- (21) Sun, T.; Seff, K. Silver Clusters and Chemistry in Zeolites. *Chem. Rev.* **1994**, *94*, 857–870.
- (22) Meitzner, M. B. a. G. *EXAFS Near Edge Structure 3*; Springer Proceedings in Physics, 1984; Vol. 2.
- (23) Zhang, H.; Huang, X.; Li, L.; Zhang, G.; Hussain, I.; Li, Z.; Tan, B. Photoreductive Synthesis of Water-Soluble Fluorescent Metal Nanoclusters. *Chem. Commun.* **2012**, *48*, 567–569.
- (24) Henglein, A. Small-Particle Research: Physicochemical Properties of Extremely Small Colloidal Metal and Semiconductor Particles. *Chem. Rev.* **1989**, *89*, 1861–1873.
- (25) Zhang, J.; Xu, S.; Kumacheva, E. Photogeneration of Fluorescent Silver Nanoclusters in Polymer Microgels. *Adv. Mater.* **2005**, *17*, 2336–2340.
- (26) Diez, I.; Ras, R. H. A. Fluorescent silver nanoclusters. *Nanoscale* **2011**, *3*, 1963–1970.
- (27) Xu, H.; Suslick, K. S. Sonochemical Synthesis of Highly Fluorescent Ag Nanoclusters. *ACS Nano* **2010**, *4*, 3209–3214.
- (28) Liu, S.; Lu, F.; Zhu, J.-J. Highly Fluorescent Ag Nanoclusters: Microwave-Assisted Green Synthesis and Cr³⁺ Sensing. *Chem. Commun.* **2011**, *47*, 2661–2663.
- (29) Diez, I.; Kanyuk, M. I.; Demchenko, A. P.; Walther, A.; Jiang, H.; Ikkala, O.; Ras, R. H. A. Blue, Green and Red Emissive Silver Nanoclusters Formed in Organic Solvents. *Nanoscale* **2012**, *4*, 4434–4437.
- (30) Lin, C.-A. J.; Lee, C.-H.; Hsieh, J.-T.; Wang, H.-H.; Li, J. K.; Shen, J.-L.; Chan, W.-H.; Yeh, H.-I.; Chang, W. H. Synthesis of Fluorescent Metallic Nanoclusters toward Biomedical Application: Recent Progress and Present Challenges. *J. Med. Biol. Eng.* **2009**, *29*, 276–283.
- (31) Kim, Y.-G.; Oh, S.-K.; Crooks, R. M. Preparation and Characterization of 1–2 nm Dendrimer-Encapsulated Gold Nanoparticles Having Very Narrow Size Distributions. *Chem. Mater.* **2003**, *16*, 167–172.
- (32) Kitazawa, H.; Albrecht, K.; Yamamoto, K. Synthesis of a Dendrimer Reactor for Clusters with a Magic Number. *Chem. Lett.* **2012**, *41*, 828–830.
- (33) Petty, J. T.; Zheng, J.; Hud, N. V.; Dickson, R. M. DNA-Templated Ag Nanocluster Formation. *J. Am. Chem. Soc.* **2004**, *126*, 5207–5212.
- (34) Choi, S.; Dickson, R. M.; Yu, J. Developing Luminescent Silver Nanodots for Biological Applications. *Chem. Soc. Rev.* **2012**, *41*, 1867–1891.
- (35) Kennedy, T. A. C.; MacLean, J. L.; Liu, J. Blue Emitting Gold Nanoclusters Templated by Poly-cytosine DNA at Low pH and Polyadenine DNA at Neutral pH. *Chem. Commun.* **2012**, *48*, 6845–6847.
- (36) Liu, G.; Shao, Y.; Ma, K.; Cui, Q.; Wu, F.; Xu, S. Synthesis of DNA-Templated Fluorescent Gold Nanoclusters. *Gold Bull.* **2012**, *45*, 69–74.
- (37) Guiying, L.; Yong, S.; Fei, W.; Shujuan, X.; Jian, P.; Lingling, L. DNA-Hosted Fluorescent Gold Nanoclusters: Sequence-Dependent Formation. *Nanotechnology* **2013**, *24*, 015503.
- (38) Lourdu Xavier, P.; Chaudhari, K.; Baksi, A.; Pradeep, T. Protein-Protected Luminescent Noble Metal Quantum Clusters: An Emerging Trend in Atomic Cluster Nanoscience. *Nano Rev.* **2012**, *3*, 14767.
- (39) Xie, J.; Zheng, Y.; Ying, J. Y. Protein-Directed Synthesis of Highly Fluorescent Gold Nanoclusters. *J. Am. Chem. Soc.* **2009**, *131*, 888–889.
- (40) Chaudhari, K.; Xavier, P. L.; Pradeep, T. Understanding the Evolution of Luminescent Gold Quantum Clusters in Protein Templates. *ACS Nano* **2011**, *5*, 8816–8827.

- (41) Baksi, A.; Xavier, P. L.; Chaudhari, K.; Goswami, N.; Pal, S. K.; Pradeep, T. Protein-Encapsulated Gold Cluster Aggregates: The Case of Lysozyme. *Nanoscale* **2013**, *5*, 2009–2016.
- (42) Anand, U.; Ghosh, S.; Mukherjee, S. Toggling Between Blue and Red-Emitting Fluorescent Silver Nanoclusters. *J. Phys. Chem. Lett.* **2012**, *3*, 3605–3609.
- (43) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. Synthesis of Thiol-Derivatised Gold Nanoparticles in a Two-Phase Liquid–Liquid System. *J. Chem. Soc., Chem. Commun.* **1994**, 801–802.
- (44) Alvarez, M. M.; Khoury, J. T.; Schaaff, T. G.; Shafiqullin, M. N.; Vezmar, I.; Whetten, R. L. Optical Absorption Spectra of Nanocrystal Gold Molecules. *J. Phys. Chem. B* **1997**, *101*, 3706–3712.
- (45) Dolamic, I.; Knoppe, S.; Dass, A.; Bürgi, T. First Enantioseparation and Circular Dichroism Spectra of Au₃₈ Clusters Protected by Achiral Ligands. *Nat. Commun.* **2012**, *3*, 798.
- (46) Philip, R.; Chantharasupawong, P.; Qian, H.; Jin, R.; Thomas, J. Evolution of Nonlinear Optical Properties: From Gold Atomic Clusters to Plasmonic Nanocrystals. *Nano Lett.* **2012**, *12*, 4661–4667.
- (47) Lu, Y.; Chen, W. Sub-Nanometre Sized Metal Clusters: From Synthetic Challenges to the Unique Property Discoveries. *Chem. Soc. Rev.* **2012**, *41*, 3594–3623.
- (48) Hakkinen, H. The Gold–Sulfur Interface at the Nanoscale. *Nat. Chem.* **2012**, *4*, 443–455.
- (49) Ghosh, A.; Udayabhaskararao, T.; Pradeep, T. One-Step Route to Luminescent Au₁₈SG₁₄ in the Condensed Phase and Its Closed Shell Molecular Ions in the Gas Phase. *J. Phys. Chem. Lett.* **2012**, *3*, 1997–2002.
- (50) Wu, Z.; MacDonald, M. A.; Chen, J.; Zhang, P.; Jin, R. Kinetic Control and Thermodynamic Selection in the Synthesis of Atomically Precise Gold Nanoclusters. *J. Am. Chem. Soc.* **2011**, *133*, 9670–9673.
- (51) Yu, Y.; Luo, Z.; Yu, Y.; Lee, J. Y.; Xie, J. Observation of Cluster Size Growth in CO-Directed Synthesis of Au₂₅(SR)₁₈ Nanoclusters. *ACS Nano* **2012**, *6*, 7920–7927.
- (52) Zhu, M.; Lanni, E.; Garg, N.; Bier, M. E.; Jin, R. Kinetically Controlled, High-Yield Synthesis of Au₂₅ Clusters. *J. Am. Chem. Soc.* **2008**, *130*, 1138–1139.
- (53) Branham, M. R.; Douglas, A. D.; Mills, A. J.; Tracy, J. B.; White, P. S.; Murray, R. W. Arylthiolate-Protected Silver Quantum Dots. *Langmuir* **2006**, *22*, 11376–11383.
- (54) Collier, C. P.; Saykally, R. J.; Shiang, J. J.; Henrichs, S. E.; Heath, J. R. Reversible Tuning of Silver Quantum Dot Monolayers Through the Metal–Insulator Transition. *Science* **1997**, *277*, 1978–1981.
- (55) Nishida, N.; Yao, H.; Ueda, T.; Sasaki, A.; Kimura, K. Synthesis and Chiroptical Study of D/L-Penicillamine-Capped Silver Nanoclusters. *Chem. Mater.* **2007**, *19*, 2831–2841.
- (56) Udayabhaskararao, T.; Pradeep, T. Luminescent Ag₇ and Ag₈ Clusters by Interfacial Synthesis. *Angew. Chem., Int. Ed.* **2010**, *49*, 3925–3929.
- (57) Udayabhaskararao, T.; Nataraju, B.; Pradeep, T. Ag₉ Quantum Cluster through a Solid-State Route. *J. Am. Chem. Soc.* **2010**, *132*, 16304–16307.
- (58) Chakraborty, I.; Udayabhaskararao, T.; Pradeep, T. Luminescent Sub-Nanometer Clusters for Metal Ion Sensing: A New Direction in Nanosensors. *J. Hazard. Mater.* **2012**, *211–212*, 396–403.
- (59) Yuan, X.; Luo, Z.; Zhang, Q.; Zhang, X.; Zheng, Y.; Lee, J. Y.; Xie, J. Synthesis of Highly Fluorescent Metal (Ag, Au, Pt, and Cu) Nanoclusters by Electrostatically Induced Reversible Phase Transfer. *ACS Nano* **2011**, *5*, 8800–8808.
- (60) Negishi, Y.; Arai, R.; Niihori, Y.; Tsukuda, T. Isolation and Structural Characterization of Magic Silver Clusters Protected by 4-(tert-Butyl)benzyl Mercaptan. *Chem. Commun.* **2011**, *47*, S693–S695.
- (61) Dhanalakshmi, L.; Udayabhaskararao, T.; Pradeep, T. Conversion of Double Layer Charge-Stabilized Ag@Citrate Colloids to Thiol Passivated Luminescent Quantum Clusters. *Chem. Commun.* **2012**, *48*, 859–861.
- (62) Chakraborty, I.; Udayabhaskararao, T.; Pradeep, T. High Temperature Nucleation and Growth of Glutathione Protected Ag₇₅ Clusters. *Chem. Commun.* **2012**, *48*, 6788–6790.
- (63) Cathcart, N.; Kitaev, V. Silver Nanoclusters: Single-Stage Scalable Synthesis of Monodisperse Species and Their Chiroptical Properties. *J. Phys. Chem. C* **2010**, *114*, 16010–16017.
- (64) Bakr, O. M.; Amendola, V.; Aikens, C. M.; Wenseleers, W.; Li, R.; Dal Negro, L.; Schatz, G. C.; Stellacci, F. Silver Nanoparticles with Broad Multiband Linear Optical Absorption. *Angew. Chem., Int. Ed.* **2009**, *48*, S921–S926.
- (65) Cathcart, N.; Mistry, P.; Makra, C.; Pietrobon, B.; Coombs, N.; Jelokhani-Niaraki, M.; Kitaev, V. Chiral Thiol-Stabilized Silver Nanoclusters with Well-Resolved Optical Transitions Synthesized by a Facile Etching Procedure in Aqueous Solutions. *Langmuir* **2009**, *25*, 5840–5846.
- (66) Farrag, M.; Thämer, M.; Tschurl, M.; Bürgi, T.; Heiz, U. Preparation and Spectroscopic Properties of Monolayer-Protected Silver Nanoclusters. *J. Phys. Chem. C* **2012**, *116*, 8034–8043.
- (67) Rao, C. N. R.; Kalyanikutty, K. P. The Liquid–Liquid Interface as a Medium to Generate Nanocrystalline Films of Inorganic Materials. *Acc. Chem. Res.* **2008**, *41*, 489–499.
- (68) Mrudula, K. V.; Udayabhaskararao, T.; Pradeep, T. Interfacial Synthesis of Luminescent 7 kDa Silver Clusters. *J. Mater. Chem.* **2009**, *19*, 4335–4342.
- (69) Chakraborty, I.; Govindarajan, A.; Erusappan, J.; Ghosh, A.; Pradeep, T.; Yoon, B.; Whetten, R. L.; Landman, U. The Superstable 25 kDa Monolayer Protected Silver Nanoparticle: Measurements and Interpretation as an Icosahedral Ag₁₅₂(SCH₂CH₂Ph)₆₀ Cluster. *Nano Lett.* **2012**, *12*, 5861–5866.
- (70) Sugi, K. S.; Chakraborty, I.; Udayabhaskararao, T.; Jyoti Sarita, M.; Pradeep, T. Evolution of Atomically Precise Silver Clusters to Superlattice Crystals. *Part. Part. Syst. Charact.* **2013**, *30*, 241–243.
- (71) Wu, Z.; Lanni, E.; Chen, W.; Bier, M. E.; Ly, D.; Jin, R. High Yield, Large Scale Synthesis of Thiolate-Protected Ag₇ Clusters. *J. Am. Chem. Soc.* **2009**, *131*, 16672–16674.
- (72) Lu, Y.; Chen, W. Size Effect of Silver Nanoclusters on Their Catalytic Activity for Oxygen Electro-reduction. *J. Power Sources* **2012**, *197*, 107–110.
- (73) Xiang, H.; Wei, S.-H.; Gong, X. Structures of [Ag₇(SR)₄][−] and [Ag₇(DMSA)₄][−]. *J. Am. Chem. Soc.* **2010**, *132*, 7355–7360.
- (74) Wu, Z.; Jiang, D.-e.; Lanni, E.; Bier, M. E.; Jin, R. Sequential Observation of Ag_nS₄[−] (1 ≤ n ≤ 7) Gas Phase Clusters in MS/MS and Prediction of Their Structures. *J. Phys. Chem. Lett.* **2010**, *1*, 1423–1427.
- (75) Leelavathi, A.; Udayabhaskararao, T.; Pradeep, T. Supported Quantum Clusters of Silver As Enhanced Catalysts for Reduction. *Nanoscale Res. Lett.* **2011**, *6*, 123.
- (76) Bootharaju, M. S.; Pradeep, T. Investigation into the Reactivity of Unsupported and Supported Ag₇ and Ag₈ Clusters with Toxic Metal Ions. *Langmuir* **2011**, *27*, 8134–8143.
- (77) Sun, Y.; Balasubramanian, K.; Udayabhaskararao, T.; Pradeep, T. First Principles Studies of Two Luminescent Molecular Quantum Clusters of Silver, Ag₇(H₂MSA)₇ and Ag₈(H₂MSA)₈, Based on Experimental Fluorescence Spectra. *J. Phys. Chem. C* **2011**, *115*, 20380–20387.
- (78) Chen, W.-T.; Hsu, Y.-J.; Kamat, P. V. Realizing Visible Photoactivity of Metal Nanoparticles: Excited-State Behavior and Electron-Transfer Properties of Silver (Ag₈) Clusters. *J. Phys. Chem. Lett.* **2012**, *3*, 2493–2499.
- (79) Bootharaju, M. S.; Deepesh, G. K.; Udayabhaskararao, T.; Pradeep, T. Atomically Precise Silver Clusters for Efficient Chlorocarbon Degradation. *J. Mater. Chem. A* **2013**, *1*, 611–620.
- (80) Harkness, K. M.; Tang, Y.; Dass, A.; Pan, J.; Kothalawala, N.; Reddy, V. J.; Cliffl, D. E.; Demeler, B.; Stellacci, F.; Bakr, O. M.; McLean, J. A. Ag₄₄(SR)₃₀^{4−}: A Silver–Thiolate Superatom Complex. *Nanoscale* **2012**, *4*, 4269–4274.
- (81) Kumar, S.; Bolan, M. D.; Bigioni, T. P. Glutathione-Stabilized Magic-Number Silver Cluster Compounds. *J. Am. Chem. Soc.* **2010**, *132*, 13141–13143.
- (82) Guo, J.; Kumar, S.; Bolan, M.; Desireddy, A.; Bigioni, T. P.; Griffith, W. P. Mass Spectrometric Identification of Silver Nanoparticles: The Case of Ag₃₂(SG)₁₉. *Anal. Chem.* **2012**, *84*, 5304–5308.

- (83) Chandrasekar, A.; Pradeep, T. Luminescent Silver Clusters with Covalent Functionalization of Graphene. *J. Phys. Chem. C* **2012**, *116*, 14057–14061.
- (84) Remya, K. P.; Udayabhaskararao, T.; Pradeep, T. Low-Temperature Thermal Dissociation of Ag Quantum Clusters in Solution and Formation of Monodisperse Ag₂S Nanoparticles. *J. Phys. Chem. C* **2012**, *116*, 26019–26026.
- (85) Yuan, X.; Tay, Y.; Dou, X.; Luo, Z.; Leong, D. T.; Xie, J. Glutathione-Protected Silver Nanoclusters as Cysteine-Selective Fluorometric and Colorimetric Probe. *Anal. Chem.* **2013**, *85*, 1913–1919.
- (86) Wang, C.; Xu, L.; Wang, Y.; Zhang, D.; Shi, X.; Dong, F.; Yu, K.; Lin, Q.; Yang, B. Fluorescent Silver Nanoclusters as Effective Probes for Highly Selective Detection of Mercury(II) at Parts-per-Billion Levels. *Chem.—Asian J.* **2012**, *7*, 1652–1656.
- (87) Singh, A. K.; Kanchanapally, R.; Fan, Z.; Senapati, D.; Ray, P. C. Synthesis of Highly Fluorescent Water-Soluble Silver Nanoparticles for Selective Detection of Pb(II) at the Parts per Quadrillion (PPQ) Level. *Chem. Commun.* **2012**, *48*, 9047–9049.
- (88) Adhikari, B.; Banerjee, A. Facile Synthesis of Water-Soluble Fluorescent Silver Nanoclusters and Hg(II) Sensing. *Chem. Mater.* **2010**, *22*, 4364–4371.
- (89) Muhammed, M. A. H.; Aldeek, F.; Palui, G.; Trapiella-Alfonso, L.; Mattoussi, H. Growth of In Situ Functionalized Luminescent Silver Nanoclusters by Direct Reduction and Size Focusing. *ACS Nano* **2012**, *6*, 8950–8961.
- (90) Redón, R.; Ramirez-Crescencio, F.; Fernández-Osorio, A. L. Solventless Synthesis of Iridium(0) Nanoparticles. *J. Nanopart. Res.* **2011**, *13*, 5959–5965.
- (91) Mathew, A.; Sajanlal, P. R.; Pradeep, T. Selective Visual Detection of TNT at the Sub-Zeptomole Level. *Angew. Chem., Int. Ed.* **2012**, *51*, 9596–9600.
- (92) Pei, Y.; Zeng, X. C. Investigating the Structural Evolution of Thiolate Protected Gold Clusters from First-Principles. *Nanoscale* **2012**, *4*, 4054–4072.
- (93) Kurashige, W.; Yamaguchi, M.; Nobusada, K.; Negishi, Y. Ligand-Induced Stability of Gold Nanoclusters: Thiolate versus Selenolate. *J. Phys. Chem. Lett.* **2012**, *3*, 2649–2652.
- (94) Negishi, Y.; Igarashi, K.; Munakata, K.; Ohgake, W.; Nobusada, K. Palladium Doping of Magic Gold Cluster Au₃₈(SC₂H₄Ph)₂₄: Formation of Pd₂Au₃₆(SC₂H₄Ph)₂₄ with Higher Stability than Au₃₈(SC₂H₄Ph)₂₄. *Chem. Commun.* **2012**, *48*, 660–662.
- (95) Yang, H.; Lei, J.; Wu, B.; Wang, Y.; Zhou, M.; Xia, A.; Zheng, L.; Zheng, N. Crystal Structure of a Luminescent Thiolated Ag Nanocluster with an Octahedral Ag₆⁴⁺ Core. *Chem. Commun.* **2013**, *49*, 300–302.
- (96) Yang, H.; Wang, Y.; Zheng, N. Stabilizing Subnanometer Ag(0) Nanoclusters by Thiolate and Diphosphine Ligands and Their Crystal Structures. *Nanoscale* **2013**, *5*, 2674–2677.
- (97) Ferrando, R.; Jellinek, J.; Johnston, R. L. Nanoalloys: From Theory to Applications of Alloy Clusters and Nanoparticles. *Chem. Rev.* **2008**, *108*, 845–910.
- (98) Teo, B. K.; Keating, K.; Kao, Y. H. Observation of Plasmon Frequency in the Optical Spectrum of Au₁₈Ag₂₀ Cluster: The Beginning of the Collective Phenomenon Characteristics of the Bulk? *J. Am. Chem. Soc.* **1987**, *109*, 3494–3495.
- (99) Teo, B. K.; Shi, X.; Zhang, H. Cluster of Clusters. Structure of a Novel Gold–Silver Cluster [(Ph₃P)₁₀Au₁₃Ag₁₂Br₈](SbF₆) Containing an Exact Staggered-Eclipsed-Staggered Metal Configuration. Evidence of Icosahedral Units As Building Blocks. *J. Am. Chem. Soc.* **1991**, *113*, 4329–4331.
- (100) Negishi, Y.; Iwai, T.; Ide, M. Continuous Modulation of Electronic Structure of Stable Thiolate-Protected Au₂₅ Cluster by Ag Doping. *Chem. Commun.* **2010**, *46*, 4713–4715.
- (101) Kumara, C.; Dass, A. (AuAg)₁₄₄(SR)₆₀ Alloy Nanomolecules. *Nanoscale* **2011**, *3*, 3064–3067.
- (102) Kumara, C.; Dass, A. AuAg Alloy Nanomolecules with 38 Metal Atoms. *Nanoscale* **2012**, *4*, 4084–4086.
- (103) Malola, S.; Häkkinen, H. Electronic Structure and Bonding of Icosahedral Core–Shell Gold–Silver Nanoalloy Clusters Au_{144-x}Ag_x(SR)₆₀. *J. Phys. Chem. Lett.* **2011**, *2*, 2316–2321.
- (104) Koivisto, J.; Malola, S.; Kumara, C.; Dass, A.; Häkkinen, H.; Pettersson, M. Experimental and Theoretical Determination of the Optical Gap of the Au₁₄₄(SC₂H₄Ph)₆₀ Cluster and the (Au/Ag)₁₄₄(SC₂H₄Ph)₆₀ Nanoalloys. *J. Phys. Chem. Lett.* **2012**, *3*, 3076–3080.
- (105) Guidez, E. B.; Mäkinen, V.; Häkkinen, H.; Aikens, C. M. Effects of Silver Doping on the Geometric and Electronic Structure and Optical Absorption Spectra of the Au_{25-n}Ag_n(SH)₁₈⁻ (n = 1, 2, 4, 6, 8, 10, 12) Bimetallic Nanoclusters. *J. Phys. Chem. C* **2012**, *116*, 20617–20624.
- (106) Liu, H.; Zhang, X.; Wu, X.; Jiang, L.; Burda, C.; Zhu, J.-J. Rapid Sonochemical Synthesis of Highly Luminescent Non-toxic AuNCs and Au@AgNCs and Cu (II) Sensing. *Chem. Commun.* **2011**, *47*, 4237–4239.
- (107) Mohanty, J. S.; Xavier, P. L.; Chaudhari, K.; Bootharaju, M. S.; Goswami, N.; Pal, S. K.; Pradeep, T. Luminescent, Bimetallic AuAg Alloy Quantum Clusters in Protein Templates. *Nanoscale* **2012**, *4*, 4255–4262.
- (108) Huang, T.; Murray, R. W. Luminescence of Tiopronin Monolayer-Protected Silver Clusters Changes to That of Gold Clusters upon Galvanic Core Metal Exchange. *J. Phys. Chem. B* **2003**, *107*, 7434–7440.
- (109) Udayabhaskararao, T.; Sun, Y.; Goswami, N.; Pal, S. K.; Balasubramanian, K.; Pradeep, T. Ag₇Au₆: A 13-Atom Alloy Quantum Cluster. *Angew. Chem., Int. Ed.* **2012**, *51*, 2155–2159.
- (110) Fields-Zinna, C. A.; Sampson, J. S.; Crowe, M. C.; Tracy, J. B.; Parker, J. F.; deNey, A. M.; Muddiman, D. C.; Murray, R. W. Tandem Mass Spectrometry of Thiolate-Protected Au Nanoparticles Na_xAu₂₅(SC₂H₄Ph)_{18-y}(S(C₂H₄O)₃CH₃)_y. *J. Am. Chem. Soc.* **2009**, *131*, 13844–13851.