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Tuning Properties in Silver Clusters

Chakra P. Joshi, Megalamane S. Bootharaju, and Osman M. Bakr*

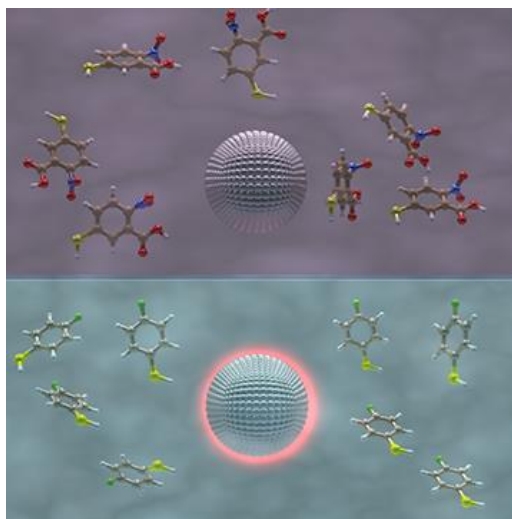
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Abstract

The properties of Ag nanoclusters are not as well understood as those of their more precious Au cousins. However, a recent surge in the exploration of strategies to tune the physicochemical characteristics of Ag clusters addresses this imbalance, leading to new insights into their optical, luminescence, crystal habit, metal-core, ligand-shell and environmental properties. In this Perspective, we provide an overview of the latest strategies along with a brief introduction of the theoretical framework necessary to understand the properties of silver nanoclusters and the basis for their tuning. The advances in cluster research and the future prospects presented in this Perspective will eventually guide the next large systematic study of nanoclusters, resulting in a single collection of data similar to the periodic table of elements.

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TOC graphics



The discovery of the periodic table and the subsequent understanding of atomic properties of elements in the early 20th century initiated many exciting research areas in chemistry. These areas laid the foundation of the cluster field which came into being decades later – *i.e.* the exploration of the properties of new exotic species consisting of a few to hundreds of atoms known as giant atoms, superatoms, magic clusters, or simply clusters.¹⁻⁷ The uncommon characteristics associated with these clusters were highlighted by Richard Feynman in his famous lecture at the American Physical Society meeting in 1959.¹ Around the same time, Becker *et al.*² experimentally demonstrated the possibility for control over atomic/molecular clusters. These clusters are fascinating not only because of their small size but also because of their resemblance to molecules. Later developments of sophisticated instruments and experimental designs in the 1980s helped characterize metal and non-metal clusters, such as Na_{*n*}⁸ and fullerene C₆₀⁹, with unprecedented atomic precision. Despite having the same carbon building block as coal, graphite, and diamond, fullerene C₆₀ exhibits unusual properties, which motivated the cluster community to find analogies in other inorganic systems. In the meantime, advances in theoretical

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3 and computational modeling of these clusters aided in breathtaking developments in cluster
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5 science.
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9 Although metal clusters are considered a part of the broader class of metal nanoparticles
10 (NPs), they have a much shorter history and their manifested characteristics may only be
11 understood based on quantized electronic interactions. However, metal NPs of tens to hundreds
12 of nanometers have been used by artists since the Middle Ages and before to stain glass with
13 colorful hues. Although these artisans were unaware of the exact source and nanoscale nature of
14 the material that helped emanate these beautiful colors, later plasmonic NPs were observed to
15 cause these phenomena.¹⁰⁻¹¹
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26 In 1857, Faraday reported the first formal synthesis of metal NPs, i.e., the synthesis of a
27 red Au NP solution.¹² He immediately attributed the color of the solution to the size of the Au
28 particles even though he lacked evidence to substantiate this hypothesis. Almost a century later
29 in 1951, with the arrival of electron microscopy, Turkevich *et al.*¹³ proved Faraday's prediction
30 correct and observed ~3-10-nm NPs. Around the same time, McPartlin *et al.*¹⁴ reported ultra-
31 small Au NPs, i.e., [Au₁₁(PPh₃)₇(SCN)₃] with sizes of ~1 nm. Notably, both Faraday's Au NPs¹²
32 and the Au₁₁ cluster¹⁴⁻¹⁵ produced a similar red solution despite their drastically different sizes.
33 The red appearance of Faraday's NPs^{11, 13} was attributed to surface plasmons whereas molecular-
34 like electronic transitions¹⁵ were thought to cause the reddening of the Au₁₁ cluster solution.
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48 Following the footsteps of Brust *et al.*,¹⁶ Whetten and co-workers^{5-6, 17} reported the
49 synthesis of 5.6, 8.7, 10.4 and 29 kDa Au species/clusters in their work of late-1990s and early-
50 2000s, coining the concept of gold NP 'molecules'. However, purification and complete isolation
51 of these ~1-2-nm clusters remained elusive, resulting in a poor estimation of their precise
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3 molecular formula.⁵ Successive work by the Tsukuda group³ in a similar system led to the
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6 isolation and unambiguous determination of the molecular formula of several magic gold-
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8 glutathione $Au_m(SG)_n$ species, including $Au_{10}(SG)_{10}$, $Au_{15}(SG)_{13}$, $Au_{18}(SG)_{14}$, $Au_{22}(SG)_{16}$,
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10 $Au_{22}(SG)_{17}$, $Au_{25}(SG)_{18}$, $Au_{29}(SG)_{20}$, $Au_{33}(SG)_{22}$ and $Au_{39}(SG)_{24}$. This seminal work in the mid-
11
12 2000s by the Tsukuda group³ spurred research on Au clusters and on other metal compositions.
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16 After Au, Ag was an obvious candidate because of its low price, largely unexplored
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18 properties and shared similarities with Au, despite its notorious lack of stability. A few
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20 unconfirmed reports focused on the precise composition of Ag NPs;¹⁸⁻¹⁹ however, in the late-
21
22 2000s, Bakr and Stellacci *et al.*²⁰ discovered Ag NPs with precise formula that displayed non-
23
24 plasmonic nature.²¹ These non-plasmonic Ag NPs were called IBANs (Intensely and Broadly
25
26 Absorbing Ag NPs).²⁰ Analogous to the $Au_m(SG)_n$ species, IBANs have a precise molecular
27
28 formula of $[Ag_{44}(SR)_{30}]^{4-}$ and are < 2 nm in size.²⁰⁻²¹ Since then, a handful of precise thiolated
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30 Ag clusters have been characterized with atomic precision.^{4, 22-26} For example, recent work on
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32 the glutathione Ag system by the Bigioni group led to the isolation of various magic $Ag_m(SG)_n$
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34 species that mostly remained uncharacterized except for the $Ag_{32}(SG)_{19}$ species.²³ A species with
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36 the same optical spectrum as $Ag_{32}(SG)_{19}$ was assigned by Bertorelle *et al.*²² as $Ag_{31}(SG)_{19}$. This
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38 discrepancy in the mass characterization of similar optical species may be due to the ease of
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40 fragmentation and rearrangement of atoms in the gas phase in a mass spectrometer. However, the
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42 structure could be decisively determined in the solid state using single-crystal X-ray diffraction if
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44 the cluster could be successfully crystallized. Thus, the ground-breaking work of the Kornberg
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46 group,²⁷ which revealed the crystal structure of $Au_{102}(p-MBA)_{44}$, paved the way for subsequent
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48 crystal structure determination of other metal clusters, such as $Ag_{44}(p-MBA)_{30}$ ²⁸ and
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50 $Ag_{44}(SPhF_2)_{30}$ ²⁹ with a charge of 4-. This landmark achievement not only revealed the molecular
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structure and metal-thiolate interface of the clusters with unprecedented detail but also provided enormous impetus for the explosive growth in the theoretical and computational fields to understand and predict the fundamental properties associated with the existing and emerging metal clusters.

Decades earlier, before the actual crystallization of the thiol-protected Au/Ag clusters,²⁷⁻²⁹ significant theoretical work was performed to understand and predict the properties of bare metal clusters and was known as the superatom theory.^{8, 30-31} These gas-phase metal clusters were assumed to behave like giant atoms and therefore follow the same rules as atoms, such as orbital hybridization, Hund's rule, and the Aufbau principle. Therefore, superatom theory is no different from atomic theory even though superatoms are composed of a few tens to thousands of atoms and have the Jellium foundation.^{8, 30} The Jellium model assumes that positive charges are spread evenly over the sphere and are inert (Figure 1a).^{8, 30} This assumption indeed qualitatively explained various properties related to superatoms.^{8, 31}

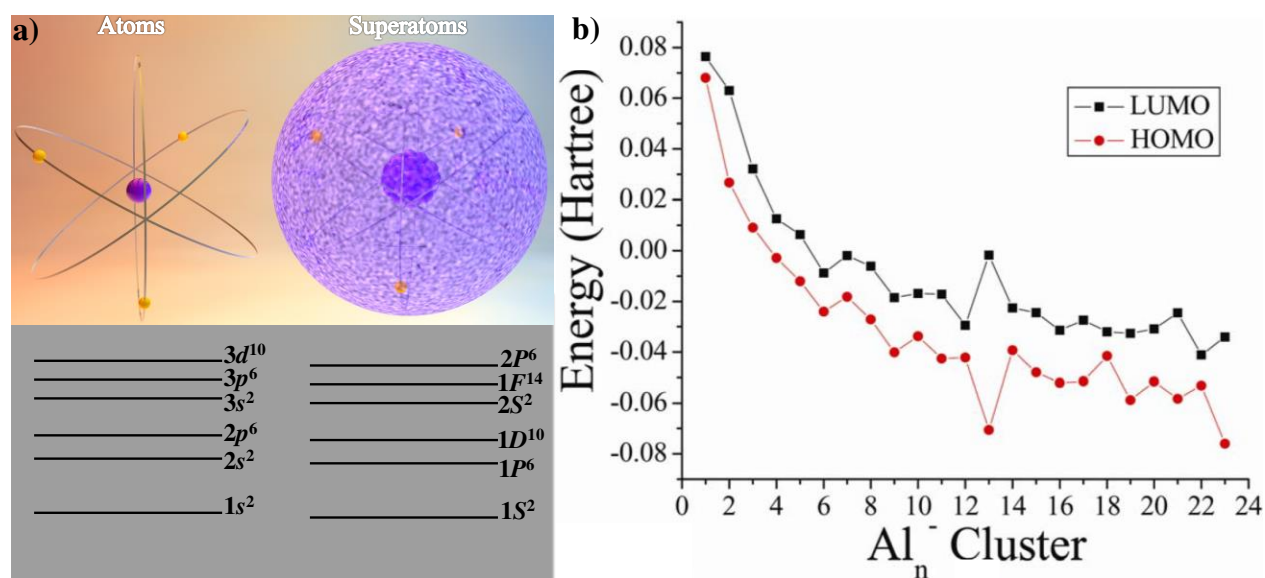


Figure 1. a) A cartoon showing the electron orbitals of an atom (lowercase s, p, d, ...) and superatom (uppercase S, P, D, ...) with a confined and smeared nuclear region and b) A

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3 theoretical plot of energy associated with the HOMO and LUMO levels of Al_n^- clusters as a
4 function of size.³² Figure 1(b) reprinted from ref. [³²] with written permission.
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9 For instance, consider the Na_n cluster. Sodium has one $3s$ electron in its valence shell and is
10 known to form bare Na_n clusters in the gas phase.⁸ Following the observation that some Na_n
11 species were more stable than others, Knight and coworkers⁸ rationalized this discrepancy based
12 on the electronic shell-closing rule of the superatom theory, where large HOMO-LUMO gaps
13 created by a closed shell conferred stability to bare Na_n clusters analogous to those of inert gases.
14
15 The resemblance between the filling of the superatomic orbitals of these bare metal clusters to
16 the filling of atoms inspired Häkkinen's group³³ to extend this idea to ligand-protected metal
17 clusters that follow the electronic shell closure rule described below:^{31, 33}
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$$28 \quad 1S^2 \mid 1P^6 \mid 1D^{10} \mid 2S^2 1F^{14} \mid 2P^6 1G^{18} \mid 2D^{10} 3S^2 1H^{22} \mid \dots \dots,$$

29
30
31 where the vertical lines indicate a shell-closure with a very large HOMO-LUMO gap. The
32 uppercase characters S, P, D, F, $\dots \dots$ represent the angular momentum quantum numbers of the
33 superatomic orbitals, and 1, 2, 3, $\dots \dots$ correspond to radial nodes. Using the electronic shell-
34 closing rule, one can obtain closed shells for $n_e = 2, 8, 18, 20, 34, 40, 58, \dots \dots$, where n_e is the
35 total free electrons available in a cluster.³³ For example, the stability of Na_{40} and Al_{13}^- clusters^{8, 34}
36 can be explained based on the electronic shell closure. The Na_{40} and Al_{13}^- clusters^{8, 34} contain 40
37 $Na(3s^1)$ and 13 $Al(3s^2 3p^1)$ atoms, resulting in a total of 40 and 39 valence electrons, respectively.
38
39 The inclusion of a negative charge associated with the Al_{13}^- cluster results in a total of 40
40 valence electrons. This electron count corresponds to a closed shell ($n_e = 40$) with a
41 configuration of $1S^2, 1P^6, 1D^{10}, 2S^2, 1F^{14}, 2P^6$ imparting exceptional stability to these gas phase
42 clusters (Figure 1b).
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3 Although the electronic shell-closing rule is useful in explaining the stability of clusters,
4 it also suggests the existence of a limited number of stable clusters with closed electronic shells.
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6 Research work by Brust and coworkers on Au-thiolates provided some insights to stabilize
7 clusters' metal core with ligands.¹⁶ However, this idea was later viewed more generally as
8 describing a metal core that can coordinate, deposit, or access electrons from an electron
9 reservoir in the form of surface ligands to maintain a coveted closed electronic shell, thereby
10 ensuring stability. The idea of ligands as a surrounding electron reservoir then spread to Ag and
11 other metals,^{4-5, 19} where ligands are believed to satisfy the dangling bonds present on a cluster.¹⁶
12
13 By considering ligand and metal-core interactions, Walter *et al.*³³ proposed an electron count
14 magic rule for ligand-protected metal clusters. According to the rule, for the ligand-protected Ag
15 clusters of the form $[C_x Ag_N L_M]^z$, where C is a Lewis-base-type coordinating ligand that does not
16 withdraw electrons but rather bonds to a metal core through a dative bond (e.g., phosphine and
17 amine) and L is a one-electron-withdrawing ligand (e.g., thiol), the electron-count rule is³³
18
19

$$n_e = Nv - M - z,$$

20
21 where v is the atomic valence of Ag, N is the number of core Ag atoms, M and x are the number
22 of respective ligands and z is the overall charge of the cluster. The application of the electron-
23 count rule to condensed-phase metal clusters explains why $[Au_{25}(SG)_{18}]^{-35}$ and $[Ag_{44}(SR)_{30}]^{4-28-}$
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29 with $n_e = 8$ and 18-electron cores, respectively, are very stable as their total free electron counts
correspond to closed electronic shells.³³

Despite the success of the electronic shell closure, the presence of conspicuous mass
peaks of bare metal clusters, such as Na_{12} , Na_{26} , and Na_{38} , in the gas phase⁸ and stable ligand-
protected metal clusters, such as $Au_{38}(SR)_{24}$ ³⁶, $Ag_{32}(SG)_{19}$ ^{23, 37} and $Ag_{15}(SG)_{11}$,²² in the
condensed phase appear to be exceptions to the rule. However, Clemenger attributed the stability

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3 of these Na_n clusters to their non-spherical shape caused by a distortion analogous to the Jahn-
4 Teller effect.^{31, 38} Indeed, $\text{Au}_{38}(\text{SR})_{24}$ with a 14-electron core was later crystallized³⁶ and
5
6 observed to have a non-spherical shape (prolate, face-fused bi-icosahedron). Similar non-
7
8 spherical shapes are expected for $\text{Ag}_{32}(\text{SG})_{19}$,²³ $\text{Ag}_{31}(\text{SG})_{19}$, and $\text{Ag}_{15}(\text{SG})_{11}$ ²² clusters.
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14 In addition to electronic shell closing, geometric shell closing is also applied to explain
15 the cluster stability. Depending on the geometric shape, e.g., cubic, tetrahedral, octahedral, or
16 icosahedral, certain numbers of building units are required to form a closed geometry. Consider a
17 cubic shape. It is not possible to construct a cube out of 26 or 28 spheres; this goal requires
18 precisely 27 atoms (i.e., 3^3). This type of precise requirement can be observed in the fullerene
19 C_{60} with icosahedral symmetry.⁹ Fullerene is known to have a closed geometry and hence is very
20 stable.⁹ Removing or adding an extra carbon atom to the C_{60} surface would destabilize the
21 geometry and therefore requires significant energy. Likewise, metal clusters also prefer
22 icosahedral symmetry at the core.^{7, 28-29} The number of atoms required to make a closed
23 icosahedral geometry can be determined using Mackay's³⁹ icosahedral sequence $S_n = 10n^2 + 2$,
24 where S_n represents the surface atoms of the n^{th} shell, from which one can acquire a closed
25 geometric shell configuration corresponding to 1, 13, 55, 147, 309, 561, ... core atoms.
26
27 Leuchtner *et al.*³⁴ experimentally demonstrated the importance of geometric shell by studying the
28 reactivity of Al_{13}^- , Al_{23}^- and Al_{37}^- clusters (representing 40, 70, and 112 electrons, respectively)
29 toward oxygen. Although all three clusters have a closed electronic shell, Al_{13}^- was observed to
30 be the most stable³⁴ because of its closed geometric shell (13-atom icosahedron, Figure 1b).
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32 Similar stability was reported for Ag_{13}^- clusters.⁴⁰ The open geometry associated with Al_{23}^- and
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34 Al_{37}^- ³⁴ would sustain steps on these cluster surfaces, lowering the work function and hence
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3 reducing the stability.⁴¹ For practical realization of these theories, actual clusters must be
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5 synthesized.
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8 9 **Syntheses of Ag clusters**

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12 The synthesis protocol for ligand-protected Ag clusters is rather straightforward.
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14 Generally, a Ag salt is mixed with a thiol ligand in a suitable solvent system to form a silver-
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16 thiolate complex. The silver-thiolate complex is then reduced with a strong reducing agent, such
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18 as NaBH₄, to produce Ag clusters that are successively washed and then re-dispersed in an
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20 appropriate solvent. Other synthetic routes, such as solid-state,⁴² ligand-exchange,⁴³ and anti-
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22 galvanic processes,⁴⁴ are also available. Some aqueous syntheses produce polydispersed Ag
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24 clusters such as Ag_m(SG)_n clusters^{4, 19}, whose purity and monodispersity are achieved either *via*
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26 cyclic reduction under oxidative conditions or through polyacrylamide gel electrophoresis
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28 (PAGE). By contrast, the monodispersity of organic soluble clusters, especially alloys, is
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30 improved *via* thermal processing²⁹ or chromatography⁴⁵⁻⁴⁷. Nevertheless, by tailoring the
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32 properties of the solvents and ligands, some remarkable success has been achieved in obtaining a
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34 truly single-sized product of Ag clusters in both aqueous and organic phases using one-pot
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36 synthesis approaches.^{20, 28-29, 48-49} This scaling up of cluster synthesis with no known upper limit
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38 (irrespective of pure or doped clusters, Figure 2) reminds us of the molecular nature of these
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40 clusters and could facilitate the application of clusters in photocatalysis⁵⁰ and sensing²⁴⁻²⁵ over
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42 large areas in addition to improving the fundamental understanding of their properties.
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Figure 2. Scaled-up final single-sized product of **a)** $[\text{Ag}_{44}(\text{p-MBA})_{30}]^{4-}$, 140 g²⁸; **b)** $[\text{Ag}_{44}(\text{SPhF})_{30}]^{4-}$, 10.89 g²⁹; **c)** $[\text{Ag}_{44}(\text{MNBA})_{30}]^{4-}$ clusters, 172 mg in 1 L of 1 M aqueous NaOH⁴⁸; and **d)** $\text{Au}_{25}\text{Ag}_2(\text{PET})_{18}$ alloy cluster, 0.86 g⁴⁹. Adapted from refs.[^{28-29, 48-49}] with written permission.

Factors involved in tuning the properties of Ag clusters

The physical and chemical properties of clusters are affected by their cores, ligands, and environments. By varying these factors, it is possible to tune the cluster properties. To illustrate, consider the family of magic $\text{Ag}_m(\text{SG})_n$ clusters.^{4, 51} While synthesizing the family of glutathione Ag clusters, the same environment was sustained in a reaction vessel; however, clusters purified from the gel exhibited distinct optical properties. This behavior is possible because of the different core sizes, i.e., the number of Ag atoms changed from one cluster to another. However, it is expected that the change in core atoms would subsequently lead to a different number of ligands to enclose the core appropriately, which was also observed with $\text{Au}_m(\text{SG})_n$ ³ and $\text{Au}_m(\text{PET})_n$ ⁷ clusters (PET: 2-phenylethanethiol), where a quantitative relationship was mapped between the cluster cores and their optical properties.

The properties arising from the cluster core can also be engineered by doping or alloying the cluster with other metal atoms, resulting in combined properties from both metal atoms. In general, doped clusters are synthesized by reducing a suitable ratio of different metal salt

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3 precursors in the presence of a ligand. The Zheng group²⁹ reported the doping of
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5 $[\text{Ag}_{44}(\text{SPhF}_2)_{30}]^{4-}$ with 12-Au atoms, producing completely different properties. For example, the
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7 optical spectrum of $[\text{Ag}_{44}(\text{SPhF}_2)_{30}]^{4-}$ contained eight peaks, including two shoulder peaks, and
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9 the cluster was stable for < 4 hrs.²⁹ whereas the spectrum of its 12-Au doped counterpart,
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11 $[\text{Ag}_{32}\text{Au}_{12}(\text{SPhF}_2)_{30}]^{4-}$, contained only two prominent and three shoulder peaks, and the cluster
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13 was able to survive > 12 hrs. under the harsh conditions of 80 °C.²⁹ In contrast, the Dass group⁵²
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15 reported selective replacement of 12-Au atoms of a $[\text{Au}_{25}(\text{PET})_{18}]^{-}$ core with Ag, producing a
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17 mixture of $[\text{Au}_{25-x}\text{Ag}_x(\text{PET})_{18}]^{-}$ alloy clusters. These researchers also noticed a significant change
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19 in the optical properties of $[\text{Au}_{25}(\text{PET})_{18}]^{-}$ clusters after doping. Fortunately, the core size was
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21 preserved in both cases after being alloyed with different metal atoms. Like Au, Ag mingles
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23 with other metals, such as Pd, Pt, and Ni, at the nanoscale, producing alloy clusters with various
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25 compositions, such as $[\text{Ag}_5\text{Pd}_4(\text{SePh})_{12}]^{-}$,⁴⁵ $\text{Ag}_4\text{Pt}_2(\text{DMSA})_4$,⁴⁷ and $\text{Ag}_4\text{Ni}_2(\text{DMSA})_4$.⁴⁶ The
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27 syntheses of materials of this type with different metal precursors are challenging and often lead
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29 to a mixture of clusters with different metal ratios, which are extremely difficult to purify.
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37 Galvanic exchange is also used for alloying clusters. In this process, usually a metal
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39 cluster is mixed with salt or a cluster of another metal, causing a redox reaction to occur. Using
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41 this technique, the Pradeep group⁵³ succeeded in producing a luminescent alloy cluster
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43 $\text{Ag}_7\text{Au}_6(\text{MSA})_{10}$ by reacting a mixture of $\text{Ag}_7(\text{MSA})_7$ and $\text{Ag}_8(\text{MSA})_8$ clusters with Au^{3+} ions of
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45 aqueous HAuCl_4 . These researchers proposed that the Au^{3+} ions first formed Au(I)-thiolates with
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47 excess MSA (mercaptosuccinic acid) that subsequently reacted with the cluster mixture Ag_{7-8} ,
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49 forming the luminescent cluster $\text{Ag}_7\text{Au}_6(\text{MSA})_{10}$. In addition to galvanic exchange, the anti-
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51 galvanic process was also observed to be equally effective for alloying the clusters. The Wu
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53 group⁴⁹ succeeded in alloying $[\text{Au}_{25}(\text{PET})_{18}]^{-}$ clusters with Ag simply by mixing $[\text{Au}_{25}(\text{PET})_{18}]^{-}$
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3 clusters with Ag^+ in AgNO_3 solutions, producing luminescent $[\text{Au}_{25}\text{Ag}_2(\text{PET})_{18}]^-$ clusters. In this
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5 case, the $[\text{Au}_{25}(\text{PET})_{18}]^-$ clusters reduced the Ag^+ to Ag atoms, thereby resulting in successful
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7 alloying. Although both the galvanic and anti-galvanic processes produced luminescence
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9 clusters, in both cases, the cluster size unfortunately changed because of the alloying, which
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11 complicates the determination of the most crucial factors affecting the cluster properties.
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13 Nonetheless, this reactivity of the clusters in the galvanic/anti-galvanic process stems from the
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15 reduction potential of the metals, which decreases drastically with the core size.⁵⁴ For instance,
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17 the standard reduction potential of bulk Ag changed from +0.79 V to -1.8 V when its size
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19 reached an isolated Ag atom in aqueous solution.⁵⁴ This dramatic change in the reduction
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21 potential makes clusters attractive for the galvanic and anti-galvanic processes.
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28 The environment where the clusters originate and/or are placed is also an important factor
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30 that contributes to their overall characteristics. Some environmental factors, such as
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32 temperature,⁵⁵ pH,^{22, 51} and the solvent,⁵⁶ are known to change the cluster properties. For
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34 example, the Ras group⁵⁶ demonstrated a dramatic change in the luminescence of Ag clusters,
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36 supposedly Ag_2 and Ag_3 , by changing the solvent type or using co-solvents. Although the
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38 reported Ag_2 and Ag_3 are more likely the fragments (in the mass measurement during mass
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40 spectrometry) of a larger Ag cluster, the observed luminescence tunability highlighted the
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42 important role of environmental changes. In the same manner, the Mak group⁵⁵ demonstrated the
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44 luminescence tunability of Ag_{12} clusters. Likewise, the Stellacci group²⁰⁻²¹ demonstrated the
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46 optical tunability of Ag_{44} clusters simply by raising the temperature (Figure 3a). The optical
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48 tunability of Ag_{44} clusters with temperature actually caused Ag-core growth, producing
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50 plasmonic NPs.²⁰ Despite the aforementioned environmental factors, such as solvatochromism⁵⁶
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and thermochromism,⁵⁵ a complete understanding of how the environment affects the cluster properties has not yet been achieved.

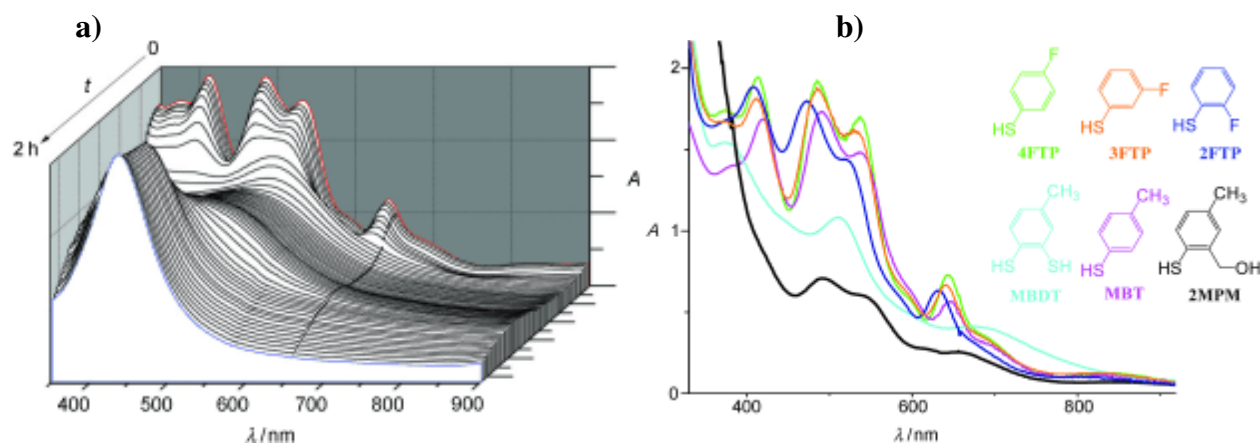


Figure 3. a) Optical spectra of $\text{Ag}_{44}(\text{SR})_{30}^{4-}$ clusters at $90\text{ }^{\circ}\text{C}$ as a function of time²⁰ and b) effect of various aryl-thiol ligands on the optical spectra of Ag clusters.²⁰ Reprinted from ref. [20] with written permission.

The ligand is another factor that changes the cluster properties. The compatibility of a cluster toward a particular solvent largely depends on the ligand. Moreover, the cluster stability depends on how well the ligands guard a sensitive core from the surrounding environment. A few examples of ligand effects on Ag clusters are highlighted here, starting with a demonstration by Bakr *et al.*²⁰ Figure 3b shows that six different aryl-thiol ligands produced similar optical spectra to Ag; however, the ligand with a substitution next to its thiol ($-\text{SH}$) group was observed to affect the optical spectrum the most. Using the HSPhF ligand, our group⁴³ quantitatively replaced the ligand shell of $[\text{Ag}_{44}(\text{MNBA})_{30}]^{4-}$ clusters while preserving the core (Figure 4). By performing this modification, we solubilized the aqueous Ag_{44} clusters into the organic phase and endowed them with luminescence. The report of Bootharaju *et al.*⁵⁷ revealed reversible tuning of the cluster size and solubility of Ag clusters *via* ligand effects. These researchers transformed $\text{Ag}_{32}(\text{SG})_{19}$ clusters³⁷, reassigned to $\text{Ag}_{35}(\text{SG})_{18}$,⁵⁷ into $[\text{Ag}_{44}(\text{SPhF})_{30}]^{4-}$ and vice

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versa by exploiting the differences in the binding energy of the Ag–S bond arising from different thiol ligands. In addition to tuning the size, other properties, such as chirality, can also be introduced to a cluster *via* the ligands, as described by Cao *et al.*⁵⁸ These researchers induced chirality in an achiral Au₂₅ cluster by capping it with a chiral ligand, such as (*R/S*)-2-amino-3-phenylpropane-1-thiol, which could be useful in modern optics. Chirality in Ag clusters has yet to be explored; however, a handful of reports probed chiral-thiol-protected Ag clusters.^{19, 59}



Figure 4. Phase transfer of aqueous $[\text{Ag}_{44}(\text{MNBA})_{30}]^{4+}$ clusters into dichloromethane (DCM) using HSPHF as a ligand and tetraphenylphosphonium bromide (TPPB) as a counter-ion.⁴³ Reprinted from ref. [43] with written permission.

Ligands can also select a particular cluster size (especially with Ag) even though the actual mechanism is not yet fully known. This capability presents a rare opportunity to study the properties of clusters of the same-core-size with various ligands. For example, selenophenol was used to reversibly produce $[\text{Ag}_{44}(\text{SePh})_{30}]^{4+}$ clusters.⁶⁰ The oxidation of $[\text{Ag}_{44}(\text{SePh})_{30}]^{4+}$ with H₂O₂ produced a Ag(I)-selenolate complex whose successive reduction with NaBH₄ yielded the original $[\text{Ag}_{44}(\text{SePh})_{30}]^{4+}$ clusters.⁶⁰ This finding demonstrates that the HSePh ligand selects the particular cluster size (Ag₄₄) that is the most thermodynamically stable among clusters of other sizes. Our recent work using thiols instead of selenols^{43, 57} also supports this finding. We examined the size-selection in a different manner; instead of exploiting reductive-oxidative conditions, as performed by the Pradeep group, we used the ligand-exchange method described

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3 in Figure 4. Here, aqueous $[\text{Ag}_{44}(\text{MNBA})_{30}]^{4-43}$ and $\text{Ag}_{35}(\text{SG})_{18}$ clusters⁵⁷ were used as starting
4 materials and were then phase transferred into DCM by the HSPhF ligand. Remarkably, after
5 ligand exchange, we obtained the same $[\text{Ag}_{44}(\text{SPhF})_{30}]^{4-}$ cluster reported earlier^{20, 29} in both
6 cases. These results demonstrated the size-selection by the HSPhF ligand is independent of the
7 original cluster size. It is speculated that the steric effects of the ligands along with the unique
8 synergism of the metal, nature of ligand, and solvent environment are responsible for the
9 selection of the thermodynamically stable cluster size.

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21 Bidentate and tridentate ligands are also interesting for tuning cluster properties, where
22 simultaneous attachment of the bidentate/tridentate thiol or phosphine groups to a metal core
23 could create a rigidity/strain within a cluster. The use of monodentate aryl-thiols, such as *p*-MBA
24 or HSPhF, is known to produce hollow icosahedral core Ag_{44} clusters,²⁸⁻²⁹ whereas the use of
25 bidentate alkyl-dithiols, such as $\text{NH}_4[\text{S}_2\text{P}(\text{OiPr})_2]^{26}$, was observed to produce non-hollow
26 icosahedral-core Ag_{21} clusters even though both the clusters contain three-dimensional protecting
27 units. Nevertheless, a fair comparison can be made only with bidentate aryl-dithiols, whose
28 effects on cluster properties have yet to be observed but are also expected to produce non-
29 hollow-core Ag clusters.

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43 Mixed ligand protection also changes the cluster properties. For instance, the use of
44 phosphine in addition to a thiol ligand completely changed the spherical shape of a purely
45 thiolated Au_{25} core³⁵ to a rod shape.⁶¹⁻⁶² This overall shape change led to poor performance of
46 the rod-shaped Au_{25} cluster in catalysis,⁶³ such as the oxidation of styrene and hydrogenation of
47 α,β -unsaturated benzalacetone. By contrast, in the case of Ag, the use of the co-ligands
48 phosphine⁶⁴ and diphosphine⁶⁵ with the same thiol (HSPhF_2) produced Ag_{14} ⁶⁴ and Ag_{16} ⁶⁵ clusters
49 instead of Ag_{44} ²⁹, which is expected when the HSPhF_2 ligand is used alone. In the former case,
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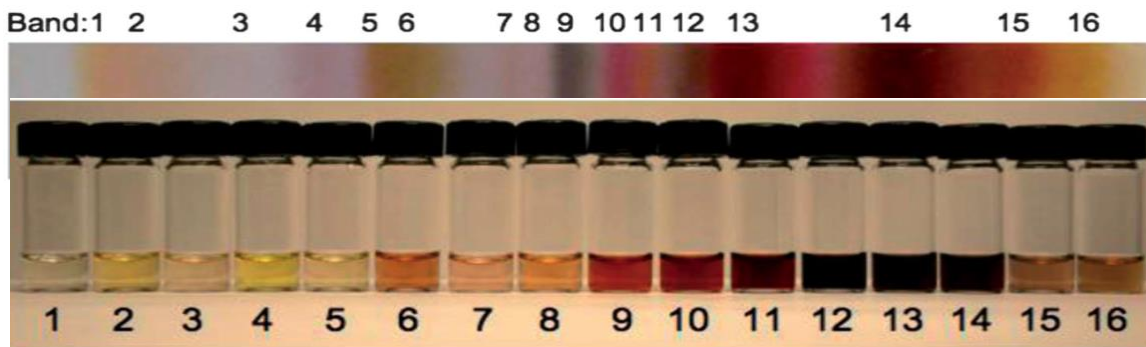
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3 phosphine preserved the Au₂₅ core while changing its shape; however, in the latter case, the
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5 phosphine roughly preserved the sphericity of the Ag₄₄ core²⁹ while shrinking its size. These
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7 changes caused by the mixed ligand systems provide an opportunity to study the fundamental
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9 changes in the properties of clusters caused by mixed ligands. A theoretical study of the ligand
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11 effects on clusters by the Jiang group⁶⁶ revealed that the stronger van der Waals forces and steric
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13 effect through a ligand are critical to the cluster stability and other related properties. Yacaman's
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15 group⁶⁷ also observed that the ligand was one of the key players affecting the cluster absorption
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17 properties.
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22 23 **Understanding the properties of Ag nanoclusters**

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27 Absorption spectroscopy is routinely used in the characterization of organic molecules
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29 and organometallic complexes because it can distinguish between different conformers and
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31 resonances. Because the number of allowed transitions is constrained by selection rules,
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33 absorption spectra can also provide valuable information about the symmetry, band gap, and
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35 electronic/geometrical structure associated with a particular system. This basic knowledge is also
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37 useful for distinguishing metal clusters with different sizes. Several gel purified magic Au_m(SG)_n
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39 clusters³ were first distinguished from each other based on their unique optical spectra, which
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41 was confirmed by their mass measurements, thus firmly establishing absorption spectroscopy as
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43 the first indispensable diagnostic tool for characterization. Similar work involving differentiating
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45 Ag_m(SG)_n clusters (Figure 5)^{4, 23, 51} was also performed *via* absorption spectroscopy even though
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47 most of these Ag_m(SG)_n clusters await mass characterization, which highlights the importance of
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49 absorption spectroscopy in cluster identification. Absorption spectra arise deep within the cluster
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51 structure due to the combined effects of the core, ligand, and environment. Some progress in this
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53 regard has been made by correlating the experimental absorption spectrum of a [Au₂₅(PET)₁₈]⁻
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3 cluster with its crystal structure in 2008 by Zhu *et al.*³⁵ via time-dependent (TD) density
4 functional theory (DFT). The appearance of the highly structured optical spectrum of
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6 $[\text{Au}_{25}(\text{PET})_{18}]^-$, unlike the ~ 525 nm peak of Au plasmons, was attributed to intra-band ($sp \rightarrow sp$)
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8 and inter-band ($d \rightarrow sp$) transitions within the cluster.³⁵ In other words, the transitions arising at
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10 the red end of the spectrum are attributed to the metal core, whereas the blue end are dominated
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12 by both metal and ligand characteristics, i.e., $-\text{S}-\text{Au}-\text{S}-\text{Au}-\text{S}-$ motifs.³⁵ Based on this
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14 information, the Aikens group²⁰ predicted the size and crystal structure of IBANs in 2009.
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16 Neither the size nor the crystal structure was precisely known at the time; however, these
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18 researchers simulated the absorption features of IBANs and predicted a size of 25 atoms (i.e.,
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20 Ag_{25}).²⁰ Later, mass spectrometry and single-crystal X-ray diffraction measurements proved
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22 otherwise, i.e., IBANs are Ag_{44} clusters.^{21, 28-29} Although the theoretical prediction using DFT did
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24 not match the experimental data for IBANs, it helped the theoretical community tremendously in
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26 further refining their predictions, such as in 2010, when Lopez-Acevedo *et al.*⁶⁸ predicted the
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28 crystal structure of $\text{Au}_{38}(\text{SR})_{24}$ using DFT before the publication of the actual experimental
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30 structure³⁶.



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Figure 5. Extracted gel bands of $\text{Ag}_m(\text{SG})_n$ clusters (top panel) and their corresponding aqueous solutions (bottom panel). Except for band 6, which is $\text{Ag}_{32}(\text{SG})_{19}$, the molecular formula for

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3 other bands are not known with atomic precision.⁵¹ Adapted from ref. [⁵¹] with written
4 permission.
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9 Despite some success in deciphering the absorption spectrum of the cluster, significant
10 work lies ahead in predicting the crystal structures and origin of such a spectrum. Determining
11 and predicting the most influencing factors to tune the optical spectra of clusters remains a
12 challenge. Some qualitative studies on tuning the optical spectra of Ag clusters based on the
13 ligand, temperature,²⁰ and core size^{4, 51} have been reported previously. Although it remains a
14 daunting task to propose the crystal structure from an optical spectrum of the known mass
15 species, attempts have been pursued to predict the crystal structures^{22, 69} for existing and
16 emerging Ag clusters, including doped clusters⁴⁶⁻⁴⁷ whose validity awaits actual crystallization of
17 the cluster.
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31 In addition to absorption, clusters also display luminescence behavior, by which it might
32 be possible to predict the cluster size if the emission is due to the bandgap (E_g) transition. This
33 potential was first recognized by Kubo⁷⁰ in 1962 with a simple scaling factor of E_f/N , i.e., the
34 energy gap in small metal clusters scales as $1/N$, where N is the total number of atoms, and E_f is
35 the Fermi energy of silver 5.49 eV^{31, 71}. The absence of fluorescence in bulk metals is due to
36 overlapping energy states that provide numerous non-radiative pathways for the decay of an
37 excited electron.⁷² However, because of the presence of discrete energy states, small metal
38 clusters exhibit fluorescence⁷³. Early work by the Whetten group⁷² attributed intraband ($sp \rightarrow sp$)
39 transitions within a metal core to the photoluminescence of < 2-nm-sized Au clusters.
40 Subsequent work from the same group on the precise cluster $\text{Au}_{28}(\text{SG})_{16}$,^{5, 74} later corrected to
41 $\text{Au}_{25}(\text{SG})_{18}$,³ provided similar arguments for the fluorescence/phosphorescence albeit with some
42 implications of the ligand effects.⁷⁴ While studying the fluorescent properties of Au clusters,
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3 Zheng *et al.*⁷⁵ (Knight *et al.*⁸ for bare Na_n clusters) empirically established a scaling factor of
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5 $E_g/N^{1/3}$ between the energy gap and the number of atoms in ligand-protected metal clusters based
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7 on the Jellium model. The Zheng *et al.*⁷⁵ relation was effective up to 20-atom Au clusters,
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9 beyond which correction factors were needed to explain the emission and cluster-size
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11 relationship.
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16 In favor of Ag clusters, the Dickson group⁷⁶ first reported fluorescent Ag clusters
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18 encapsulated by dendrimers. Huang and Murray's¹⁸ work pointed to the inter-band
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20 recombination (between *d* and *sp*) as a fluorescence source for Ag clusters. Although the exact
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22 origin of the fluorescence in precise Ag clusters remains disputable, Cathcart *et al.*¹⁹ and Bakr *et*
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24 *al.*²⁰⁻²¹ reported additional luminescence Ag clusters protected by glutathione, cysteine, and aryl-
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26 thiols. It is logical to assume that the visible luminescence from a relatively small-size cluster
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28 will be blueshifted compared with a large cluster because the HOMO-LUMO gap changes with
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30 the size. However, counter-intuitive observations (see Table 1), such as visible luminescence
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32 from a large Ag_{152} ⁶⁹ cluster compared with small IR-luminescence $[\text{Ag}_{44}(\text{SPhF})_{30}]$ ⁴⁻²⁰ cluster and
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34 a blueshift in the luminescences of $\text{Ag}_9(\text{SG})_6$ ⁷⁷ and $\text{Ag}_{15}(\text{SG})_{11}$ ²² compared with those of
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36 $\text{Ag}_8(\text{MSA})_8$ ²⁴ and $\text{Ag}_{11}(\text{SG})_7$ ²⁵, add some other parameters that affect the cluster-size and
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38 emission relationship. These luminescence-altering factors can be due ligand and surface state
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40 transitions, in addition to contributions from the cluster's surrounding environment. For example,
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42 Li *et al.*⁷⁸ and Xu *et al.*⁵⁵ demonstrated the luminescence change by understanding the
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44 temperature effects on precise Ag clusters, whereas Díez *et al.*⁵⁶ observed that the solvent rather
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46 than the size affected the emission. Recent work from the Jin group⁷⁹ on Au clusters emphasized
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48 the ligand, as they discovered that ligand→metal charge transfer (LMCT) either *via* the Au-S
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50 bond or through the electron-rich atoms/groups (e.g., N, O, -COOH, -NH₂) was responsible for
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the fluorescence. Similar LMCT in Ag clusters was observed by Pelton *et al.*⁸⁰ while studying transient-absorption spectroscopy of IBANs. A summary of the photophysical properties associated with some of the precise Ag clusters with their characterization techniques is provided in Table 1.

Table 1. A selection of atomically precise thiol- and thiol-phosphine-protected Ag clusters and their photophysical properties.

S.N.	Chemical formula	Excitation (nm)	Emission (nm)	Characterization	Ref.
1	Ag ₁₅₂ (PET) ₆₀	375	800	MALDI	69
3	Ag ₄₄ (SPhF) ₃₀ ⁴⁻	596, 643	1375	single-crystal	29
4	Ag ₃₅ (SG) ₁₈	420, 500	650	ESI-MS	57
5	Ag ₃₂ (SG) ₁₉	420, 500	680	ESI-MS	23
6	Ag ₃₂ (DPPE) ₅ (SPhF ₃) ₂₄ ²⁻	360	440	single-crystal	65
7	Ag ₂₅ (DHLLA) ₁₄	355	680	ESI-MS	81
8	Ag ₁₆ (SG) ₉	489	647	ESI-MS	77
9	Ag ₁₆ (DPPE) ₄ (SPhF ₂) ₁₄	360	440	single-crystal	65
10	Ag ₁₅ (SG) ₁₁	470	665	ESI-MS	22
11	Ag ₁₄ (SPhF ₂) ₁₂ (PPh ₃) ₈	360	536	single-crystal	64
12	Ag ₁₁ (SG) ₇	440	705	ESI-MS	25
13	Ag ₉ (MSA) ₇	625	720	ESI-MS	42
14	Ag ₉ (SG) ₆	379	495	ESI-MS	77
15	Ag ₈ (MSA) ₈	550	650	ESI-MS	24
16	Ag ₇ (MSA) ₇	350	440	ESI-MS	24

The luminescence data in Table 1 of Ag clusters were analyzed using the scaling factors reported by Kubo⁷⁰ and Zheng *et al.*⁷⁵ (Figure 6) to study the size-dependent emission properties. Both the Kubo and the Zheng *et al.* models are found to be unsuitable for explaining the entire data and therefore are unable to predict the relationship between size and emission of Ag clusters. However, unlike Au where the model of Zheng *et al.* is somewhat reasonable,⁷⁵ significant deviation is observed in the size range of ~ 8 –15 and ≥ 44 -atom in Ag clusters. Although the origin of such discrepancy is a complex problem with many potential variables and assumptions and is beyond the scope of this article; nevertheless, it can be understood that the photoluminescence may not originate only from the band-gap of clusters, which limits our ability to predict Ag cluster size spectroscopically with the emission energy *versus* E_g relation.

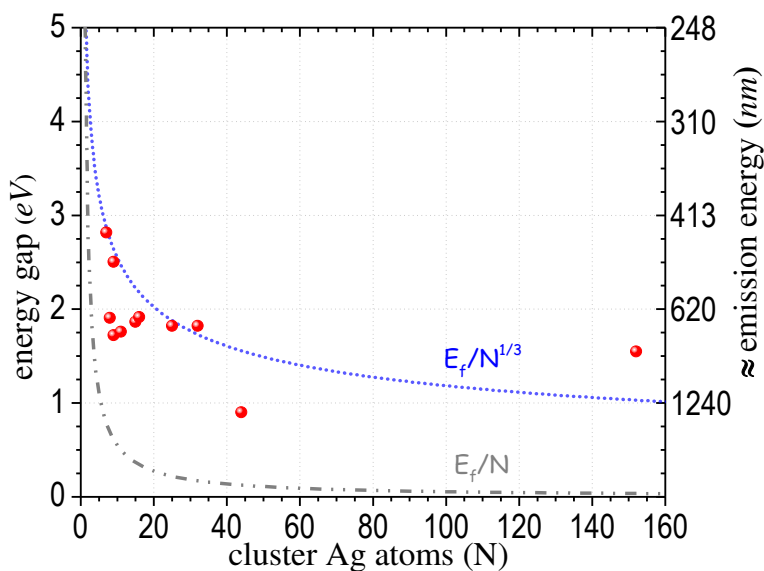


Figure 6. Correlation of the emission energy of Ag cluster size as predicted by Kubo (gray, E_f/N) and Zheng *et al.* (blue, $E_f/N^{1/3}$) scaling factors. The red spheres represent the actual emission energy of the thiolated Ag clusters.

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3 Also, when discussing spectroscopic properties related to Ag clusters, caution should be
4 exercised because Ag is prone to oxidation and is sensitive to light. Relatively few Ag clusters
5 are reported (Table 1), and some might be impure and unstable⁶⁹. Trace impurities in Ag cluster
6 samples with other sizes, especially the luminescent ones arising from oxidation or other
7 processes from the existing clusters during spectroscopic measurements, could significantly
8 affect emission spectrum. This effect adds uncertainty to the interpretation of the data and
9 therefore should be considered prior to estimation of Ag cluster size *via* emission $\propto E_g$ relation.
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21 In order to minimize the decomposition of Ag clusters with light in optical spectroscopy
22 and to identify materials close to their native states, mass spectrometry (MS) with softer
23 ionization method is essential. The Whetten group used laser desorption ionization (LDI) MS for
24 the characterization of Au clusters.^{5-6, 17} However, because of the significant fragmentations from
25 the LDI, relatively softer techniques with high resolution, such as matrix-assisted laser
26 desorption ionization (MALDI) and electrospray ionization (ESI), are more prevalent today. The
27 ESI MS, in particular, is preferred over MALDI because it neither uses light (laser) nor a
28 solidified sample with matrix. The Tsukuda³ and Griffith groups²³ characterized magic-size
29 Au_m(SG)_n and Ag₃₂(SG)₁₉ clusters, respectively, using ESI MS. The Griffith group observed that
30 the Ag thiolates were more fragile and prone to fragmentation than their Au counterparts.²³
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32 Nevertheless, MS is one of the most important tools for the characterization of clusters where the
33 molecular formula of the compound of interest is important for identification and crystallization
34 poses a significant challenge.
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52 Crystallization ensures purity of the material by consolidating molecules in a dense space
53 where single-crystal X-ray diffraction can reveal the ultimate atomic coordinates in 3D space.
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55 Detection of the intact cluster or its fragments in MS sometimes make interpreting a mass
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3 spectrum quite challenging because several processes, such as rearrangement, coordination, and
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5 fragmentation, occur in parallel in the gas phase. Most of these gas-phase metal clusters are
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7 difficult to crystallize or manipulate because they either change their properties or lose identity
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9 when they contact other species. Growing a single crystal from the solution phase of the cluster
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11 could be a possibility, although crystallization is challenging. Despite these challenges, there are
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13 reports of the crystallization of pure-thiol and mixed-ligand Ag clusters.^{28-29, 64-65}
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19 Similar to molecules, clusters prefer certain types of crystal habits. For example, graphite
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21 and diamond are composed of the same carbon building blocks; however, their respective crystal
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23 habits are completely different, i.e., tabular and octahedral. This tunability of the crystal habit
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25 results in new properties for materials. A recent report by Yao *et al.*⁸² brings this promise to the
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27 cluster community, as shown in Figure 7. These researchers were able to perform a crystal habit
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29 transition from a rhombohedral to an octahedral state for the same $[\text{Ag}_{44}(\text{p-MBA})_{30}]^{4-}$ system by
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31 swapping counter-ions⁸². In this case, the directionality provided by the counter-ions H^+ *via* H-
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33 bonding was disrupted with Cs^+ ions, which led to the change in the crystal habit. The ability to
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35 swap counter-ions with other metal-cations, such as Ca^{2+} and Al^{3+} , would allow engineers to
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37 construct new 3D shapes using $[\text{Ag}_{44}(\text{SR})_{44}]^{4-}$ as building blocks in the future, which could result
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39 in dramatically useful properties at the macro-scale that have already been achieved at the micro-
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41 scale^{28, 82}.
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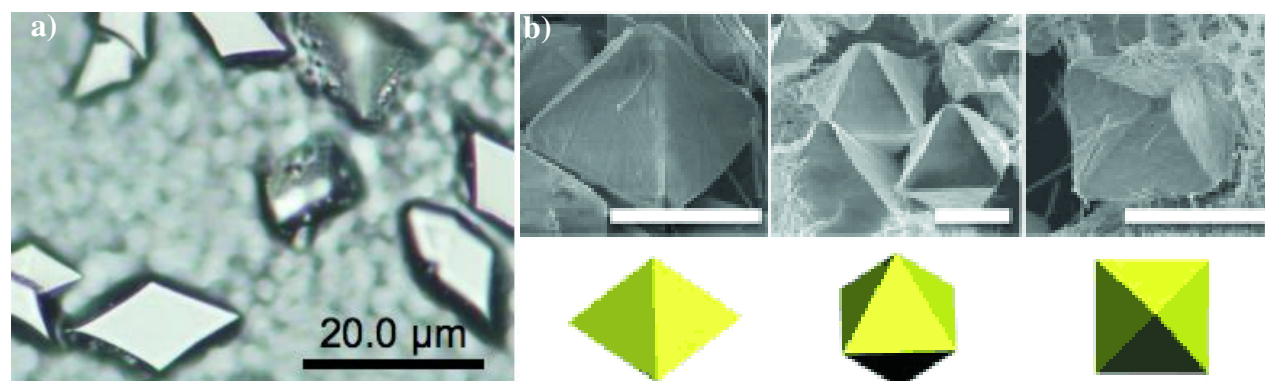


Figure 7. Crystals of $[\text{Ag}_{44}(\text{p-MBA})_{30}]^{4-}$ clusters **a)** with a rhombus shape crystallized from a dimethylformamide (DMF) solution with a completely protonated ligand as observed under an optical microscope²⁸ and **b)** electron micrograph of the octahedron-shaped crystals grown from dimethylsulfoxide (DMSO)/water using Cs^+ counter-ions⁸² (scale bar = 10 μm). Adapted from refs. ²⁸ and ⁸² with written permission.

Manifestation of fundamental properties such as the optical-activity and reactivity is key to understanding metal clusters better and can ultimately be achieved using single-crystal X-ray diffraction for both aqueous²⁸ and organic²⁹ soluble Ag clusters. Surprisingly, single-crystal X-ray diffraction revealed a completely different protecting layer for Ag clusters than for Au clusters, where mono ($-\text{S}-\text{Au}-\text{S}-$) and dimeric ($-\text{S}-\text{Au}-\text{S}-\text{Au}-\text{S}-$) motifs were predominant (Figure 8).³⁵⁻³⁶

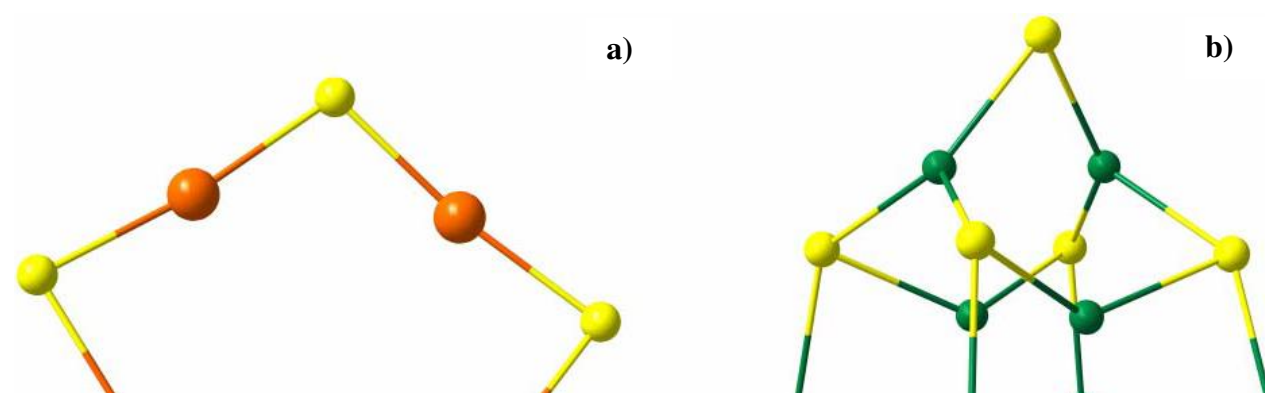


Figure 8. Structure of the cluster-protecting motifs Au₂S₃ (left) and Ag₂S₅ (right) observed in Au and Ag clusters, respectively.^{28-29, 35} Color legend of spheres: Au–orange, Ag–green, and S–yellow. Adapted from ref. [²⁹] with written permission.

As observed in Figure 8, the Au clusters are protected with one-dimensional motifs whereas the Ag clusters crystallized so far are protected with three-dimensional motifs. Although the ubiquitous nature of the three-dimensional Ag₂S₅ motif has yet to be proven, it can be argued that the many one-dimensional motifs would provide better coverage for a cluster core than the three-dimensional motif. This hypothesis is also supported by the fact that [Ag₄₄(*p*-MBA)₃₀]⁴⁻ contains ~50% void space²⁸ in the crystal volume, making it highly affected by its surrounding, which could explain the relatively low stability of Ag clusters compared with Au clusters. In stark contrast, our observations of year-long ambient stability in other Ag clusters, such as aqueous [Ag₄₄(MNBA)₃₀]⁴⁻⁴⁸ and Ag₃₅(SG)₁₈⁵⁷, clearly indicate the opposite physicochemical behavior.

Perspectives

The syntheses of Ag clusters involve multi-step and hours-long processes^{20, 29} with few exceptions²⁸. For instance, the synthesis of [Ag₄₄(SR)₃₀]⁴⁻ requires days based on the protocol of Bakr *et al.*²⁰ whereas a similar composition can be obtained in a one-pot synthesis in an hour using the procedure described by Desireddy *et al.*²⁸. This shortening of the synthesis time is crucial for materials processing and applications on industrial scales. Nevertheless, the key factors behind this drastic reduction in synthesis time have not been seriously considered. In

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3 addition, in $\text{Ag}_m(\text{SG})_n$ clusters, what factors determine the values of m and n remains a mystery
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6 both experimentally and theoretically and therefore require attention.
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9 Silver has received less attention than has gold from the beginning even though it is
10 inexpensive. This inferiority of silver over gold was due to its susceptibility to oxidation.
11 However, at the nanoscale, Ag is not as susceptible to oxidation as indicated by the resistance of
12 some Ag clusters, such as $\text{Ag}_{35}(\text{SG})_{18}$ ⁵⁷ and $[\text{Ag}_{44}(\text{MNBA})_{30}]^{4-48}$. Many magic clusters in the
13 $\text{Au}_m(\text{SG})_n$ family³ have been successfully characterized with atomic precision because they are
14 stable. Years have passed since the isolation of 20+ magic $\text{Ag}_m(\text{SG})_n$ clusters;⁴ however, few²²⁻²³
15 of these clusters have been characterized. This lack of progress in the characterization of Ag
16 clusters lies in either cluster stability or instrumental limitations. Stability appears to be a critical
17 factor despite the significant technical know-how acquired from the characterization of
18 analogous $\text{Au}_m(\text{SG})_n$ clusters because the instability associated with Ag clusters can ruin a
19 sample, as decayed products accumulate over time, resulting in poor data and confusion. For
20 example, four research groups independently working on the same glutathione Ag system
21 detected $\text{Ag}_m(\text{SG})_n$ species with very similar absorption features that were assigned as
22 $\text{Ag}_{35}(\text{SG})_{18}$ ⁵⁷, $\text{Ag}_{32}(\text{SG})_{19}$,²³ $\text{Ag}_{31}(\text{SG})_{19}$,²² and $\text{Ag}_{16}(\text{SG})_9$ ⁷⁷.
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43 Although some clues for improving the stability of Ag clusters were revealed from a
44 single-crystal structure of Ag_{44} ²⁸⁻²⁹ and other Ag species⁶⁴⁻⁶⁵, significant work needs to be
45 performed before actual manipulation of the Ag cluster stability can be achieved. Among all
46 available Ag species,^{20, 28-29, 48} aqueous $[\text{Ag}_{44}(\text{MNBA})_{30}]^{4-}$ is observed to be the most stable with
47 an 18-electron core. However, this cluster undergoes rapid ligand exchange with different aryl-
48 thiols in a matter of seconds, producing less-stable species, such as $[\text{Ag}_{44}(\text{SPhF})_{30}]^{4-}$ and $\text{Ag}_{44}(\text{2-}$
49 naphthalenethiol)₃₀⁴⁻ with a Ag_{44} core intact.⁴³ A question remains unanswered: Why would the
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3 cluster sacrifice its stability to migrate into a less-stable state? Arguments that an excess ligand
4 pushes the equilibrium in favor of the ligand exchange are reasonable. However, reversibility
5 was not observed when excess MNBA ligand was used to obtain the original $[\text{Ag}_{44}(\text{MNBA})_{30}]^{4-}$
6 from the $[\text{Ag}_{44}(\text{SPhF})_{30}]^{4-}$ clusters in our experiments.
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13 In addition, unlike Au, where the same ligand PET can produce different size $\text{Au}_m(\text{PET})_n$
14 clusters,⁷ Ag is known to form the same Ag_{44} cluster with different aryl thiols.^{20, 43} This limits
15 our ability to diversify cluster size; however, a subtle yet important empirical factor for cluster
16 size tuning is often lost. For tuning the size of Ag clusters, researchers should look at those aryl
17 thiols that have substitution adjacent to the thiol group. This subtle change in ligands could
18 unlock the key to producing Ag clusters of different sizes, which needs to be considered.
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28 Another concern is the superatom theory. The electronic and geometric shell closure
29 ideas of the superatom theory represent significant theoretical advancements in explaining the
30 stability associated with clusters. However, some clusters do not have closed structures (Figure
31 9), do not obey superatom theory but are very stable. Therefore, the superatom theory requires
32 modification to include clusters with open shells. Moreover, having a closed electronic shell does
33 not guarantee that the cluster is a superatom even though it is one criterion. For example, the
34 $[\text{Au}_{23}(\text{SC}_6\text{H}_{11})_{16}]^-$ cluster^{7, 83} has an $8e^-$ core, analogous to the $[\text{Au}_{25}(\text{PET})_{18}]^-$ cluster; however,
35 DFT analysis based on the experimental crystal structure proved that this cluster was not a
36 superatom. In this case, where the superatom theory has a limited use, Clemenger³⁸ suggested
37 that the clusters would undergo distortion to lower their energies; however, a concrete theory is
38 not available yet. Thus, we should be cautious regarding the superatom theory. Deeper
39 understanding may imply that it is feasible in principle to synthesize arbitrary Ag_m clusters
40 (where $m = 1, 2, 3, 4, \dots$) although these clusters may vary in the stability. In the future, we
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could have numerous Ag_m clusters with various properties that could go beyond the periodic table of elements to meet our needs. We believe that emerging Ag clusters may follow a particular trend described by the stability curve presented in Figure 9.

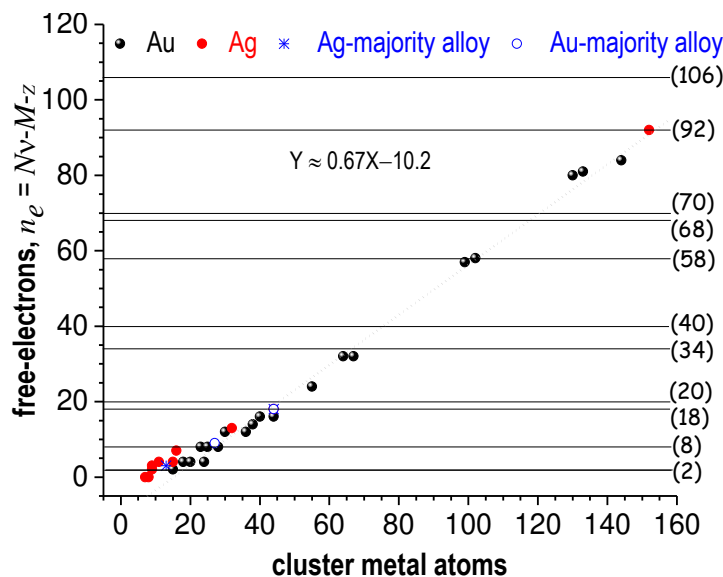


Figure 9: Stability belt of ligand-protected metal clusters obtained after analysis of the free electrons present in the thiol-protected Ag_mL_n and Au_mL_n , and their alloys. The numbers inside the parentheses indicate electron-shell closure, and the dotted line is the actual fit to Au_mL_n clusters with a slope of $\approx 2/3$ (data compiled from Table 1 and refs. [7, 49, 53, 29, and 84])

It is apparent from Figure 9 that ligand-protected metal clusters follow a certain trend described by the plot of n_e versus cluster metal atoms. Notably, the clusters populate themselves around a line with a slope of $2/3$. Therefore, the magic size clusters maintain a magic ratio of approximately 2 free electrons for every 3 metal atoms with some intercept value (Figure 9). We expect that emerging Ag clusters would follow the trend described by the stability curve because it would be difficult to synthesize a mono-thiol protected clusters that deviate considerably from the projection of the stability curve. We also studied the plot of $(n_e - |z|)$ versus cluster core atoms

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3 (not shown) but did not find much difference because the majority of clusters are neutral.
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6 Regardless of the superatom theory, this stability curve can serve as a guide for predicting the
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8 sizes of Ag_m clusters that can be synthesized, which could be studied like the periodic table of
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10 elements. Furthermore, the stability curve also suggests a threshold of a cluster size of ~ 15
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12 atoms, beyond which the core atom count in a cluster would always be greater than the ligand
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14 count.
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18 Finally, impending chaos is on the horizon for the systematic study and organization of
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20 existing and emerging ligand-protected metal clusters. Therefore, a healthy debate on this matter
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22 is expected in the scientific community. Attempts toward the systematic study of bare gas-phase
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24 metal clusters in a 3D periodic table have been discussed in the literature;⁸⁵⁻⁸⁶ however, this
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26 effort has not been made for ligand-protected metal clusters. Our views in this regard are
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28 presented below.
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33 Natural elements are arranged in the standard form of the periodic table as a function of
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35 their increasing atomic numbers such that no two elements have the same position in the 7×18
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37 grid table (Figure 10, top panel). However, the arrangement of clusters is different; these
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39 structures possess a few hundred atoms clinging together, resulting in an additional dimension
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41 that is not needed for atoms. Moreover, existing and emerging clusters would easily outnumber
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43 the total elements by a large margin, thus complicating their systematic study, given the number
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45 of ways that atoms can be arranged in a 3D cluster space.
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50 Nevertheless, placing Ag_mL_n clusters in a periodic table similar to Mendeleev's is an
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52 option. However, finding a reasonable basis for the arrangement of clusters in the most
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54 meaningful manner is challenging. We have many candidates for bases: the total atomic number
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3 or weight, cluster electron configuration, cluster energy, electronegativity, length, etc. Using the
4 total atomic number or weight as a basis, which is obtained by summing the contributions from
5 all the atoms present in a cluster, appears unsuitable because it would produce a very large
6 number. Superatom/cluster electronic configuration, i.e., categorizing clusters into S, P, D, F, G,
7 blocks is possible; however, some clusters do not follow the superatom theory. The
8 exclusion of non-superatoms or superatoms with zero free electrons or in a negative state (i.e.,
9 the case of a greater ligand than metal count) could be a serious problem in this case. An
10 arrangement based on either the total energy or electronegativity of a cluster is less likely
11 because of the fractional numbers and the high probability of similar values for many different
12 clusters. Arranging clusters according to their length is promising because the nanoscale
13 properties depend on the length scale. However, defining a precise length is difficult because of
14 the variability in cluster shapes. Therefore, we think that organizing clusters based on the core
15 metal atom count would simplify the task as we can have very precise numbers 1, 2, 3, 4, 5,
16 similar to the atomic numbers in the periodic table of elements. Depending on the shape, size,
17 and cluster properties, we do expect the same-size clusters to be assigned to a single or multiple
18 cells. However, the length and width of the periodic table for Ag_mL_n clusters currently remain
19 changeable due to inadequate data.

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Despite these issues, the question arises of how the periodic table of clusters would look when they are arranged as a function of increasing core atoms. Certainly, it would be much different from the periodic table of elements (Figure 10, top panel). Unlike the periodic table of elements, periodicity will be lost with clusters. Therefore, the future periodic table of clusters would look like a megapixel photograph, where a pixel would represent either a superatom or a non-superatom cluster. This photograph of clusters (abbreviated here as “clusterograph”) would

have local or regional similarities among different clusters across the entire grid (highlighted in red, yellow, green, blue and violet) but no recurring periodicity. Furthermore, in contrast to the periodic table of elements, similar superatom clusters, such as $[\text{Ag}_{44}(\text{SPhF})_{30}]^{4+}$, $[\text{Ag}_{44}(\text{SPhF}_2)_{30}]^{4+}$ and $[\text{Ag}_{44}(\text{SPhF}_3)_{30}]^{4+}$, would be given a single cell even though each cluster contains a different ligand. We believe that most elements in the periodic table of elements such as Cu, Au, Pd, and Pt would have their own clusterograph as we demonstrate here for Ag in Figure 10, bottom panel. Interpreting these clusterographs would be more appropriate for computers than for humans.

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	* La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	† Ac															

*57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
†89 Ac	90 Th	91 Pa	92 U											

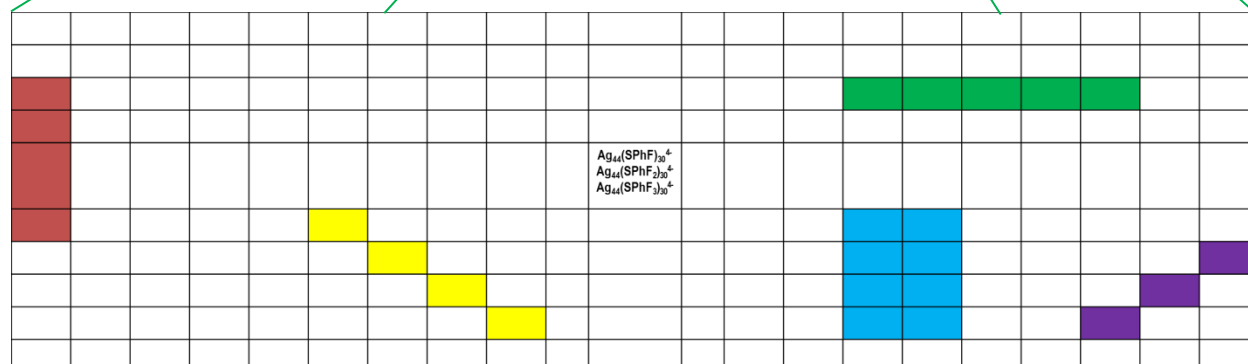


Figure 10. Elemental periodic table (top) along with a proposed clusterograph of Ag clusters (bottom). The yellow, green, red, blue, and violet shading highlights the similarities in the properties of different Ag clusters at the local or regional levels.

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Quotes:

1. Geometric shell closing is also applied to explain the cluster stability. Depending on the geometric shape, e.g., cubic, tetrahedral, octahedral, or icosahedral, certain numbers of building units are required to form a closed geometry
2. For tuning Ag cluster size, researchers should look at those aryl thiols that have substitution adjacent to the thiol group. This subtle change in ligand could unlock the key for other size Ag clusters
3. Magic size clusters maintain a magic ratio of approximately 2 free electrons for every 3 metal atoms with some intercept