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Item Type	Article
Authors	Krishnadas, Kumaranchira Ramankutty; Natarajan, Ganapati; Baksi, Ananya; Ghosh, Atanu; Khatun, Esma; Pradeep, Thalappil
Citation	Krishnadas KR, Natarajan G, Baksi A, Ghosh A, Khatun E, et al. (2018) Metal-ligand interface in the chemical reactions of ligand protected noble metal clusters. Langmuir. Available: http://dx.doi.org/10.1021/acs.langmuir.8b03493.
Eprint version	Post-print
DOI	10.1021/acs.langmuir.8b03493
Publisher	American Chemical Society (ACS)
Journal	Langmuir
Rights	This document is the Accepted Manuscript version of a Published Work that appeared in final form in Langmuir, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see https://pubs.acs.org/doi/10.1021/acs.langmuir.8b03493.
Download date	09/08/2022 08:44:35
Link to Item	http://hdl.handle.net/10754/630269

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Langmuir, **Just Accepted Manuscript** • DOI: 10.1021/acs.langmuir.8b03493 • Publication Date (Web): 06 Dec 2018

Downloaded from http://pubs.acs.org on December 11, 2018

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Metal-ligand interface in the chemical reactions of ligand protected noble metal clusters

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ABSTRACT

We discuss the role of the metal-ligand (M-L) interfaces in the chemistry of ligand protected, atomically precise noble metal clusters, a new and expanding family of nanosystems, in solution as well as in gas phase. A few possible mechanisms in which the structure and dynamics of M-L interfaces could trigger intercluster exchange reactions are presented first. How interparticle chemistry can be a potential mechanism of Ostwald ripening, a well-known particle coarsening process, is also discussed. Reaction of Ag_{59}(2,5-DCBT)$_{32}$ (DCBT = dichlorobenzenethiol) with 2,4-DCBT leading to the formation of Ag_{44}(2,4-DCBT)$_{30}$ is presented, demonstrating the influence of the ligand structure in ligand-induced chemical transformations of clusters. We also discuss structural isomerism of clusters such as $Ag_{44}(SR)_{30}$ (-SR = alkyl/aryl thiolate) in gas phase wherein

the occurrence of isomerism is attributed to the structural rearrangements in the M-L bonding network. Interfacial bonding between $Au_{25}(SR)_{18}$ clusters leading to the formation of cluster dimers and trimers is also discussed. Finally, we show that desorption of phosphine and hydride ligands on a silver cluster, $[Ag_{18}(TPP)_{10}H_{16}]^{2+}$ (TPP = triphenylphosphine) in gas phase, lead to the formation of a naked silver cluster of precise nuclearity, such as Ag_{17}^{+}. We demonstrate that the nature of the M-L interfaces, *i.e.*, the oxidation state of metal atoms, structure of the ligand, M-L bonding network, *etc*., play key roles in the chemical reactivity of clusters. The structure, dynamics and chemical reactivity of nanosystems in general are to be explored together to obtain new insights into their emerging science.

Introduction

Metal-ligand (M-L) interfaces play key roles in dictating the physical properties, chemical reactivity and interparticle interactions of ligand protected metal nanosystems. Atomically precise noble metal clusters,[1,2]such as $Au_{102}(SR)_{44}$,[3] $M_{25}(SR)_{18}$ (M=Ag/Au),[4-5] $Ag_{44}(SR)_{30}$,[6-7]*etc*. (–SR = alkyl/aryl thiolate), serve as convenient models to investigate the properties of M-L interfaces owing to their well-defined compositions, structures and molecule-like properties.[8-10] Such clusters have a well-defined metal core protected by a ligand shell. Feasibility to incorporate a variety of ligands such as phosphines,[11-13] thiols,[7, 14-19] selenols,[20-22] alkynes,[23]*etc*., also make them suitable systems to study M-L interfaces. Early in the literature, these clusters were referred to as "monolayer protected clusters",[24] assuming that the ligands form an extended, ordered layer on particle surfaces,[25] which in turn resemble crystallographic planes of the corresponding metals. Single crystal X-ray crystallography revealed that the M-L interfaces in many of these clusters, assume well-defined, short M_xL_y oligomeric units. For example,

$Au_{25}(SR)_{18}$ is composed of a Au_{13} core and six $Au_2(SR)_3$ units, often referred to as staple motifs. Similarly, $Ag_{44}(SR)_{30}$ consists of an Ag_{32} core protected by six $Ag_2(SR)_5$ mounts. This structural model has been referred to as the 'divide and protect' model[26] wherein these clusters are viewed as a core containing a precise number of metal atoms protected by a specific number of M_xL_y oligomeric units. Structural correlations between these clusters and that of M-L complexes and self-assembled monolayers have also been identified.[27]Recently, a few other structural models[28-30]in which these clusters have been considered as interlocked rings, instead of distinct staples or mounts, have been proposed to understand the properties of these clusters. Irrespective of the structural model, the actual structure of the ligands, their spatial distribution on the cluster surface, binding modes of the ligands with the metal atoms, oxidation states of metal atoms, *etc*., need to be considered in order to understand the M-L interfaces in these clusters.

The nature of ligands such as the type of the tail groups (alkyl, aryl, *etc*.) and the positions[31](ortho, meta and para) of functional groups (-CH_3, -COOH, *etc*.) in them drastically influence the nuclearity, geometry, solubility and other properties of clusters.[32-33] Weak van der Waals and/or π-π interactions between the ligands is shown to be responsible for their chiroptical properties,[34-35] supramolecular interactions,[36] and cluster assemblies.[37-39] Electronic interaction between the ligands and the metal core influences optical absorption[40], and luminescence[41-42] features. Metal atoms in the staples serve as the true catalytic sites in such clusters. A variety of chemical transformations of these clusters such as ligand exchange,[43-47] metal atom substitution[48-53], ligand-induced core etching[54-55] and core transformation,[56-58]*etc*., were reported in the last few years. Recently, reactions between clusters in solution phase were also reported.[59-64] These reactions invariably involve the metal atoms and ligands in the staple or mount motifs of these clusters.[65-68] Dynamic nature of the staple motifs or mounts[69-74] and reactions of these

clusters have been studied, mostly in the solution phase. Gas phase stability, dynamics of these M-L interfaces and resulting chemical reactivity of ligand protected clusters remain poorly understood. In order to understand the chemical reactivity of these clusters, a better understanding of their M-L interfaces is essential.

In this *Feature* article, we discuss the role of M-L interfaces in dictating the solution as well as gas phase reactions of ligand protected atomically precise noble metal clusters. We discuss the role of the staples or mount motifs in such clusters in triggering the intercluster exchange reactions. We propose that interparticle chemistry, as demonstrated between atomically precise clusters, can be helpful to understand the chemical events behind Ostwald ripening, a well-known particle coarsening process. Next, we show that ligand-induced transformation of Ag_{59}(2,5-DCBT)$_{32}$ to Ag_{44}(2,4-DCBT)$_{30}$ (DCBT = dichlorobenzenethiol) occurs in solution phase through the dissociation of metal ligand fragments.[75] Then we discuss three examples wherein gas phase dynamics and reactivity of M-L interfaces are demonstrated. We present ion mobility mass spectrometric studies showing that ligand protected clusters such as $Ag_{44}(SR)_{30}$ exhibit structural isomerism in gas phase wherein the isomerism is attributed to the structural rearrangements in the metal-ligand bonding network.[76] Interfacial bonding between $Au_{25}(SR)_{18}$ clusters leading to the formation of cluster dimers and trimers is also presented.[77] Finally, we show that desorption of phosphine and hydride ligands on a silver cluster, $[Ag_{18}(TPP)_{10}H_{16}]^{2+}$ in gas phase, lead to the formation of naked silver clusters of specific nuclearity, such as Ag_{17}^{+}.[78] We conclude the article with a summary and brief discussion of the future perspectives.

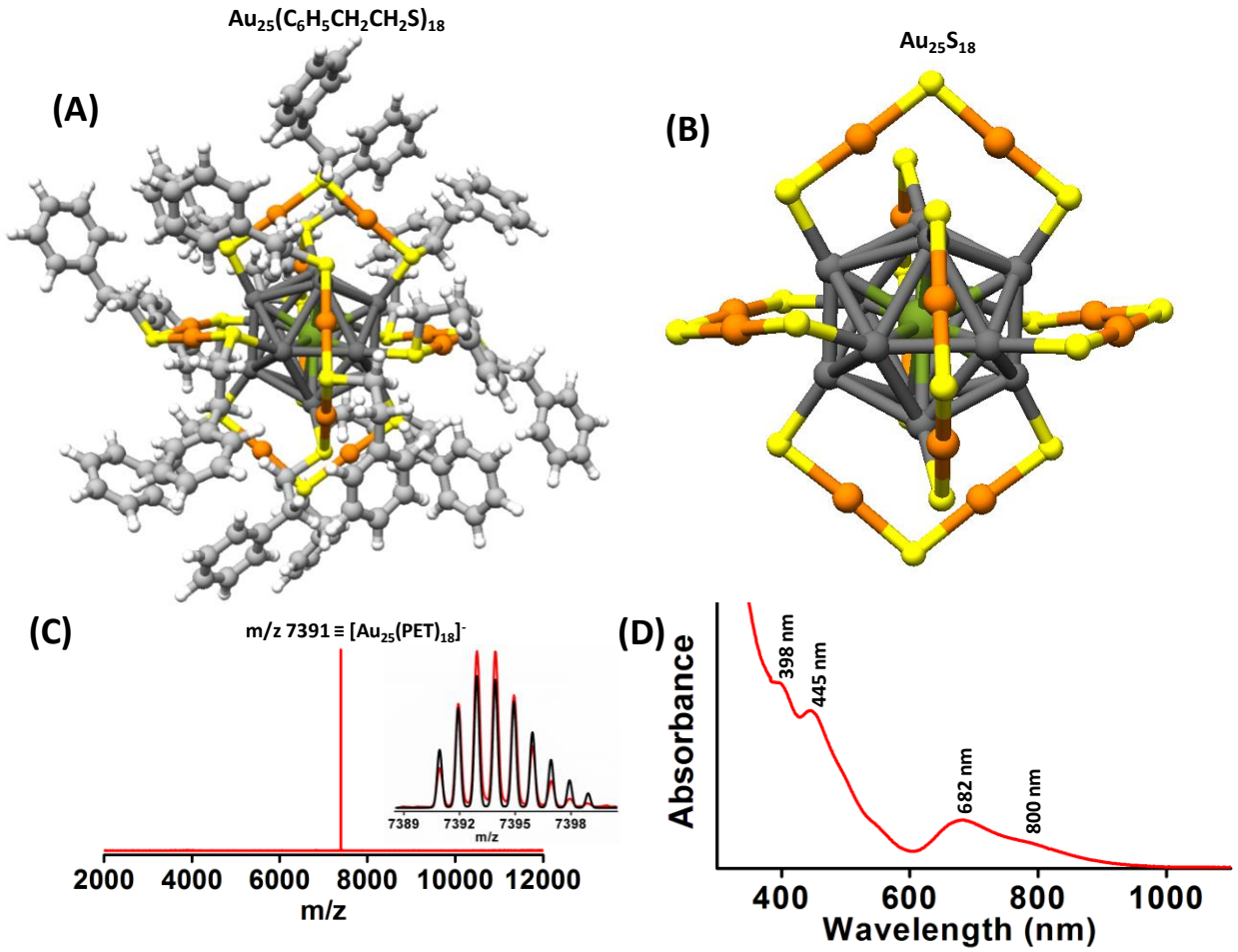

Figure 1. Crystal structure of $Au_{25}(C_6H_5CH_2CH_2S)_{18}$ (A), schematic showing the icosahedral core and the six $Au_2(SR)_3$ staples (B), negative ion ESI MS spectrum (C) and UV/Vis absorption spectrum of $Au_{25}(C_6H_5CH_2CH_2S)_{18}$ (D). The $C_6H_5CH_2CH_2$ groups of the ligands are omitted in (B), for clarity. The figures are intended to highlight the ligand-core interface. Color codes of atoms: Au atoms in the icosahedral core (black), in the center of Au_{13} icosahedron (Green), in the staples (Orange), sulfur (Yellow), carbon (Grey) and hydrogen (White). Distinct features in the mass and the UV/Vis spectra are also marked in (C) and (D). Isotopic resolution of the molecular ion feature of $Au_{25}(C_6H_5CH_2CH_2S)_{18}$ at m/z 7391 is shown in the inset of (C) along with a comparison of the theoretical (black) and experimental (red) spectrum.

Intercluster reactions: What is the role of metal ligand interface?

As mentioned above, thiolate-protected noble metal clusters have traditionally been viewed as composed of a core consisting of a definite core of metal atoms, protected with a well-defined shell of metal-ligand oligomeric complexes. Single crystal X-ray crystallographic structure of $Au_{25}(C_6H_5CH_2CH_2S)_{18}$, for example, is shown in Figures 1A and 1B. This cluster consists of an inner Au_{12} icosahedral core (black spheres in Figures 1A and 1B) encapsulating a central Au atom (green spheres in Figures 1A and 1B) and the ligands are distributed in six, distinct $Au_2(SR)_3$ staple motifs (see orange and yellow spheres in Figure 1B). The composition and charge state of these clusters are further confirmed through electrospray ionization mass spectrometry (ESI MS) as well, as shown in Figure 1C. High resolution spectrum shows the isotopic features. Although Au has only one isotope, the isotopes of S (^{32}S, ^{33}S, ^{34}S and ^{36}S), C (^{12}C and ^{13}C) and H (^{1}H and ^{2}H) produce a rich spectrum. Such richness can be used to confirm the composition of the cluster by comparing with the theoretical spectrum. Electronic structure calculations show that the distinct electronic absorption features of these clusters (see Figure 1D) originate from various transitions in their discrete electronic energy levels. Thus, crystallography and electronic structure calculations support this structural model of these ligand-protected noble metal clusters. However, in order to understand the chemical reactivity of these clusters, it is necessary to consider other structural models. We discuss some of these aspects in the preceding sections.

Recently, intercluster reactions, resulting in the exchange of metal atoms, ligands and metal ligand fragments between them have been demonstrated.[59-60, 62-63] However, the mechanisms of such reactions, especially how such reactions are triggered, remain unknown. In this section, we discuss a few possible ways by which the structure and dynamics of M-L interfaces trigger

intercluster reactivity. For this, we consider the reaction between two structurally and compositionally analogous noble metal clusters, $Ag_{25}(SR)_{18}$ and $Au_{25}(SR)_{18}$.[59] As mentioned above, these clusters have traditionally been viewed as composed of a distinct M_{13} core protected by $M_2(SR)_3$ (M= Ag/Au) staples. According to the superatom theory,[27] valence electrons of metal atoms in their staples are localized by polar covalent bonds with sulfur atom of the ligands. Furthermore, each of the $M_2(SR)_3$ staples localizes the valence electron of one of the metal atoms in the M_{13} core. Therefore, all of the metal atoms in the six $M_2(SR)_3$ staples and six of the metal atoms in the M_{13} core are considered to be in +1 oxidation state. The remaining seven electrons and an acquired negative charge make the eight electron superatom, $[Au_{25}(SR)_{18}]^-$. In the crystal structure, the charge neutrality is provided by the metal ions or ammonium ions. The studies presented in this article are performed with this $Au_{25}(SR)_{18}$ anions in solution, although this may not be mentioned explicitly.

We think that the difference in the oxidation states of metal atoms in the core and the staples, as explained above, play a crucial role in triggering the intercluster reactions. Because of this difference in oxidation states, redox-like reactions could occur between two clusters. Let us consider two such possibilities, taking the reaction between $Ag_{25}(SR)_{18}$ and $Au_{25}(SR)_{18}$ as an example. In the first case, an $Ag_{25}(SR)_{18}$ molecule reacts with the $Au_2(SR)_3$ staples of the $Au_{25}(SR)_{18,}$ wherein Au of $Au_2(SR)_3$ staples is in +1 oxidation state. Note that redox reactions between silver clusters and Au(I)-thiolates are known.[79] Alternatively, an $Au_{25}(SR)_{18}$ molecule reacts with the $Ag_2(SR)_3$ staples of the $Ag_{25}(SR)_{18}$, wherein Ag of $Ag_2(SR)_3$ staple is in +1 oxidation state. Such reactions between $Au_{25}(SR)_{18}$ and Ag(I)-thiolates are also known.[80] It remains still unclear how the difference in oxidation states of metal atoms in the core and the staples contributes to the chemical reactivity of these clusters. Apart from these possibilities, it

has also been intuitively suggested in the reaction between $Au_{25}(SR)_{18}$ and $Ag_{44}(SR)_{30}$ that the interaction between these two intact clusters could result in the formation of small, reactive fragments such as $Ag(SR)_2^-$ which react with the $Au_2(SR)_3$ staples of $Au_{25}(SR)_{18}$ resulting in exchange of metal atoms, ligands and M-L fragments.[62] In this context, it is important to understand how far the chemistry of these clusters differ from that of the M-L complexes. In other words, do these clusters behave as unique entities in their reactions wherein the overall electronic structures of both of the reacting clusters need to be considered in order to explain their reactivity (rather than attributing their chemistry as due to the reaction between one of the clusters and the staples or the mounts of the other, as explained earlier)?

A new structural model, namely, the Borromean rings model,[28] has been proposed for the noble metal cluster $Au_{25}(SR)_{18}$ by Natarajan *et al*., wherein $Au_{25}(SR)_{18}$, has been considered as part of three interlocked $Au_8(SR)_6$ rings surrounding the central Au atoms (see Figure 2). In this, all the metal and sulfur atoms, except the central metal atom, belong to a unique structural component, the $Au_8(SR)_6$ ring. This model suggests that disconnecting any ring leads to two unlinked rings, which is a defining characteristic of the Borromean rings bonding topology (see Figure 2B). The Borromean rings model also applies to a silver cluster, $Ag_{25}(SR)_{18}$, which is a structural analogue of $Au_{25}(SR)_{18}$. Natarajan *et al.*, also noted that interlocked metal-thiolate ring structures have been found in the core and staple structures of a few gold-thiolate clusters which have crystal structures available, both smaller and larger than $Au_{25}(SR)_{18}$, namely $Au_{10}(SR)_{10}$,[81] $Au_{20}(SR)_{16}$[82] and $Au_{144}(SR)_{60}$[30, 83]. They suggested that the interlocked ring structures form a strong framework for the clusters and may possibly represent a unified viewpoint for the structure of monolayer protected clusters. According to this interlocked-ring structural model, these clusters being formed out of and stabilized by ring structures, are more

dynamic in nature than one would expect from the core/staple model, because in the latter, the M_{13} core has been viewed as distinct, compact structural unit which is difficult to undergo any structural distortion. Furthermore, if the cluster existed in solution as distinct, structurally rigid Au_{13} core and $Au_2(SR)_3$ staples, exchange of metal atoms into the core would not have been feasible. However, exchange of metal atoms in the core also occurs during the reaction between $Ag_{25}(SR)_{18}$ and $Au_{25}(SR)_{18}$ suggesting that the icosahedral Au_{13} core is flexible and dynamic in nature, as experimentally proven by Tsukuda *et al*.[29] Ghosh *et al*. have shown that dynamics of M-L interfaces can be controlled by using dithiolates which bind to the metal core in a bidentate fashion and thereby reducing the flexibility of the metal-ligand bonding network.[84] Hence, we think that an interlocked-ring model of the structure can better explain the enhanced dynamics of M-L interfaces and reactivity of clusters.

Even though the mechanistic details are not known, it has been suggested that interactions between the M-L interfaces might occur in the initial stages of these reactions. In the reaction between $Au_{25}(SR)_{18}$ and $Ag_{25}(SR)_{18}$, we detected a dimeric species, $[Ag_{25}Au_{25}(DMBT)_{18}(PET)_{18}]^{2-}$, which could be one of the intermediates of the reaction.[56] DFT calculations revealed that this adduct could be formed through a weak covalent bonding between them through inter-staple metal sulfur bonds.[59] Recently, Zhang *et al*., attempted to detect such intermediates during the reaction between $Au_{38-x}Ag_x(SR)_{24}$ and $Au_{38}(SR)_{24}$ using *in situ* X-ray absorption fine structure (XAFS) measurements.[66] However, detection of exchanged Ag atoms in the staples was not successful, possibly due to shorter residence time of the exchanged Ag atoms in the staples.

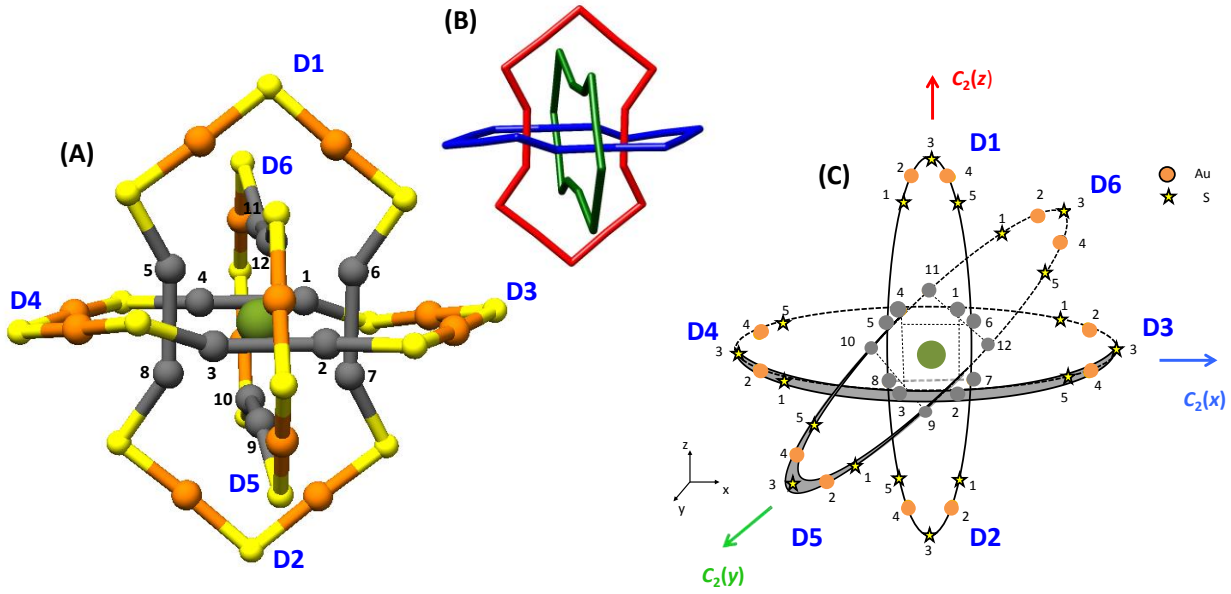

Figure 2. (A)A visualization of $Au_{25}S_{18}$ as the ring structure consisting of three interlocked (Au_8S_6)-rings. (B) The topological configuration of the Borromean rings, with the three rings Au_8S_6 rings being colored red, blue and green. (C)A 2D schematic diagram of the Borromean rings formed by planar-projection of the$Au_{25}S_{18}$ ring structure shown in (A), wherein the Au_8S_6 rings formed by pairs of coplanar staples are shown as ellipses. Gold atoms in the icosahedral core are shown by grey circles and yellow stars represent the positions of S atoms of the thiolate ligand. The core Au atoms are numbered from 1 to 12 and the staple atoms are numbered clockwise from end of the staple, from 1 to 5. The lines that join core Au atoms on opposite ends of the same staple are shown by the dotted lines. The three perpendicular C_2 axes are marked with the associated Cartesian axes directions in brackets. The staple directions are labeled by the six staple locants D1 to D6, marked in blue. In each Au_8S_6 ring, there are three sets of coplanar staples, *i.e.*, D1-D2, D3-D4 and D5-D6. Color codes of atoms in (A): Au atoms in the icosahedral core (grey), centre of the Au_{13} icosahedron (Green), staples (Orange), Sulfur (Yellow). (Adapted with permission from, Ref. 28)

Ostwald ripening and interparticle reactions

Ostwald ripening is one of the important mechanisms of nanocrystal growth[85] wherein larger particles grow larger at the expense of smaller ones in solution. Thermodynamic driving force behind this process is the difference in surface energies of (smaller and larger) particles in a polydisperse solution/dispersion. Smaller particles possess higher surface energy and hence, they disappear more easily compared to the larger particles in the same solution/dispersion. Ostwald ripening occurs by the diffusion of the smaller particles, towards the larger particles and subsequent reactions between them resulting in the growth of the particle.[85] This makes the larger particles grow larger in size, consuming or reducing the size of the smaller ones. However, it remains unclear how the constituents (atoms, ions or molecules) of smaller particles are transported to the larger ones, *i.e.*, by a direct interparticle exchange or exchange of their fragments, in such processes. Details of chemical events in such processes are not known clearly. It was shown that in the case of noble metal clusters, exchanges of metal atoms, ligands and metal ligand fragments occur through direct interaction or collision between the reacting clusters. How do these two processes *i.e.*, intercluster exchange and Ostwald ripening, differ from each other? Can Ostwald ripening be interpreted or understood as interparticle exchange reactions between larger particles and smaller ones?

Let us discuss this briefly in the context of ligand protected metal nanosystems. For example, consider a dispersion of thiolate-protected metal nanoparticles, which are typically polydisperse in their sizes. In such a mixture, smaller particles could be more reactive compared to the larger ones, also for reasons other than the surface energy differences, such as change in the oxidation states, differences in the redox potentials of (smaller and larger) particles, differences in metal-ligand binding modes, *etc*. as mentioned previously in the context of atomically precise clusters.

Do such factors contribute to the interparticle reactions (between larger and smaller particles) resulting in Ostwald ripening?

In the intercluster exchange reactions reported so far, the size, structure, composition (*i.e.*, number of metal atoms and ligands) and charge state remain unaltered. This could be due to the tendency of these clusters to retain their compact, highly symmetric, geometrically and electronically stable structures. Furthermore, these clusters are molecule-like and are of comparable sizes wherein electronic factors, such as shell closing effects, rather than geometrical factors determine the stability. However, in Ostwald ripening, particle size changes, as mentioned above. In this context, it is interesting to check whether there is a clear particle size limit, at which an intercluster/interparticle exchange reaction and an Ostwald ripening can be discriminated by the change or constancy of the particle size? Maran *et al*., have recently reported the formation of $Au_{38}(SR)_{24}$from a smaller cluster, $Au_{25}(SR)_{18}$ which they referred to as "gold fusion". However, it remains unclear whether this reaction can be understood as an example of Ostwald ripening of atomically precise clusters.[86] The above discussion imply that it is important to investigate what are the (surface/interfacial) chemical events *between* particles in an Ostwald ripening process, at least in the context of ligand protected nanosystems.

Ligand's influence on cluster transformations

Atomically precise clusters of a wide variety of nuclearity, geometry and protecting ligands are reported in the last decade. However, it remains unknown how the actual structure of the ligands influences the nuclearity and geometry of the clusters. One of the ways to investigate this aspect is to study the reactions of ligand protected clusters with free ligands. Often, exchange of ligands occurs in these reactions without altering the overall structure and charge states of the clusters.[45-

[47, 87] However, in some cases, reactions of a cluster with a new type of ligand transforms the cluster to completely new entities.[53, 88]

Khatun *et al*. demonstrated that such a reaction wherein a monothiolate protected cluster, Ag_{59} upon the reaction with 2,4-DCBT ligand, slowly converts it to $Ag_{44}(DCBT)_{30}$.[75] Note that the ligands 2,4-DCBT and 2,5-DCBT differ only in the positions of the substituent Cl groups (isomeric thiols). This reaction demonstrates that such minute changes in the structure of the ligands drastically changes the nuclearity of cluster. This could be due to the position dependent (ortho, para, or meta) changes in the electron donating or withdrawing inductive (+I or –I) effects of the methyl groups of the ligands. The π- π interactions and steric hindrance between the substituent groups might also play a role in these transformations. Mass spectrometric measurements reveal that the reaction involves the formation of small metal-ligand fragments of clusters (see Figure 3). Exchange of ligands were proposed to be the initial stages of such transformations[89]; however, in this case, no ligand exchanges were observed as the molecular masses of both thiols were the same. The use of different thiol such as, FTP (4-fluorothiophenol) and CTP (4-chlorothiophenol) shows ligand exchanged peaks. Another reason could be the sensitivity of certain structural motifs such as staples, mounts, *etc*., towards the structure of the incoming ligands, *i.e.*, the M-L motifs may not be able to accommodate the incoming ligands retaining their geometry and bonding network. Simulations and experimental techniques with better temporal resolution are essential to probe such dynamics of the M-L interfaces.

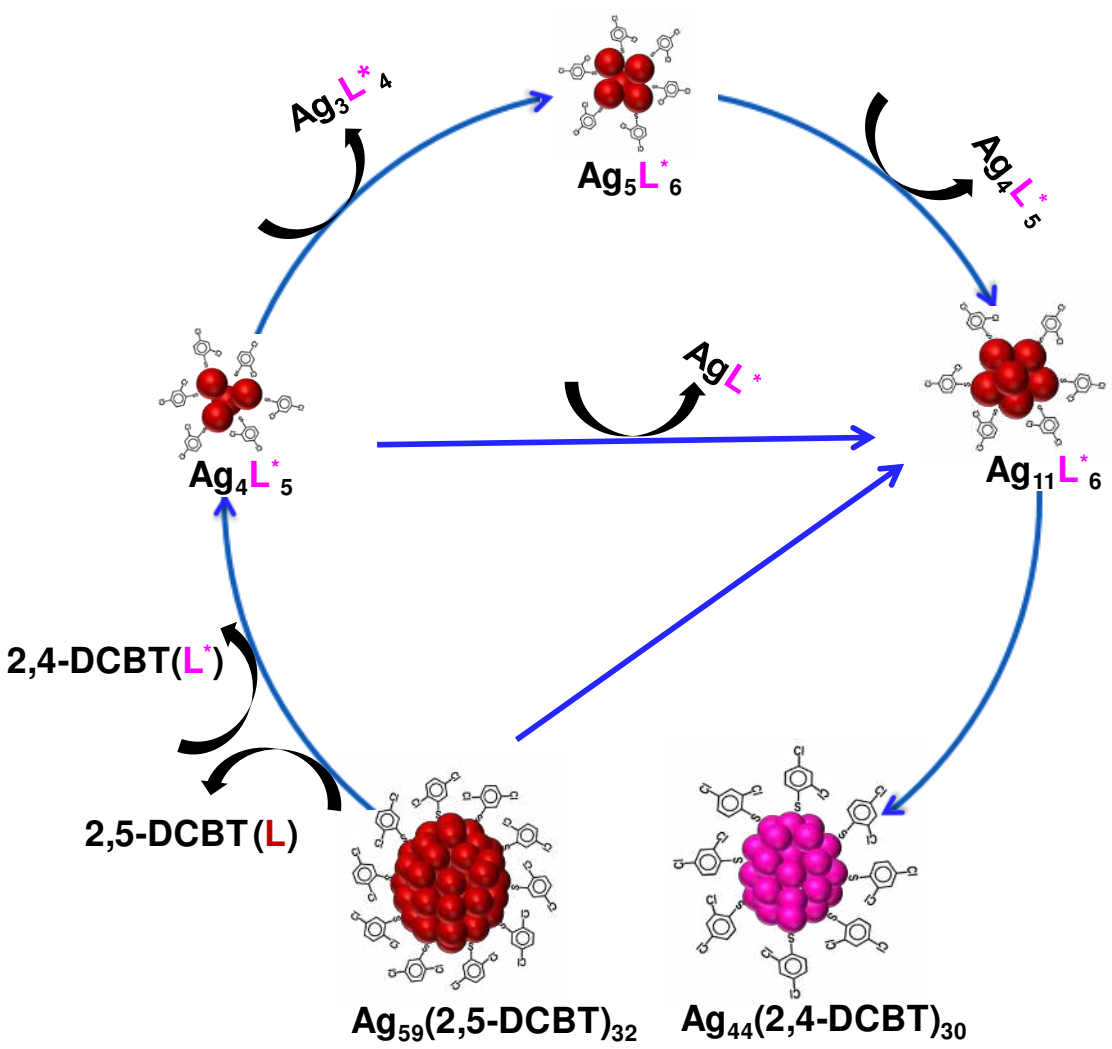

Figure 3. Schematic of theligand-induced conversion pathway of $Ag_{59}(2,5\text{-DCBT})_{32}$ to $Ag_{44}(2,4\text{-DCBT})_{30}$. L and L* denote 2,5-DCBT and 2,4-DCBT, respectively (Reproduced with permission from, Ref. 75)

Gas phase dynamics and reactivity of M-L interfaces

Dynamics of M-L interfaces have been studied mostly in the solution phase, however, such studies of the structure, dynamics and reactivity of isolated, ligand protected metal clusters in gas phase remains largely unexplored. One of the techniques for probing the gaseous phase dynamics

of molecular systems is ion mobility mass spectrometry (IM MS).[90] This technique has been traditionally used for gas phase analysis of small molecules[90] and conformational studies of proteins;[76] however, recently, it has been utilized for probing the thiolate protected metal clusters as well.[91]In this technique, molecules are ionized and taken to the gaseous phase using standard mass spectrometric techniques and then, they are separated according to their mobility in presence of a buffer gas. The mobility of the molecules depends on their mass to charge ratio, size and shape. Here we present the results of IM MS measurements of $Ag_{44}(SR)_{30}$. Crystal structure of $Ag_{44}(SR)_{30}$ shows that it consists of a Ag_{32} core protected by six $Ag_2(SR)_5$ mounts. $Ag_{44}(SR)_{30}$ is an interesting system in this regard because of its multi-shell structures and unusual geometry of $Ag_2(SR)_5$ mounts. Furthermore, this cluster occurs in different charge states in the gas phase. For these experiments, $Ag_{44}(SR)_{30}$ clusters were brought to the gas phase using conventional electrospray ionization (ESI) technique. Ion mobility measurements on these clusters reveal the presence of structural isomers, as depicted in Figure 4.[76] Here we have used a model system, $Ag_{44}(SH)_{30}$ to represent the structure.

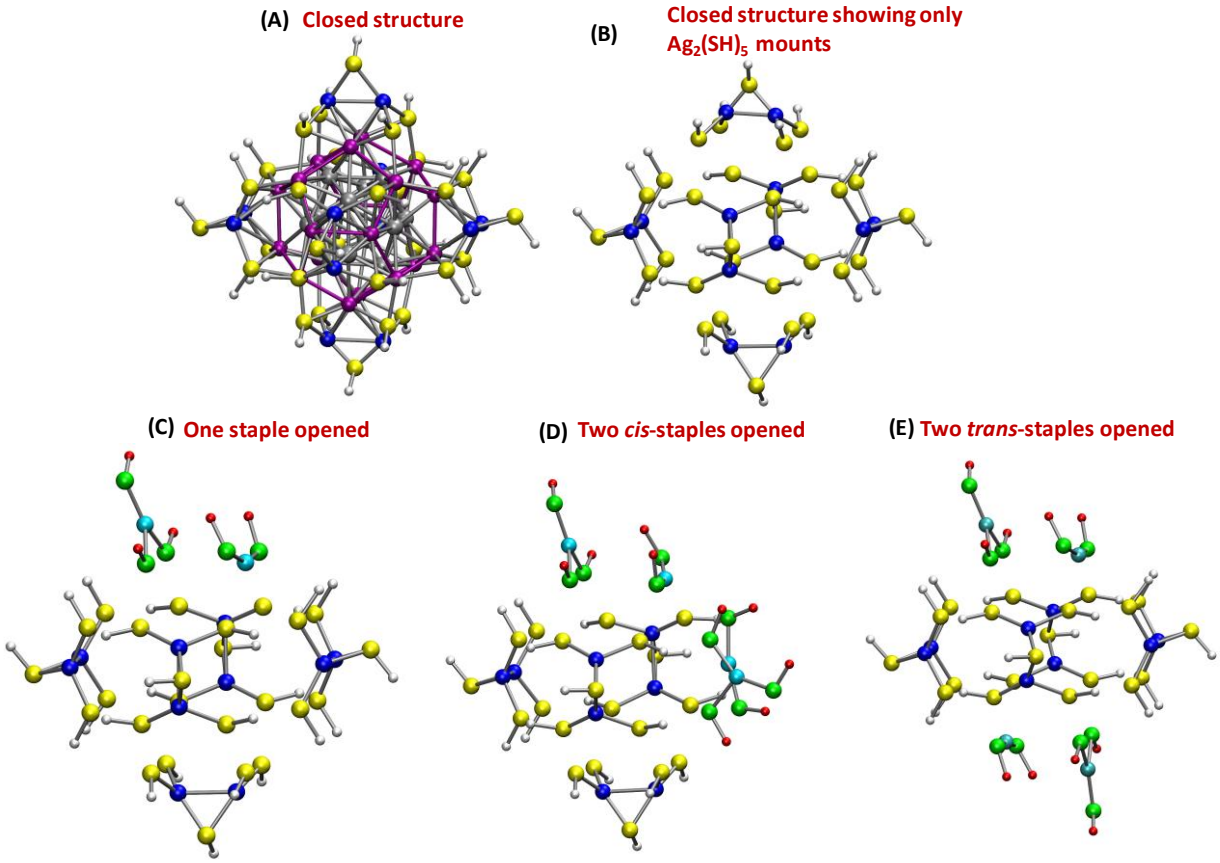

Figure 4. Schematic structures of the isomers of $[Ag_{44}(SH)_{30}]^{4-}$. Geometries of $[Ag_{44}(SH)_{30}]^{4-}$ with (A) and without (B) the core atoms, and its three structural isomers (C-E) with one staple opened (C), two cis-staples opened (D), and two trans staples opened (E) structures. Closed $Ag_2(SH)_5$ mounts in (A)-(E) are shown in blue (silver), yellow (sulfur) and white (hydrogen) colors. Open $Ag_2(SH)_5$ mounts in (C)-(E) are shown in cyan (silver), green (sulfur) and red (hydrogen) colors. Since the structure of the Ag_{12} icosahedron (gray in A) and the Ag_{20} dodecahedron (pink in A) are retained in their isomers, these core atoms are not shown in (C)-(E) for clearly distinguishing the changes in the staple arrangements in its isomers. Since the actual ligands are not shown here, additional structural isomers due to the difference in the ligand conformations are not presented here. (Adapted with permission from, Ref. 76)

Density functional theory (DFT) calculations suggest that the difference in the isomerism arises due to the difference in the bonding network of the metal-ligand interface in these clusters. Note that the $Ag_2(SR)_5$ mounts have complicated bonding compared to those in the $Au_2(SR)_3$ staples and therefore, it is likely that some of the bonds in the $Ag_2(SR)_5$ mounts could break, leading to more stable, open structures. However, these isomers possess the same Ag_{32} core structure as in the crystal structure. Note that these structures possess exactly the same molecular formulae, $Ag_{44}(SR)_{30}$, and differ from each other only in terms of the structures of a few of their mount motifs and hence, they are structurally isomeric. Hence, this study reveals that rearrangements in the metal ligand interface can generate structural isomerism in these clusters. However, if the real ligands are involved, their confirmations also have to be taken into account when their structural isomerism is discussed. However, such an analysis is beyond the scope of this article.

In another example of ion mobility mass spectrometric experiments, we show that $Au_{25}(SR)_{18}$ clusters form dimers, $[Au_{50}(SR)_{36}]^{2-}$, for example, and trimers in gas phase experiments. DFT calculations show that these dimers were formed by the bonding between the $Au_2(SR)_3$ staple motifs, as shown in Figure 5.[77] Spectroscopic evidence of such bonding in gas phase is not available so far, however, inter-staple bonding has been detected in crystals.[38]Note that this type of inter-staple bonding has not altered the total number of metal atoms, ligands and the charge states of individual clusters in these dimers. Furthermore, existence of such isomers further support the dynamic nature of the metal ligand interface in such clusters. Also, we think that the Borromean rings model is better suited to explain the formation of such dimers because the longer $Au_8(SR)_6$ rings are expected to be more dynamic in nature, compared to the shorter $Au_2(SR)_3$ staples, which could facilitate their breaking and reforming, leading to intercluster bonding.

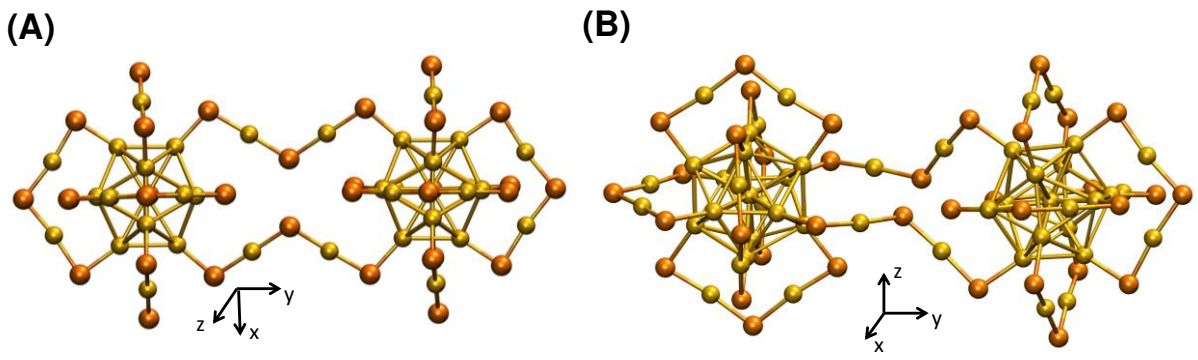

Figure 5. Interfacial bonding between clusters resulting in the formation of dimers. (A and B) DFT-optimized structures of possible structural isomers of $[Au_{50}(SR)_{36}]^{2-}$ considering inter-cluster bonding via common Au_2S_3 staples. In (A), there is bonding between the two clusters by two parallel Au_2S_3 chains. The view shown is along the negative z-direction (top view). In (B), a twisted linkage between the Au_2S_3 staples of two clusters is shown with the cluster on the right being rotated by 90′ anticlockwise about the x-axis, and it is coming out of the paper. Cartesian axes are shown. The ligand R-groups have been removed for clarity. Color codes of atoms: gold (orange), sulphur (yellow). (Adapted with permission from, Ref. 77)

Desorption of ligands: New route for naked metal clusters

The strength of the chemical bond between the metal atoms and the anchoring atom of the ligands (Au-S bond in $Au_{25}(SR)_{18}$, for example) largely determines the stability of the clusters. Fragmentation behavior of these clusters was also studied using mass spectrometry[91-92] and computations[93]. For example, phosphines are known to bind to metal atoms less strongly, compared to thiolates, through weak covalent bonds. In this context, it is interesting to test whether it is possible to detach the ligands from phosphine protected noble metal clusters, in gaseous or liquid phase, so that naked clusters, with precise nuclearity, are generated.

Conventionally, naked metal clusters are generated by techniques such as laser ablation or electrospray which require sophisticated instrumentation for mass selection.

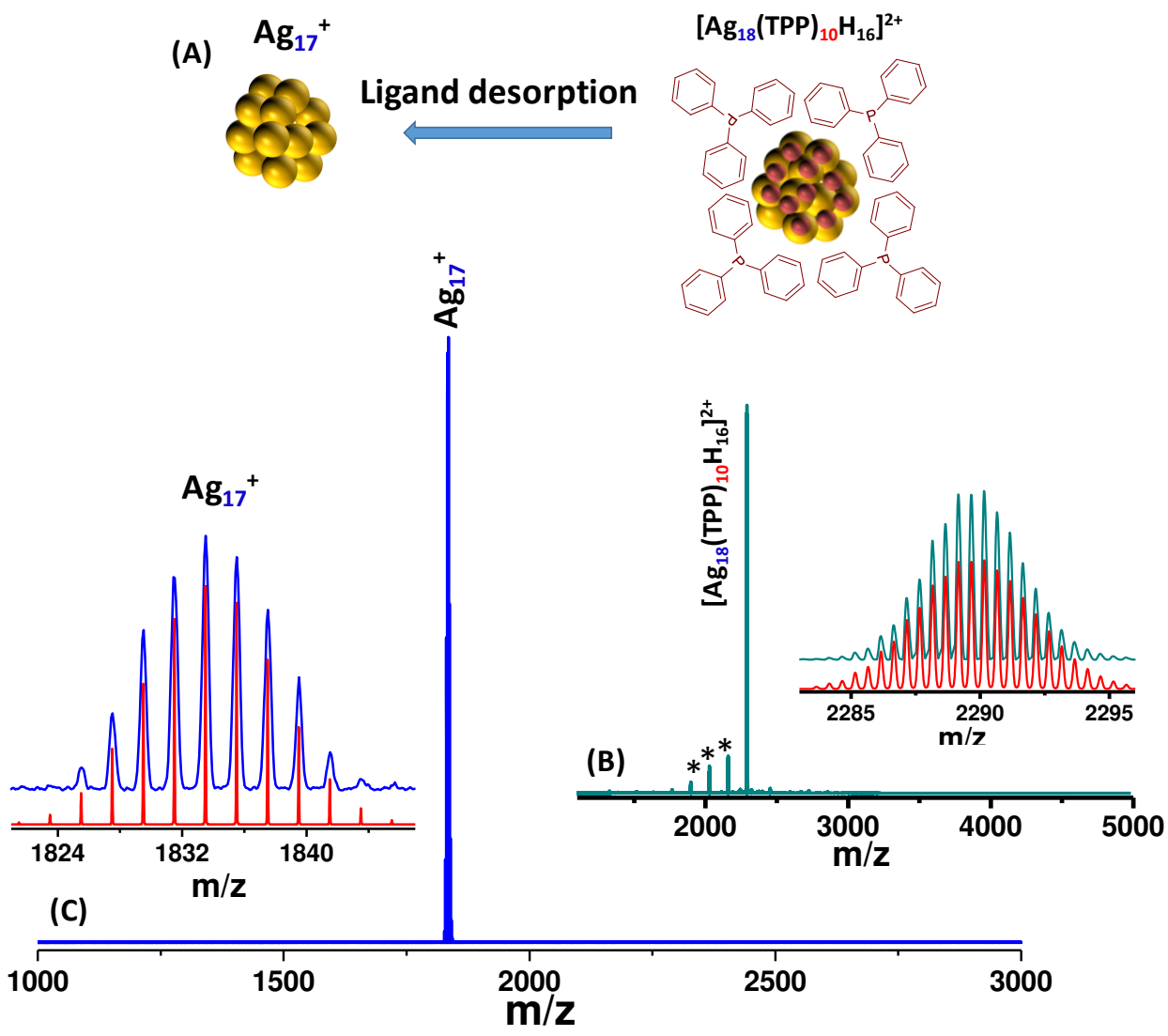

Figure 6. Schematic of the desorption of triphenylphosphine (TPP) ligands from $[Ag_{18}(TPP)_{10}H_{16}]^{2+}$ leading to the formation of naked, Ag_{17}^{+} (A), ESI mass spectrum of $[Ag_{18}(TPP)_{10}H_{16}]^{2+}$ (B), Ag_{17}^{+} (C). Insets of (B) and (C) shows the matching of the theoretical (red) and experimental (blue in C, green in B) isotopic patterns of the corresponding ions. Color codes of atoms in (A): silver (yellow), hydrogen (red). (Adapted with permission from, Ref. 78)

Ghosh *et al*., demonstrated that it is indeed possible to generate atomically precise naked metal clusters from a silver cluster, $[Ag_{18}(TPP)_{10}H_{16}]^{2+,}$ protected by phosphine and hydride ligands. $[Ag_{18}(TPP)_{10}H_{16}]^{2+}$ can be sequentially desorbed to generate naked silver clusters of specific nuclearity, such as Ag_{17}^{+}.[78] For this, $[Ag_{18}(TPP)_{10}H_{16}]^{2+}$ was introduced to gas phase using an ESI source. Sequential fragmentation of the ligands was carried out by successively increasing the ionization voltages in the ESI set up. Figure 6 shows that $[Ag_{18}(TPP)_{10}H_{16}]^{2+}$ initially transforms to $Ag_{17}H_{14}^{+}$ which finally loses all the hydride ions, generating Ag_{17}^{+}. Note that the desorption of ligands in this case occurred through the breaking of the bond between the metal and the anchoring atom of the ligand, *i.e.*, Ag-P bond. This is in contrast to the case of thiolate protected clusters wherein the S-C bond breaks and metal-sulfur bond is retained. The formation of naked clusters from thiolate protected clusters has never been observed. This could be attributed to the fact that the Ag/Au-S bond is much stronger than the Ag-P bond. Similarly, ligands such as pyridine or its analogues might also act as weaker ligands to these types of clusters, and such systems also could lead to the formation of naked clusters. However, the example presented above indicates that desorption of ligands depends on the nature of the ligands as well as the strength of the bond between the metal atom and the anchoring atom of the ligands. Such ligand desorption can occur also in ambient air, leading to naked clusters.[94]

Summary and future perspectives

In summary, we presented a few examples demonstrating the role of the structure and dynamics of metal-ligand interface in dictating the chemical reactivity of monolayer protected noble metal clusters in solution as well as in the gas phase. We suggested that the difference in the oxidation states of metal atoms at the M-L interface could be a key factor triggering intercluster reaction. The structure of the M-L ligand bonding network (staples *vs* mounts, monodentate *vs* bidentate, *etc*.) and dynamics (Interlocked (Borromean) rings model *vs* core-staple model) dictate the type as well as the extent of the exchange processes. Furthermore, these studies imply that a single structural model is inadequate to explain spontaneous reactions between these clusters; consideration of multiple structural models is essential for a better understanding of their properties.

We proposed that interparticle chemistry may not be limited to metal clusters, but such reactions might also occur in other nanosystems, which could be a potential mechanism in particle coarsening processes such as Ostwald ripening. We also showed that the nature of the ligands, *i.e.*, their structure and electron donating withdrawing properties, is crucial in controlling the geometry and nuclearity of these clusters. The dynamics of the M-L interfaces is not limited to the solution phase; structural rearrangements and interfacial bonding occurs in gas phase as well, leading to the formation of geometrical isomers and cluster assemblies. Finally, we showed that the ligands can be desorbed completely in the gas phase, leading to the formation of atomically precise naked metal clusters. This study indicates that phosphines can be promising ligands for generating naked clusters of other metals as well.

Even though, we demonstrated that a number of factors concerning the M-L interfaces, such as oxidation states of metal atoms, actual structure of the ligands, *etc*., are important when considering the chemistry of these clusters, contribution of each of these factors has not been understood in isolation. Among the reasons is the limitation in making many of the clusters, by varying only one aspect alone at one time, such as specific ligands.

Probing the interfacial properties for these clusters is essential for creating cluster assembled materials and new types of hybrid materials comprising of distinctly different types of nanosystems. Probing the kinetics and thermodynamics and real time monitoring of interfacial phenomena in these clusters are rarely addressed. Gas phase dynamics of these clusters remain largely unexplored. Probing the chiroptical properties of these clusters in gaseous phase could be a potential new direction in this regard. Further efforts are needed to clearly understand the contribution metal-ligand interfaces in dictating the geometric structures, dynamics and chemical reactivity of ligand protected metal clusters. We think that the dynamic interfacial chemistry is not limited to metal clusters, and hence, the structure, dynamics and chemical reactivity of nanosystems in general are to be explored in greater detail, which might unveil new directions in materials chemistry.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest

ACKNOWLEDGMENT

K.R.K., A.G. and E.K. thank the UGC for their senior research fellowships. A.B. thanks IIT Madras for an Institute Post-Doctoral Fellowship. We thank the Department of Science and Technology for constantly supporting our research program.

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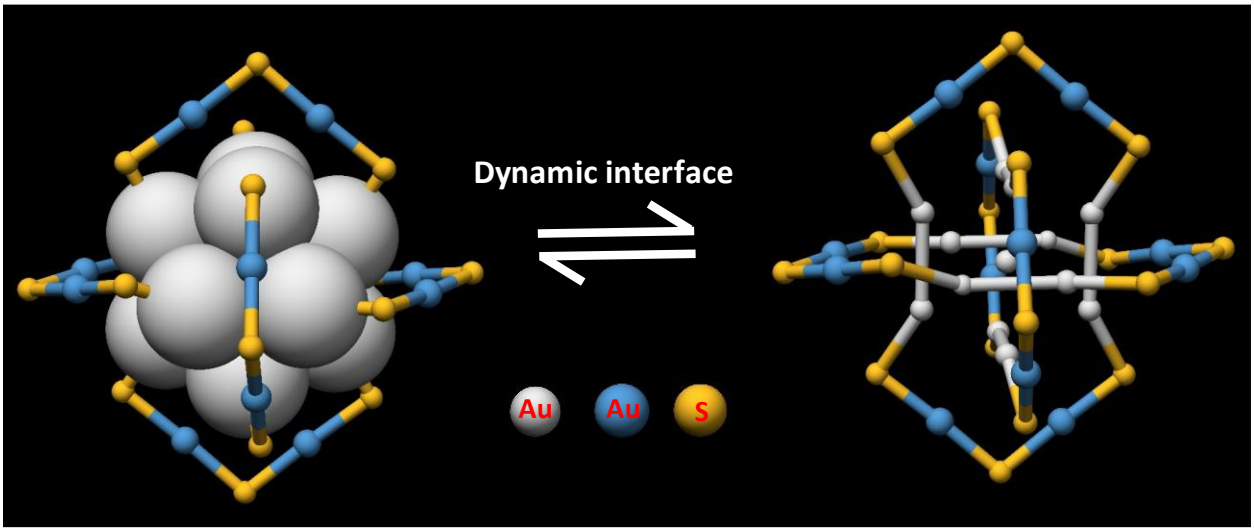
Image for the Table of Contents



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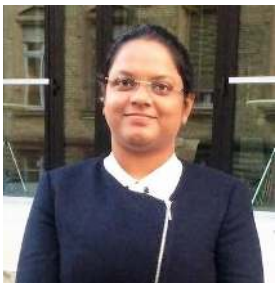

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