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Silver Clusters

Doubly Charged Silver Clusters Stabilized by Tryptophan: Ag_4^{2+} as an Optical Marker for Monitoring Particle Growth**

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Metal clusters can serve as ultimate building blocks for nanometer-scale devices because of their unique optical and electronic properties, which are size and structure dependent.[1] However, an important issue for optical and electronics applications is the influence of charges that can affect the formation and the electronic properties of such nanosystems. As the size of the cluster decreases, the charging that occurs during the photoexcitation or the charge transport in the device may even destroy the metal moiety as a result of strong Coulomb repulsion. Small multiply charged systems, in particular silver clusters, have been studied extensively in the gas phase.[2,3] Although isolated metal clusters with double charge (e.g. Ag_n^{2+}) are not stable for $n<7$,[3] stabilization can be provided by the environment. Indeed, the attachment of protective ligands such as complex chemical[4] or biomolecular[5,6] templates was used to stabilize multiply charged clusters. In particular, small multiply charged silver clusters were observed and stabilized in solution during the formation of colloidal Ag nanoparticles.[7] The Ag_4^{2+} tetramer was even suggested as the main precursor for the particle formation and was investigated by optical spectroscopy.[8,9] Encapsulation of multiply charged small silver clusters within biomolecular templates[6] is particularly attractive because it can provide both stabilization and functionalization of the metal cluster, thus forming new hybrid complexes with remarkable optical and photostability properties. In this case, the mechanism for stabilization usually involves the formation of salt-bridged structures.[10] The recent progress in the synthesis of stabilized metal nanoclusters challenges the understanding of their electronic, spectroscopic, and chemical properties at the molecular level—these issues have not been addressed to date. Gas phase studies offer the opportunity to produce and study hybrid systems under well-defined conditions.[11–13] Gas phase electronic spectroscopy has succeeded in giving structural information on isolated and microhydrated molecular ions. Combined with theoretical investigations, it provides a conceptual framework to unravel optical properties of multiply charged clusters and in particular the influence of stabilizing templates.

In our combined theoretical and experimental study, we investigate an Ag_4 metal cluster and its interaction with a tryptophan (Trp) molecule, which can be used as a reducing agent for the synthesis of silver nanoparticles.[14] We demonstrate that this hybrid system exhibits an unambiguous optical fingerprint of the doubly charged silver cluster (Ag_4^{2+}) stabilized by a salt-bridge (SB) interaction with the organic moiety. Thus, we propose the use of its optical signature as a marker to monitor early stages of seeding processes for particle growth.

Nanohybrids composed of a unit of the aromatic amino acid tryptophan and small silver clusters were produced in the gas phase by combining electrospray ionization and multiple stage mass spectrometry. The $[(Trp-H)+Ag_4]^+$ complex containing Ag_4^{2+} was formed in a trapping cell by collision-induced fragmentation of the precursor ion $[(Trp)_2-3H+4Ag]^+$. A similar approach to producing complexes of silver clusters with amino acids has already been proposed by Khairallah and O'Hair[15] and Tabarin et al.[16].

Theory predicts favorable formation of these complexes as a result of the interaction of the deprotonated carboxylic group and the cluster in the SB structure. Two types of salt-bridged structures arise from exploration of structural properties (for details see Figure SM1 in the Supporting Information): 1) the lowest energy structure SB1 (Figure 1 a) contains a doubly charged Ag_4 cluster bound to the COO^- moiety and interacting with the indole ring. The distribution of the charge in this hybrid system is illustrated by the electrostatic potential map shown in Figure 2. This map shows strong localization of positive charges on the Ag_4 subunit while the negative charge is distributed over the COO group. The natural bonding orbital (NBO) analysis shows that a net charge of $+1.76$ e is localized on the Ag_4 subunit, thus proving

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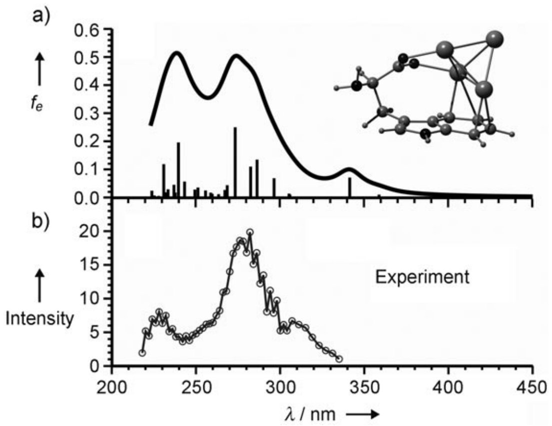

Figure 1. a) Calculated absorption spectrum for the lowest energy structure SB1 of $[(\text{Trp}-\text{H})+\text{Ag}_4]^+$ characterized by Ag_4^{2+} subunit (shown in inset). The f_e values represent the oscillator strengths (black sticks). The broadening of the lines is simulated by a Lorentzian function with a width of 20 nm (black line). b) Experimental photofragmentation yield of $[(\text{Trp}-\text{H})+\text{Ag}_4]^+$.

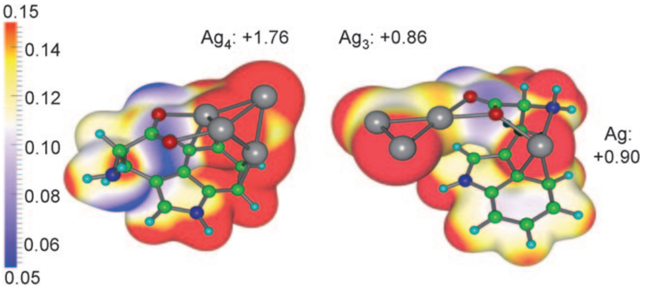

Figure 2. Calculated molecular electrostatic potential map for two prototype structures SB1 (left) and SB2 (right) of the $[(\text{Trp}-\text{H})+\text{Ag}_4]^+$ complex projected onto the constant electron density surface with an isovalue of 0.005. The color scale corresponds to the strength of the electrostatic potential. The NBO charges (in e) on silver subunits are also given, thus illustrating strong charge localization on Ag_4^{2+} in SB1.

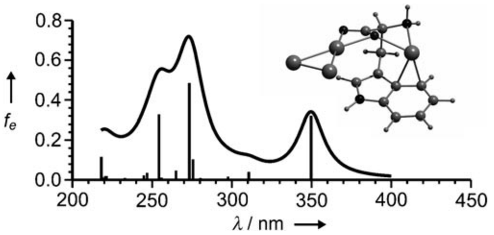

Figure 3. Calculated absorption spectrum for structure SB2 of the $[(\text{Trp}-\text{H})+\text{Ag}_4]^+$ complex containing an Ag_3^+ subunit (shown in inset). The f_e values represent the oscillator strengths (black sticks). The broadening of the lines is simulated by a Lorentzian function with a width of 20 nm (black line).

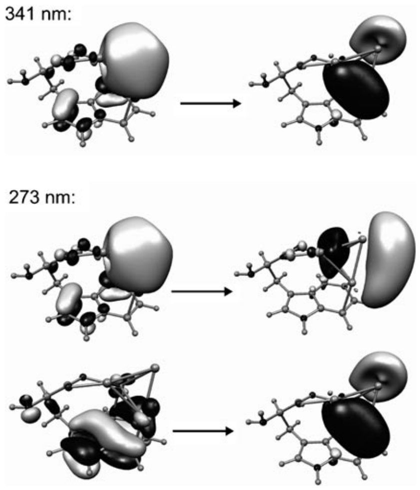

Figure 4. Leading excitations involved in the intense transitions of $[(\text{Trp}-\text{H})+\text{Ag}_4]^+$ corresponding to transitions located at 341 and 273 nm (SB1 isomer).

the presence of a doubly charged metal moiety. 2) Structure SB2 (Figure 3) which according to the CC2 method is more than 1 eV higher in energy than SB1, is characterized by the presence of a singly charged Ag_3^+ subunit, and an additional Ag^+ ion bound to the COO^- group (Figure 2).

The calculated absorption spectrum for structure SB1 (Figure 1 a) shows two broad absorption bands between 220 nm and 330 nm with maxima at 240 and 275 nm; this result is in agreement with the measured photofragmentation-yield spectrum shown in Figure 1 b. In contrast, the calculated absorption spectrum for structure SB2 (Figure 3) is red-shifted with respect to SB1 and does not match the experimental photofragmentation spectrum. Moreover, the electrostatic potential map for the SB2-type structure shown also in Figure 2 illustrates that the localization of positive charge in the Ag_3 subunit is not very pronounced as the NBO analysis shows that the net charge is only +0.86 e. Both the higher stability as well as the optical properties allow us to conclude that the experimentally measured photofragmentation spectrum implies the presence of a doubly charged Ag_4 cluster interacting with tryptophan. In SB1, the excitation within Ag_4^{2+} accompanied by the charge transfer between the metallic and organic subunits (Figure 4 and Figure SM2) is mainly responsible for the leading absorption features.

In fact, the band arising from the transition at 341 nm has its main contribution from excitation within the metal part, while the transitions at 286, 282, and the most intense transition at 273 nm are characterized by strong mixing of the metal-localized excitations with charge-transfer excitations. In general, the excitations involving the organic part of the complex become more important with rising transition energy, thus the transition located at 240 nm is dominantly due to excitations within the environment of the organic subunit (see Figure SM2. Because of these features, the observed spectrum shown in Figure 1 is a fingerprint of Ag_4^{2+} stabilized by a salt-bridge structure (SB1) with a negatively charged environment. Importantly, the observed spectrum is not the sum of the spectra of the subunits $(\text{Trp}-\text{H})^-$ and Ag_4^{2+} (see Figure SM3 in the Supporting Information), but reflects the interaction of both subunits in the hybrid system.

In contrast, the excitations leading to dominant transitions in the SB2 structure located at 349, 273, and 254 nm (see

Figure SM4) occur within the Ag_3^+ subunit without the involvement of the environment.

As mentioned in the introduction, Ag_4^{2+} was observed as a precursor in primary steps of colloidal aggregation.[7–9] It was shown that the nature and the stoichiometry of the precursor play key roles in the final size and morphology of the resulting nanoparticles.[18] The absorption spectrum of Ag_4^{2+} solvated with methanol has been reported to display a broad band in the near-UV region centered at 300 nm.[8] This spectrum is significantly broader and red-shifted as compared to the calculated spectrum of the bare Ag_4^{2+} cluster, which displays a dominant absorption band located at 246 nm (see Figure SM3). Note that the solution spectrum was obtained by pulse radiolysis, where environmental factors influence the absorption. In fact, the absorption spectrum of Ag_4^{2+} in methanol closely resembles our experimental and theoretical photofragmentation spectra of the $[(Trp-H)+Ag_4]^+$ complex. This outcome demonstrates that the observed spectrum is characteristic for Ag_4^{2+} embedded in an organic environment.

Finally, we show that Ag_4 is the smallest doubly charged silver system that can be stabilized by tryptophan. This fact results from the particularly low second ionization potential of Ag_4 ($Ag_4^+ \rightarrow Ag_4^{2+} + e^-$; see Figure SM5), which favors the formation of the complex. This is not the case for smaller Ag species. As previously observed, Ag_3 bound to tryptophan in $TrpAg_3^+$ is singly charged.[11] The even smaller species Ag_2^{2+} is not bound as a consequence of the electrostatic repulsion and the absence of valence electrons. Moreover, our theoretical and experimental findings (see Figure SM6) show that tryptophan does not stabilize Ag_2^{2+}, and the predicted complex exhibits a COO^-Ag^+ SB bonding with an additional interaction between Ag^+ and the tryptophan molecule. Note that for metals with a significant contribution of *d* electrons to bonding, such as gold, the formation of doubly charged dimers can occur (e.g. Au_2^{2+}).[17]

In conclusion, by the combined experimental and theoretical study of the optical spectrum of an isolated hybrid system built around an Ag_4 cluster, we were able to rationalize the effect of the environment on the doubly charged metallic subunit. We show that the coupling between electronic excitations of the doubly charged metal core and charge-transfer-type excitations between the ligand and the metal moieties is responsible for a strong absorption below 250 nm. We have also demonstrated that singly and doubly charged metal species in hybrid systems can be discriminated by their different optical properties. This study will allow identification of seed precursors and provide mechanistic insights into the aggregation and growth of nanoparticles.

Experimental Section

The nanohybrids composed of a unit of the aromatic amino acid tryptophan and a small silver cluster were produced in the gas phase by combining electrospray ionization and multiple stage mass spectrometry.[16,19] The electrolyte solution was prepared by mixing a solution of silver nitrate salt (500 μM in H_2O/CH_3OH 1:1 (v/v)) and a solution of amino acid (500 μM in H_2O/CH_3OH 1:1 (v/v)) in a ratio of 1:1. Photodissociation measurements were obtained using a modified LCQ ion trap coupled to a tunable optical parametric oscillator (OPO) laser.[20] The laser light was focused at the center of the trap and the trapped ions were irradiated for 500 ms (10 laser shots). Mass spectra obtained after laser irradiation were recorded. The yield of fragmentation (σ) was measured as a function of the laser wavelength ($\sigma = \ln((\text{parent}+\Sigma\text{frag})/\text{parent})/\phi$), where ϕ is the laser fluence, parent is the intensity of the parent signal, and Σfrag represents the total intensity of the photofragment signals).

The structural properties and absorption spectra of the studied systems have been determined using the approximated coupled cluster method CC2 by employing the resolution of identity (RI) approximation. The TZVPP basis set for C, O, N, and H atoms has been used.[22] For structural properties the 19 electron relativistic effective core potential of the Stuttgart group together with the TZVP basis set was used for silver.[21] For absorption properties the 11 electron RECP with atomic orbital basis set, which was developed for an accurate description of excited states of silver clusters, was employed.[23]

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