1. Origin of Magic Stability of Thiolated Gold Clusters: A Case Study on $\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18}$

The present work aims to test the validity of the electronic shell model for $\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18}$ by monitoring the charge state of the Au:S core and thereby to elucidate the origin of magic stability. Electrospray ionization mass spectrometry revealed that the Schiffirin method yields $[\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18}]^x$ with a distribution of charge states, which shifts toward negative values with reduction time. The stable ions $[\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18}]^{1+}$ and $[\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18}]^{1–}$ can be synthesized by chemical oxidation and reduction of $[\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18}]^0$, respectively. These findings lead us to conclude that electronic shell closing is not a crucial factor for the high stability of $[\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18}]^x$ ($x = 1–, 0, 1+$). We ascribe magic stability to the core-in-cage structure predicted theoretically.

![Figure 1. Optical absorption spectra (left) and ESI mass spectra (right) of $[\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18}]^x$ with different charge states.](image1)

2. Ubiquitous 8 and 29 kDa Gold: Alkanethiolate Cluster Compounds: Mass-Spectrometric Determination of Molecular Formulas and Structural Implications

The molecular formula and charge state distributions of thus-far known, ubiquitous alkanethiolate-protected gold clusters with core-masses of 8 and 29 kDa were assessed using electrospray ionization mass spectrometry (ESI-MS). The 8 and 29 kDa clusters were determined to be composed of single species, $[\text{Au}_{38}(\text{SC}_n)_{24}]^z$ and $[\text{Au}_{144}(\text{SC}_n)_{59}]^z$, respectively, with charge states of $z \geq 0$. Possible geometric structures for $\text{Au}_{38}(\text{SC}_n)_{24}$ and $\text{Au}_{144}(\text{SC}_n)_{59}$ are discussed based on the structures of relevant systems that have been recently determined experimentally and theoretically; $[\text{Au}_{25}(\text{SR})_{18}]^{1–}$ and $\text{Au}_{102}(\text{SR})_{44}$, in which the Au cores are protected by monomers $[\text{–SR–Au–SR–}]$ and/or dimers $[\text{–SR–Au–SR–Au–SR–}]$. Their preferential formation and chemical robustness are proposed as being associated with high stability due to geometric factors, while the Au-thiolate interface takes on common motifs regardless of the underlying Au core.

![Figure 2. LDI and ESI mass spectra of $[\text{Au}_{38}(\text{SC}_6\text{H}_{18})_{24}]^z$ (left) and $[\text{Au}_{144}(\text{SC}_6\text{H}_{18})_{59}]^z$ (right).](image2)

3. Thermosensitive Gold Nanoclusters Stabilized by Well-Defined Vinyl Ester Star Polymers: Reusable and Durable Catalysts for Aerobic Alcohol Oxidation

Au nanoclusters of less than 4 nm with a narrow size distribution were prepared and supported in thermosensitive vinyl ether star polymers obtained by living cationic polymerization. The thermosensitivity of the star polymers
permitted easy separation of the clusters from the reaction mixture without any negative aggregation. Thus, the Au clusters could be recovered for reuse several times to induce alcohol oxidation with similar reactivity in each run.

4. Ligand exchange of \( \text{Au}_{25}\text{SG}_{18} \) Leading to Functionalized Gold Clusters: Spectroscopy, Kinetics, and Luminescence

Ligand exchange offers an effective way to modify the properties of the recently prepared quantum clusters of gold. To tune optical and photoluminescence properties of one of the most stable quantum clusters of gold, \( \text{Au}_{25}\text{SG}_{18} \) (SG-glutathione thiolate), we functionalized it by the exchange of -SG with functionalized-SG and with an altogether different ligand, namely, 3-mercapto-2-butanol (MB). The products were characterized by various techniques such as optical absorption (UV-vis), Fourier-transform infrared (FTIR), nuclear magnetic resonance (NMR), X-ray photoelectron (XPS), and luminescence spectroscopies, mass spectrometry, and thermogravimetry (TG). Analyses of the TG data helped to establish the molecular composition of the products. Ligand exchange reaction was monitored by NMR spectroscopy, and it was found that the exchange reaction follows a first order kinetics. The XPS study showed that after the exchange reaction there was no change in the chemical nature of the metal core and binding energy values of Au 4f \(_{7/2}\) and 4f \(_{5/2}\), which are similar in both the parent and the exchanged products. Photo-luminescence studies of these clusters, done in the aerated conditions, showed that the excitation spectrum of the MB-exchanged product is entirely different from the acetyl- and formyl-glutathione exchanged products. The inherent fluorescence and solid-state emission of these clusters were observed. This intense emission allows optical imaging of the material in the solid state. The emission is strongly temperature dependent.

The synthesis of a diverse variety of clusters and their chemical stability and intense luminescence offer numerous applications in areas such as energy transfer, sensors, biolabeling, and drug delivery.

5. Electronic Structure of Dendrimer-Au Hybrid Nanoparticle: Hard X-Ray Photoemission Study

We have carried out the hard X-ray photoemission study of dendrimer-Au hybrid nanoparticles/nanoclusters supported on the HOPG substrates. From the detailed line-shape analysis for Au 4f core-level photoemission spectrum of dendrimer-Au hybrid nanoparticles with mean diameter of 2.6 nm, it is found that Au 4f core-level spectrum consists of three components. We attribute these components to the interior Au atoms, surface Au atoms, and surface Au atoms bonded to dendrimers. Furthermore, we have investigated the valence-band photoemission spectra. From these results, we discuss the electronic structures and interfacial properties of dendrimer-Au hybrid nanoparticles/nanoclusters.

References

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