

Single Crystal XRD Structure and Theoretical Analysis of the Chiral $\text{Au}_{30}\text{S}(\text{S}-t\text{-Bu})_{18}$ Cluster

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Background

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Article

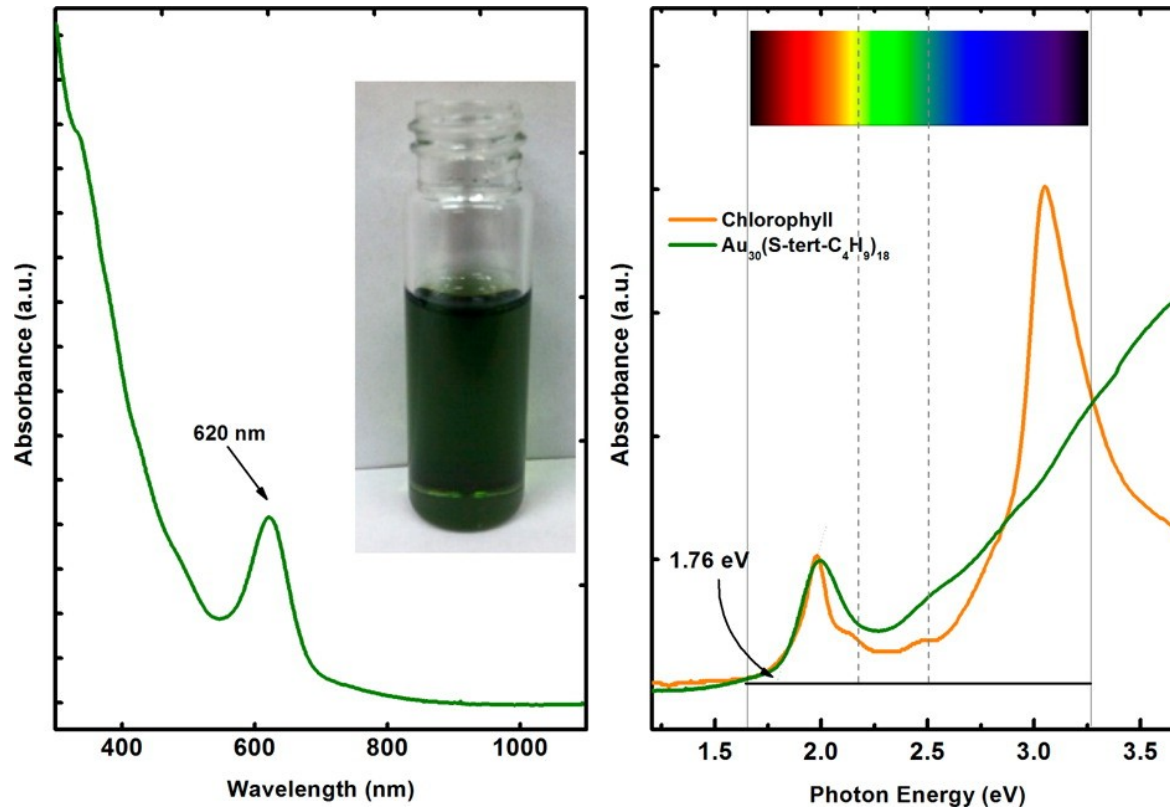
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Green Gold: $\text{Au}_{30}(\text{S-}t\text{-C}_4\text{H}_9)_{18}$ Molecules

David Crasto and Amala Dass*

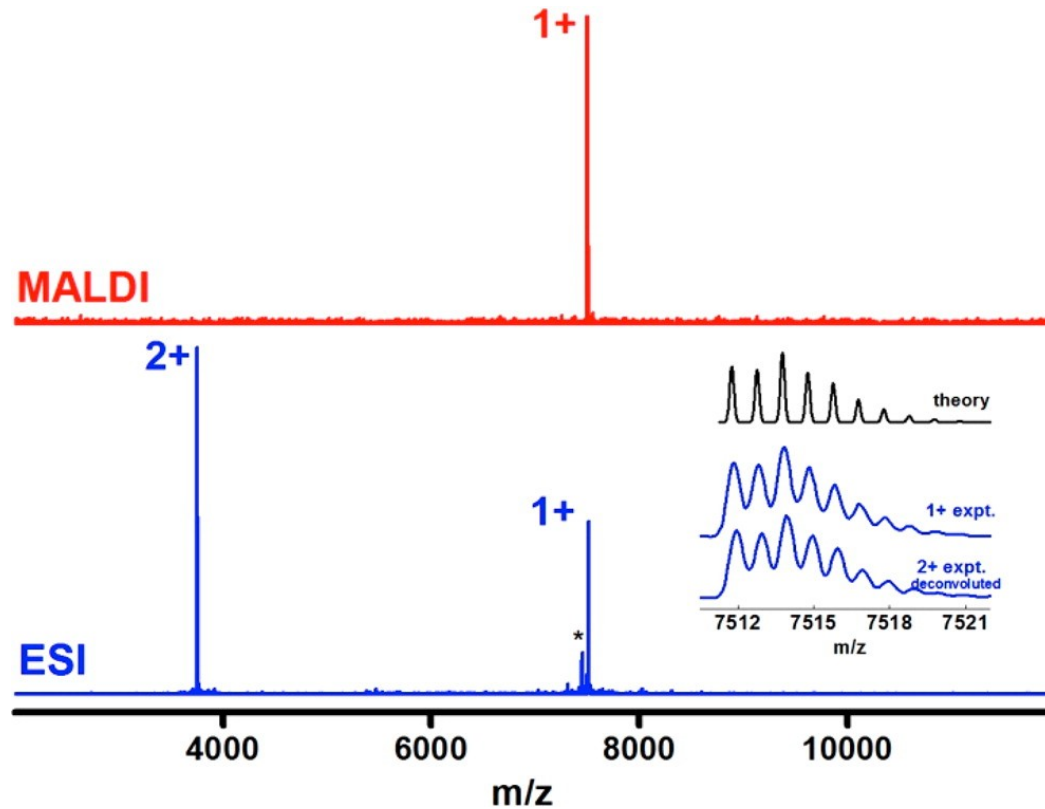
Department of Chemistry and Biochemistry, University of Mississippi, University, Mississippi 38677, United States

Results and discussion



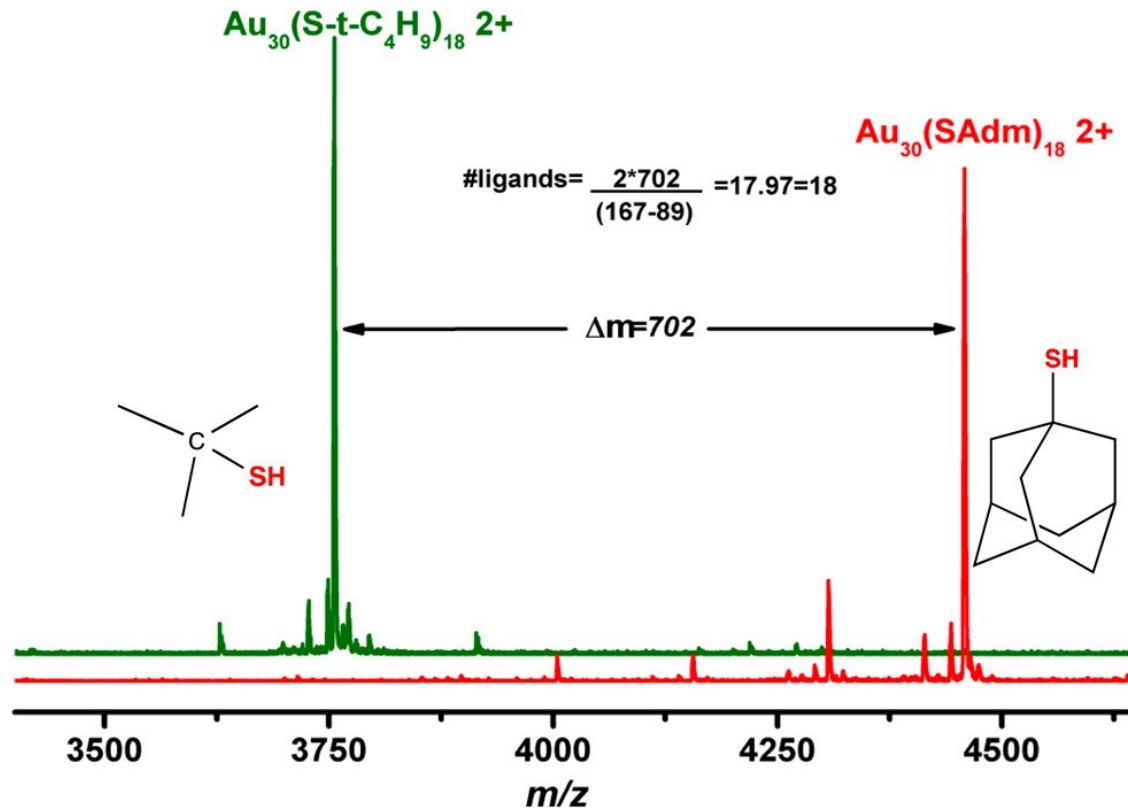
(left) UV-vis-NIR spectrum of $\text{Au}_{30}(\text{S-}t\text{-C}_4\text{H}_9)_{18}$ (olive curve) molecules in toluene. The photograph shows the green color of the toluene solution of the title molecule. (right) Absorbance plotted against photon energy (eV) for the $\text{Au}_{30}(\text{S-}t\text{-C}_4\text{H}_9)_{18}$ molecules compared with chlorophyll, displaying the determination of the optical band gap found to be 1.76 eV. Although this large-band gap characteristic of the nanoparticle is seen in differential pulse voltammetry (see Figure S3, Supporting Information), difficulty in obtaining a signal has hindered a determination of the electrochemical gap.

Results and discussion



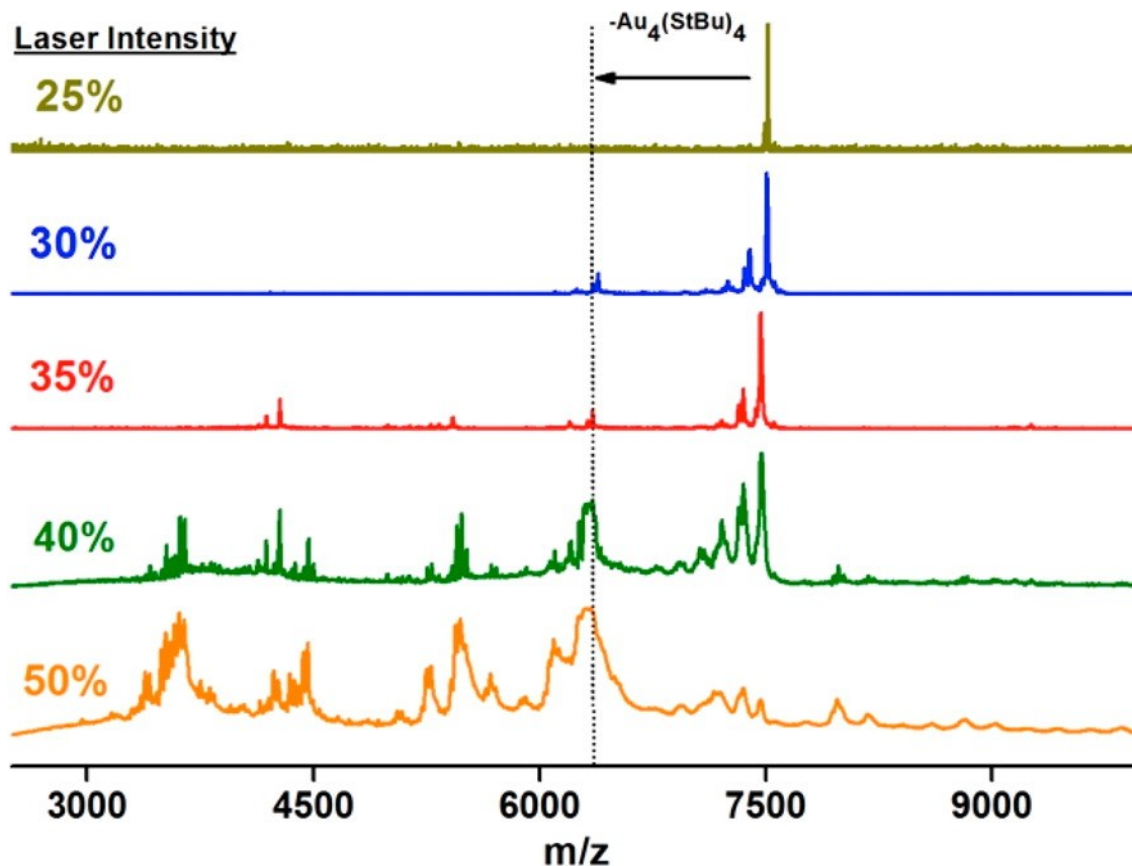
Mass spectrometry. ESI (blue) and MALDI-TOF (red) mass spectra of $\text{Au}_{30}(\text{S-}t\text{-C}_4\text{H}_9)_{18}$. Asterisk indicates fragmentation corresponding to the loss of one ligand. Inset shows the comparison between theoretical and experimental mass spectrum (1+ and deconvoluted 2+ ions) of $\text{Au}_{30}(\text{S-}t\text{-C}_4\text{H}_9)_{18}$. No $\text{Au}_{25}(\text{SR})_{18}$ was observed in either mass spectra.(6)

Results and discussion



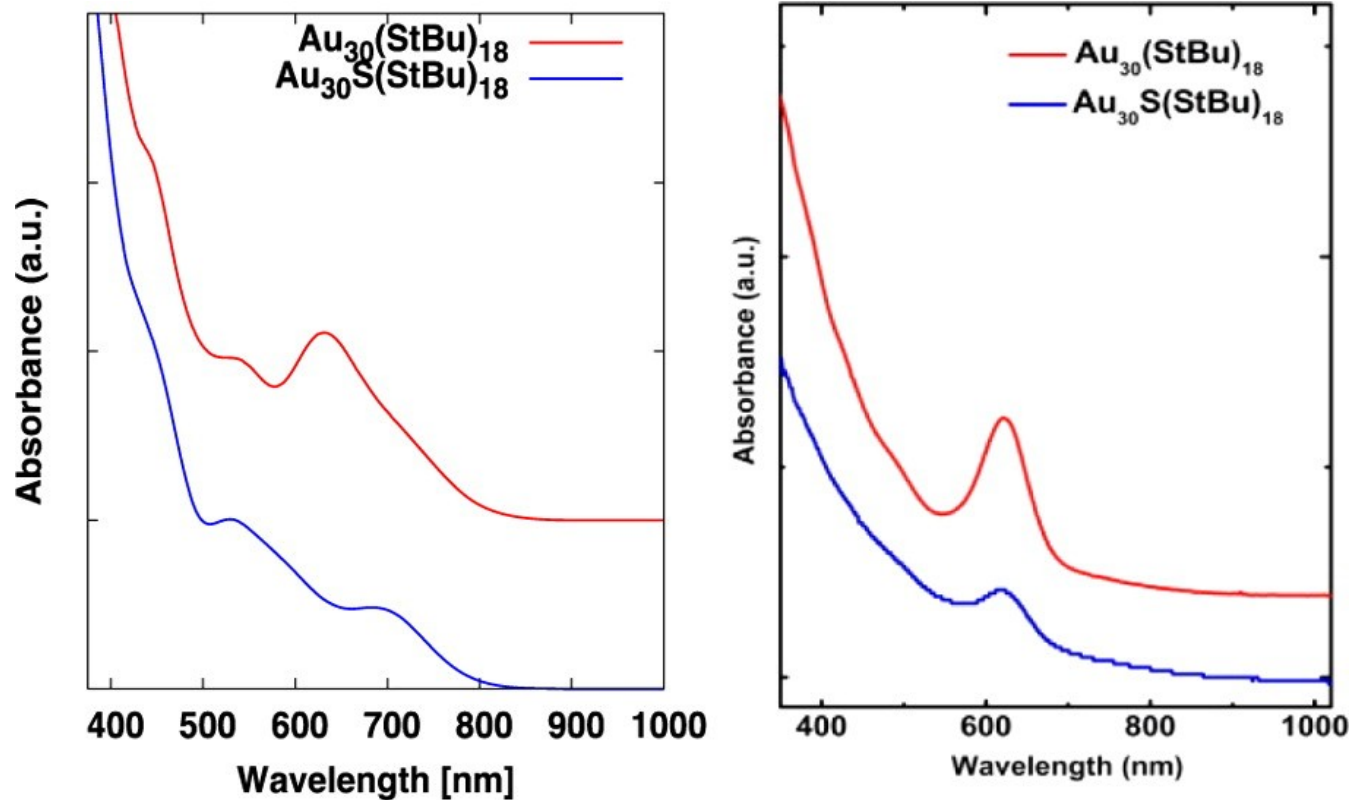
High-resolution ESI mass spectrum displaying the 2+ charge state for $\text{Au}_{30}(\text{SAdm})_{18}$ at an m/z of 4458, in addition to the 2+ for $\text{Au}_{30}(\text{S-t-C}_4\text{H}_9)_{18}$ at an m/z of 3756.

Results and discussion



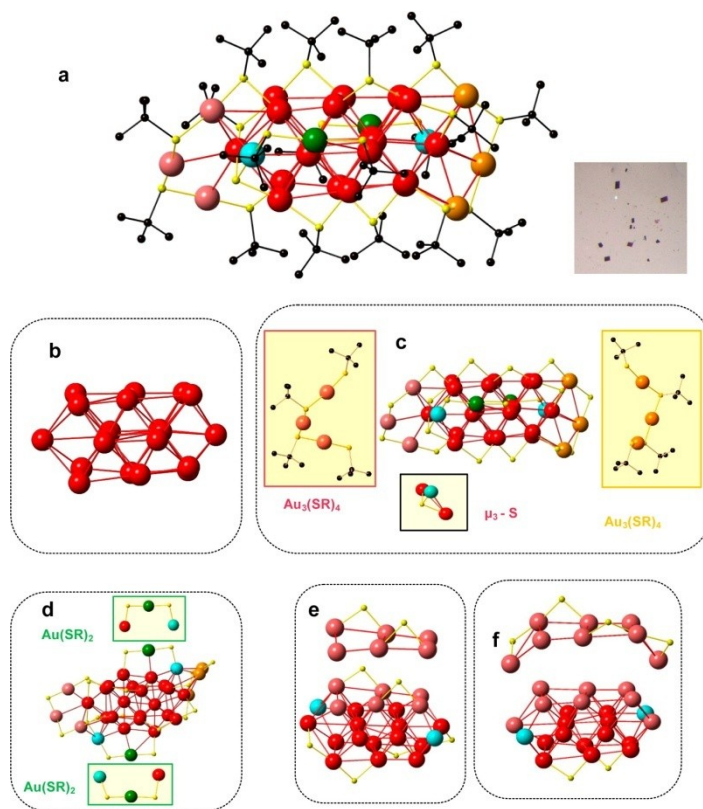
MALDI mass spectrum of $\text{Au}_{30}(\text{S-}t\text{-C}_4\text{H}_9)_{18}$ at various laser intensities. The top spectrum is acquired at threshold laser fluence displaying the molecular ion with minimal fragmentation. As the laser fluence is increased in the lower spectra, fragmentation increases, including the loss of Au_4L_4 species as observed before.(18)

In this paper



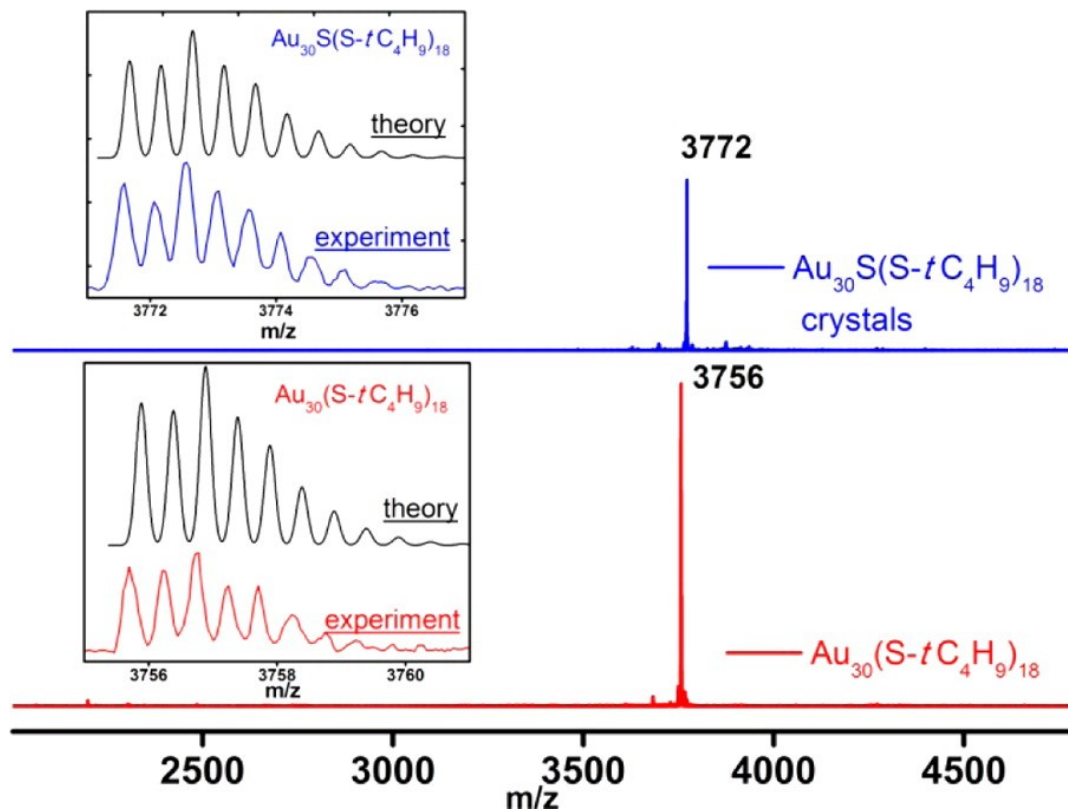
(Left) Calculated and (right) experimental optical absorption spectra of $\text{Au}_{30}\text{S}(\text{S-}t\text{-Bu})_{18}$ and $\text{Au}_{30}(\text{S-}t\text{-Bu})_{18}$. The only clearly distinguishable feature between the two different clusters is the peak at 630 nm. Note that the blue curve in (b) is measured from a sample that still contains trace amounts of $\text{Au}_{30}(\text{S-}t\text{-Bu})_{18}$.

Results and discussion



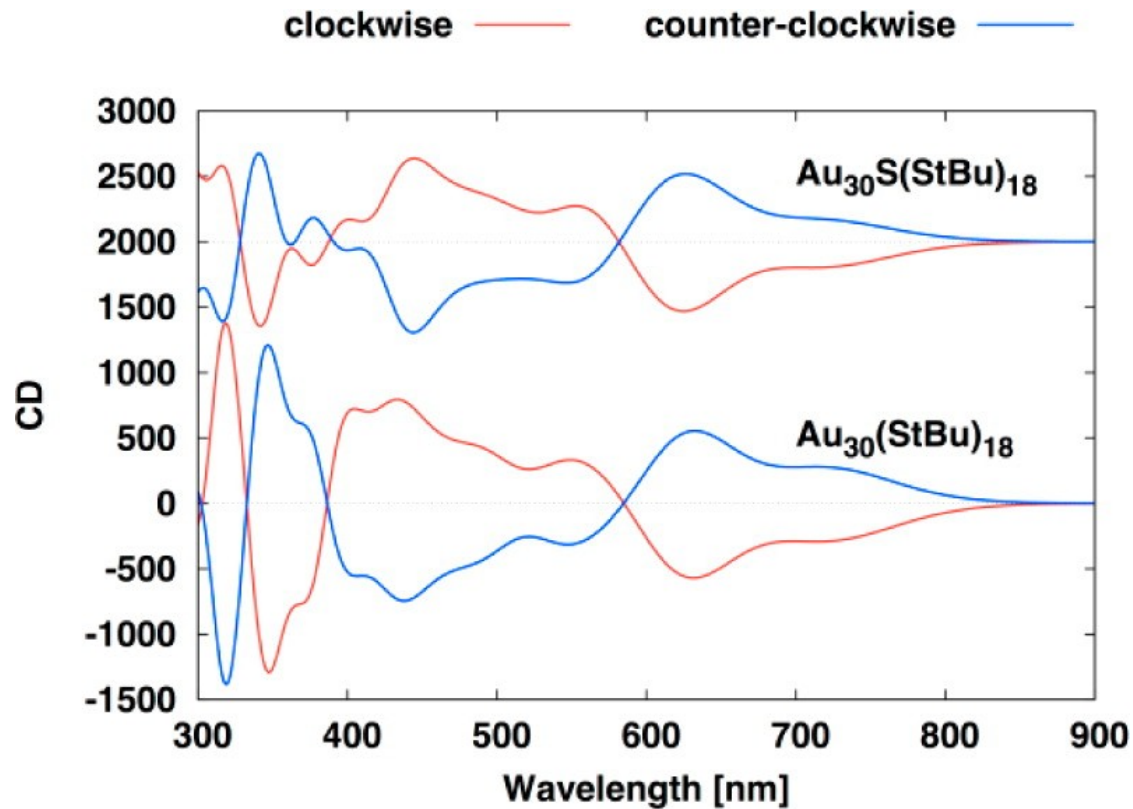
Single crystal XRD structure. (a) Total structure of $\text{Au}_{30}\text{S}(\text{S}-t\text{-Bu})_{18}$ (hydrogen atoms are omitted for clarity); (b) Au_{20} interpenetrating bicuboctahedral core geometry; (c) $\text{Au}_{30}\text{S}_{19}$ geometry showing the triply coordinated μ_3 -sulfur and the two trimeric $[-\text{SR}-\text{Au}-\text{SR}-\text{Au}-\text{SR}-\text{Au}-\text{SR}-]$ units, highlighted in the orange and pink boxes inset; (d) $\text{Au}_{30}\text{S}_{19}$ geometry showing the two monomeric $[-\text{SR}-\text{Au}-\text{SR}-]$ units, highlighted in the green box as inset (carbon atoms are omitted in (c) and (d) for clarity); (e and f) the positions of the rest of the SR groups on the Au_{22} bicuboctahedral substructure. The picture inset in (a) shows an optical photograph of the crystals.

Results and discussion



ESI-mass spectra of crystallite particles (blue) and $\text{Au}_{30}(\text{S}-t\text{Bu})_{18}$ (red). The solution of the crystallite particles clearly support the presence of the 19th sulfur, offering additional chemical evidence for the X-ray structure.

Results and discussion



Calculated CD-spectra of $\text{Au}_{30}\text{S}(\text{S-}t\text{-Bu})_{18}$ and $\text{Au}_{30}(\text{S-}t\text{-Bu})_{18}$ clusters for both enantiomers based on the crystal structure of $\text{Au}_{30}\text{S}(\text{S-}t\text{-Bu})_{18}$.

Summary and conclusion

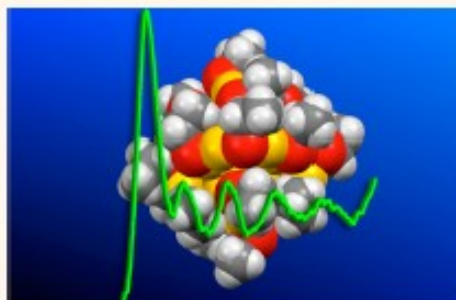
- They have resolved experimentally and explained computationally the structural and the optical properties of $\text{Au}_{30}\text{S}(\text{S-t-Bu})_{18}$ and $\text{Au}_{30}(\text{S-t-Bu})_{18}$ clusters.
- $\text{Au}_{30}(\text{S-t-Bu})_{18}$ is converted to $\text{Au}_{30}\text{S}(\text{S-t-Bu})_{18}$ during the crystallization process.
- They have a gold–thiolate protecting layer which consists of a novel triply coordinated sulfur (in case of $\text{Au}_{30}\text{S}(\text{S-t-Bu})_{18}$) and bridging SR-groups, as well as monomeric $\text{Au}(\text{SR})_2$ and trimeric $\text{Au}_3(\text{SR})_4$ units.
- The aspect ratio of the core and the optical properties are changed merely by one sulfur atom.

Au₂₅(SEt)₁₈, a Nearly Naked Thiolate-Protected Au₂₅ Cluster: Structural Analysis by Single Crystal X-ray Crystallography and Electron Nuclear Double Resonance

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ABSTRACT X-ray crystallography has been fundamental in discovering fine structural features of ultrasmall gold clusters capped by thiolated ligands. For still unknown structures, however, new tools capable of providing relevant structural information are sought. We prepared a 25-gold atom nanoduster protected by the smallest ligand ever used, ethanethiol. This cluster displays the electrochemistry, mass spectrometry, and UV–vis absorption spectroscopy features of similar Au₂₅ clusters protected by 18 thiolated ligands. The anionic and the neutral form of Au₂₅(SEt)₁₈ were fully characterized by ¹H and ¹³C NMR spectroscopy, which confirmed the monolayer's properties and the paramagnetism of neutral Au₂₅(SEt)₁₈.⁰ X-ray crystallography analysis of the latter provided the first known structure of a gold cluster protected by a simple, linear alkanethiolate. Here, we also report the direct observation by electron nuclear double resonance (ENDOR) of hyperfine interactions between a surface-delocalized unpaired electron and the gold atoms of a nanoduster. The advantages of knowing the exact molecular structure and having used such a small ligand allowed us to compare the experimental values of hyperfine couplings with DFT calculations unaffected by structure's approximations or omissions.



KEYWORDS: gold nano clusters · Au₂₅ · Au₂₅(SEt)₁₈ · X-ray crystallography · ENDOR · paramagnetism

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Lesson from this work!



1. Sometime we have also seen sulfide attached cluster in the mass spectrum, but it was very hard to convince sir that it is indeed possible. Now, from the crystal structure we came to know that: yes, it is possible!!!
2. More and more reports of crystal structure suggest that it is getting very difficult to establish the existence of cluster without a single crystal. Either you will get JACS, or else it will be very difficult to go in JPC/JMC also.
3. Getting a crystal is not about choosing the ligands, its about the purity and the procedure or may be some tricks from an expert.