

Mixed-Monolayer-Protected Au₂₅ Clusters with Bulky Calix[4]arene Functionalities

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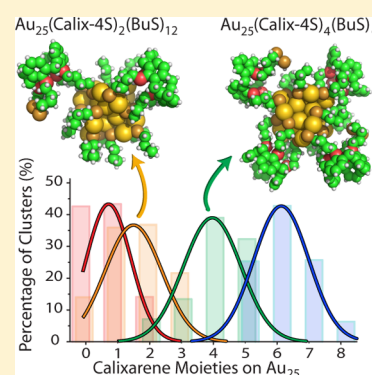
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S Supporting Information

ABSTRACT: Although various complex, bulky ligands have been used to functionalize plasmonic gold nanoparticles, introducing them to small, atomically precise gold clusters is not trivial. Here, we demonstrate a simple one-pot procedure to synthesize fluorescent magic number Au₂₅ clusters carrying controlled amounts of bulky calix[4]arene functionalities. These clusters are obtained from a synthesis feed containing binary mixtures of tetrathiolated calix[4]arene and 1-butanethiol. By systematic variation of the molar ratio of ligands, clusters carrying one to eight calixarene moieties were obtained. Structural characterization reveals unexpected binding of the calix[4]arenes to the Au₂₅ cluster surface with two or four thiolates per moiety.



SECTION: Physical Processes in Nanomaterials and Nanostructures

Metal clusters in the size range below 2 nm are interesting materials because of their size-dependent properties, which differ from the properties of larger nanoparticles, bulk metal, or single atoms.^{1–3} Within this size range, cluster sizes can be controlled with atomic precision, thus allowing precise investigations of structure–function relationships. These metal cores are typically passivated by an organic ligand shell, and therefore, these species are often referred to as monolayer-protected clusters (MPCs). Gold clusters passivated by thiolates, Au_n(SR)_m, are one of the most studied MPCs because of their high stability. Due to the stability, these clusters can be prepared by wet chemistry methods in ambient conditions and processed like ordinary chemicals. As a result of developments in synthetic procedures, separation methods, and analysis techniques, several stable “magic number” MPCs, such as Au₂₅(SR)₁₈, Au₃₈(SR)₂₄, Au₁₀₂(SR)₄₄, and Au₁₄₄(SR)₆₀, have been isolated, and reasons for their stability have been recognized.^{1,4,5}

Various bulky or structurally complex thiols (e.g., drug analogues, cyclodextrin derivatives, DNA oligonucleotides, polymers, dendrimers) have been used to produce plasmonic gold MPCs with applications including sensing,⁶ diagnostics,⁷ and drug delivery.⁸ However, most studies related to magic number MPCs are focused on using simple alkane- or arenethiols,^{9–11} though more complex, bulky ligands could bring valuable functionalities also to smaller clusters. This

shortcoming stems from major difficulties in reaching atomic precision by direct synthesis with structurally complex thiols. Atomically precise mixed-monolayer-protected clusters (MMPCs), on the other hand, can be realized by using, for example, ligand exchange reactions to existing magic number MPCs.^{12–14} However, ligand exchange of bulky ligands is often severely hampered by kinetic effects (i.e., steric hindrance), thus restricting the extent of exchange or even making ligands completely unusable.¹⁵ To overcome this hindrance, we investigate here a novel approach for synthesis of magic number MMPCs prepared directly by using thiol mixtures. This procedure enables a straightforward incorporation of functional, bulky ligands, whereas secondary small ligands facilitate size-focusing to discrete magic numbers and provide additional chemical stability by filling the possible defect sites on MMPCs.

Without doubt, capping clusters with specific functional groups is crucial regarding possible applications. Calixarenes are an interesting group of compounds that possess specific host–guest interactions with organic as well as metal cations.¹⁶ Because of these interactions, calixarenes find applications, for example, in ion-sensitive electrodes and sensors,¹⁷ stationary

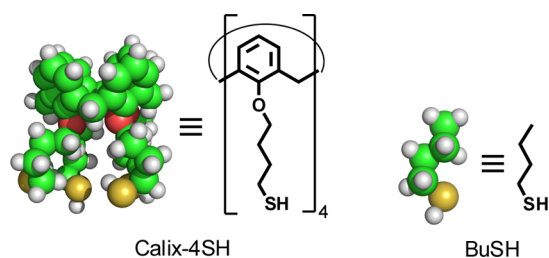
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phases in chromatography,¹⁸ and catalysis.¹⁹ After the first report of calixarene-protected gold nanoparticles by Arduini et al.,²⁰ there has been an increased interest toward calixarene-modified gold nanostructures.^{21–25} Recently, atomically precise MPCs (Au_{11}) with five phosphine-bound calixarene moieties were realized by de Silva et al.,²⁶ and their structure was theoretically verified by Chen et al.²⁷ Important to note is that the number of calixarene ligands was fixed, and their bulkiness led to incomplete capping, leaving the gold core partly exposed.

Here, we aim at a one-pot synthesis for atomically precise MPCs with a tunable number of bulky ligands, where a second smaller ligand would allow a complete ligand monolayer to cover the gold core. A mixture of thiol-modified calix[4]arene (briefly, Calix-4SH) and 1-butanethiol (BuSH) is used to prepare atomically precise $\text{Au}_{25}(\text{Calix-4S})_x(\text{BuS})_y$ clusters passivated by a mixed monolayer of these thiols (Chart 1).

Chart 1. Structures of Thiol Ligands



Calix-4SH in cone conformation was synthesized using a reported protocol;²⁸ details are given in the Supporting Information. Cone conformation, locked by four 4-mercaptobutanolate chains, was chosen to facilitate multidentate binding to the cluster surface. By systematically varying the Calix-4SH concentration in the synthesis feed, we are able to control the amount of calixarene functionalities on the clusters. To the best of our knowledge, there are no previous reports of creating atomically precise cluster cores carrying thiolated calixarenes. In addition, no studies of fluorescent gold clusters prepared using a mixed ligand feed could be found in the literature.

Au_{25} clusters passivated with mixtures of Calix-4SH and BuSH were synthesized by modifying the method by Qian et al.¹⁰ Details of the synthetic procedure can be found in the Supporting Information. Briefly, a mixture of Calix-4SH and BuSH was added to a solution containing HAuCl_4 and tetraoctylammonium bromide (TOAB) in tetrahydrofuran (THF). After the formation of colorless Au-thiolates, NaBH_4 was added in aqueous solution to obtain a polydisperse cluster mixture. This polydisperse cluster mixture was size-focused by allowing it to react until Au_{25} cluster absorption features became prominent. The clusters were purified by repeated centrifugal washing with methanol followed by size-exclusion chromatography (SEC) to ensure removal of free Calix-4SH from the final cluster product. SEC served well to separate free Calix-4SH as well as a minor portion of larger cluster species from the final product (Figure 1, inset). The Au_{25} cluster yields were typically 12–20%.

Absorption spectroscopy was initially used to get information about the core size of the clusters. Prominent absorption features were observed from all cluster samples at 680, 442, 400, and 320 nm, which are well-known features of the $\text{Au}_{25}(\text{SR})_{18}$ cluster core (Figure 1). In addition, details in the absorption spectrum revealed the charge state of the cluster. It has been shown that a broad absorption at 800 nm is an

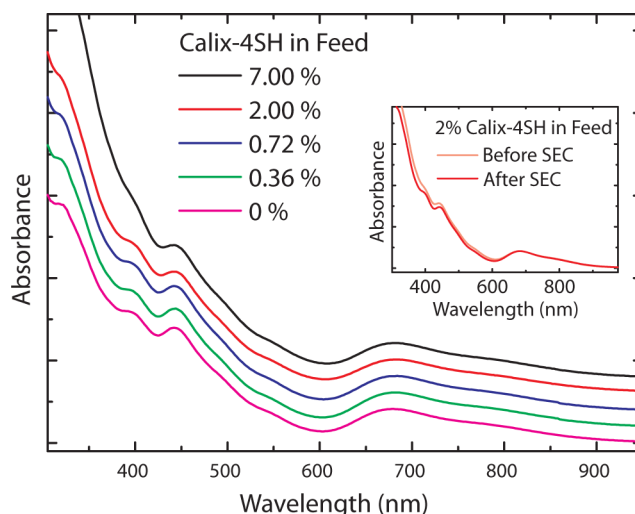


Figure 1. UV-vis absorption spectra of Au_{25} clusters with varying Calix-4SH concentration (spectra are vertically shifted for clarity). The inset shows spectra before and after SEC.

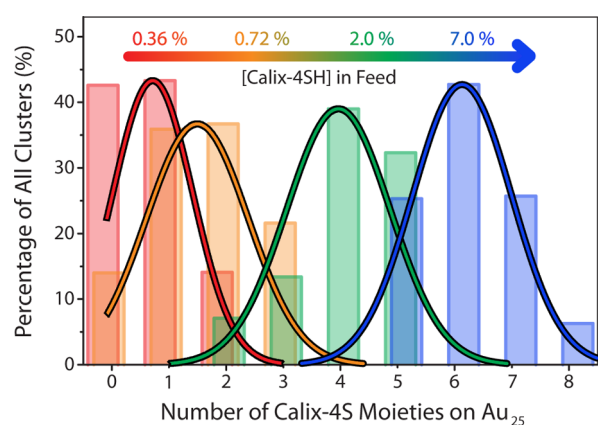
indication of a negatively charged, reduced gold core as well as a ratio of 1.2 between ~ 400 and ~ 440 nm absorptions.^{29,30} All Calix-4S-functionalized cluster samples showed these features, thereby indicating a majority of negatively charged cluster cores as observed also in previous reports from similar syntheses.^{10,29,30} The counterion of these negatively charged clusters was TOA^+ , which was detected in the nuclear magnetic resonance (NMR) spectra of all $\text{Au}_{25}(\text{Calix-4S})_x(\text{BuS})_y$ clusters.

To further analyze the structure of the clusters, the ligand compositions were probed by electrospray ionization mass spectrometry (ESI-MS) and NMR analyses. The negative polarization ESI-MS spectra were, surprisingly, dominated by the pure $\text{Au}_{25}(\text{BuS})_{18}$ cluster. In positive polarization measurements, however, more abundant $\text{Au}_{25}(\text{Calix-4S})_x(\text{BuS})_y$ clusters could be observed, with x ranging from 0 to 8 (neutral clusters as Cs^+ adducts and anionic clusters as 2Cs^+ adducts). Apart from Au_{25} , no other cluster sizes were observed in ESI-MS. Au_{25} clusters are easily oxidized by atmospheric oxygen, as reported by Jin's group.²⁹ We also observed the same phenomenon, and the rate of oxidation was more pronounced with dried samples compared to clusters stored in THF solution. In vacuum-dried samples, signs of oxidation could be noticed in hours, and the samples were fully oxidized in a few days. Comparison of negative and positive polarization mass spectra shows that oxidation is more pronounced in the case of $\text{Au}_{25}(\text{Calix-4S})_x(\text{BuS})_y$ clusters than for $\text{Au}_{25}(\text{BuS})_{18}$. However, when stored free of oxygen, in the dark and at 4°C , clusters exhibited no change in their spectral features even after 2 months of storage.

As expected, the use of a thiol mixture led to varying ligand compositions in the final products (see Table 1 for results from a sample with 0.36% Calix-4SH in the synthesis feed; data from other samples are presented in the Supporting Information). However, it can be easily observed that the amount of Calix-4S units attached to clusters clearly correlates with the amount of Calix-4SH inserted into the synthesis feed (Figure 2). Samples with 0–2, 1–3, 2–5, and 5–8 calixarene units were obtained by varying the Calix-4SH feed in the 0.36–7.0% range of the amount of BuSH. Even though this kind of synthesis with a binary mixture of thiols will rarely end up in a single ligand

Table 1. Cluster Compositions in Sample with 0.36% Calix-4SH in the Synthesis Feed

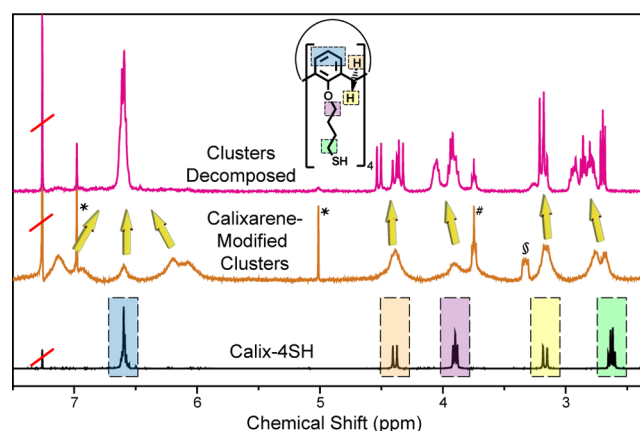
ion composition (+ <i>n</i> Cs ⁺)	Calix-4S		BuS
	tetradentate	bidentate	
Au ₂₅ (BuS) ₁₈	0	0	18
Au ₂₅ (Calix-4S)(BuS) ₁₄	1	0	14
Au ₂₅ (Calix-4S)(BuS) ₁₆	0	1	16
Au ₂₅ (Calix-4S) ₂ (BuS) ₁₀	2	0	10
Au ₂₅ (Calix-4S) ₂ (BuS) ₁₂	1	1	12
Au ₂₅ (Calix-4S) ₂ (BuS) ₁₄	0	2	14

**Figure 2.** Variation of the amount of Calix-4S units on clusters when increasing the Calix-4SH content in the synthesis feed. For better visibility of the trend, the normal distribution for each sample has been overlaid on the histogram.

composition, we were still able to maintain good control on the final ligand compositions.

Au₂₅ clusters are known to be passivated by 18 thiolate ligands, arranged as 6 RS-(Au-SR)₂ units on top of a 13-atom icosahedral gold core.^{31–33} All ions observed in our ESI-MS analysis could be interpreted to have 18 thiolates attached to the gold surface, suggesting that the well-known Au₂₅(SR)₁₈ structure is retained regardless of the ligand composition. The clusters are also eight-electron “superatoms” as negatively charged species after the synthesis. The cluster compositions observed in ESI-MS measurements revealed interesting details on the binding of Calix-4S units. Interestingly, the vast majority of clusters (>99%) had an even number of BuS ligands attached. This suggests that Calix-4SH ligands are attached to the cluster surface predominantly with two or four thiolates because binding with one or three thiolates would also result in species containing an odd number of BuS. Binding only with two or four thiolates is also evident in clusters containing only one calixarene unit; Au₂₅(Calix-4S)(BuS)₁₅ and Au₂₅(Calix-4S)(BuS)₁₇ were not observed in ESI-MS analysis. Binding with two or four thiolates also supports our recent study of Calix-4S protected nanoparticles, in which a binding with an average of three thiolates was observed (unpublished results).

Calix-4SH binding to gold with two thiolates leaves the two other thiolates dangling. Chemical structure of the dangling thiols was investigated with ESI-MS and NMR studies. In NMR spectra, all resonances were broadened due to the existence of different ligand compositions and also various isomers in each composition due to different Calix-4S binding sites on Au₂₅. The signals from thiol-neighbor methylene protons at 2.6 ppm were shifted downfield from free calixarene signals,

**Figure 3.** ¹H NMR spectra of Calix-4SH (bottom) and calixarene-modified Au₂₅ clusters before (middle) and after (top) the Iodine Death reaction (7.0% Calix-4SH in the feed). Signals arising from the different parts of Calix-4SH are marked in color, and the signals from THF, THF stabilizing agent butylated hydroxytoluene, and TOA⁺ are marked with #, *, and §, respectively.

suggesting no free thiol groups being present in the system (Figure 3). Additionally, the mass accuracies in ESI-MS experiments suggest no thiol groups being present in the clusters. Absence of S–H bonds was further confirmed by infrared absorption spectroscopy (see the Supporting Information). Therefore, it can be proposed that two dangling thiolates of bidentately bound Calix-4SH form a disulfide bridge with each other. Also, the peak positions in ¹H NMR studies support the formation of disulfides, as seen from the downfield shifts of CH₂ protons next to sulfur atoms.

The intensities of peaks in ESI-MS are influenced by the ionization efficiencies and transmission efficiencies of the ions through the ESI-MS interface. Considering the chemical and physical similarities of calixarene-decorated clusters, their ionization and transmission efficiencies can be approximated to be independent of ligand composition, thus allowing semiquantitative analysis of abundances of clusters with different ligand compositions (Figure 2). In addition to ESI-MS, the average ligand composition was probed with ¹H NMR analysis. The cluster cores were decomposed with the Iodine Death reaction, which quantitatively liberates the alkanethiolate monolayer as disulfide compounds and thus allows determination of ligand concentrations through integration of NMR signals.^{24,34} The average ligand compositions measured by these independent methods are well in line with each other (Table 2).

It is worth noticing that the amount of calixarene finally attached to clusters is very high compared to the amount used in the synthesis. In all samples, the ratio *n*(Calix-4S)/*n*(BuS) on the cluster surface was 20–25 times higher than the *n*(Calix-4SH)/*n*(BuS) ratio in the synthesis feed. This highly efficient binding is likely caused by the multidentate nature of Calix-4SH as it does not detach easily during the size-focusing process in which larger clusters are etched into Au₂₅ cores. Hence, polythiolated molecules are highly useful in cluster syntheses with thiol mixtures. Incorporation of thiols into complex molecules is often a tedious task, and cluster synthesis typically consumes large amounts of thiol ligands (usually Au/S ≤ 1/5). By using a mixture of thiols, the consumption of Calix-4SH is minimized because Calix-4SH efficiently binds to the cluster surface and a large excess of commercially available BuSH acts

Table 2. Average Ligand Compositions of Au₂₅ Clusters

Calix-4SH in the feed, %	<i>n</i> (Calix-4S)/ <i>n</i> (BuS) on clusters, %		average composition ^a
	NMR	ESI-MS	
0.36	8	5	Au ₂₅ (Calix-4S) ₁ (BuS) ₁₆
0.72	17	11	Au ₂₅ (Calix-4S) ₂ (BuS) ₁₄
2.0	51	52	Au ₂₅ (Calix-4S) ₄ (BuS) ₈
7.0	152	155	Au ₂₅ (Calix-4S) ₆ (BuS) ₄

^aRounded to integers.

as a secondary passivating ligand and, even more importantly, as an etchant that allows one to reach atomic precision of the gold core. It is also worth mentioning that ligand exchange of Calix-4SH to Au₂₅(BuS)₁₈ clusters could not be accomplished, most probably due to the bulkiness of the incoming Calix-4SH ligand. Therefore, the use of thiol mixtures is the only suitable option for preparing clusters with Calix-4SH ligand.

The ¹H NMR spectra of clusters showed an interesting resonance pattern in the aromatic region consisting of a center signal and doublet side signals (Figure 3). The side signals were present in all samples, and their positions were independent of the amount of Calix-4S moieties on the cluster surface. Signals in the aromatic region were further investigated by 2D NMR measurements (see the Supporting Information). In COSY and TOCSY spectra, couplings were observed only between the doublets of the side signals, indicating that all three resonances (~7.1, 6.6, and 6.1 ppm) form separate spin systems. In the ROESY spectrum, however, an additional coupling was observed between the side signals at 7.1 and 6.1 ppm. This coupling suggests that these protons belong to a specific type of cluster-bound Calix-4S, which is further supported by the symmetric shape and magnitude of the side signals. The center signal at 6.6 ppm shows no coupling in ROESY, indicating that it originates from a cluster-bound Calix-4S with a chemical shift similar to the aromatic signal from free Calix-4SH.

Considering the 2/4 thiolate binding mechanism indicated by ESI-MS analysis, it is reasonable to suggest that the center signal originates from Calix-4S binding with four thiolates and the side signals from species binding with two thiolates. The side signals arise from a conformational distortion of the symmetric calixarene cup to a pinched cone conformation. "Locking" to a pinched cone conformation has been observed in tetrakis(*n*-alkoxy)calix[4]arenes at low temperatures, while the interconversion between cone and pinched cone conformations is rapid at room temperature.³⁵ Functionalization of upper and lower rims has also been used to lock calix[4]arenes to pinched cone conformation through covalent and hydrogen-bonding interactions.^{35–38} On the contrary, conformational locking to a pinched cone by a steric impediment, as seen now in Au₂₅ cluster surfaces, has not been previously reported. It is worth noticing that the pinched cone conformation is not observed on larger nanoparticle surfaces protected by dithiolated²⁴ or tetrathiolated calix[4]arenes (unpublished results). Therefore, the origin of the preferential pinched cone formation can be attributed to the high surface curvature of the subnanometer-sized Au₂₅ core, which sets specific requirements on the S–Au binding positions.

The effect of ligand composition on cluster fluorescence was also investigated. All clusters showed fluorescence in the near-infrared region (800 nm), and their quantum yields varied slightly (0.1–0.3%) with the amount of Calix-4S (see the Supporting Information). However, fluorescence from Au₂₅ clusters also strongly depends on the oxidation state of the

cluster core, as reported by Wu and Jin.³⁹ As the clusters easily oxidize, it is difficult to separate the effect of the ligand composition from slight variations in the oxidation state of clusters. It is worth noting that the shape of the excitation spectra is similar to the absorption spectra of clusters, a feature not present in existing literature of Au₂₅ clusters.^{12,39}

In conclusion, atomically precise Au₂₅ clusters passivated with Calix-4SH and BuSH were prepared in a robust one-pot synthesis by using a mixture of thiols in the synthesis feed. This type of synthesis could provide a general strategy for the incorporation of other bulky ligands to cluster surfaces. By varying the molar ratio of the ligands, clusters carrying up to eight calixarene moieties could be obtained. Calix-4SH was found to preferentially bind to a high curvature Au₂₅ surface by two or four thiolates, and in the case of two thiolate binding, the calixarene cavity undergoes a distortion to a pinched cone conformation due to steric impediment. These clusters show promising potential for building cluster assemblies via host–guest interactions, which is a matter of further study.

■ ASSOCIATED CONTENT

📄 Supporting Information

Details of the synthesis procedures and characterization techniques as well as further UV–vis, IR, NMR, and ESI-MS data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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