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

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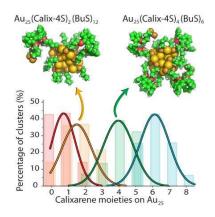
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ABSTRACT: Although various complex, bulky ligands have been used to functionalize plasmonic gold nanoparticles, introducing them to small, atomically precise gold clusters is not trivial. Here we demonstrate a simple one-pot procedure to synthesize 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.

TOC GRAPHICS



KEYWORDS: Gold, clusters, functionalization, calixarene

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 sensing⁶, diagnostics⁷ and drug delivery⁸. 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 e.g. ligand exchange reactions to existing magic number MPCs.^{12–14} However, ligand exchange of bulky ligands are 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

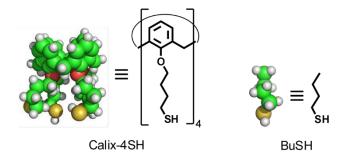
procedure enables a straightforward incorporation of functional, bulky ligands whereas secondary small ligands facilitate size-focusing to discrete magic numbers and provide additional chemical stability by filling the possible defect sites on MMPCs.

Without doubt, capping clusters with specific functional groups is crucial regarding possible applications. Calixarenes are an interesting group of compounds that possesses specific host-guest interactions with organic as well as metal cations. Because of these interactions, calixarenes find applications, for example, in ion-sensitive electrodes and sensors, stationary phases in chromatography and catalysis After the first report of calixarene-protected gold nanoparticles by Arduini et al. there has been an increased interest towards calixarene-modified gold nanostructures. Recently, atomically precise MPCs (Au₁₁) with five phosphine-bound calixarene moieties were realized by de Silva et al²⁶ and their structure was theoretically verified by Chen et al²⁷. 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 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 Au₂₅(Calix-4S)_x(BuS)_y clusters passivated by a mixed monolayer of these thiols (Chart 1). Calix-4SH in cone conformation was synthesized using a reported protocol²⁸, details are given in the Supporting Information. Cone conformation, locked by four 4-mercaptobutanolate chains, was chosen to facilitate multidentate binding to 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.

Chart 1. Structures of Thiol Ligands



Au₂₅ 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 HAuCl₄ and tetraoctylammonium bromide (TOAB) in tetrahydrofuran (THF). After the formation of colorless Au-thiolates, NaBH₄ was added in aqueous solution to obtain a polydisperse cluster mixture. This polydisperse cluster mixture was size-focused by allowing it to react until Au₂₅ 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 Au₂₅ cluster yields were typically 12–20 %.

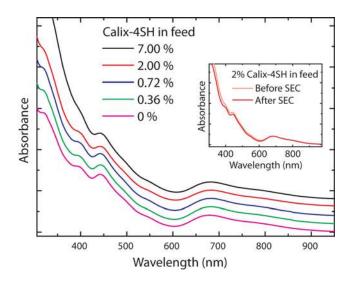


Figure 1. UV-vis absorption spectra of Au₂₅ clusters with varying Calix-4SH concentration (spectra are vertically shifted for clarity). The inset shows spectra before and after size-exclusion chromatography.

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 nm, 442 nm, 400 nm and 320 nm which are well-known features of Au₂₅(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 indication of a negatively charged, reduced gold core as well as a ratio of 1.2 between ~400 nm 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 counter-ion of these negatively charged clusters was TOA⁺ which was detected in the nuclear magnetic resonance (NMR) spectra of all Au₂₅(Calix-4S)_x(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 pure Au₂₅(BuS)₁₈ cluster. In positive polarization measurements, however, more abundant Au₂₅(Calix-4S)_x(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 Au₂₅, no other cluster sizes were observed in ESI-MS. Au₂₅ 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 few days. Comparison of negative and positive polarization mass spectra shows that oxidation is more pronounced in the case of Au₂₅(Calix-4S)_x(BuS)_y clusters than for Au₂₅(BuS)₁₈. However, when stored free of oxygen, in dark and at 4 °C, clusters exhibited no change in their spectral features even after two 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 sample with 0.36 % Calix-4SH in synthesis feed, data from other samples is 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 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 composition, we were still able to maintain good control on the final ligand compositions.

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

Ion composition (InCot)	Calix-4S		DuC
Ion composition (+nCs ⁺)	Tetradentate	Bidentate	- BuS
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

Au₂₅ clusters are known to be passivated by 18 thiolate ligands, arranged as six 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 8 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 even number of BuS ligands attached. This suggests that Calix-4SH ligands are attached to cluster surface predominantly with two or four thiolates since binding with one or three thiolates would also result in species containing odd numbers 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 2 or 4 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-neighboring methylene protons at 2.6 ppm were shifted downfield from free calixarene signals 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 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.

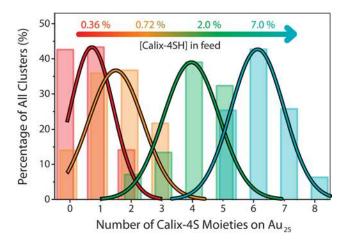


Figure 2. Variation of the amount of Calix-4S units on clusters when increasing the Calix-4SH content in synthesis feed. For better visibility of the trend, normal distribution for each sample has been overlaid on the histogram.

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 semi-quantitative 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 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).

Table 2. Average Ligand Compositions of Au₂₅ Clusters

Calix-4SH _ in feed, %	n(Calix-4S)/n(BuS) on clusters, %		- A
	NMR	ESI-MS	Average composition*
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	$Au_{25}(Calix-4S)_6(BuS)_4$

^{*} Rounded to integers

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 cluster surface was 20–25 times higher than the n(Calix-4SH):n(BuSH) 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 to complex molecules is often a tedious task and cluster synthesis typically consumes large amounts of thiol ligands (usually Au/S \leq 1/5). By using a mixture of thiols, the consumption of Calix-4SH is minimized since Calix-4SH efficiently binds to cluster surface and a large excess of commercially available BuSH acts as a secondary passivating ligand and, even more importantly, as an etchant that allows reaching 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 cluster surface. Signals in the aromatic region were further investigated by 2D NMR measurements (see 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 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.

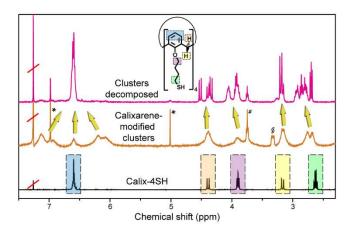


Figure 3. ¹H NMR spectra of Calix-4SH (bottom) and calixarene-modified Au₂₅ clusters before (middle) and after (top) iodine death reaction (7.0 % Calix-4SH in feed). Signals arising from the different parts of Calix-4SH are marked in color, and the signals from THF, THF stabilizing agent butylated hydroxytoluene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

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 cone–pinched cone exchange is rapid in room temperature.³⁴ 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.^{36–38} 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 pinched cone conformation is not observed on larger nanoparticle surfaces protected by dithiolated²⁴ or tetrathiolated calix[4]arenes (unpublished results). Therefore, the origin of 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 to 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 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 interests.

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REFERENCES

(1) Jin, R. Quantum Sized, Thiolate-Protected Gold Nanoclusters. Nanoscale 2010, 2,

343-362.

(2) Zheng, J.; Nicovich, P. R.; Dickson, R. M. Highly Fluorescent Noble-Metal Quantum Dots.

Annu. Rev. Phys. Chem. 2007, 58, 409-431.

(3) Díez, I.; Ras, R. H. A. Fluorescent Silver Nanoclusters. *Nanoscale* **2011**, *3*, 1963–1970.

(4) Maity, P.; Xie, S.; Yamauchi, M.; Tsukuda, T. Stabilized Gold Clusters: from Isolation

Toward Controlled Synthesis. *Nanoscale* **2012**, *4*, 4027–4037.

(5) Häkkinen, H. The Gold–Sulfur Interface at the Nanoscale. *Nat. Chem.* **2012**, *4*, 443–455.

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- (6) Saha, K.; Agasti, S. S.; Kim, C.; Li, X.; Rotello, V. M. Gold Nanoparticles in Chemical and Biological Sensing. *Chem. Rev.* **2012**, *112*, 2739–2779.
- (7) Lu, F.; Doane, T. L.; Zhu, J.-J.; Burda, C. Gold Nanoparticles for Diagnostic Sensing and Therapy. *Inorg. Chim. Acta* **2012**, *393*, 142–153.
- (8) Ghosh, P.; Han, G.; De, M.; Kim, C. K.; Rotello, V. M. Gold Nanoparticles in Delivery Applications. *Adv. Drug Deliv. Rev.* **2008**, *60*, 1307–1315.
- (9) Qian, H.; Jin, R. Ambient Synthesis of Au₁₄₄(SR)₆₀ Nanoclusters in Methanol. *Chem. Mater.* **2011**, 23, 2209–2217.
- (10) Qian, H.; Liu, C.; Jin, R. Controlled Growth of Molecularly Pure Au₂₅(SR)₁₈ and Au₃₈(SR)₂₄ Nanoclusters from the Same Polydispersed Crude Product. *Sci. China Chem.* **2012**, 55, 2359–2365.
- (11) Tang, Z.; Robinson, D. A.; Bokossa, N.; Xu, B.; Wang, S.; Wang, G. Mixed Dithiolate Durene-DT and Monothiolate Phenylethanethiolate Protected Au₁₃₀ Nanoparticles with Discrete Core and Core-Ligand Energy States. *J. Am. Chem. Soc.* **2011**, *133*, 16037–16044.
- (12) Shibu, E. S.; Habeeb Muhammed, M. A.; Tsukuda, T.; Pradeep, T. Ligand Exchange of Au₂₅SG₁₈ Leading to Functionalized Gold Clusters: Spectroscopy, Kinetics, and Luminescence. *J. Phys. Chem. C* **2008**, *112*, 12168–12176.
- (13) Niihori, Y.; Matsuzaki, M.; Pradeep, T.; Negishi, Y. Separation of Precise Compositions of Noble Metal Clusters Protected with Mixed Ligands. *J. Am. Chem. Soc.* **2013**, *135*, 4946–4649.

- (14) Knoppe, S.; Michalet, S.; Bürgi, T. Stabilization of Thiolate-Protected Gold Clusters Against Thermal Inversion: Diastereomeric Au₃₈(SCH₂CH₂Ph)₂₄–2x(R–BINAS)_x. *J. Phys. Chem. C* **2013**, *117*, 15354–15361.
- (15) Astruc, D.; Daniel, M.-C.; Ruiz, J. Dendrimers and Gold Nanoparticles as Exo-Receptors Sensing Biologically Important Anions. *Chem. Commun.* **2004**, 2637–2649.
- (16) Gutsche, C. D. In "Calixarenes: an Introduction"; Stoddart, J. F., Ed.; Monographs in Supramolecular Chemistry; The Royal Society of Chemistry; 2nd edition: London, **2008**; Vol. 1.
- (17) Arora, V.; Mohindra, H. M.; Singh, S. P. Calixarenes as Sensor Materials for Recognition and Separation of Metal Ions. *Arkivoc* **2007**, *2*, 172–200.
- (18) Mokhtari, B.; Pourabdollah, K.; Dalali, N. Applications of Nano-Baskets of Calixarenes in Chromatography. *Chromatographia*, **2011**, *73*, 829–847.
- (19) Cacciapaglia, R; Mandolini, L. in "Calixarenes in Action"; Mandolini, L.; Ungaro, R., Eds.; Imperial College Press: London, **2000**; pp. 241-264.
- (20) Arduini, A.; Demuru, D.; Pochini, A.; Secchi, A. Recognition of Quaternary Ammonium Cations by Calix[4]arene Derivatives Supported on Gold Nanoparticles. *Chem. Commun.* **2005**, 645–647.
- (21) Ha, J.-M.; Solovyov, A.; Katz, A. Postsynthetic Modification of Gold Nanoparticles with Calix[4]arene Enantiomers: Origin of Chiral Surface Plasmon Resonance. *Langmuir* **2009**, *25*, 153–159.

- (22) Dionisio, M.; Maffei, F.; Rampazzo, E.; Prodi, L.; Pucci, A.; Ruggeri, G.; Dalcanale, E. Guest-Controlled Aggregation of Cavitand Gold Nanoparticles and N-Methyl Pyridinium-Terminated PEG. *Chem. Commun.* **2011**, *47*, 6596–6598.
- (23) Ciesa, F.; Plech, A.; Mattioli, C.; Pescatori, L.; Arduini, A.; Pochini, A.; Rossi, F.; Secchi, A. Guest Controlled Assembly of Gold Nanoparticles Coated with Calix[4]arene Hosts. *J. Phys. Chem. C* **2010**, *114*, 13601–13607.
- (24) Pulkkinen, P. M. S.; Wiktorowicz, S.; Aseyev, V.; Tenhu, H. Complexation of Calix[4]arene Protected Gold Nanoparticles with Pyridinium and Bipyridinium Compounds. *RSC Adv.* **2013**, *3*, 733–742.
- (25) Pescatori, L.; Boccia, A.; Ciesa, F.; Rossi, F.; Grillo, V.; Arduini, A.; Pochini, A.; Zanoni, R.; Secchi, A. The Effect of Ligand Denticity in Size-Selective Synthesis of Calix[n]arene-Stabilized Gold Nanoparticles: A Multitechnique Approach. *Chem. Eur. J.* **2010**, *16*, 11089–11099.
- (26) de Silva, N.; Ha, J.-M.; Solovyov, A.; Nigra, M. M.; Ogino, I.; Yeh, S. W.; Durkin, K. A.; Katz, A. A Bioinspired Approach for Controlling Accessibility in Calix[4]arene-Bound Metal Cluster Catalysts. *Nat. Chem.* **2010**, *2*, 1062–1068.
- (27) Chen, X.; Häkkinen, H. Protected but Accessible: Oxygen Activation by a Calixarene-Stabilized Undecagold Cluster. *J. Am. Chem. Soc.* **2013**, *135*, 12944–12947.
- (28) Ha, J.-M.; Katz, A.; Drapailo, A. B.; Kalchenko, V. I. Mercaptocalixarene-Capped Gold Nanoparticles via Postsynthetic Modification and Direct Synthesis: Effect of Calixarene Cavity-Metal Interactions. *J. Phys. Chem. C* **2009**, *113*, 1137–1142.

- (29) Zhu, M.; Eckenhoff, W. T.; Pintauer, T.; Jin, R. Conversion of Anionic [Au₂₅(SCH₂CH₂Ph)₁₈]⁻ Cluster to Charge Neutral Cluster via Air Oxidation. *J. Phys. Chem. C* **2008**, *112*, 14221–14224.
- (30) Parker, J. F.; Weaver, J. E. F.; McCallum, F.; Fields-Zinna, C. A.; Murray, R. W. Synthesis of Monodisperse [Oct₄N⁺][Au₂₅(SR)₁₈⁻] Nanoparticles, with Some Mechanistic Observations. *Langmuir* **2010**, *26*, 13650–13654.
- (31) Heaven, M. W.; Dass, A.; White, P. S.; Holt, K. M.; Murray, R. W. Crystal Structure of the Gold Nanoparticle [N(C₈H₁₇)₄][Au₂₅(SCH₂CH₂Ph)₁₈]. *J. Am. Chem. Soc.* **2008**, *130*, 3754–3755.
- (32) Zhu. M.; Aikens, C. M.; Hollander, F. J.; Schatz, G. C.; Jin, R. Correlating the Crystal Structure of A Thiol-Protected Au₂₅ Cluster and Optical Properties. *J. Am. Chem. Soc.* **2008**, 130, 5883–5885.
- (33) Akola, J.; Walter, M.; Whetten, R. L.; Häkkinen, H.; Grönbeck, H. On the Structure of Thiolate-Protected Au₂₅. *J. Am. Chem. Soc.* **2008**, *130*, 3756–3757.
- (34) Templeton, A. C.; Hostetler, M. J.; Kraft, C. T.; Murray, R. W. Reactivity of Monolayer-Protected Gold Cluster Molecules: Steric Effects. *J. Am. Chem. Soc.* **1998**, *120*, 1906–1911.
- (35) Arduini, A.; Fabbi, M.; Mantovani, M.; Mirone, L.; Pochini, A.; Secchi, A.; Ungaro, R. Calix[4]arenes Blocked in a Rigid Cone Conformation by Selective Functionalization at the Lower Rim. *J. Org. Chem.* **1995**, *60*, 1454–1457.
- (36) Hudrlik, P. F.; Arasho, W. D.; Hudrlik, A. M. The Wurtz-Fittig Reaction in the Preparation of C-Silylated Calixarenes. *J. Org. Chem.* **2007**, *72*, 8107–8110.

- (37) Casnati, A.; Sansone, F.; Ungaro, R. Peptido- and Glycocalixarenes: Playing with Hydrogen Bonds around Hydrophobic Cavities. *Acc. Chem. Res.* **2003**, *36*, 246–254.
- (38) Scheerder, J.; Vreekamp, R. H.; Engbersen, J. F. J.; Verboom, W.; van Duynhoven, J. P. M.; Reinhoudt, D. N. The Pinched Cone Conformation of Calix[4]arenes: Noncovalent Rigidification of the Calix[4]arene Skeleton. *J. Org. Chem.* **1996**, *61*, 3476–3481.
- (39) Wu, Z.; Jin, R. On the Ligand's Role in the Fluorescence of Gold Nanoclusters. *Nano Lett.* **2010**, *10*, 2568–2573.