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The ligand exchange reaction between monodisperse Au_{25}(2-PET)$_{18}$ (2-PET: 2-phenylethylthiolate) clusters and 1,1′-binaphthyl-2,2′-dithiol (BINAS) was long thought to induce decomposition of the cluster (Si *et al.*, *J. Phys. Chem. C*, 2009). We repeated the experiment and analyzed the reaction products using MALDI-TOF mass spectrometry. The spectra clearly indicate successful ligand exchange, bidentate binding of the BINAS ligand and intact Au_{25} clusters. The reaction products are identified as Au_{25}(2-PET)$_{18-2x}$(BINAS)$_x$ (x = 1–4) for a 24 h reaction with a 50-fold molar excess of BINAS. Two likely binding motifs are discussed. Analysis of atomic distances in both the cluster and the free ligand indicates interstaple binding connecting the central sulfur atom of the protecting $(SRAu)_2SR$ with the outer sulfur atom of a second unit. The results presented have implications on the binding position of BINAS in $Au_{38}(SR)_{24-2x}$(BINAS)$_x$ clusters.

Introduction

Ligand exchange reactions are commonly used to alter the properties of thiolate-protected gold clusters, $[Au_m(SR)_n]^z$.[1–13] The reactions allow convenient access to functionalized (*e.g.* chirally) monolayer-protected gold clusters. While a monodentate incoming thiol is expected to replace the leaving thiol at the same position within the cluster,[13] the situation is much more complicated for bidentate di-thiols, such as 1,5-pentanedithiol,[14] toluene-3,4-dithiol[3] or 1,1′-binapthyl-2,2′-dithiol.[7–9,15] These di-thiols are either conformationally flexible or their sulfur–sulfur distance is short enough that bidentate binding to the cluster is expected, thus replacing two leaving thiolates. This has been confirmed using MALDI-TOF mass spectrometry.[3,14]

$Au_{25}(SR)_{18}$ clusters are frequently used targets for investigations of ligand exchange reactions in clusters. The cluster consists of an Au_{13} core which is protected by six protecting units $(SRAu)_2SR$ (dimeric units or 'staples').[16–20] The cluster, in its anionic state, can be interpreted as an 8-electron superatom complex, as indicated by a change from *P* to *D* symmetry between HOMO and LUMO.[20,21] In a series of articles, both $Au_{25}(SR)_{18}$ and $Au_{38}(SR)_{24}$ clusters were reacted with an excess of BINAS.[7–9,15] The Au_{25} cluster was assumed to decompose under the influence of BINAS,[15] but it should be noted that at the time the study was conducted, MALDI-TOF mass spectrometry[2] was not yet available for analysis. The decomposition of the cluster was based on a change in the absorption spectrum, which is very typical for $Au_{25}(SR)_{18}$. It was argued that the dimeric protecting units in $Au_{25}(SR)_{18}$ cannot bind BINAS in a bidentate fashion. This would lead to steric stress, inducing decomposition to smaller clusters of unknown composition. In contrast, $Au_{38}(SR)_{24}$ (and $Au_{40}(SR)_{24}$) were found to remain intact, but incorporate BINAS only incompletely. Furthermore, the reaction proceeds slowly.[7,8] The incomplete exchange leads to clusters $Au_{38}(SR)_{24-2x}$(BINAS)$_x$ (with x = 1–3). Following the argumentation outlined above for Au_{25}, it was suggested that BINAS is bound regioselectively at the monomeric protecting units SRAuSR in $Au_{38}(SR)_{24}$.[22] The crystal structure of $Au_{38}(SR)_{24}$ also shows only three short staples.[23] Based on this, it was proposed that BINAS is a suitable ligand to read out the number of short protecting units in clusters of unknown structure.[7] It should, however, be noted that the ligand exchange reaction between Au_{38} and BINAS drastically slows down even after the first exchange step.[9]

We herein report the mass spectrometric assignment of the reaction products of the ligand exchange reaction between Au_{25}(2-PET)$_{18}$ clusters and BINAS (Scheme 1). We repeated the reaction at a higher molar excess of BINAS (50 : 1) than in the previous study (5 : 1) in order to accelerate the reaction.[15] Circular dichroism spectra were recorded and compared to those reported earlier in order to establish successful repetition of the experiment. The reaction products were then analyzed using MALDI-TOF mass spectrometry and assigned. It turns out that the cluster does in fact survive the exchange reaction.

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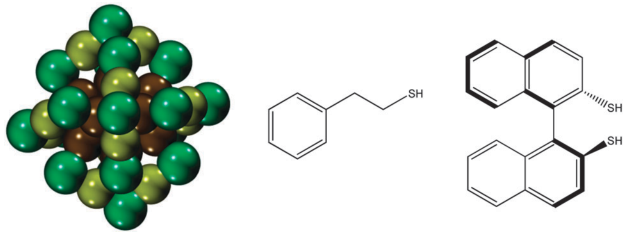

Scheme 1 Left: structure of the Au_{25}(2-PET)$_{18}$ cluster (the PET-groups are removed for clarity). Brown, Au_{Core}; yellow, Au_{Adatom}; cyan, sulfur. Center: 2-phenytlethylthiol (2-PET). Right: *S*-1,1′-binapthyl-2,2′-dithiol (BINAS).

We propose, in agreement with earlier studies conducted by the groups of Murray and Dass,[3,14] an interstaple binding motif for BINAS. The results also urge revision of the interpretation of the regioselective exchange reaction between Au_{38}(2-PET)$_{24}$ and BINAS.

Experimental

All chemicals were purchased from commercial suppliers and used as received. BINAS was synthesized from BINOL as reported earlier.[9] Au_{25}(2-PET)$_{18}$ clusters were prepared as by-products of the synthesis of Au_{38}(2-PET)$_{24}$ and isolated using size-exclusion chromatography.[7,22] Typically, the clusters are gained in the neutral state (greenish in color),[19] as confirmed by the absence of the absorption feature above 700 nm.

Ligand exchange reactions were performed at room temperature. 3 mg of Au_{25} clusters were dissolved in 6 mL methylene chloride and a 50-fold molar excess of *S*-BINAS was added. At defined times (3, 8 and 24 h), aliquots of about 2 mL were taken and the solvent was removed *via* rotary evaporation. The residue was dissolved in the minimum volume of tetrahydrofuran and passed over a short size-exclusion column (1 cm in diameter, 15 cm in length). This removes excess thiol, which is expected to have longer elution times due to its smaller hydrodynamic volume as compared to the clusters. A yellow solution was obtained. The solvent was removed and the clusters were washed with methanol.

UV-Vis spectra

Absorption spectra were measured on a Varian Cary 50 UV-Vis spectrometer. Quartz cuvettes of 1 cm path length were used. All spectra were measured in methylene chloride.

Circular dichroism

CD spectra were measured on a JASCO J-810 spectrophotometer with a quartz cuvette of 5 mm path length. All spectra were measured in methylene chloride. Several scans were averaged to improve the signal-to-noise ratio. FFT filters were applied to smoothen the curves. Anisotropy factors $g = \Delta A/A = \theta[\text{mdeg}]/(32\,980 * A)$ were calculated using the absorption spectra provided by the CD spectrometer.

MALDI-TOF mass spectra

MALDI-TOF mass spectra were obtained on a Shimadzu Biotech Axima mass spectrometer in linear mode. DCTB was used as matrix.[2]

Results and discussion

Au_{25}(2-PET)$_{18}$ clusters were synthesized and isolated as reported earlier. The clusters were obtained in the neutral form, $[Au_{25}(2\text{-PET})_{18}]^0$, according to their color in solution (greenish) and absorption spectra (Fig. 1).[18]

MALDI-TOF mass spectrometry[2] shows one peak at $m/z = 7394$. Ligand exchange was performed at a higher BINAS-to-cluster ratio (50 : 1) than in the previous[15] study (5 : 1). We chose this higher ratio in order to accelerate the reaction. Over the course of the reaction, a slight color change from greenish to yellow was observed. After purification of the clusters, UV-Vis and CD spectra were recorded. With increasing reaction time, the absorption spectra show a loss of the characteristic features of Au_{25} clusters (Fig. 2). The peaks at 670, 450 and 400 nm become less defined and the weak tail above 700 nm vanishes almost completely. This is in agreement with the observed color change from greenish to yellow. Nevertheless, the absorption spectra are not completely featureless, even after an extended reaction time (24 h). Note that in similar experiments by the groups of Murray and Dass, a change in the optical properties of Au_{25} using bidentate ligands has been observed as well.[3,14]

Optical activity is induced into the clusters after reaction with BINAS (Fig. 3). With increasing reaction time, the spectra become more pronounced and additional features are observed, *e.g.* a shoulder at 475 nm. At short reaction times, the spectra

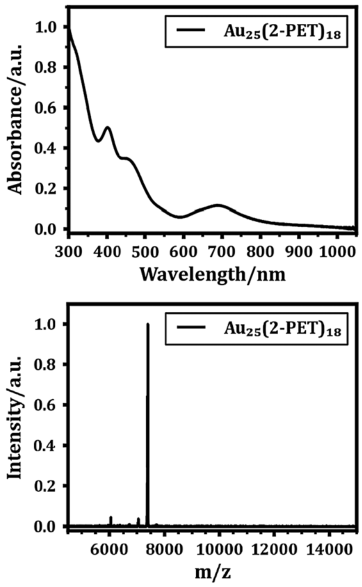

Fig. 1 UV-Vis (top) and MALDI-TOF spectra (bottom) of Au_{25}(2-PET)$_{18}$ clusters after synthesis and size-selection. The typical absorption features (400, 450 and 700 nm) and the absence of a shoulder above 700 nm indicate presence of $Au_{25}(SR)_{18}$ in its neutral form. The MALDI-TOF spectrum shows one single peak at $m/z = 7394$. The small peaks at lower masses are well-known fragments.

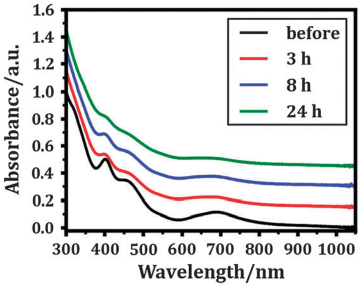

Fig. 2 UV-Vis spectra of $Au_{25}(2\text{-PET})_{18}$ prior (black) and after ligand exchange with *S*-BINAS. With increasing reaction time, the spectra are less defined, but maintain their basic features. Spectra are normalized at 300 nm and off-set for clarity.

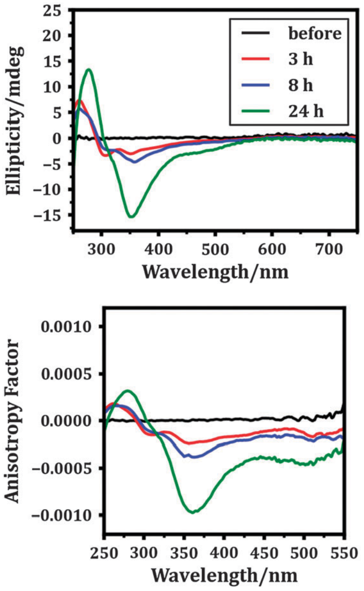

Fig. 3 CD spectra (top) and anisotropy factors (bottom) of $Au_{25}(2\text{-PET})_{18}$ clusters prior (black) and after ligand exchange with *S*-BINAS. While the unreacted cluster shows no optical activity – as expected – with extended reaction time, stronger optical activity is observed.

look very similar to those reported earlier:[15] (negative) peaks at 350 and 310 nm. At an extended reaction time (24 h), the positive feature at 260 nm is red-shifted (to 280 nm). Overall, the data seem to confirm that chiral BINAS ligands have been successfully incorporated into the ligand shell of the clusters, since no optical activity is observed prior to the reaction. The similarity in the CD spectra reported earlier and those presented here allows the conclusion that the reaction is widely repeatable (apart from the fact that a different reaction rate has to be assumed due to the change in the Au-to-BINAS ratio in the reaction). Note that the CD spectra are quite different from the ones reported for Au_{25} clusters covered by glutathione, camphorthiol or 1-methyl-2-phenylethylthiolate.[24–26] The CD spectra of the former two are quite similar. The optical activity of this cluster is thought to arise from the mixing of sulfur orbitals into the relevant cluster states.[18,27] The mixing likely depends on the orientation of the thiolates (*cis–trans*). It is therefore not surprising that the rigid BINAS induces different CD responses than monothiols.

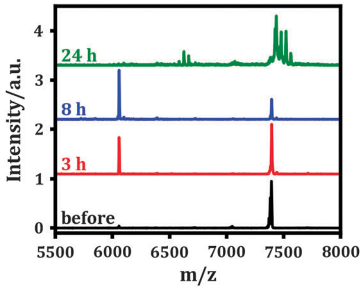

Fig. 4 MALDI-TOF mass spectra of $Au_{25}(2\text{-PET})_{18}$ clusters prior to (black) and after ligand exchange with *S*-BINAS. After a 24 h reaction time, a new set of signals with masses higher than the original cluster (m/z = 7394) is found, indicating formation of $Au_{25}(2\text{-PET})_{18-2x}(\text{BINAS})_x$. The peak at m/z = 6058 is the well-known $Au_{21}(SR)_{14}$ fragment.[29]

Based on the drastic change of the optical properties of the sample under the influence of the BINAS ligand (Fig. 3), it was concluded that the cluster decomposes.[15] It was argued that it seems unlikely that the BINAS ligand binds to the dimeric protecting units, SRAuSRAuSR, in a bidentate fashion. A similar argumentation was used to explain the limited ligand exchange between $Au_{38}(SR)_{24}$ and $Au_{40}(SR)_{24}$ clusters and BINAS.[7–9] It was argued that – in contrast to $Au_{25}(SR)_{18}$ – the exchange with $Au_{38}(SR)_{24}$ (and $Au_{40}(SR)_{24}$) is regioselective and takes place at short staples only. However, the reaction products of the exchange reaction between $Au_{25}(2\text{-PET})_{18}$ and BINAS were not assigned on a mass spectrometric basis in the earlier work. Lopez-Acevedo and Häkkinen proposed structures derived from $Au_{25}(SR)_{18}$, in which the Au_2SR_3 units are replaced by short $AuSR_2$ units.[28] The resulting structures $Au_{13}(Au_2SR_3)_{6-x}(AuSR_2)_x$ (or $Au_{25-x}(SR)_{18-x}$) should be stable and maintain their 8-electron superatomic electronic structure. The resulting derived cluster structures could likely form if BINAS binds to short staples only, leaving the Au_{13} core and the overall electronic situation intact.

In order to clarify the fate of the Au_{25} cluster after reaction with BINAS, MALDI-TOF mass spectra were measured (Fig. 4). At short reaction times, only a small fraction of clusters seems to have reacted (Fig. 5, top). Of note, a series of signals with masses higher than m/z = 7394 is found (Fig. 5, bottom). The signals have a spacing of m/z = 42. This corresponds to the mass difference between BINAS-di-thiolate and two 2-PET ligands. After a 24 h reaction time, these peaks are clearly visible. A peak at m/z = 7561 corresponds to the cluster $Au_{25}(2\text{-PET})_{10}(\text{BINAS})_4$. No signs of decomposition are found. In some of the spectra, a signal group centering at *ca.* m/z = 6630 is observed, consisting of several peaks with a m/z = 42 spacing. It is clear that the peaks above m/z = 7394 belong to intact $Au_{25}(2\text{-PET})_{18-2y}(\text{BINAS})_y$. In order to test whether the signal group at m/z = 6630 fulfils the general formula $Au_{25-x}(2\text{-PET})_{18-x-2y}(\text{BINAS})_y$ (replacement of long staples by short as proposed by Lopez-Acevedo and Häkkinen), we calculated all masses of these clusters for x = 0, 1, … 6 and y = 0, 1, … 6. However, none of these calculated masses is close to those observed in the mass spectra, indicating that the derived structures that were proposed are not formed.

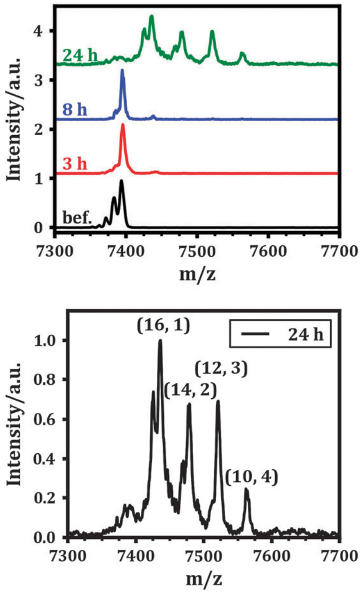

Fig. 5 Top: zoom into the MALDI-TOF mass spectra of $Au_{25}(2\text{-PET})_{18}$ before and after exchange with *S*-BINAS. The signals at m/z = 7394 are those of the unreacted Au_{25} cluster. Only very little material seems to be exchanged after 3 and 8 h. Bottom: zoom into the MALDI-TOF mass spectrum of the 24 h sample. The annotated signals have a spacing of m/z = 42, indicating bidentate binding of BINAS. The reaction products have a composition $Au_{25}(2\text{-PET})_{18-2x}(S\text{-BINAS})_x$ (x = 0–4). Notation in the figure is: (18 − 2x, x).

Instead, we consider these signals to be fragments of the $Au_{25}(2\text{-PET})_{18-2x}(\text{BINAS})_x$ clusters. It is also interesting to note that the intensity of the peaks corresponding to the distribution of the different exchange species (Fig. 5, bottom) is far from those obtained statistically. This shows that the rates of the different exchange steps are quite different.

Both Murray and Dass reported mass spectrometric studies of $Au_{25}(SR)_{18}$ clusters that were reacted with bidentate thiols.[3,14] In both studies, intact $Au_{25}(SR)_{18-2y}(\text{di-thiolate})_y$ clusters were identified. Dass and co-workers also studied the binding situation of the di-thiolate using density functional theory.[14] As result, interstaple binding was proposed to be the most favorable (this has also been proposed by Murray). In this, the di-thiolate connects to staples by binding to the central sulfur atom of one unit and one of the outer sulfur atoms of a neighboring unit, at least for certain di-thiolates. It is obvious that in this binding motif not more than six di-thiolates can be incorporated into the ligand shell of $Au_{25}(SR)_{18}$. We assume that a similar (if not the same) binding motif is found in the case of BINAS and Au_{25}. Nevertheless, there are two different interstaple binding modes possible: (a) the central atom of the first unit is connected to an outer sulfur atom of the second unit (**IBM-1**) and (b) one of the outer sulfur atoms of the first unit is connected to an outer atom of the second unit (**IBM-2**). The situation is highlighted in Fig. 6. We calculated the average anchoring position for the ligands in **IBM-1** and **IBM-2** based on the crystal structure data of $Au_{25}(2\text{-PET})_{18}$ published by Murray.[17] While the first has an average distance of *ca.* 4.05 Å, the distance increases to 5.04 Å for **IBM-2**. The sulfur–sulfur distance in BINAS is *ca.* 4.1 Å, as predicted by quantum chemical calculations.[30] This value is very close to that found for **IBM-1**.

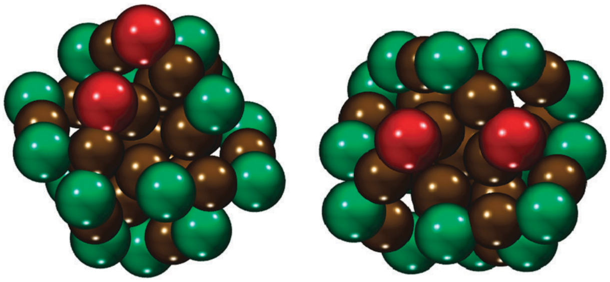

Fig. 6 Two possible binding positions for the BINAS ligand in Au_{25}: left: connection between the central sulfur atom of the first unit with an outer sulfur atom of the second unit, **IBM-1** and right: connection between the outer sulfur atoms of the two units (**IBM-2**). The respective sulfur atoms are highlighted in red. The average distance between the sulfur atoms is *ca.* 4.05 Å (**IBM-1**) and 5.05 Å (**IBM-2**).

The data presented here clearly show that $Au_{25}(SR)_{18}$ does not necessarily decompose under exposure to BINAS. It follows that the ligand can tolerate the presence of dimeric protecting units. In consequence, the interpretation of the data obtained for ligand exchange with $Au_{38}(2\text{-PET})_{24}$ may be revised:[7,8] the six dimeric units are arranged into two subgroups that form triblade fans very similar to those found in $Au_{25}(SR)_{18}$. Locally, this is very similar to $Au_{25}(SR)_{18}$ (average S–S distance for **IBM-1:** *ca.* 4.15 Å).[23] The limited exchange observed in $Au_{38}(SR)_{24}$ may be due to kinetic reasons; the reactions drastically slows down even after the first reaction step.[9]

Conclusions

In summary, we have repeated the ligand exchange reaction between $Au_{25}(2\text{-PET})_{18}$ clusters and bidentate BINAS. Our goal was to assign the reaction products using MALDI-TOF mass spectrometry. It was found that the cluster survives the exchange reaction without noticeable decomposition, although its optical properties are drastically changed. Clusters with the general formula $Au_{25}(2\text{-PET})_{18-2y}(\text{BINAS})_y$ are formed. We assume that the binding motif between the cluster and the di-thiolate is very similar to the ones proposed by Murray and Dass, that is, the bidentate thiol connects two neighboring staples (interstaple cross linking). No signs of 8-electron superatom complexes (general formula $Au_{25-x}(SR)_{18-x-2y}(\text{di-thiolate})_y$) with replaced protecting units are found.

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