Ligand Exchange on Au$_{25}$ Cluster with Chiral Thiols

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Ligand exchange on [Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$$^-$] [TOA$^+$] is studied with two chiral ligands *R/S*-BINAS and NILC/NIDC in THF with induction of metal-based optical activity. Under the applied condition the ligand exchange is only partial, showing that also within a mixed ligand shell significant optical activity can be induced. The ligand exchange resulted in the change of particle size as observed by UV−vis spectroscopy.

The study of chirality on extended metal surfaces, that is, chirality in two dimensions, is now an established field of research.[1−4] The interest in such systems is manifold ranging from the fundamental understanding of symmetry breaking over the question about the origin of homochirality to the important field of chiral technology. Chirality on subnanometer-sized metal nanoparticles is yet less known but becomes an emerging field of research partly due to the unique properties of these particles such as their molecule-like discrete electronic structures.[5−11] A promising method to impart chirality to metal nanoparticles is the adsorption of a chiral molecule, which creates a locally chiral environment near the metal surface. This may lead to a "chiral footprint" on the nonchiral (nanoparticle) surface, that is, the slight distortion of the metal surface atoms involved in the adsorbate complex toward a chiral arrangement. The adsorbed molecules may also transfer chirality onto the electronic structure of the nonchiral metal.

In terms of subnanometer metal clusters, a great attention has been given to various types of gold clusters because of its relative ease of synthesis and isolation. Various types of molecular gold clusters are already isolated such as Au$_{10}$, Au$_{15}$, Au$_{18}$, Au$_{22}$, Au$_{25}$, Au$_{29}$, Au$_{33}$, and Au$_{39}$.[12] Among them Au$_{25}$ is established to be particularly stable. Very recently several groups reported on the synthesis and crystal structure of [Au$_{25}$-(SCH$_2$CH$_2$Ph)$_{18}$$^-$] [TOA$^+$] cluster.[13−19] This cluster is composed of an icosahedral Au$_{13}$ core surrounded by staple motifs consisting of thiolates and gold atoms that are somewhat detached from the dense gold core. These motifs resemble a gold-thiolate polymer structure and were already discovered in the crystal structure of Au$_{102}$(p-mercaptobenzoic acid)$_{44}$.[20] A number of protocols have been developed for the synthesis of this interesting Au$_{25}$ cluster, but yield and purity remain a major concern. Recently, Au$_{25}$ clusters stabilized by glutathione (GSH),

a tripeptide, were found to exhibit an extraordinary stability against core etching. The crystal structure of this particular cluster is still unresolved,[21,22] but a recent NMR study on this cluster indicates a similar structure as was found for [Au$_{25}$-(SCH$_2$CH$_2$Ph)$_{18}$$^-$] [TOA$^+$].[23]

Ligand exchange is a convenient method enabling the incorporation of a molecule to these clusters in order to get the desired properties, for example, chirality.[24] It has been shown that the thiolate ligands on Au$_{25}$ clusters can be exchanged.[16] Thus, it should be possible to functionalize [Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$$^-$] [TOA$^+$] with chiral molecules by simple ligand exchange and therefore impart chirality on the molecular cluster. However, there remains the question concerning the fate of the cluster upon ligand exchange.

In this communication, we report the ligand exchange on [Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}$$^-$] [TOA$^+$] (from here on read as Au$_{25}$, unless otherwise mentioned) with two chiral molecules, viz., *R/S*-1,1′-binaphthyl-2,2′-dithiol (BINAS) and *N*-isobutyryl-L-cysteine (NILC)/*N*-isobutyryl-D-cysteine (NIDC) in THF solvent. BINAS has two thiol groups and is therefore not compatible with the structure of the staples found in [Au$_{25}$-(SCH$_2$CH$_2$Ph)$_{18}$$^-$], which consist of SR−Au−SR−Au−SR units, that is, three thiols per staple. Furthermore, within these staples the S−Au−S angle is close to linear, which cannot be achieved with one gold atom in between the two sulfur atoms of BINAS due to sterical reasons.

We have used the method developed by Murray et al. as it produces reasonable amounts of pure Au$_{25}$ clusters.[13] In a typical reaction, 256 mg (0.468 mmol) of TOAB was dissolved in dichloromethane to which was added 0.08 mL of phenylethanethiol and 0.062 mL of thiophenol (1:1 mmol ratio) using a syringe followed by 150 mg (0.381 mmol) of HAuCl$_4$·3H$_2$O dissolved in milli-Q water. The above mixture was stirred in ambient condition for 16 h, which resulted in the formation of a transparent light yellow color polymer and then added 155 mg (4.0 mmol) of NaBH$_4$ dissolved in milli-Q water all at once. Immediately after borohydride treatment, the solution changed to yellow color and finally to deep brown. The resulting mixture was kept stirring for 24 h for complete reduction. The solution

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SCHEME 1
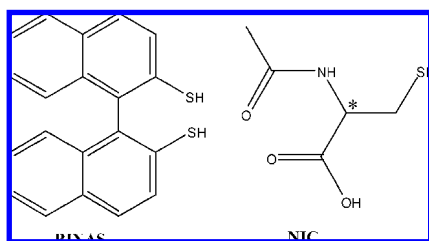
was next dried by rotary evaporation to remove the majority of the dichloromethane and precipitated thrice with ethanol. The precipitates were filtered with a 0.2 μm PTFE membrane. After the second and third precipitation with ethanol, the precipitate did not show any band in the UV−vis spectrum characteristic of Au$_{25}$, whereas the orange-yellow supernatant showed the characteristic bands of Au$_{25}$. The reaction described above lead to a mixture of Au$_{25}$ and other gold clusters. An easy way to extract the Au$_{25}$ from the mixture was repeated precipitation with ethanol and collecting the supernatant. Practically, only two precipitations were sufficient to extract the Au$_{25}$ from the mixture. Interestingly, the crystal structure of the Au$_{25}$ prepared according to this procedure shows that the cluster is capped with phenylethanethiol while thiophenol was not observed.[13]

For the ligand exchange reaction, about 1.0 mg of Au$_{25}$ was treated separately with 3.86 mg of *R/S*-BINAS and 2.32 mg of NILC/NIDC (corresponding to a 5-fold excess of the incoming ligand), respectively in 2 mL of THF under argon atmosphere. The reaction mixture was kept stirring in a closed vessel under argon for 5 h, during which the yellow-orange colored solution changed to yellow-green. The resultant solution was then ultracentrifuged (MWCO 5000 DA membrane filter) and washed with THF repeatedly to free from the excess ligand. The resultant residue after filtration was dissolved in an equivalent amount of THF for spectral characterization.

The chemical structure of chiral molecules BINAS and NIC is shown in Scheme 1. The two molecules are completely different from each other both in terms of structure as well as concerning their optical activity. Thus, the induced chirality on Au$_{25}$ with these two ligands was anticipated to be quite different. The CD spectrum of the reaction product after 2 h of exchange

showed the peaks of the neat ligands but the absence of any optical activity due to metal-based transitions. Also the color of the solution remained unchanged and the UV−vis spectrum showed the band of Au$_{25}$ and of free ligands after 2 h. After 5 h reaction time, an optical activity was observed and the color of the solution was changed.

Figure 1A shows the CD spectrum of Au$_{25}$ before ligand exchange. As expected this cluster is optically inactive. Upon exchange with BINAS, intense bands at 305, 352, and 390 nm are observed in the CD spectra with opposite sign for clusters covered by the enantiomers of BINAS. These CD spectra are considerably different from the one of free BINAS, which shows CD signals below 310 nm.[9] The appearance of CD bands above 310 nm in Figure 1A is a clear indication of metal based optical activity, which arises due to the exchange of achiral PhCH$_2$CH$_2$S by chiral BINAS on the Au$_{25}$ cluster. As observed previously for gold nanoparticles directly prepared in presence of BINAS, the *R* and the *S* enantiomers lead to positive and negative bands, respectively.[9] Figure 1B shows the corresponding UV−vis spectra of Au$_{25}$ before and after exchange with BINAS. The spectrum before ligand exchange is characteristic of Au$_{25}$ with bands at 400, 450, and 670 nm as reported previously by various groups.[14,15,22,25,26] But after exchange with BINAS, the characteristic bands for Au$_{25}$ vanish and a new band at ∼600 nm is observed. This goes hand in hand with a change of the color of the solution from yellow-orange to yellow-green and a slight blue shift of the absorption onset. Particularly the latter observation is clear indication for the formation of smaller clusters[8,12] by removal of some of the gold atoms from Au$_{25}$ as will be discussed later.

To demonstrate that the metal-based optical activity is ligand dependent, another chiral ligand NILC/NIDC was used under identical reaction conditions. Figure 2A shows the CD spectra of Au$_{25}$ before and after exchange with *N*-isobutyryl-cysteine (NIC). The CD spectra show the development of optical activity with a mirror image relationship for the two enantiomers with bands at 318, 362, and 400 nm. Again these CD spectra are different from the ones of neat NIC but bear some similarity with those of Au$_{15}$(NIC)$_{13}$.[8] Also, the CD spectra are totally different from the ones obtained by the exchange with BINAS. This shows that the optical activity in the gold cluster is ligand dependent. Figure 2B shows the corresponding UV−vis spectra
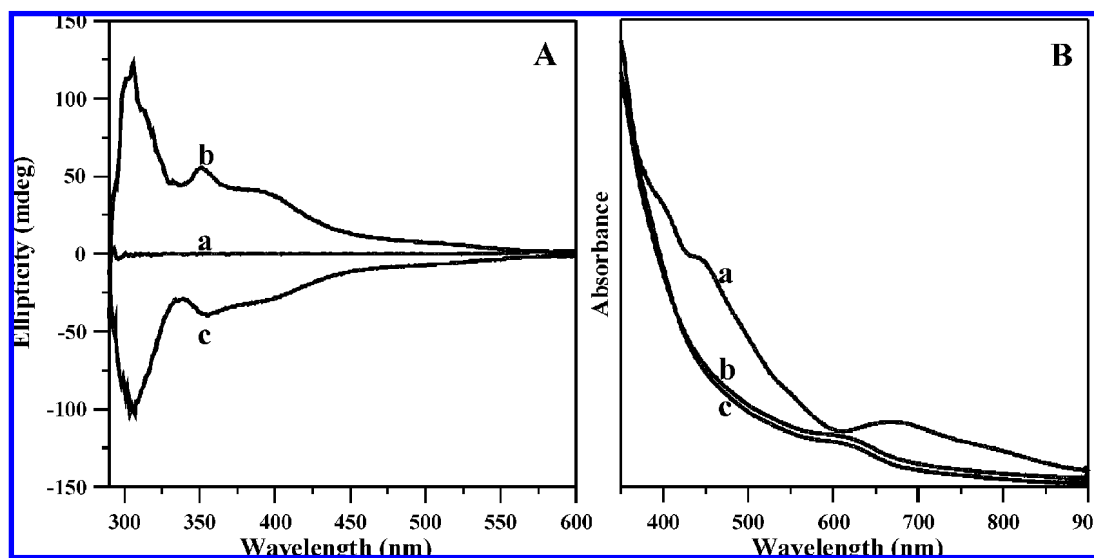

Figure 1. (A) CD spectra of Au$_{25}$ (a) before exchange with *R/S*-BINAS, (b) after exchange with *R*-BINAS, and (c) after exchange with *S*-BINAS; (B) UV−vis absorption spectra of the corresponding samples.
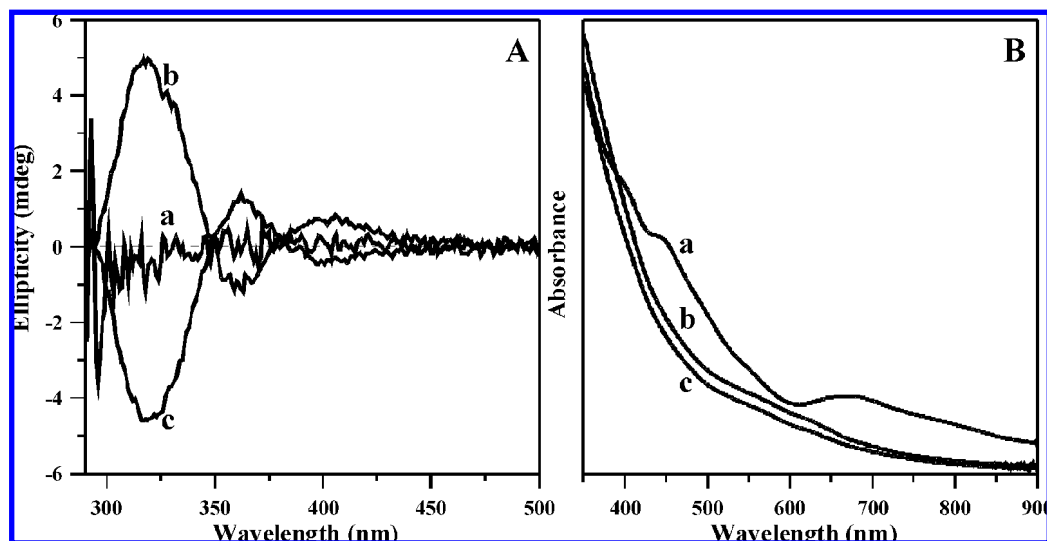
Figure 2. (A) CD spectra of Au$_{25}$ (a) before exchange with NILC/NIDC, (b) after exchange with NILC, and (c) after exchange with NIDC; (B) UV−vis absorption spectra of the corresponding samples.
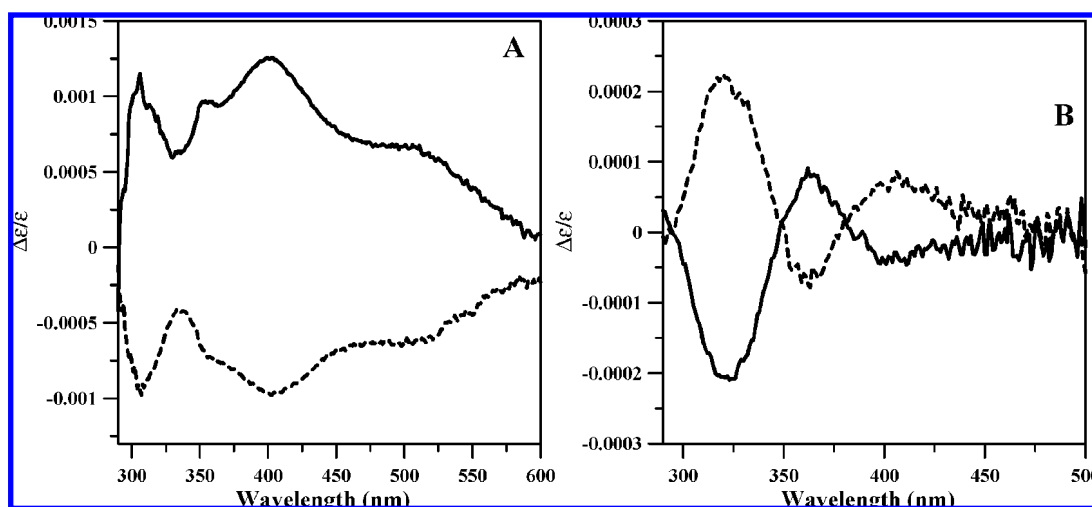

Figure 3. (A) Anisotropy factor of Au$_{25}$ after exchange with *R*-BINAS (solid line) and *S*-BINAS (dashed line); (B) Anisotropy factor of Au$_{25}$ after exchange with NILC (dashed line) and NIDC (solid line).

of the Au$_{25}$ cluster before and after exchange with NIC. The spectra alter upon ligand exchange indicating the formation of clusters of different size. In both cases discussed above, the spectra indicate that there is some chemical modification of the Au$_{25}$ cluster in presence of excess incoming ligands (BINAS and NIC). It should be noted that the resulting clusters are stable for at least some days as evidenced by constant UV−vis spectra and optical activity.

By comparison of Figure 1 and Figure 2, it becomes obvious that the extent of optical activity is clearly larger after exchange with BINAS compared to exchange with NIC. In order to quantitatively support the difference between the induced optical activity by BINAS and NIC, the anisotropy factor ($\Delta A/A$) was calculated and is given in Figure 3. The maximum anisotropy factor induced by BINAS is more than five times larger than the one induced by NIC. This result can be compared to the reported anisotropy ratios for size-selected NIC- and BINAS-stabilized gold particles of the same size range that were prepared directly with the respective thiol.[27] There it was also found that BINAS-stabilized gold nanoparticles showed considerably stronger anisotropy ratio. This shows that BINAS is particularly suitable to impart optical activity to gold nanoparticles. Interestingly, both for the BINAS and NIC case the

anisotropy factor was reported to be larger by a factor of 2.5 to 3 for the particles directly prepared with the respective thiols compared to the exchange method reported here. This may indicate that under the conditions applied here the ligand exchange is not complete (see later). It should be noted that the extent of the ligand exchange may also be different in the two cases. However, the observation that the color change occurred within about the same time after addition of the ligand, indicates that the ligand exchange rates are not completely different for the two systems.

The change in the UV−vis spectra strongly indicates that during the ligand exchange the size of the cluster is changing and that smaller clusters are formed. In contrast, there are reports on the chemical etching of Au$_{25}$GSH$_{18}$ (gold-glutathione) cluster with free glutathione, in which it was found that Au$_{25}$GSH$_{18}$ exhibits an extraordinary stability against core etching.[21,22] This may be because GSH is quite bulky and therefore better able to shield the gold core. On the other hand, the change in size observed here may be connected to the higher affinity of BINAS and NIC to gold compared to HSCH$_2$CH$_2$Ph. In fact, the thiols used here have more than one possibility to interact with gold (BINAS, two thiols; NIC, thiol and acid group).

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The recently reported crystal structure of [Au$_{25}$-(SCH$_2$CH$_2$Ph)$_{18}^-$] [TOA$^+$][13] by Murray and co-workers may give some hint about possible mechanisms of the core etching. Three types of gold atoms were found; one is at the center, 12 form the vertices of the icosahedron around the central atom, and the remaining 12 gold atoms are stellated on 12 of the 20 faces of the Au$_{13}$ icosahedron. The icosahedral Au$_{13}$ core is protected by six (−SR−Au−SR−Au−SR−) oligomers. Two sulfur environments are observed in the structure, 6 sulfur atoms are in the middle of the oligomers, and 12 are located at their ends. The excess ligands in solution may thus break these oligomeric −SR−Au−SR−Au−SR− bridging molecules and bind to the remaining Au structure. This may be the reason for the formation of smaller clusters. Furthermore, during washing the supernatant showed light yellow color, which may arise from gold cluster fragments originating from Au$_{25}$ or Au(I)−SR oligomers that might be formed during the ligand exchange. These species are very small and easily passed through the membrane filter.

Recently, the ligand exchange reaction of the same Au$_{25}$ cluster as we used in this study by hexanethiol and thiophenol was studied by mass spectrometry.[16] For partially exchanged particles a relatively broad distribution of composition was found in both cases. This means that not only one compound Au$_{25}$N$_x$M$_{18-x}$ (with only one value of x) was found, where N and M are the incoming and exchangeable ligands, respectively, but also other species (with different values of x). In fact, distributions containing up to about nine different compositions were detected. It was furthermore found that the exchange is relatively slow and depends on the nanoparticle concentration and the ratio between incoming and exchangeable thiol ligands. For example, at a nanoparticle concentration of 2 mg/mL and a ratio of 3:1 (incoming/exchangeable ligands) it took about eight hours to exchange about seven thiolates. After 24 h, the exchange reaction was still not complete. On the basis of this study, it is relatively safe to assume the following: (i) After five hours of exchange at a ratio of 5:1 (incoming/exchangeable ligands), not all the ligands are exchanged, that is, we deal with a mixed ligand layer. (ii) A distribution of particles with different composition (different number of exchanged ligands) is obtained. In addition, as shown above, ligand exchange also leads to smaller clusters. Considering these points, it is surprising that still quite strong CD signals can be observed. This is an indication that only a few chiral ligands are needed to induce significant optical activity in the metal-based electronic transitions of such small gold particles.

In conclusion, ligand exchange on [Au$_{25}$(SCH$_2$CH$_2$Ph)$_{18}^-$]-[TOA$^+$] was performed with two chiral ligands *R/S*-BINAS and NILC/NIDC in THF with induction of metal-based optical activity. The CD spectra were completely different for the two thiols. Under the applied condition the ligand exchange was only partial, showing that also within a mixed ligand shell significant optical activity can be induced. The observations are consistent with a chiral footprint model, where the chiral ligands impart a chiral footprint onto the particle surface. The ligand exchange resulted in the change of particle size as observed by UV−vis spectroscopy.

References and Notes

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