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Chiroptical Properties of Intrinsically Chiral Thiolate-protected Gold Clusters

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Abstract: Chiral thiolate-protected gold clusters of atomic precision have gained increasing interest in recent years due to their potential use in catalysis, sensing or bioapplications. While the protection of gold clusters with chiral ligands is a rather trivial task, it was found that the clusters can bear intrinsically chiral features, most obvious in the arrangement of the protecting ligands on the surface of the cluster. Recent efforts showed the separation of the enantiomers of such intrinsically chiral gold clusters. This technique can be used for the prediction of chirality in structurally unknown clusters. Activation barriers for the racemization of $Au_{38}(SR)_{24}$ were determined. As this involves a huge rearrangement of the ligands, the flexibility of the gold-thiolate interface is demonstrated. Furthermore, the ligand exchange reactions between intrinsically chiral clusters and bidentate chiral thiols were studied. A limited, regioselective exchange was found. Most importantly, the reaction is diastereoselective and allows tailoring of gold clusters that are protected with a defined layer of ligands.

Keywords: Circular dichroism · Gold clusters · Nanoparticles · Stereochemistry

1. Introduction

Ligand-protected gold clusters with the general formula $Au_m(SR)_n$ (SR: thiolate, 10 < m < 200) have attracted significant interest in recent years.[1] Their interesting, strongly size-dependent behavior allows their properties to be tailored for application in catalysis[2] and sensing.[3] Moreover, the clusters are an ideal system for theoretical studies and the gold-thiolate interface bears certain resemblance to self-assembled monolayers.[1b,4] Compared to the latter, clusters are solution-based model systems that allow a broader range of characterization methods.

The field was born in 1994, when Brust *et al.* published a short communication on the synthesis of monolayer-protected gold nanoparticles.[5] The nanoparticles have typical diameters of 1–3 nm and their properties differ drastically from colloids gained from the Turkevich method (*e.g.* absence of a localized surface plasmon resonance).[6] It was soon realized that this new class of gold nanoparticles has strong, molecule-like properties and only certain sizes are formed.[7] Detailed theoretical analysis showed that the nanoclusters can be treated using a modified jellium model, which explains both electronic and geometric structure and stability of certain sizes.[8]

Chirality, on the other hand, is one of the most investigated fields of chemical research. It is ubiquitous in biological systems. Asymmetric synthesis is of paramount importance for drug design and triggers the development of chiral catalysts. Chirality in nanostructures also became important in the metamaterials and optics community.[9] It was found that chirality can be bestowed onto gold nanoclusters by protection with chiral ligands.[10] Moreover, crystal structure determination revealed that gold clusters can bear intrinsic chirality that does not require the use of chiral protecting ligands.[11] Given the tunability of properties in thiolate-protected gold clusters (*e.g.* solubility depending on the polarity of the ligand) and the development of synthetic routes towards monodisperse gold clusters,[1a-c] the chirality of such systems has gained ever-increasing attention.[10b]

This review seeks to discuss the recent progress made in the field of chiral thiolate-protected gold clusters. Emphasis will be placed on the structures and (chiroptical) properties of intrinsically chiral clusters. A second focus is ligand-exchange reactions introducing chiral thiolate ligands into the ligand shell of the clusters.

2. Crystal Structures of Thiolate-protected Gold Clusters

A milestone in the development of the field and understanding of thiolate-protected gold clusters was made in 2007, when Jadzinsky *et al.* presented the first total structure determination of the $Au_{102}(p\text{-}MBA)_{44}$ cluster (*p*-MBA: *para*-mercaptobenzoic acid).[11a] The structure confirms a prediction made in 2006: the interface between the gold cluster and the thiolate ligands exhibits bridged binding motifs (‘divide-and-protect’), in which Au atoms are stabilized between two sulfur atoms.[12] The motifs, coined ‘staple motifs’, occur in monomeric (SR-Au-SR) and dimeric (SR-Au-SR-Au-SR) fashions. It should be noted that the organic backbones of the ligands can in principle adopt different relative configurations (*cis/trans*) with respect to the S-Au-S bonds. The sulfur atoms become stereogenic centers. A similar situation was found in self-assembled monolayers of thiolates on Au(111) surfaces.[13]

The Au_{102} cluster consists of a Au_{79} core, which is protected by 21 staple motifs, of which two are dimeric and nineteen are monomeric. Interestingly, the units are arranged in a chiral fashion. Since the protecting ligand is achiral, both enantiomers are found in the unit cell and the compound is racemic.

The seminal crystal structure of $Au_{102}(p\text{-}MBA)_{44}$ was closely followed by the structure of $[Au_{25}(2\text{-}PET)_{18}]^{-1/0}$ (2-PET: 2-phenyethylthiolate, $\text{-}SCH_2CH_2Ph$).[8e,14] The Au_{25} cluster is not intrinsically chiral,

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but deserves brief discussion due to its prominence. The anionic cluster consists of an $(\mathrm{Au}_{13})^-$ icosahedron which is protected by six long staples. The units form two triblade fans of three staples each, which intertwine and have opposite handedness. This creates a center of inversion. In the anionic form, the counterion imposes some distortions to the structure, whereas the charge-neutral form is distortion-free.[14c]

Jin and coworkers presented the crystal structure of $\mathrm{Au}_{38}(\text{2-PET})_{24}$ in 2010 (Fig. 1).[11b] The structure was correctly predicted by Lopez-Acevedo *et al.*,[15] which differed from a previously reported prediction by Pei *et al.*, who presented an achiral isomer.[16] $\mathrm{Au}_{38}(\mathrm{SR})_{24}$ is composed of an Au_{23} core and is protected by six long and three short staples. The core is a face-fused bi-icosahedron and the three short staples are arranged along the equator of the core. The six dimeric units are split into two subgroups of triblade fans of the same handedness and protect the polar sites of the core. The unit cell of the crystal contains both enantiomers of the cluster. In the following, the left-handed enantiomer of the cluster will be termed *A*-$\mathrm{Au}_{38}(\mathrm{SR})_{24}$ (*A*: anticlockwise) and the right-handed enantiomer *C*-$\mathrm{Au}_{38}(\mathrm{SR})_{24}$ (*C*: clockwise).

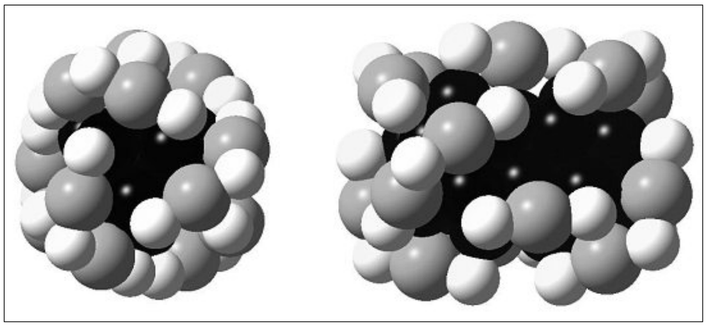

Fig. 1. Structure of $\mathrm{Au}_{38}(\text{2-PET})_{24}$ in top (left) and side (right) view. The $-\mathrm{CH}_2\mathrm{CH}_2\mathrm{Ph}$ groups have been removed for clarity. Black: $\mathrm{Au}_{\mathrm{Core}}$, grey: $\mathrm{Au}_{\mathrm{Adatom}}$, white: sulfur. The presented structure is the left-handed enantiomer.

3. Chirality and Chiroptical Spectroscopy of Thiolate-protected Gold Clusters

The protection of gold clusters with chiral thiolates leads to strong responses in the circular dichroism (CD) spectra. This was first established in 1998[10a] and since then, several studies of different ligand types have been carried out.[17] The shape and strength of the CD spectra is both size-and ligand-dependent. As in other chiral compounds, enantiomeric ligands induce mirror-imaged CD spectra.[10b] Conformational analysis of the ligand is possible using vibrational circular dichroism.[17c,18] While the database of CD spectra of clusters with different size and chiral ligands is still scarce, it is difficult to compare the influence of ligands on the chiroptical properties of a cluster of given size. An example is the $\mathrm{Au}_{25}(\mathrm{SR})_{18}$ cluster. While the CD spectra of Au_{25} protected with L-glutathionate (L-SG) and camphor-10-thiolate are quite similar,[10a,17g] strong differences were found for the spectrum of $[\mathrm{Au}_{25}(\mathrm{pet}^*)_{18}]^-$ (pet*: 2-methyl-2-phenylethylthiolate).[17f] This may be ascribed to the induction of absolute configuration at the sulfur atoms of the protecting staples, which may be similar for camphorthiolate and L-SG, but different for pet*.[17g] Experimental verification of this interpretation is lacking, however.

4. Chiroptical Properties of Intrinsically Chiral Gold Clusters

While it is confirmed that chirality can be an intrinsic property of thiolate-protected gold clusters,[11] their CD spectra remained unknown since the compounds were gained as racemates and resolution of enantiomers or asymmetric synthesis of the clusters were not available. A NMR study showed that it is possible to probe the chirality of $\mathrm{Au}_{38}(\text{2-PET})_{24}$ using the diastereotopicity of the methylene group protons in the ligands.[19] However, it should be noted that the analysis of the NMR spectra was based on the knowledge of the structure of $\mathrm{Au}_{38}(\mathrm{SR})_{24}$. The assignment of handedness is not possible and prediction of chirality in clusters of unknown structure is difficult, since the different chemical shifts might stem from different chemical environments of the ligands. For instance, NMR analysis of ligand-symmetry equivalence has been presented by Wong *et al.*[20]

Motivated by the findings of intrinsic chirality in thiolate-protected gold clusters, a chiral HPLC method was developed that allowed us to separate the enantiomers of Au_{38} clusters.[21] The method allows near baseline separation of the enantiomers. Both peaks show the same (characteristic) absorption spectra of $\mathrm{Au}_{38}(\text{2-PET})_{24}$ and are optically active. While the chirality of $\mathrm{Au}_{38}(\mathrm{SR})_{24}$ is no mystery, the $\mathrm{Au}_{40}(\mathrm{SR})_{24}$ cluster is structurally unknown.[22] A variation of the HPLC method allows the separation of the cluster into two different fractions, which both show optical activity with mirror-image relationship.[23] This is the first example in which experimental results suggest intrinsic chirality, most likely due to the arrangement of the protecting ligands as in Au_{38} and Au_{102}. The isolated enantiomers of $\mathrm{Au}_{38}(\text{2-PET})_{24}$ and $\mathrm{Au}_{40}(\text{2-PET})_{24}$ show strong optical activity (Fig. 2). For Au_{40}, the CD spectra give detailed insight into the electronic structure of the cluster as compared to the rather featureless absorption spectrum.[23]

Assignment of handedness is possible for the enantiomers of $\mathrm{Au}_{38}(\text{2-PET})_{24}$. Lopez-Acevedo *et al.* presented simulated CD spectra for the right-handed isomer.[15] Comparison with experiment shows that the enantiomer eluting last from the HPLC column matches the simulated spectrum in sign and transition energies (Fig. 3a). Previously reported CD spectra of $\mathrm{Au}_{38}(\text{L-SG})_{24}$ bear great resemblance to the CD spectrum of *C*-$\mathrm{Au}_{38}(\text{2-PET})_{24}$, which indicates that synthesis of gold clusters using chiral ligands is diastereoselective.[24] It seems that the chiral L-SG ligand has minor influence on the spectral properties of Au_{38} and that the CD spectrum is dominated by the chiral arrangement of the protecting ligands (Fig. 3b and 3c).

The fact that the enantiomers of Au_{38} and Au_{40} can be separated and characterized at ambient conditions raises the question of their stability against inversion. The behavior of enantiopure Au_{38} was studied at elevated temperatures and a significant decrease in optical activity was observed

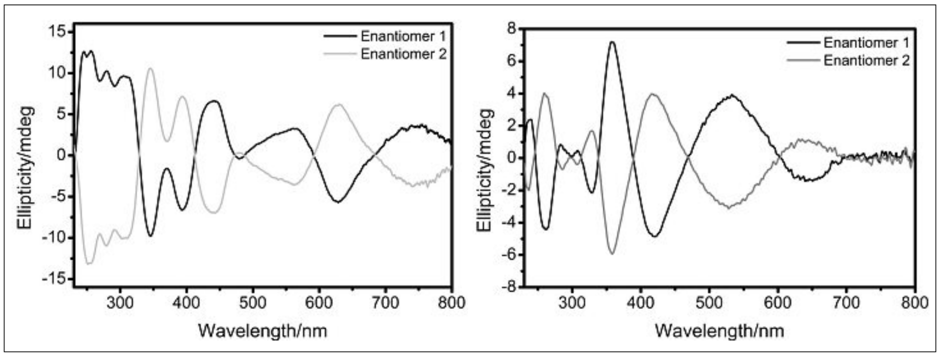

Fig. 2. CD spectra of $\mathrm{Au}_{38}(\text{2-PET})_{24}$ (left) and $\mathrm{Au}_{40}(\text{2-PET})_{24}$ (right). The black traces are the spectra of the enantiomer eluting first, the gray traces correspond to the enantiomer eluting last from the HPLC column.

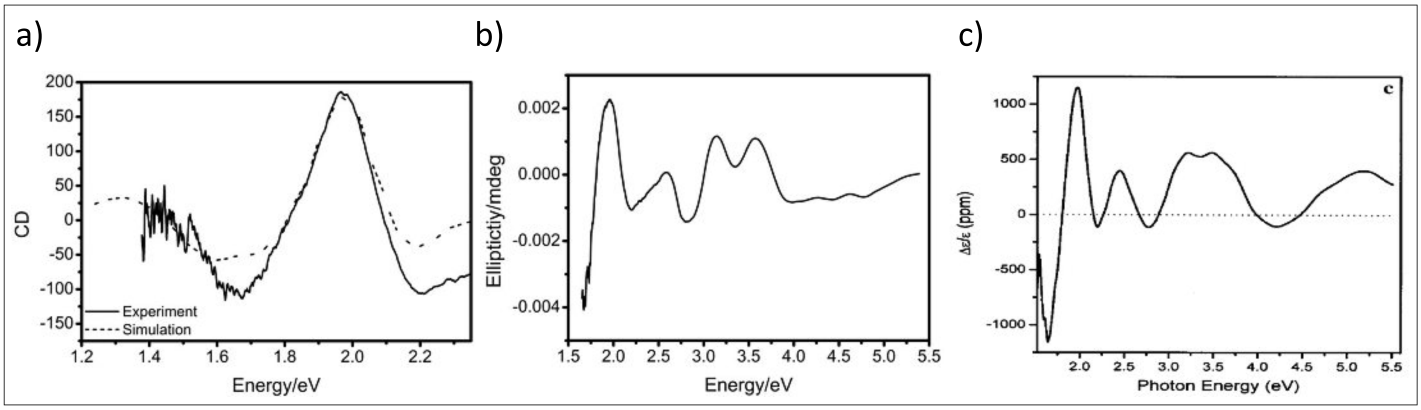

Fig. 3. a) CD spectrum of the enantiomer of $Au_{38}(2\text{-}PET)_{24}$ that elutes last from the column[21] in comparison with a computed spectrum of *C*-$Au_{38}(SCH_3)_{24}$.[15] The good match allows assignment of handedness. b) CD spectrum of *C*-$Au_{38}(2\text{-}PET)_{24}$ in eV. c) CD spectrum of Au_{38}(L-SG)$_{24}$. Reprinted with permission from ref. [24]. Copyright (2000) American Chemical Society. Comparison of b) and c) reveals the minor influence of the chiral L-SG ligand on the spectral properties (contribution of L-SG in the UV).

within minutes at temperatures above 70 °C.[25] HPLC control showed that the cluster is converted into its enantiomer without decomposition. The activation barrier for the racemization was determined to be *ca.* 28.1 kcal/mol. This value is surprisingly low bearing in mind that typical Au–S binding energies are in the range of 50 kcal/mol and several bonds have to be rearranged.[26] Two possible mechanisms were suggested. Most importantly, the low activation barrier highlights the flexibility of the gold-thiolate interface.

5. Ligand Exchange Reactions with Chiral Thiols

The post-synthetic exchange of ligands is a commonly used technique to introduce functionalities into clusters. The clusters are treated with an excess of incoming thiols and successful exchange is indicated by a change of properties, most obvious in the MALDI mass spectra of the cluster. Other changing properties include solubility, electrochemical gaps,[27] spectral properties,[28] liquid crystalline behavior,[17e,29] *etc.* The introduction of chiral ligands into (intrinsically achiral or racemic) clusters that are protected with achiral ligands leads to the induction of Cotton effects to the cluster.[30]

Well-defined clusters protected by 2-PET were exposed to chiral 1,1'-binaphthyl-2,2'-dithiol (BINAS) and place exchange reactions were monitored with MALDI mass spectrometry.[30,31] Two important findings were made: i) The incoming BINAS ligand replaces two of the leaving 2-PET ligands. No monodentate binding of BINAS was found in the mass spectra. ii) For $Au_{38}(SR)_{24}$, the exchange stops at incorporation of three BINAS ligands. Since $Au_{38}(SR)_{24}$ contains three monomeric staples this finding indicates that BINAS exchanges selectively at monomeric staples. This is further supported by experiments with Au_{25}.[32] The latter cluster contains only dimeric staples and seems to decompose when interacting with BINAS. This finding could be used for the determination of structural parameters: Exchange experiments with BINAS on $Au_{40}(2\text{-}PET)_{24}$ suggest presence of six monomeric staples (exchange up to six BINAS ligands).[30,31] This would mean that a Au_{26} core is protected with six monomeric and four dimeric units.

Taking into account that the $Au_{40}(2\text{-}PET)_{24}$ cluster can be split into two enantiomeric species with strong optical activity using chiral HPLC[23] and considering new transmission electron microscopy measurements (that suggest an aspect ratio of 2:1 for the core),[33] a structure was proposed based on DFT calculations.[34] The proposed structure consists of a dimer of Au_{13} icosahedrons in edge-to-edge contact with an angle of 90°. The core is protected by six monomeric and four dimeric units, which are arranged in a chiral fashion. Of note, the 16-electron cluster can be interpreted as a dimer of 8-electron superatoms in the sense of the superatom complex model.[8a,c,d,35] The simulated UV-Vis and CD spectra of the minimum energy isomer are in good agreement with experimental data. The cluster serves as an example of a previously unknown type of cluster materials, in which superatomic units serve as building blocks.

The chiral BINAS ligand induces strong Cotton effects onto the racemic mixture of the Au_{38} and Au_{40} clusters.[30,31] A detailed analysis showed that the evolution of optical activity in $Au_{38}(2\text{-}PET)_{24\text{-}2x}(BINAS)_x$ and $Au_{40}(2\text{-}PET)_{24\text{-}2x}(BINAS)_x$ follows a nonlinear curve with respect to the average number of BINAS ligands found in the samples.[31] The interpretation of these effects is not trivial due to the presence of several species contributing to the optical activity in different ways. One possibility for the observed nonlinearity may be diastereoselective ligand exchange in which a BINAS ligand of given handedness shows preference for one of the two enantiomers of the racemic clusters.

A diastereoselective ligand exchange reaction was demonstrated on pure *rac*-$Au_{38}(2\text{-}PET)_{24}$ clusters which were reacted with *R*-BINAS.[36] The reaction was monitored *in situ* with HPLC and the rate constants were determined for both enantiomers of Au_{38}. It was found that *R*-BINAS reacts faster with *A*-$Au_{38}(2\text{-}PET)_{24}$ (*ca.* four times faster than with *C*-$Au_{38}(2\text{-}PET)_{24}$, Fig. 4). The substituted diastereomers are deactivated for further exchange (six times slower for the left-handed clusters, not interpretable for the right-handed ones). It should be noted that the observations discuss the kinetics of the reaction and do not allow conclusions on the relative stability of the diastereomers. Isolation of the diastereomeric products from the reaction mixture using HPLC was not possible so far, since the peaks of the individual species overlap in the HPL chromatograms (this does not majorly affect the kinetic analysis). However, the method should in principle allow the isolation of clusters with defined mixed-ligand shells (number of ligands exchanged, regioselectivity and control over stereochemistry).

6. Conclusions and Outlook

In summary, recent years have seen strong progress in the understanding of the chirality of thiolate-protected clusters. The crystal structures of Au_{38} and Au_{102} revealed intrinsic chirality of the clusters which does not require chiral ligands. Separation of the enantiomers of Au_{38} is possible. In a similar manner, enantiomers of $Au_{40}(SR)_{24}$ clusters were obtained, demonstrating intrinsic chirality of this cluster of unknown structure. The racemization

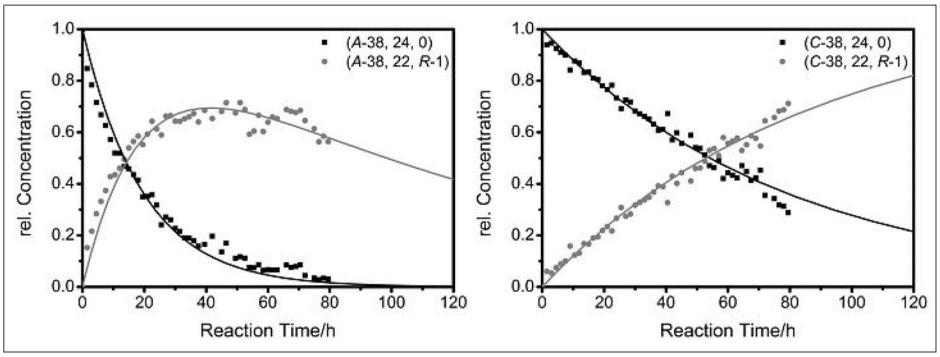

Fig. 4. Relative concentrations of the unexchanged enantiomers of Au_{38}(2-PET)$_{24}$ (black dots) in comparison with the species containing one *R*-BINAS ligand (gray dots). The plot on the left is for the left-handed clusters, the plot on the right corresponds to the right-handed clusters. The left-handed cluster reacts about four times faster than the right-handed one. The left-handed cluster proceeds to react with BINAS, as indicated by the decrease of the concentration of *A*-Au_{38}(2-PET)$_{22}$(*R*-BINAS)$_1$ after about 40 h of reaction time.

barrier of $Au_{38}(SR)_{24}$ was determined to be 28.1 kcal/mol, which is low compared to typical Au–S bond energies. The results demonstrate the high flexibility of the gold-thiolate interface, which will have implications on catalytic activity and fundamental understanding. Ligand exchange experiments between chiral ligands and Au_{38}/Au_{40} demonstrate a regioselective exchange using bidentate BINAS. The reaction is diastereoselective when Au_{38}(2-PET)$_{24}$ is reacted with BINAS. This allows the synthesis and isolation of chiral gold clusters with tailored ligand layers for applications in catalysis and sensing.

Future work should be assigned to answering the question whether or not chirality is a ubiquitous feature of thiolate-protected gold clusters. The racemization barriers of other cluster sizes should be determined and experimental and theoretical effort should be put towards a deeper understanding of the flexibility of the ligand layer. This is a prerequisite for tailoring properties of clusters for applications. Site- and diastereoselective ligand exchange reactions should be investigated in order to yield nanomaterials with defined mixed ligand layers. Catalytic activity should be tested.

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