Ligand dependence of the synthetic approach and chiroptical properties of a magic cluster protected with a bicyclic chiral thiolate

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Chiral gold clusters stabilised by enantiopure thiols were prepared, size-selected and characterised by circular dichroism and mass spectrometry. The product distribution is found to be ligand dependent. Au_{25} clusters protected with camphorthiol show clear resemblance of their chiroptical properties with their glutathionate analogue.

Thiolate-protected gold clusters (<200 Au atoms) have recently become an intensively studied field. Their optical, magnetic and electrochemical properties differ widely from bigger nanoparticles (>2 nm) that exhibit surface plasmon resonances.1 Whereas the general properties (optical spectrum, electronic structure) of selected clusters (e.g. Au_{25}(SR)$_{18}$, Au$_{38}$(SR)$_{24}$: SR: thiolate) are well-understood, their chiroptical properties are barely studied. Several examples of chiral gold nanoclusters have been presented in the past2–8 and successful synthesis of chiral Au$_{25}$(SR)$_{18}$. Therefore, the observed optical activity has to be linked to the chirality of the adsorbed thiolates (SR).

A reasonable explanation for the observed optical activity in the Au$_{25}$(SR)$_{18}$ system is the mixing of sulfur orbitals into the states involved in the respective transitions.2 Surprisingly, the only two available CD spectra of Au$_{25}$(SR)$_{18}$, where SR is glutathionate3 and 2-methyl-2-phenylethylthiolate,2 respectively, are quite different, whereas their absorption spectrum is very similar. In order to understand the subtle effect of the ligand on the optical activity we considered a different ligand system.

We hereby present the synthesis of a novel camphor-10-thiolate-protected gold cluster system (in the following Au$_{25}$(CamS)$_{18}$). A one-phase size-focusing approach was used which yields Au$_{25}$(CamS)$_{18}$ as a major product (along with others, see below).17,18

The crude reaction mixture was size-separated using gel permeation chromatography (GPC).8,19 The isolated fractions were characterised by MALDI mass spectrometry, UV-Vis spectroscopy and Electronic Circular Dichroism (CD). In a similar approach, we used 1-phenylethylthiol (1-PET, Scheme 1). This ligand yields a polydisperse mixture of clusters, showing that the success of the one-phase approach towards Au$_{25}$ is a strongly ligand-dependent process.

The ligands were prepared according to published protocols (details in the ESI†).20,21 The bicyclic structure of camphorthiol contains two fixed stereogenic centres. 1-PET is a structural isomer of the widely used 2-phenylethylthiol. The applied one-phase approach avoids the use of phase transfer reagents such as TOAB, which are difficult to remove from the product. It was shown in earlier studies that the approach yields pure Au$_{25}$(SR)$_{18}$ clusters using simple alkanethiol ligands.17,18

In the camphorthiol case we gained a mixture of clusters of different sizes. GPC separation yielded three fractions labelled as 1, 2 and 3 according to increasing elution times (decreasing hydrodynamic volume). The UV–Vis spectrum of fraction 2 is in accordance to those reported for Au$_{25}$ clusters. The spectra of fractions 1 and 3 are featureless and do not allow direct assignment of the cluster sizes (ESI†).

![Scheme 1](image)  

**Scheme 1** Structures of 1S,4R-camphorthiol (left) and S-1-phenylethylthiol (right).
MALDI mass spectra of the isolated fractions were measured using DCTB as matrix (spectrum of fraction 2 in Fig. 1, top). Fraction 1 is—in agreement with the UV-Vis spectra—a polydisperse mixture of particles heavier than Au25. The mass range (11,000–20,000 Da) indicates clusters composed of 38 to 100 Au atoms. A detailed assignment of the signals is hard to achieve as fragment peaks overlap with signals of unfragmented clusters. The mass spectrum of fraction 2 shows only one major signal, assigned to Au25 (calcd. 8223 Da), as expected from the UV–Vis spectra. However, the mass found is slightly higher than expected (8260 Da, internal calibration done with addition of Au25-(2-PET)18, Au38(2-PET)24 and Au40(2-PET)24, 2-PET: phenylethylthiolate). Upon reduction of gold with sodium borohydride, the keto-group in the camphorthiol ligand might have been reduced, leading to an increase in mass (calcd. 8260 Da). The spectra are highly reproducible between different reaction batches, regardless of enantiomeric purity of the ligand (the racemic ligand gives a similar size distribution). Slightly different synthesis conditions may explain the slight shift towards higher average mass in the S-1-PET batch (Fig. 2, top). We attempted to size-select the clusters with GPC but no significant separation was achieved probably due to the quasi-continuous size-distribution of the clusters. The fact that no Au25 was found in the mass spectra (expected position marked in the ESI†) is highly surprising and reveals the ligand-dependency of the applied one-phase approach (or stability of Au25(1-PET)18). Interestingly, the steric demand of 1-PET compared to CamSH (bicyclic) or glutathione (tripeptide) seems to be less and is therefore not expected to be the reason for the non-formation of Au25(1-PET)18. The question concerning the stability of Au25 that is protected by different ligands remains open at this stage.

CD spectra of the isolated fractions of Auₙ(CamS)ₘ and Auₙ(1-PET)ₘ were measured for both enantiomers (Fig. 3, top (Au25) and ESI†). In the camphorthiol-case, the spectra exhibit good mirror-image relationships; the same is observed for the 1-PET-protected clusters (to a lesser extend which may be due to the varying size distributions between synthesis batches, ESI†). As the strength of the CD spectrum is a concentration-dependent property, anisotropy factors $g = \Delta A/A$ were calculated.
Comparison of the CD spectra of Au25(CamS)18 with protected clusters, but no mass assignment was performed for these.8 A similar trend has been observed earlier in binaphthyldithiol-protected clusters, but no mass assignment was performed for these.6 The spectrum of Au25(1S, 4R-CamS)18 is very similar in sign and transition energies.

The observed maximum anisotropy factors drop from 1 × 10−2 (fraction 3) over 3 × 10−4 (fraction 2) to 1 × 10−4 (fraction 1). A similar trend has been observed earlier in binaphthyldithiol-protected clusters, but no mass assignment was performed for these.6 Comparison of the CD spectra of Au25(CamS)18 with the ones reported by Jin and Whetten reveals some interesting points.2,6 When comparing to the spectra of Au25(pet*)18 (pet*: 2-methyl-2-phenylethylthiolate), the difference in the spectral shape is striking.7 In contrast, there is a remarkable resemblance with the spectrum of Au25(SG)18 (SG: l-glutathionate) (Fig. 3).5,6 Glutathionate and camphorothiolate are both rather bulky ligands in contrast to pet*. Within the staples (SR-Au-SR-Au-SR) mentioned above the ligands can adopt different relative orientations, corresponding to different absolute configurations at the sulfur atom.16,24 We propose that this configuration at the sulfur atoms, through mixing of sulfur orbitals into the relevant electronic states,24 dominates the optical activity rather than the actual structure of the ligand. The bulkiness of SG and CamS may result in a similar relative arrangement (stERIC demand), in contrast to the small pet* ligand (that also may be stabilised by aromatic interactions with each other).

The presented camphorothiolate system exhibits the first example in which an enantiopure, bicyclic ligand is used to protect gold clusters; 1-PET is the first ligand in which the thiolate function is directly attached to the stereogenic centre. The one-phase approach for Au25 synthesis was shown to be ligand dependent, leading to a polydisperse mixture in the camphorothiolate case and no Au25 in the 1-PET case. During the synthesis of Au25 clusters the carbonyl group of adsorbed camphorothiolate was reduced probably due to the catalytic activity of the gold cluster. The CD spectra of Au25(CamS)18 show good agreement with the one of Au25(SG)18, in contrast to Au25(pet*)18. We conclude that it is the relative orientation of the ligands with respect to the staples, caused by stERIC demand, rather than the actual structure of the ligand, which dictates the optical activity of Au25. This may help to factorize the contributions of different levels of chirality to the overall chiroptical activity of gold clusters.

Notes and references