Nanoscale

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Cite this: DOI: 10.1039/c2nr30498h

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PAPER

Strong non-linear effects in the chiroptical properties of the ligand-exchanged Au_{38} and Au_{40} clusters†

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Received 29th February 2012, Accepted 18th April 2012
DOI: 10.1039/c2nr30498h

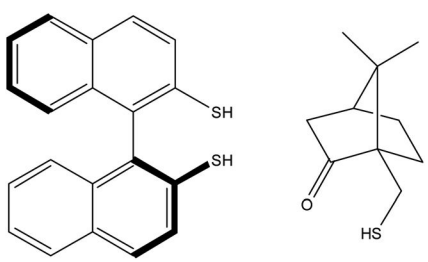
Ligand exchange reactions on size-selected $Au_{38}(2\text{-PET})_{24}$ and $Au_{40}(2\text{-PET})_{24}$ clusters (2-PET: 2-phenylethylthiol) with mono- and bi-dentate chiral thiols were performed. The reactions were monitored with MALDI mass spectrometry and the arising chiroptical properties were compared to the number of incorporated chiral ligands. Only a small fraction of chiral ligands is needed to induce significant optical activity to the clusters. The use of bidentate 1,1′-binaphthyl-2,2′-dithiol (BINAS) leads to slow exchange, but the optical activity measured is strong. Moreover, a non-linear behaviour between optical activity and the number of chiral ligands is found in the BINAS case for both Au_{38} and Au_{40}, which may indicate different exchange rates of enantiopure BINAS with the enantiomers of inherently chiral (but racemic) clusters. This is ascribed to effects arising from the bidentate nature of BINAS. In contrast, the use of monodentate camphor-10-thiol (CamSH) leads to comparably fast exchange on both clusters. The arising optical activity is weak. This is the first study where chiroptical effects are directly correlated with the composition of the ligand shell.

Introduction

The study of thiolate-protected gold nanoclusters (or nanomolecules) with molecular features (non-linear, size-dependent optical spectra, electrochemical properties…) has evolved as a vastly studied field in chemistry and material sciences.[1–3] The possible application of such systems as (biological) sensors and as catalysts stimulates research efforts[4,5] as well as fundamental questions concerning the evolution of electronic and structural properties as the clusters become larger thus showing particle-like behaviour such as a surface plasmon resonance (*ca.* 320 atoms and more).[6–8]

A gold cluster $Au_m(SR)_n$ (SR: thiolate) is a defined system with precise numbers for m and n. Not all combinations of m and n are found, but certain ones fulfill the superatom complex model and extraordinary stability is assigned to them (*e.g.* $Au_{25}(SR)_{18}$, 8e).[9–13] Interestingly, the clusters $Au_{38}(SR)_{24}$ (14e) and $Au_{40}(SR)_{24}$ (16e) do not obey a "magic number" (assuming a neutral native charge state). This may be explained by a non-spherical geometry of the Au clusters. The non-spherical Au_{23} core of Au_{38} has recently been confirmed by X-ray structure determination.[14–16] The cluster consists of a fused biicosahedral Au_{23} core that is protected by six dimeric $Au_2(SR)_3$ and three monomeric $Au(SR)_2$ staples. Within these staples, the thiolates have a bridged binding mode and an Au adatom is stabilised between two sulphur atoms.[17] In contrast, little is known about $Au_{40}(SR)_{24}$.[18] Identified as a by-product in the synthesis towards Au_{38}, a Au_{26} core protected by six monomeric and four dimeric staples has been *proposed*.[19]

In a recent study, we performed thiolate-for-thiolate ligand exchange on Au_{38} and Au_{40} clusters.[19] We followed the reaction with both MALDI mass spectrometry (amount of ligands exchanged) and circular dichroism (evolution of the chiroptical properties). The in-depth study of the chiroptical properties of partially exchanged clusters was not possible in this study since Au_{38} and Au_{40} were coexisting in the reaction and product mixtures; thus, the observed CD spectra comprise a mixture of different cluster sizes. In the meantime, a method for separation



Scheme 1 Structures of *S*-1,1′-binaphthyl-2,2′-dithiol (*S*-BINAS, left) and 1*R*,4*S*-camphor-10-thiol (1*R*,4*S*-CamSH, right).

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† Electronic supplementary information (ESI) available: UV-Vis spectra of exchanged clusters and additional MALDI mass spectra. See DOI: 10.1039/c2nr30498h

of the two clusters was developed, that allows the study of both clusters individually.[20] We synthesised and isolated Au_{38}(2-PET)$_{24}$ and Au_{40}(2-PET)$_{24}$ clusters and performed ligand exchange with mono- and bidentate chiral thiols, namely camphor-10-thiol (CamSH) and 1,1′-binaphthyl-2,2′-dithiol (BINAS) (Scheme1). The reactions were monitored with mass spectrometry and CD spectroscopy; special attention was paid to the relationship of the strength of the chiroptical response and the extent of the ligand exchange. A strongly non-linear behaviour between the strength of the CD signals and the amount of incorporated BINAS is found for both Au_{38} and Au_{40}, but the behaviour is significantly different for the two clusters.

Methods and materials

General remarks

All chemicals were purchased from standard suppliers and used without further purification. Nanopure water (>18 MΩ) was used. The ligands were synthesised according to the literature.[21,22]

Spectroscopy/mass spectrometry

UV-Vis spectra were recorded on a Varian Cary 50 spectrometer in methylene chloride (1 cm pathlength) and normalised at 300 nm. CD spectra were recorded on a JASCO J-815 spectrophotometer in methylene chloride (5 mm pathlength). The signal of the blank solvent was subtracted and FFT filters were applied to smooth the curves. Anisotropy factors $g = \Delta A/A = \theta$ [mdeg]/ $32980 \times A$ were calculated using the UV-Vis spectra provided by the CD spectrometer. MALDI mass spectra were obtained on a Bruker Autoflex (nitrogen laser at near threshold fluence, positive mode) using a 1 : 1000 analyte : matrix ratio.[23] A [3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) matrix was used. MALDI spectra were normalised at the maximum intensity.

Synthesis of the starting material[19]

Au_{38}(2-PET)$_{24}$ and Au_{40}(2-PET)$_{24}$ clusters were synthesised and isolated as reported earlier.[19,20]

Step 1. A solution of tetrachloroauric acid trihydrate in methanol (1 g in 200 mL) was mixed with an aqueous solution of glutathione (3.1 g in 100 mL) at room temperature. The resulting suspension was stirred at 0 °C for 15 min and an aqueous solution of sodium borohydride (1.1 g in 60 mL) was added. The reaction mixture was stirred for 1 h and the black product was allowed to settle. After decanting, the clusters were suspended in methanol and centrifuged.

Step 2. The clusters prepared in Step 1 were redissolved in water (10 mL), 10 mL acetone and 15 mL 2-phenylethylthiol were added. The system was heated to 80 °C, during which phase transfer occurred. The organic phase was diluted with methylene chloride and washed with water. The aqueous phase was discarded. After removal of the solvent, the crude product was washed with methanol and filtered over a recovered cellulose filter. This was repeated several times. The clusters were then redissolved in methylene chloride and passed over a PTFE syringe filter to remove the insoluble material.

Size-selection of the clusters[20]

The purified clusters from Step 2 were dissolved in a minimum amount of tetrahydrofuran, given on a size exclusion column (SEC, BioBeads S-X1, 1 m length, 2.5 cm in diameter) and eluted with tetrahydrofuran. The fractions containing Au_{38}(2-PET)$_{24}$ and Au_{40}(2-PET)$_{24}$ as major components were collected individually and refined by SEC several times until no further improvement of monodispersity was achieved. The resulting clusters were checked with MALDI mass spectrometry for sufficient monodispersity.

Ligand exchange reactions[19]

In a typical reaction, Au_{38}(2-PET)$_{24}$ or Au_{40}(2-PET)$_{24}$ clusters (*ca.* 3–5 mg per reaction) were dissolved in 2 mL of methylene chloride per mg of the material. A 100-fold molar excess (with respect to the clusters) of the chiral ligand was added and the solutions were stirred at room temperature under inert gas atmosphere. Aliquots of 0.5–1 mL were taken at different reaction times and extensively washed with methanol prior to subjecting the samples to CD/UV-Vis spectroscopy and MALDI analysis.

Results and discussion

Characterisation of the isolated clusters

The clusters were characterised with UV-Vis spectroscopy and fragmentation-free MALDI mass spectrometry.[23] In the case of Au_{38}, a single signal at 10 778 Da (calcd: 10 778.08 Da) is observed; for Au_{40}, a signal at 11 172 Da (calcd: 11 172.02 Da) is found. Both samples were regarded as "pure" based on MALDI sensitivity (apart from small (<5%) unassigned impurities in Au_{40}). The optical spectra of the two clusters are in agreement with those reported earlier.[20] Both spectra do not show optical activity, indicating true racemates or absence of intrinsic chirality, although enantiopure L-glutathionate was used in the precursor clusters during synthesis (ESI†). For Au_{38}, this is in agreement with HPLC data.[24]

Ligand exchange of Au_{38} and Au_{40} with (bidentate) BINAS

Ligand exchange between Au_{38}(2-PET)$_{24}$ and enantiopure *S*-BINAS was performed in a 100-fold molar excess of the incoming ligand with respect to the cluster (roughly, a 4.2-fold excess with respect to the 2-PET ligands). Aliquots were taken at different reaction times, washed with ethanol and characterised with UV-Vis and CD spectroscopy. The extent of exchange was monitored with MALDI spectrometry.

UV-Vis spectra of the samples show no hints of decomposition; the distinct features of Au_{38} clusters are still observable after 72 h. When comparing carefully, it becomes apparent that the spectra are less defined at longer reaction times. On the one hand, this is due to normalisation at 300 nm, at which the adsorbed BINAS absorbs stronger than the replaced 2-PET. (In the ESI†, absorption spectra normalised at different wavelengths are compared.) On the other hand, it seems that adsorption of BINAS leads to characteristic changes in the UV-Vis spectra, altering the absorption properties of the whole cluster. The

spectra appear less defined and some transitions seem slightly red-shifted, *e.g.* at 629 nm.

The mass spectra only show existence of Au_{38} clusters and no other cluster sizes are found (for full spectra, see ESI†). Moreover, we recorded CD spectra of the samples and calculated their anisotropy factors $g = \Delta A/A$ over the spectral range. As reported earlier, the exchange is slow compared to the use of monodentate thiols and stops at the incorporation of three BINAS ligands (each one replacing two 2-PET ligands).[19] We ascribe this behaviour to selective binding to short staples in the Au_{38} structure (which is limited to three).[14–16] The bidentate binding of BINAS is shown by a mass increase of 42 Da (signals with a spacing of +180.23 Da relative to the starting material – corresponding to monodentate binding – are not observed, Fig. 1, left). The signal set consists of four species $Au_{38}(2\text{-PET})_{24-2x}(BINAS)_x$ (x = 0–3). We determined the average number of BINAS ligands found from the relative intensity of the peaks in the MALDI spectra (resulting in non-Daltonian average formulae, *e.g.* $Au_{38}(2\text{-PET})_{23.37}(BINAS)_{0.315}$) and compared to the corresponding anisotropy factor of the sample (of the 370 nm signal, denoted with an arrow in Fig. 1, right). The data of different reaction batches match well and clearly show a non-linear behaviour (Fig. 3, left) that is, the optical activity of the clusters is not simply proportional to the number of adsorbed chiral ligands.

In analogy to the above-described exchange reaction between $Au_{38}(2\text{-PET})_{24}$ and BINAS, we performed the thiolate-for-thiolate exchange reaction between $Au_{40}(2\text{-PET})_{24}$ and BINAS. Again, no hint of a monodentate binding of BINAS to the cluster is found, all signals in the set correspond to replacement of two 2-PET ligands by one BINAS ligand. The exchange stops at six BINAS ligands, as reported earlier (Fig. 2, left).[19] No information on the structure of Au_{40} is available but based on the exchange experiments, we propose that the cluster has six short staple binding sites with which BINAS selectively exchanges. Of note, the exchange is very fast up to four BINAS ligands ($x = 4$, within 1 hour) but seems to proceed remarkably slower in the formation of $x > 4$ species. This leads to almost pure mixed ligand species with $x = 4$ after 12–14 h and may have structural reasons, too. Again, the average BINAS coverage per sample was calculated and compared to the maximum anisotropy factor (that is, similarly to Au_{38}, close to 370 nm). Again, the resulting curve is not linear, but is of completely different character (Fig. 3, right) compared to the Au_{38} case.

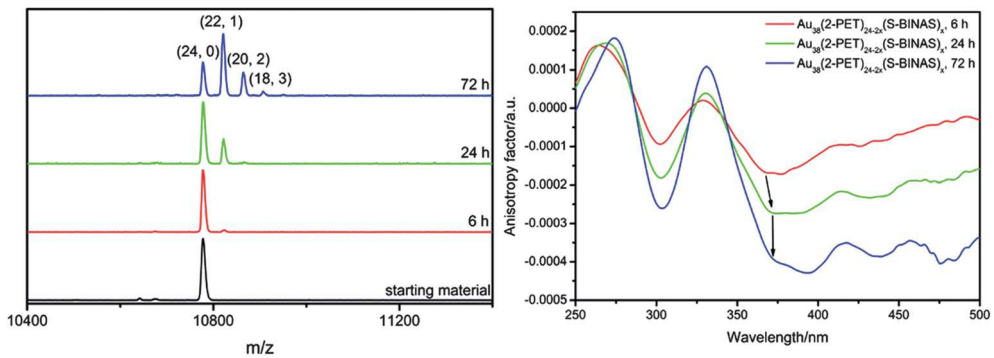

Fig. 1 Left: MALDI mass spectra of $Au_{38}(2\text{-PET})_{24}$ before (bottom trace) and after 6, 24 and 72 h of exchange with BINAS (bottom to top). All samples contain a significant amount of the unreacted starting material. Right: anisotropy factors after 6, 24 and 72 h. The arrows denote the signal at 370 nm that is compared to the average number of BINAS ligands found in the mass spectra (see text).

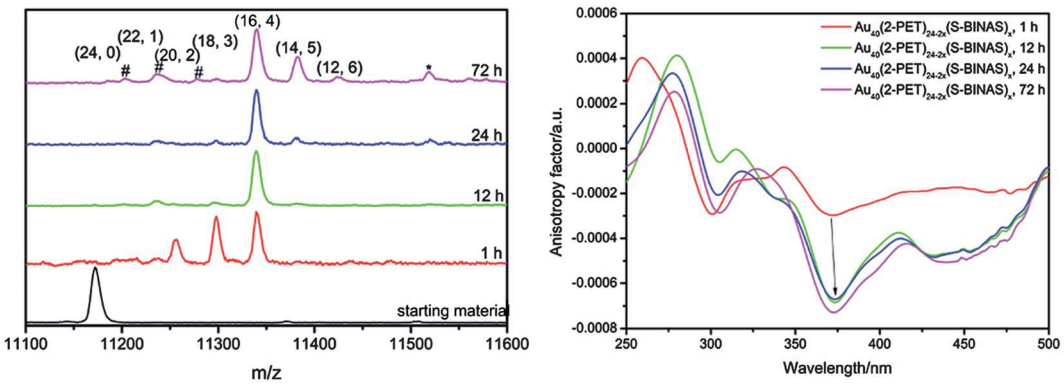

Fig. 2 Left: MALDI mass spectra of $Au_{40}(2\text{-PET})_{24}$ before (bottom trace) and after 1, 12, 24 and 72 h of exchange with BINAS (bottom to top). No species incorporating seven BINAS ligands are observed. The starting material is fully consumed within one hour, indicating a drastically faster reaction than in Au_{38}. Right: anisotropy factors after 6, 24 and 72 h. The arrow denotes the signal at 370 nm that is compared to the average number of BINAS ligands found in the mass spectra (compare text).

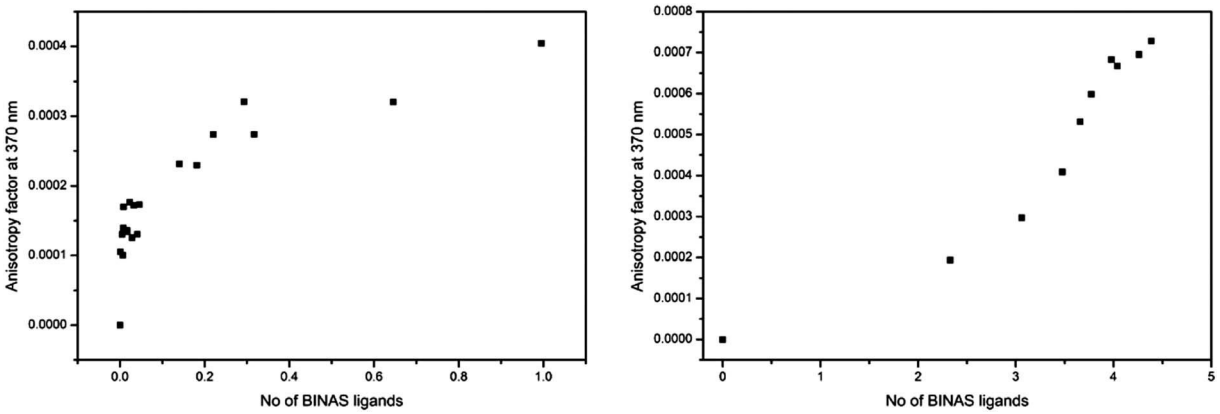

Fig. 3 Left: anisotropy factor (at 370 nm) of $Au_{38}(2\text{-PET})_{24-2x}(BINAS)_x$ compared to the average number of BINAS ligands determined by mass spectrometry (*x*-axis); right: the same comparison with $Au_{40}(2\text{-PET})_{24-2x}(BINAS)_x$. It becomes obvious that in both cases the evolution of the optical activity is non-linear with respect to the number of chiral ligands present. Absolute values for the anisotropy factors were used as the response is negative at 370 nm when *S*-BINAS is used.

The data presented comprise (to the best of our knowledge) the first direct correlation between the composition of a ligand shell and an evolving property (optical activity in this case) of a truly monodisperse gold cluster system. This should allow drawing some interesting conclusions. However, one should bear in mind that the analysed solutions after some time of ligand exchange contain several species and therefore the optical activity observed is a superposition of the optical activities of all the individual species. The latter, all of the Au_{38} clusters, have different composition, *i.e.* different numbers of 2-PET and BINAS in their ligand shell, and are different stereoisomers due to the chirality of Au_{38} and BINAS, resulting in a rather complex situation.

The resulting curves for Au_{38} and Au_{40} (number of chiral ligands *vs.* resulting optical activity) show distinct nonlinear behaviour. Only a small fraction of chiral ligands is needed to induce a strong chiroptical response in Au_{38} and the influence of additional ligands is comparably weaker, whereas the opposite is the case for Au_{40}. As the crystal structure reveals, $Au_{38}(2\text{-PET})_{24}$ is intrinsically chiral by the arrangement of the protecting ligand staples (but racemic).[14,15] Assuming that the general structure of the cluster is maintained, incorporation of enantiopure ligands leads to a diastereomeric situation. *rac*-$Au_{38}(2\text{-PET})_{24}$ is converted to L-$Au_{38}(2\text{-PET})_{24-2x}(S\text{-BINAS})_x$ and D-$Au_{38}(2\text{-PET})_{24-2x}(S\text{-BINAS})_x$ (for exchange with *S*-BINAS; L and D denote the handedness of the staple arrangement on the Au_{23} core). It is reasonable to assume different CD responses of diastereomers, in contrast to enantiomers in which mirror-imaged CD spectra are observed. Moreover, the reaction of Au_{38} with BINAS is slow and all samples contain the starting material ($x = 0$). For $x = 1$, we have to consider a mixture of four chiral species (L-$Au_{38}(2\text{-PET})_{24}$, D-$Au_{38}(2\text{-PET})_{24}$, L-$Au_{38}(2\text{-PET})_{22}(S\text{-BINAS})_1$ and D-$Au_{38}(2\text{-PET})_{22}(S\text{-BINAS})_1$). The use of *R*-BINAS leads to the corresponding enantiomeric species (L-$Au_{38}(2\text{-PET})_{22}(S\text{-BINAS})_1$ is the enantiomer of D-$Au_{38}(2\text{-PET})_{22}(R\text{-BINAS})_1$) of the mixtures, which explains the mirror-image CD spectra when *R*- and *S*-BINAS exchange are compared.[19]

The contribution of the different species to the observed CD spectrum depends on the relative exchange rates of enantiopure

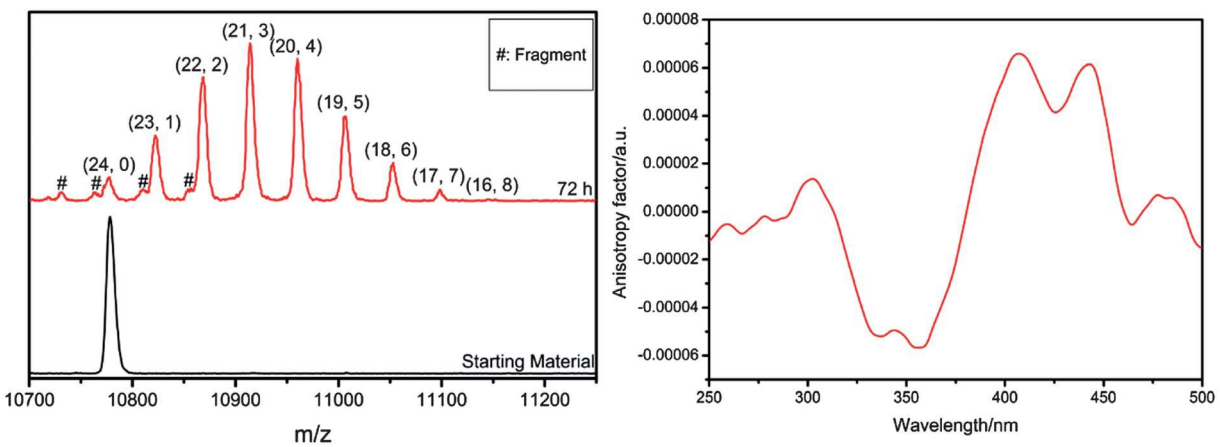

Fig. 4 Left: MALDI mass spectra of $Au_{38}(2\text{-PET})_{24}$ before (black) and after 72 h of exchange with CamSH. Species up to $Au_{38}(2\text{-PET})_{16}(CamS)_8$ are found. Right: the anisotropy factor plot of $Au_{38}(2\text{-PET})_{24-x}(CamS)_x$ after 72 h. The induced optical activity (up to 7×10^{-5}) is remarkably weak compared to exchange with BINAS.

BINAS with racemic Au_{38}. Two principal situations can be distinguished. (I) If both enantiomers of the original cluster react with BINAS with the same rate, the CD spectra of $Au_{38}(2\text{-PET})_{24}$ cancel (racemic mixture) and they do not contribute to the resulting *observed* CD spectrum (but – of note – to the anisotropy factor, since the clusters contribute to the overall absorption of the samples). In this case, the resulting *observed* CD spectra reflect the differential spectrum of the individual spectra of L-$Au_{38}(2\text{-PET})_{22}(S\text{-BINAS})_1$ and D-$Au_{38}(2\text{-PET})_{22}(S\text{-BINAS})_1$ and the anisotropy factors might therefore be drastically lower (or – at least – different) than, for example, for diastereopure D-$Au_{38}(2\text{-PET})_{22}(S\text{-BINAS})_1$ (or L-$Au_{38}(2\text{-PET})_{22}(S\text{-BINAS})_1$). If, case II, enantiopure BINAS reacts faster with one of the cluster enantiomers, $Au_{38}(2\text{-PET})_{24}$ is not racemic anymore thus contributing to the observed optical activity in addition to the exchanged species (L-$Au_{38}(2\text{-PET})_{22}(S\text{-BINAS})_1$ and D-$Au_{38}(2\text{-PET})_{22}(S\text{-BINAS})_1$). The situation is similar for $x = 2$ and 3, but more complicated since six ($x = 2$) or eight ($x = 3$) chiral species have to be considered.

How can this explain the nonlinear behaviour in the evolution of optical activity? First of all, the composition changes from sample to sample as ligand exchange progresses, leading to a different (average) number of incorporated BINAS ligands and different optical activity. The CD spectra for the $x = 1$, 2, 3 species do not have to be identical, resulting in different strengths and possibly even sign at a given wavelength. Moreover, the UV-Vis absorption changes with increasing the number of chiral ligands because BINAS itself absorbs below *ca.* 350 nm and slightly alters the absorption spectrum of the cluster (see ESI†). This would alter (lower) the calculated anisotropy factor at 370 nm even without increase of optical activity. In contrast, the proportion of the unreacted ($x = 0$) Au_{38} in the sample decreases with time and its contribution to the total absorbance is less, hence the anisotropy factor should rise. Clearly, this situation is complex but different concurring reactions leading to products of a different CD sign and anisotropy factor seems to suit as a good model to explain the non-linear behaviour in the arising optical activity of Au_{38}.

There is no information on the structure of Au_{40} clusters and the nonlinearity observed may be explained by a similar model. The opposite behaviour of the curve in Fig. 3 (compared to Au_{38}) may be explained by concurring species of opposite sign at the given wavelength.

The superposition of different CD spectra of several species ($x = 0$, 1, 2, 3) may thus explain the nonlinear behaviour of the anisotropy factor at one wavelength as a function of the *average* number of exchanged BINAS ligands. This holds true for both Au_{38} and Au_{40} and due to the complexity of the mixture and without further information it is difficult to draw further conclusions. However, for the Au_{38} case and at the beginning of the exchange the discussion can be deepened. Fig. 1 (left) shows that after 24 h only two masses are observed corresponding to the un-exchanged $Au_{38}(2\text{-PET})_{24}$ (two enantiomers) and the $Au_{38}(2\text{-PET})_{22}(S\text{-BINAS})_1$ (two diastereomers) species. Most importantly, up to an average number of about 0.25 of exchanged BINAS no higher exchange products ($x > 1$) can be distinguished. Fig. 3, left, however, shows that the first non-linearity in the curve is found at an average number of exchanged BINAS of about 0.1. In this regime only $x = 0$ and $x = 1$ species exist and the non-linear behaviour has to have reasons other than higher exchange products ($x > 1$) with different CD spectra. Case (I) discussed above, *i.e.* the case where the two enantiomers of the Au_{38} cluster react with the same rate with BINAS, is not compatible with the observed non-linear behaviour in Fig. 3. In this case the observed CD spectrum is the difference between the CD spectra of D-$Au_{38}(2\text{-PET})_{22}(S\text{-BINAS})_1$ and L-$Au_{38}(2\text{-PET})_{22}(S\text{-BINAS})_1$ at identical concentrations. The strength of the CD signal is then linearly proportional to the concentration of the species and therefore to the average number of exchanged BINAS. This holds also true for the anisotropy factor for low exchange numbers x. These considerations may be taken as an indication that the exchange of *S*-BINAS does not have the same rate for the two enantiomers of the Au_{38} cluster (case II above) or in other words that the ligand exchange is enantioselective.

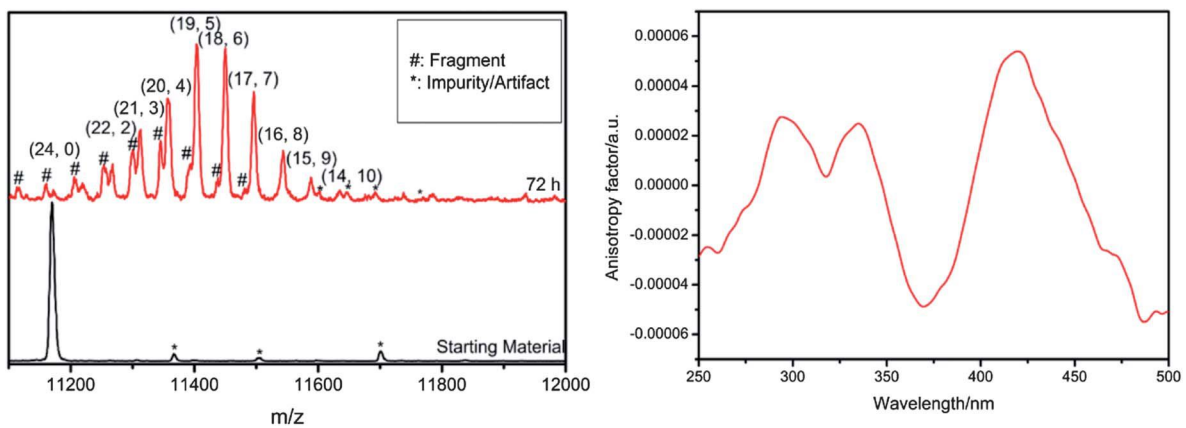

Fig. 5 Left: MALDI mass spectra of $Au_{40}(2\text{-PET})_{24}$ before (black) and after 72 h of exchange with CamSH. Species up to $Au_{40}(2\text{-PET})_{14}(CamS)_{10}$ are found. Right: the anisotropy factor plot of $Au_{40}(2\text{-PET})_{24-x}(CamS)_x$ after 72 h. The induced optical activity (up to 6×10^{-5}) is remarkably weak compared to exchange with BINAS (up to *ca.* 7.5×10^{-4}).

Ligand exchange of Au_{38} and Au_{40} with (monodentate) CamSH

In analogy to the experiments described above, we performed ligand exchange with enantiopure 1*S*,4*R*-camphor-10-thiol. Again, a 100-fold molar excess (with respect to the cluster) was used; note that since camphorthiol is monodentate, the number of "offered" thiolate groups is only half, compared to exchange with BINAS. Again, the UV-Vis spectra give no hint for decomposition of the clusters. CD spectra were measured for the 72 h samples and – in contrast to exchange with BINAS – rather weak optical activity was found (g_{max} up to 7×10^{-5} for Au_{38} and 6×10^{-5} for Au_{40}, Fig. 4 and 5). We did not record CD spectra for all data points, as the responses are too weak for shorter reaction times and, thus, are not interpretable.‡ As a major contrast to exchange with BINAS, odd numbers of 2-PET ligands are exchanged, which is attributed to the monodentate nature of CamSH. The number of found camphorthiolate ligands exceeds the number of thiolate binding sites in the short staples for both clusters (six and twelve, respectively; assuming the model is correct). This indicates indifferent exchange behaviour of the incoming ligand with respect to the different binding sites of the clusters. Similar behaviour was found for thiophenol (which seems to convert into $Au_{36}(SR)_{23}$ at long reaction times).[19,25] The incomplete exchange may be attributed to the rather bulky and rigid bicyclical structure of camphorthiol, which might not replace the flexible 2-phenylethyl ligand. The arising weak optical activity as compared to BINAS may be due to weak enantiodiscriminating interactions for monodentate CamSH in contrast to the bidentate BINAS, which appears to be more sensitive to the intrinsic chirality of the clusters.

The shape of the CD spectra of BINAS- and CamS-exchanged Au_{38} is different. The influence of the ligands on the shape of the CD responses was shown for Au_{25} clusters.[26,27] For Au_{38}, this interpretation is complicated by the fact that the cluster is inherently chiral and diastereomeric effects (superposition of different spectra) cannot be excluded. Mono- and bidentate binding may also influence the chiroptical responses.

Conclusions

In conclusion, we performed ligand exchange reactions on monodisperse Au_{38} and Au_{40} clusters covered with 2-phenylethanethiol and incoming mono- and bi-dentate ligands. The use of the bidentate BINAS ligands induces strong optical activity to the clusters. We determined the average number of replaced ligands for numerous samples and compared to the evolving chiroptical response. In both clusters, a strong non-linear behaviour is found that characteristically differs between the two species. A model involving selective exchange with respect to the handedness of the cluster is discussed. The observed non-linear behaviour of the optical activity with respect to the average number of exchanged ligands may indicate enantioselectivity in the exchange reaction, which appears to be enhanced by the bidentate nature of BINAS. In contrast, the use of the monodentate camphorthiol leads to weak chiroptical responses. This is the first study on comparison of evolving properties with respect to a (changing) ligand shell composition on monodisperse cluster systems.

‡ The direct synthesis of full-camphorthiol protected clusters as reference failed (we used a similar etching approach as was used for the synthesis of the starting materials. Since camphorthiol is a solid and phase separation during the etching reaction is desirable, we dissolved the thiol in chloroform).

Acknowledgements

We gratefully acknowledge the University of Geneva and the Swiss National Foundation (SK, TB) and the University of Mississippi and the National Science Foundation 0903787 (AD) for financial support. Prof. Stefan Matile (UniGe) is gratefully acknowledged for providing the CD spectrometer. We thank Prof. Serafino Gladiali (Italy) for the donation of BINAS.

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