Structures and chiroptical properties of the BINAS-mono substituted Au38(SCH3)24 cluster†

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The structure and optical properties of a set of R-1,1′-binaphthyl-2,2′-dithiol (R-BINAS) mono substituted A-Au38(SCH3)24 clusters are studied by means of time dependent density functional theory (TD-DFT). While it was proposed earlier that BINAS selectively binds to monomer motifs (SR-Au-SR) covering the Au23 core, our calculations suggest a binding mode that bridges two dimer (SR-Au-SR-Au-SR) motifs. The more stable isomers show a negligible distortion induced by BINAS adsorption on the Au38(SCH3)24 cluster which is reflected by similar optical and Circular Dichroism (CD) spectra to those found for the parent cluster. The results furthermore show that BINAS adsorption does not enhance the CD signals of the Au38(SCH3)24 cluster.

In recent years, interest in thiolate-protected gold clusters has grown since the first report of optical and chiroptical properties of glutathionate-protected gold clusters by Whetten et al. finding strong optical activity.1 Due to lack of structural information at that time the origin of optical activity could not be determined (except for the fact that a chiral ligand is used for protection of the cluster), although several mechanisms were proposed.1,2 Nowadays, several structures of thiolate-protected gold clusters are available.3 For example the Au102(SR)44 and Au138(SR)24 clusters show intrinsic chirality of their Au–S framework whereas the latter is achiral for the thiolate-protected Au25 cluster.3–6 Moreover, it was established that Au38(SR)24 and Au39(SR)24 clusters show strong circular dichroism signals even if covered by achiral thiols7 whereas the anionic Au32(SR)18 cluster shows rather week optical activity when covered by chiral thiols and no optical activity when covered by achiral thiols.1a,b–10 Taking into account the different symmetry of the two cluster Au–S frameworks (D3 for the Au32(SR)24 cluster3 and Ci for the Au25(SR)18 cluster11,12) one can conclude that the more intense optical activity observed in the thiolate-protected Au32 cluster is related to its intrinsically chiral structure. In the Au32(SR)18 cluster,11,12 the observed optical activity in the presence of a chiral thiol is thought to be induced by a chiral distortion of the initially achiral structure by chiral thiols such as glutathione, while the phenylethanol thiolate (SCH2CH2Ph) ligand gives a null CD signal.1b,c,13,14 Conversely, in the case of much smaller chiral Au48(SR)n (n = 12–15, 16–20; m = 9–12, 12–16) clusters, the whole cluster structure (core and ligand shell) is responsible of the intense CD signals.6

Our knowledge of the structure of the Au–S interface is based on the X-ray crystallography of the Au102(SR)44 cluster showing that the S and Au atoms form staple motifs which are bound to an Au70 core.13 These motifs have been obtained from theoretical calculations,14,15 and were systematically studied.12,18 The S atoms become stereogenic centers upon adsorption of the ligands (achiral). In addition the staples form a chiral pattern on the cluster surface. In a similar way, the Au38(SR)24 cluster consists of three SR-Au-RS (short or monomer) and six SR-Au-SR-Au-RS (long or dimer) motifs covering a face-fused biicosahedral Au23 core (Fig. 1).9,15 The six dimer motifs form a staggered arrangement at the ends of the prolate Au23 core while the three monomer motifs are located at its equator.4,5

Ligand exchange reactions, pioneered by Murray and coworkers, are a useful method to post-synthetically alter the properties of monolayer-protected gold clusters by introducing new functionalities.16 Recently, Wang and co-workers reported the synthesis of a novel thiolate-protected gold cluster with outstanding stability, optical and electrical properties in which compositionally both di-thiolates and mono-thiolates are present

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†Electronic supplementary information (ESI) available: Comparison of calculated and experimental optical absorption and CD spectra of the A-M enantiomer; bond distribution of the A-38 enantiomer, and four studied regioisomers; tables with the excitation energies, oscillator strengths and weights of the electronic transitions; xyz relaxed coordinates of studied regioisomers, frontier orbitals of the relaxed structures. See DOI: 10.1039/c3nr03403h
actions were investigated by the early-stage reactions at the core late.

Assuming conservation of the cluster size, monodentate thiolates through which the dithiols were found to replace monothiolate ligand interfaces between the thiolate ligands and excess thiols, protected Au25 cluster, showing conservation of the cluster in the protective monolayer. The Au–thiolate bonding interactions were investigated by the early-stage reactions at the core–ligand interfaces between the thiolate ligands and excess thiols, through which the dithiols were found to replace monothiolate ligands at 1 : 2 stoichiometry ratio, while addition of monothiols into dithiolate monolayer instead of exchange was observed. Assuming conservation of the cluster size, monodentate thiolates are expected to bind to the adsorption site of the leaving thiolate. The situation is complicated and the possible adsorption sites may be a consequence of the structure of the di-thiolate, as its conformational flexibility and the distance of the thiolate groups have to be taken into account. For instance, decomposition of Au25(SR)18 clusters was thought to occur, but a recent assignment of the reaction products shows that the cluster in fact survives the exchange with BINAS (Fig. 2). Other place exchange reactions with di-thiolate ligands were performed on the thiolate-protected Au25 cluster, showing conservation of the cluster size. As yet, little effort was put into the study of the binding mode of di-thiolates. Noteworthy, Dass and co-workers studied the Au25(2-PET)16(1,5-pentanedithiolate)1 cluster using density functional theory (DFT). Bridging between two protecting units was found to be the most stable configuration (interstaple binding). Given the high conformational flexibility of 1,ω-alkane di-thiolate, it is unknown whether or not the proposed binding motif can be transferred to other kinds of di-thiolates.

Recent ligand exchange reactions between the intrinsically chiral Au38(2-PET)24 cluster and bidentate BINAS indicated a selective binding of BINAS to the short (or monomeric) staples, SR-Au-SR. Specifically, it was found by mass spectrometry that only up to three BINAS ligands can replace up to six 2-PET ligands even at longer exchange times. Because the known Au38 cluster contains three short staples, it was argued that ligand exchange of BINAS may take place selectively at the short staples. Later it was found that the ligand exchange rate for the second exchange is much slower than for the first one. Therefore the observed limited exchange could simply be due to kinetic reasons. In order to shine light on these issues the present study aims at elucidating the stability of BINAS at different binding sites on the cluster (inter- vs. intrastaple binding). We herein report a computational study of the structure, optical and chiroptical properties of derivative structures of the Au38(SR)18 cluster with the general formula Au38(SCH3)22(BINAS)1. Methylthiolate was chosen as model for the 2-phenylethylthiolate ligand. Motivated by the observed preference of the left-handed enantiomer of the thiolate-protected Au38 cluster for a BINAS with a R handedness in ligand exchange experiments, an initial set of four isomers with the anticlockwise enantiomer of Au38(SCH3)22 (A-38) and R-BINAS was considered, which differ in the adsorption site of the BINAS. Structural optimizations of Au38(SCH3)22(BINAS)1 regioisomers were performed without symmetry restrictions and their energies and optical absorption and CD spectra were calculated by using the ADF package. Indeed, a good match for interstaple binding was found, giving rise to revision of the previous explanation for the limited exchange. This study also reveals a negligible influence of the adsorbed BINAS molecule on the chiroptical properties of the thiolate-protected Au38 cluster. All DFT-GGA calculations were carried out using the PBE functional for the exchange and correlation (XC) terms, the Slater type basis sets employed in the geometry optimizations are of polarized triple (TZP) quality with a [1s2–4f14] frozen core for Au, a [1s2– 2p6] frozen core for S, and a [1s2] frozen core for C. The energy convergence criterion is tightened to 10−4 Hartree, and the gradient convergence criterion is tightened to 10−3 Hartree per Å. Moreover, ADF includes scalar relativistic effects through the Zeroth Order Regular Approximation (ZORA). Time-dependent DFT, as implemented in ADF, was utilized for the study of the optical and chiroptical properties, through the calculation of its excitation energies, and oscillator and rotatory strengths. To calculate the optical absorption and circular dichroism spectra, particularly in the low energy region (0.5–2.5 eV), the lowest 200 excited (singlet) states were considered, using the same XC functional and basis set as for the structural calculations. To test the reliability of the present TD-DFT methodology, a comparison between calculated optical absorption and CD spectra of the
Au\textsubscript{38}(SCH\textsubscript{3})\textsubscript{24} cluster with experimental data was performed, indicating a good agreement, as it is shown in the ESI section (Fig. S1†). Relaxed atomic coordinates for all regioisomers are provided in the ESI† section also.

Initial Cartesian coordinates of enantiomers of the pure Au\textsubscript{38}(SR)\textsubscript{24} cluster were extracted from the available crystal structure.\textsuperscript{44} In order to label the two enantiomers in the unit cell of the Au\textsubscript{38}(SCH\textsubscript{3})\textsubscript{24} cluster we have orientated each enantiomer along their C\textsubscript{3} axis and observed the arrangement of their dimer motifs. For example, Fig. 2 shows an anti-clockwise rotation of dimer motifs of the A-38 enantiomer. The assignment of the handedness of the cluster was recently done by a comparison between measured and calculated CD spectra.\textsuperscript{5,7}a The regioisomers considered here maintain both the handedness of BINAS and of the thiolate-protected Au\textsubscript{38} cluster but they differ in the position of BINAS ligand. Fig. 3 shows the optimized regioisomers where \textbf{I1} shows R-BINAS linked between two vicinal dimer motifs, \textbf{I2} holds R-BINAS adsorbed between vicinal monomer and dimer motifs, \textbf{I3} has R-BINAS linked to one monomer motif, and in \textbf{I4} R-BINAS is linked to one dimer motif. By comparison of the relative energies of the optimized structures (Table 1), it emerges that more stable regioisomers correspond to R-BINAS bound between two gold adatoms located at vicinal staple motifs (interstaple mode). The energy difference between \textbf{I1} and \textbf{I2} is of 0.44 eV, and both regioisomers have R-BINAS linked in an interstaple mode being favoured over the regioisomer with R-BINAS bound to one motif only (intrastaple binding mode, \textbf{I3} and \textbf{I4}).

In a previous study of the Au\textsubscript{25}(SCH\textsubscript{3})\textsubscript{16}(1,5-pentanedithiolate)\textsubscript{3} cluster,\textsuperscript{20} the interstaple binding mode was found to be energetically favored over intrastaple binding. Here, we have calculated an energy difference of 1.05 eV between R-BINAS linked to gold adatoms of vicinal dimer motifs (\textbf{I1}) and R-BINAS linked to one dimer motif (\textbf{I4}). The calculated trend of R-BINAS to link in an interstaple mode is in contrast to what has been proposed in the past based on the number of exchanged BINAS molecules in ligand exchange experiments.\textsuperscript{21a} Since the preferred binding site for the BINAS ligand is found to be an interstaple motif between dimeric staples (\textbf{I1}), the initially proposed selective binding to monomeric staples may not hold true.\textsuperscript{21a,22} Instead, it seems likely that the limited exchange is due to kinetic reasons, since it was found that the reaction drastically slows down after the first exchange step.\textsuperscript{21b}

The structure of the optimized pure A-38 enantiomer is built by 72C–H, 24C–S, 48S–Au, and 104Au–Au bonds. Au–Au bonds are included in the range 2.83–3.27 Å. Au–Au bonds forming the Au\textsubscript{23} core (Au(core)–Au(core)) are distributed in the following manner: 12 bonds that involve two center Au atoms bound to the Au\textsubscript{21} shell; 57 bonds forming the Au\textsubscript{21} shell and three bonds between Au atoms that represent the icosahedral face-fused. \textbf{I1} and \textbf{I2} regioisomers show bond distances comparable to the original A-38 cluster (see Fig. S2† for comparison) which can be interpreted as a slight or null distortion induced by R-BINAS adsorption. The negligible distortion may be due to a similar S–S distance on R-BINAS before and after its adsorption to Au adatoms in staple motifs.

Bond length analysis of the optimized \textbf{I3} regioisomer shows that bonds between the two central atoms of the Au\textsubscript{13} units and their respective Au\textsubscript{12} shells have an average bond length of 2.87 Å, whereas all missing Au–Au bonds are in the range

![Fig. 3](image-url)
The Au–S bonds between Au(core) and S atoms forming the monomer motifs are around 2.44 Å, and bonds between Au(core) and S atoms in the dimer motifs are circa 2.43 Å. Au–S bonds in the monomer and dimer motifs have an average bond length of 2.35 Å. It was found that once R-BINAS is bound to a monomer motif (I3), it induces a distortion resulting in two Au–S bonds between 2.38 and 2.55 Å. The C–H bonds of methyl and R-BINAS ligands are around 1.1 and 1.0 Å respectively. Further structural analysis shows that all the studied regioisomers hold an entire C1 symmetry (including the ligand shell).

In order to study the distortion induced after R-BINAS adsorption, we analyzed isolated Au23 cores finding that the pure A-38 cluster has a D3 symmetry when a tolerance of 0.09 Å is applied. I1, I2 and I3 hold D3 symmetry with a tolerance of 0.10, 0.15 and 0.25 Å respectively. These results confirm that the Au23 core of the A-38 cluster is intrinsically chiral with a slightly larger distortion induced in I4 (0.28 Å) which can as well be considered as an entire C1 structure (see discussion on Fig. S2†).

It is interesting to note that the distortion of the original A-38 core goes along with a destabilization of the corresponding cluster (Fig. 4). A large relative energy was found for I4 (1.05 eV) being the main reason to discard it in the present discussion.

In general, the electronic stability of the studied regioisomers may be understood on the basis of a shell model, considering 14 delocalized valence electrons. In fact, the features of the optical absorption spectra are related to the cluster geometry, such that it can be used to distinguish between each other.\textsuperscript{26,27} The experimental absorption spectrum of the pure Au_{38}(SCH\textsubscript{2}CH\textsubscript{2}Ph)\textsubscript{24} cluster displays two characteristic signatures related to an electronic transition located at 1.99 eV, and a less defined peak located at 1.64 eV.\textsuperscript{29} Calculated optical absorption of the A-38 enantiomer (Fig. 5) shows two peaks located at 1.99 and 1.66 eV in good agreement with experimental results as can be seen on the line-shape obtained through the broadening of the associated oscillator strengths (f) represented as colored sticks. Fig. 5 shows optical absorption spectra of A-38 and all four studied regioisomers.

<table>
<thead>
<tr>
<th>Description</th>
<th>D\textsubscript{3} (Å)</th>
<th>E\textsubscript{rel}, eV</th>
<th>HL, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>I1 R-BINAS/2 dimer motifs</td>
<td>0.10</td>
<td>0.00</td>
<td>0.91</td>
</tr>
<tr>
<td>I2 R-BINAS/1 monomer and 1 dimer motif</td>
<td>0.15</td>
<td>0.44</td>
<td>0.89</td>
</tr>
<tr>
<td>I3 R-BINAS/1 monomer motif</td>
<td>0.25</td>
<td>0.88</td>
<td>0.63</td>
</tr>
<tr>
<td>I4 R-BINAS/1 dimer motif</td>
<td>0.28</td>
<td>1.05</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Fig. 4 Correlation between the Au\textsubscript{23} core distortion, HL gap values, and relative energy of studied regioisomers. The core distortion is given as the tolerance (Å) necessary to obtain a D\textsubscript{3} point group.

Fig. 5 Calculated optical absorption spectra for the A-38 enantiomer and R-BINAS substituted regioisomers. Some transitions are labeled as a, b and c in ESI.† A Gaussian broadening of 0.1 eV has been used. With asterisks are identified on A-38 spectrum two characteristic peaks along all calculated spectra.
From the structural analysis mentioned above, I1 and I2 regioisomers have a similar Au$_{23}$ core which might result in similar optical absorption spectra with respect to the A-38 cluster. This expected behaviour was confirmed by the calculated spectra shown in Fig. 5. In I2, a slightly more intense peak located at 1.65 eV was found, while I1 shows an intense peak located at 2.0 eV. However, the changes for I3 and I4 regioisomers with respect to the parent A-38 cluster are more pronounced with peaks located below 1.0 eV. Those electronic transitions under 1.0 eV, are related to weak HOMO–1 to LUMO and HOMO–LUMO electronic transitions as it will be shown later.

The A-38 optical spectrum shows a HOMO–1 to LUMO transition, located at 1.06 eV, while the I3 regioisomer shows an intense peak located at 0.98 eV attributed to HOMO–1 to LUMO+2 transition. In addition, I3 has one weak signal located around 0.69 eV related to a direct HOMO to LUMO transition. This peak under 1.0 eV was found more intense in I4. After a Kohn–Sham orbitals analysis of the four studied clusters, it was determined that the HOMO level is located at similar energies, but the LUMO level suffers an evident shift toward negative energies for I3 and I4 regioisomers (Fig. S3–S7†). The shift of the LUMO level of I3 and I4, has an effect in the character of the Kohn–Sham orbitals, in such a manner that the frontier orbitals of I3 and I4, exhibit a major character of ligand-based orbitals (Fig. S6 and S7†). In general, in thiolate-protected gold clusters, electronic transitions located under 1.0 eV are not expected to involve electronic levels with ligand character because the HL transition is characteristic of core transitions (fingerprinting). The mixing of ligand character into the frontier orbitals in I3 and I4 is therefore considered as further support to explain their higher relative energies.

In the case of I1, one peak located at 1.03 eV represents a HOMO to LUMO+1, and HOMO–1 to LUMO transitions. In I2 regioisomer one peak located at 1.04 eV is yielded by HOMO–1 to LUMO+1 and HOMO–1 to LUMO transitions.

Another peak located at 1.36 eV in A-38 is present at 1.30 eV in I3 with an enhanced oscillator strength value. At 1.47 eV is located a peak that does not have a counterpart in the A-38 spectrum. Two peaks in I3 coincide in their position with the A-38 spectrum (1.6 and 1.78 eV). In general two peaks located around 1.64 eV and 1.99 eV in A-38 can be considered characteristic along all calculated regioisomers. Further differences were found for I3 regioisomer which shows a peak around 1.25 eV with major intensity. Both strongly distorted regioisomers I3 and I4 show a largely reduced HL gap (Table 1) and transitions far below 1.0 eV, both in optical and CD spectra (Fig. 5 and 6).

Before CD spectra discussion, it is important to recall that I3 was found more distorted after BINAS adsorption and its absorption spectrum shown in Fig. 5, consistently shows less structure. This result points to a relation between lower symmetry of the core and a less structured absorption spectrum in I3. Furthermore, it is evident that the absorption spectrum does not change much for isomers I1 and I2, compared to the parent cluster, whereas for I3 (and I4) the spectra change drastically. Experimentally, it was found that one BINAS ligand has only a minor effect on the absorption spectrum, which is a further argument for interstaple binding.

The CD spectrum of the Au$_{38}$(SCH$_2$CH$_2$Ph)$_{24}$ cluster was measured after enantioseparation and the following position and phase of the peaks were found (see Fig. S1‡): 2.82(+), 2.59(−), 2.2(+) + , 1.97(−), 1.66(+) eV. The calculated CD spectrum of left handed enantiomer of Au$_{38}$ (A-38) protected with methyl ligands has the coincident peaks: 2.57(+), 2.19(−), 1.93(−), and 1.64(+) eV and we calculated additional peaks which are not reported in the experiment at 1.35(−), 1.14(−), and 1.03(+) eV. Regarding the calculated CD intensities (rotatory strengths), they are similar for peaks located at 1.93 and 1.64 eV.

Due to the fact that CD spectra are more sensitive to the structure, calculated spectra show large differences between the regioisomers. First of all, I3 and I4 show peaks located below
1.0 eV which are not present in the pure A-38 structure. One negative peak located at 1.93 eV in A-38 and two positive peaks located at approximately 1.64 and 2.42 eV are less intense in substituted R-BINAS isomers. It appears that adsorption of R-BINAS on the chiral Au$_{23}$(SCH$_3$)$_{24}$ cluster does not enhance the CD signals. This is supported by experimental findings. For I$_2$ even considerable less intense signals were found. Of note, calculated CD spectra of I$_3$ and I$_4$ are the weakest of all considered structures although their Au$_{23}$ cores are most distorted. The structural analysis let us correlate weaker CD signals to more distorted Au$_{23}$ cores for all R-BINAS-substituted regioisomers. However this assertion needs to be taken with reserve because CD signals arise not only from the Au$_{23}$ core but from the whole structure.

As is evident from Fig. 6 the calculated CD spectra of I$_1$ and I$_2$ are similar to the spectrum of A-38 in the range 1.0–2.5 eV.

It is important to notice that experimental circular dichroism curves where obtained from 1.5 to 4.5 eV. However, given the complexity of the present calculations (mostly because of the high use of memory), theoretical curves span the range from 0.5 to 2.5 eV. In other words, comparison of experimental and theoretical curves is limited to the spectral region comprises between 1.5 and 2.5 eV.

Fig. 7a depicts the experimental curve of A-Au$_{38}$(SCH$_2$CH$_2$Ph)$_{22}$(R-BINAS)$_1$ against the calculated CD of the I$_1$ regioisomer. The experimental and calculated spectra of I$_1$ agree on at least three peaks (position and sign); two positive peaks located around 1.68 and 2.45 eV, and one negative peak located around 1.97 eV which relative intensity is reproduced, while one positive peak located around 2.18 eV was found less intense and with opposite sign in the calculated I$_1$ spectrum. The calculated negative peak located above 2.5 eV must be considered as not characteristic because it is on the limit of the calculated range and it might be necessary to extend that range to get a more reliable sign for it.

In the case of I$_2$ one negative peak located at 2.21 eV is less intense and positive in the experimental spectrum and one negative experimental peak around 2.0 eV is located toward low energy in the calculated one. As can be seen in Fig. 7b, position and sign of peaks of I$_2$ show less agreement with the experimental spectrum as compared to I$_1$. Overall, the CD spectrum of I$_1$ is in best agreement with the experimental one.

Conclusions

In summary, structural, electronic, optical and chiroptical properties of a set of A-Au$_{38}$(SCH$_3$)$_{22}$(R-BINAS)$_1$ regioisomers having the same handedness of the Au$_{38}$(SCH$_3$)$_{24}$ cluster and BINAS but differing in the position of BINAS adsorption were analyzed using TD-DFT. It was found that R-BINAS prefers to bind between two vicinal dimer motifs located at endings of the prolate Au$_{23}$ core. We have found that I$_1$ and I$_2$ regioisomers maintain almost intact the Au$_{23}$ core of the Au$_{38}$(SCH$_3$)$_{24}$ cluster after R-BINAS adsorption, whereas considerable distortion was found for the other adsorption sites. A-38, I$_1$ and I$_2$ show similar optical absorption and CD spectra, which is consistent with experimental findings. Furthermore, there is no evidence that adsorption of chiral R-BINAS enhances CD signals. An even less intense CD spectrum was found for the I$_3$ isomer, which shows a strong distortion in the Au$_{23}$ core. The calculations also show that the CD intensity is not only related to a more or less distorted gold core but that the whole atomic structure of the Au$_{38}$(SCH$_3$)$_{22}$(BINAS)$_1$ cluster has to be considered.

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