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COMMUNICATION

Thiolated Au₁₈ cluster: Preferred Ag sites for doping, structures, optical and chiroptical properties

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Recently the X-ray determined structure of the thiolated Au₁₈ cluster has been reported. In this communication we addressed a study of structures and chiroptical properties of thiolated Au₁₈ cluster doped with up to ten Ag atoms which have been calculated by Time dependent Density Functional Theory (TD-DFT). The number of Ag atoms was steadily varied and more stable isomers show distinct optical and Circular Dichroism (CD) spectra to that found for the parent Au₁₈ cluster. Doping with more than four Ag atoms results in the enhancement of the oscillator strength of the HOMO-LUMO peak and it is expected that this feature can be exploited for photoluminescence applications.

The doping of thiolated gold clusters have captured our interest since the first experimental report of Pd doping of the anionic Au₂₅(SR)₁₈ cluster¹ by Murray group in 2009.² In the amply studied thiolated Au₂₅ cluster, the preferred site for doping depends on the atom, for example Pd and Pt atoms prefer inner positions,³⁻⁴ Mn and Ag are located at the surface of the core,⁵⁻⁹ while Cu and Hg were found at staple-like motifs by experimental groups.¹⁰ Noteworthy is that the radius of Ag and Au atoms are similar allowing their mixing, in contrast the doping by using Cu atoms might induce more distortion into the structure. Recently, new alloys have been reported for thiolated Au₁₄₄,¹¹ Au₁₃₀¹² and Au₃₈ clusters.¹³

Ultrasmall bimetallic thiolate-protected clusters, in the case of Au₂₄Pd(SR)₁₈ and Au₃₆Pd₂(SR)₂₄, significantly are more stable against degradation in solution, laser dissociation and core etching by thiol.¹⁴ Additionally, they display molecular-like properties and the incorporation of two type of metal atoms, is reported to enhance their photoluminescence,^{7c} and their properties could be tailored by controlling their compositions.^{7b} Potential applications of bimetallic

thiolated clusters include catalysis,¹⁵ and bio-sensors.¹⁶

Regarding the smallest bimetallic cluster, an experimental study by Pradeep et. al¹⁷ and a theoretical study by Tlahuice-Flores in 2014 have revealed the structure of the Au₆Ag₇(SR)₁₃ cluster as comprised by an octahedral-like Ag₆ core and protected with two dimers and one Au₂Ag(SR)₄ motif.¹⁸ Thus, both Ag₆Au₇ and Au₂₅⁸ clusters show a clear preference to incorporate Ag atoms into their core and their frontier (HOMO and LUMO) levels have contribution from Ag, and S atoms. Therefore, the electronic excitations are influenced by foreign atoms which are incorporated to the monometallic clusters.

Thiolated Au₁₅ and Au₁₈ clusters are important systems because they have been devised as the smallest thiolated gold clusters with two and four electrons, respectively. The thiolated Au₁₅ cluster model has been reported and it was proposed as a Au₄ core protected by two trimer motifs plus a closed-pentameric [SR-Au]₅ ring,¹⁹ or protected by one heptamer and one tetramer motif.²⁰ The last model of the thiolated Au₁₅ cluster was proposed based on the superior agreement between the calculated CD spectrum, that features a prominent negative peak located at 3.48 eV, in agreement with the experimental 3.42 eV band.²⁰ Following this line, experimental work devoted to the elucidation of the structure of thiolated Au₁₈ cluster succeed recently²¹ providing to theoretical groups²² the opportunity to correct their algorithms used to propose structures and to improve our knowledge in this field.

Herein is addressed a DFT²³ study of the doping, with up to ten Ag atoms, of the X-Ray determined structure of thiolated Au₁₈ cluster.^{21b} The aim of this study is to determinate how the structure, HOMO-LUMO (HL) gap values, the oscillator strength of the lower energy peak and optical and chiroptical properties are affected by Ag doping. A systematic search of lowest-energy isomers was carried out using the PBE functional²⁴ 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 10⁻⁵ Hartree, and the gradient convergence criterion is tightened to 10⁻⁴ Hartree/Å. Scalar relativistic effects were included through the Zeroth Order Regular Approximation (ZORA).²⁵ Time-dependent DFT, as implemented in ADF package, was utilized for the study of the optical and chiroptical properties, through the calculation of its excitation energies, and oscillator and rotatory strengths.²⁶ To

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† Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: Comparison between calculated and experimental absorption spectrum of thiolated Au₁₈, an extended set of studied structures and a Table with Boltzmann weights and with electronic excitations and their oscillator strengths, and Cartesian coordinates of more stable isomers are provided. See DOI: 10.1039/x0xx00000x

calculate the optical absorption and circular dichroism spectra, particularly in the low energy region (0.5-4.0 eV), the lowest 300 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 spectrum of the $\text{Au}_{18}(\text{SCH}_3)_{14}$ cluster with experimental data was carried out, indicating a good agreement, as it is shown in the Supporting Information section (Figure S1).

The thiolated Au_{18} cluster itself is a red-emitting cluster²⁷ which is built by one Au_9 core that resembles two octahedral-like clusters linked by a shared triangular face (STF) and covered with three monomer motifs located around an axis perpendicular to the STF, while one dimer and one tetramer motifs are located at the endings of the Au_9 core. There exists one special position where one Au atom is linked to both one monomer and one dimer motif. Previously we reported an isomer constituted by one Au_8 core that was described as a bi-capped octahedral-like cluster, while the structure reported here can be seen as a tri-capped octahedral-like cluster.²² In Figure 1 is depicted the arrangement of staple-like motifs in the optimized structure that holds a 1.48 eV HL gap value. Moreover, calculated Au-Au distances in the Au_9 core (from 2.72 to 3.00 Å) are in agreement with those reported in ref. 21b (from 2.67 to 3.00 Å). The distances in staple-like motifs are calculated as 1.84 Å (S-C) and as 2.34 - 2.37 Å for Au-S bonds. Bonds between Au core and Au adatoms are comparable to Au-Au bonds in the Au_9 core. Thus, we can conclude that the interaction between the Au_9 core and staple-like motifs is strong due to the compact structure. A complete graph of calculated bond lengths is included in the SI section (Figure S2).

In order to study the effect of the Ag doping in the structure of the thiolated Au_{18} cluster, it has been explored a set of clusters by varying the position and number of Ag atoms (given by n). Starting from one Ag doping atom, a large set of isomers was obtained by testing positions both in the Au_9 core, and in the staple-like motifs. After a normal modes analysis, representatives low-energy isomers, for each composition, were selected and they are displayed in Figure 2. Furthermore, a more complete set of isomers for each n is provided in Table S1.

An interesting subject is to determinate possible sites of doping in function of the number of Ag atoms incorporated to the parent Au_{18} cluster. Mathematically, the number of isomers (NH) for each composition of Au-Ag bimetallic cluster is given as:

$$NH = N! / (n! * (N - n)!)$$

where N is the total number of gold atoms and n is the number of incorporated silver atoms.

It is important to mention that we reduced the large number of isomers for a composition of $n+1$ Ag atoms, by exploring positions close to the favoured sites from previous compositions (n). For example, we maintained the lower energy isomer for $n=4$ and play with the rest of positions to generate a set of isomers for $n=5$. Nonetheless, we make a double check in order to verify whether the trend was maintained for large values of n , for example for $n=7$ we relaxed a total of 23 isomers.

Our results regarding the Ag doping can be summarized as follows:

(1) We relaxed a set of 18 isomers for mono-substitution of Ag atoms. The preferred Ag doping is found to occur in the Au_9 core rather than into the staple-like motifs. The energy minimum is obtained when one Ag atom is located at one core atom linked to one

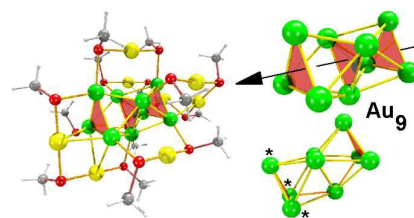


Fig. 1 Structure of the optimized $\text{Au}_{18}(\text{SCH}_3)_{14}$ cluster. The Au, S, C, and H atoms are yellow, red, gray and white, respectively. Arrow indicates an axis along the Au_9 core that it is displayed in green color, where the middle triangular face is shared by two octahedral-like units. In addition, the Au_9 core can be described as a tri-capped (indicated with asterisks) octahedral-like cluster (Right and bottom figure).

terminal S atom of the dimer motif (1.59 eV HL gap value and Ag-S of 2.59 Å). It was found that the Ag atom linked to a terminal S atom of the dimer motif is larger than Au-S bonds by circa 0.05 Å. However, when one core Ag atom is linked to the tetramer motif the cluster is 59.3 meV close in energy. The preference for Ag doping is found as follows: core atoms (0.0- 0.15 eV) > monomer (0.16-0.24 eV) > tetramer (0.19-0.22 eV) > dimer motifs (0.25-0.26 eV). The less favourable substitution of core atoms occurs at the terminal S atom of one monomer motif (0.19 eV) being its relative energy comparable with the position into the staple-like motifs. We can conclude that minimum in energy is related to positions linked to dimer motifs.

(2) We studied a set constituted by 25 isomers when $n=2$, guided by the obtained trend for mono-substitution. Two Ag atoms prefer to incorporate to STF positions, which are attached to dimer and tetramer motifs, but other two isomers with at least one Ag atom located at STF are close in energy (35 meV and 111 meV, respectively). A further analysis of the bonding displayed by the minimum of the $n=2$ structure showed that the Au-S (2.55 Å) bond is short than the Ag-S bond (2.59 Å) at linkage points of dimer and tetramer motifs. Regarding Au-Ag bonds, it was found that they are comparable to Au-Au bonds. While the two Ag atoms are separated by a distance of 3.02 Å. It is important to mention that when Ag atoms are forming part of two different staple-like motifs, the relative energy increases to more than 0.26 eV (isomer 19 in Table S1), attesting that two Ag atoms substitute core Au atoms preferentially.

(3) A set of 40 isomers was considered for $n=3$ structure. Three Ag atoms located at STF result in a minimum in energy with a calculated HL gap of 1.67 eV. They are attached both to one tetramer (Ag-S bond of 2.56 Å) and one dimer motif (Ag-S bond of 2.60 Å). Calculated Ag-Ag bonds were: 3.0, 2.85 and 2.96 Å, respectively, being those bond distances comparable to the Au-Au bonds of the un-doped cluster. Interestingly, this structure showed similar Ag-Ag, Au-Ag and Au-Au bond lengths.

Moreover, another two isomers hold two Ag atoms located at STF with relative energies of 0.14 and 0.17 eV, respectively. Interestingly, two less stable isomers have Ag atoms in almost parallel triangular faces to the energy minimum, and they are linked either to the monomer motif or to one adatom.

(4) We studied a set of 40 isomers for the $n=4$ composition. Four Ag atoms are incorporated into STF plus the special position preferentially (Fig. 2). Another two isomers have been found (29 and 46 meV), which have the STF occupied plus one Ag core atom or

one Ag atom located at the monomer motif, respectively. However, when four Ag atoms are substituting adatoms of the tetramer motif the relative energy is calculated as 0.59 eV. Structurally, the incorporation of four Ag atoms seemed to result in Ag-Au, Au-Au and Ag-Ag bonds comparable in length and dispersed in a range from 2.83 Å to 3.00 Å.

(5) Given the obtained trend in the preference of the Ag doping, we reduce the set of isomers to nine when $n=5$. Substitution of five core Au atoms in the STF, results in three isomers which are close related in energy. The most stable isomer contains, in addition, one Ag atom located at the special position (Ag-S bonds of 2.55 and 2.7 Å), and one core Ag atom linked to one monomer motif (Ag-S bond of 2.52 Å). Another isomer with one Ag atom located at the monomer motif holds a relative energy of 48 meV.

(6) For $n=6$ we considered a set of seven isomers. The minimum in energy maintained the structure of $n=5$, plus one Ag atom linked to one monomer motif (Ag-S bond of 2.52 Å). Interestingly, it is found an isomer with three Ag atoms in the STF plus three Ag atoms distributed as follows: one in the special position, one linked to one monomer motif and one incorporated into the monomer motif (5.1 meV). Another isomer (28 meV) contains in addition two core Ag atoms linked to the same monomer motif plus one Ag atom substituted in the special position.

(7) In order to make a double check of the trend in the substitution of silver atoms, in the case of seven silver atoms, we considered a set of 23 isomers. When seven Ag atoms are incorporated in the core, three stable isomers are found. They have relative energies of 0.0, 2.1, and 15.2 meV, respectively. More stable isomer holds six Ag atoms in the octahedral-like unit, that contains the special position, and one Ag atom linked to the monomer motif (Ag-S bond of 2.52 Å). When one Ag atom is located at the monomer motif, the relative energy increases up to 0.143 eV. For the minimum, it was found that Ag-S and Au-S bonds are similar and also one core Au-Au bond was found short (2.67 Å) than those Au-Au bonds found in the monometallic cluster.

(8) The number of isomers considered was reduced to three based on the trend obtained for $n=7$. Eight Ag atoms prefer to dope the core leaving free the atom close to the tetramer motif and linked to one monomer motif. Nonetheless, Ag-Au bonds in the core are clearly distinguished from those bonds linking Au atoms located in the staples motifs and Ag atoms forming the core.

(9) When $n=9$ we considered a set of 11 isomers. A total substitution of the nine core atoms was found preferentially. The Ag_9 core held Ag-Ag bond lengths from 2.77 to 3.2 Å. In contrast if Ag atoms are part of two monomers and one tetramer motifs, the isomer is 0.35 eV less stable. The incorporation of all the nine Ag atoms in the staple-like motifs yielded an isomer with a relative energy of circa 1.0 eV.

(10) In order to explore all the preferred sites for Ag doping for $n=10$, we considered 13 isomers. Ten Ag atoms prefer to incorporate to the Au_9 core plus one monomer motif (0.0 eV), or to one tetramer motif (8.8 meV). When the Ag atoms are incorporated into two monomer adatoms, one tetramer motif, and Ag_7 core, the relative energy is 0.274 eV.

The obtained trend in the Ag doping is that silver incorporates in atoms of STF and additional atoms prefer to incorporate to either core or adatoms located at monomer motifs ($n=4,5,6$). However, substitution occurs in the inner positions when $n=9$.

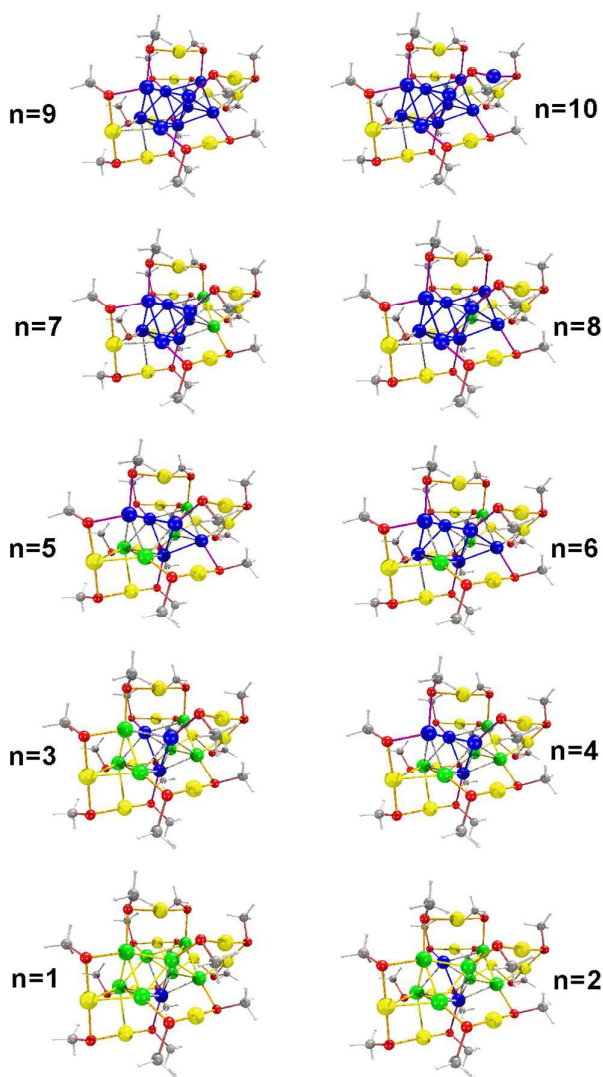


Fig 2. More stable isomers with up to ten Ag atoms ($n=1-10$) doping the parent Au_{18} the thiolated Au_{18} cluster, but it is found an isomer with a relative energy of 0.26 eV that contains five Ag atoms in the inner core and cluster. Colors are same as indicated in figure 1, but Ag atoms are shown in blue.

All the studied compositions in this report show the presence of one Ag_3 unit, located at the middle part of the structure (in the triangular shared face by two octahedral-like units). This result is in line with experimental results by Dass et al. for crystalline silver doped Au_{38} cluster.^{13a} They have attributed the presence of one Ag_3 unit, located at the shared face by two icosahedral units, to the stability conferred to the structure. We think that the combine effects of three monomeric motifs linked across one Ag_3 unit are conferring stability to the Ag doped $\text{Au}_{18}(\text{SR})_{14}$ structures also.

A further analysis of the calculated HL gaps let us know that the larger value is obtained after substituting seven Ag atoms, and followed by a structure constituted by three Ag atoms, as can be seen in Table 1. However, is important to note that large HOMO-LUMO values are not related to a major stability necessarily as will be shown latter.

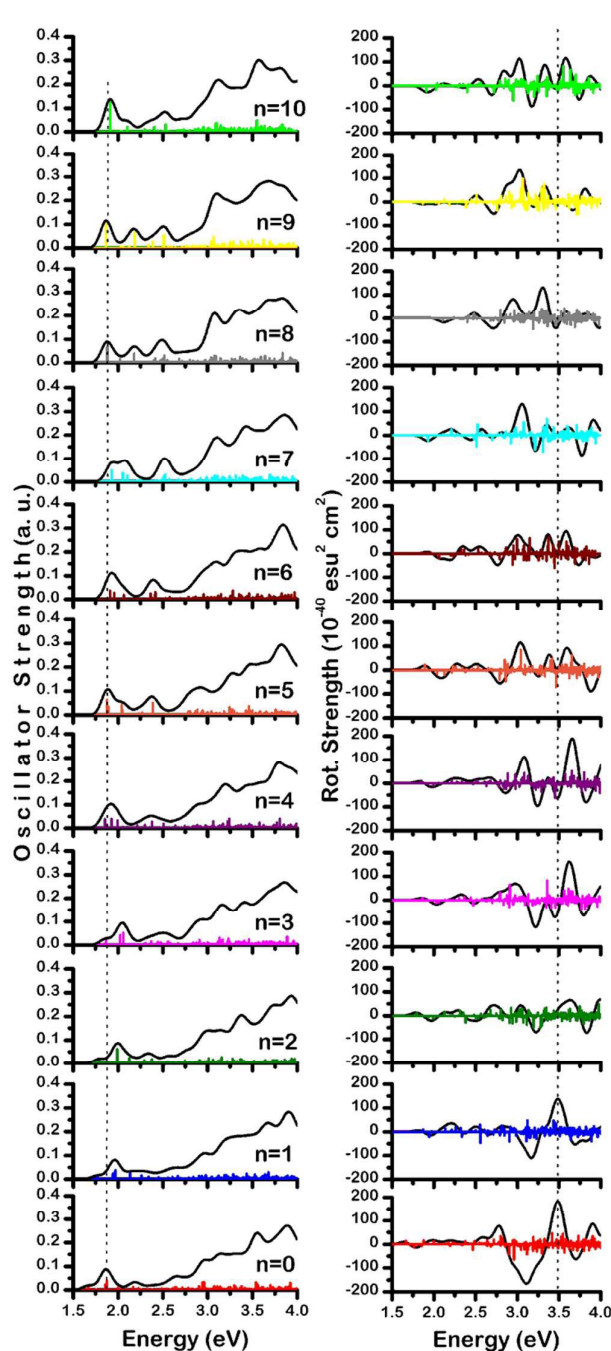
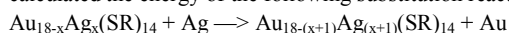


Fig 3. Calculated optical absorption (left panel) and CD spectra (Right panel) for more stable monometallic and doped clusters; n indicates the number of Ag atoms. Bottom curve corresponds with the un-doped structure. A Gaussian broadening of 0.15 eV has been used.

An important question is related to the relative stability of the doped clusters. In order to know which n yield the more stable structure, we calculated the energy of the following substitution reactions:



It was found that the lowest substitution reaction energy is obtained when $n=2$ with a reaction heat of 0.30 eV (Figure 4). This result indicates that Ag doping conduces to optimal formation of the

Table 1. Core composition and HOMO-LUMO (HL) gap of most stable $\text{Ag}_n\text{Au}_{18-n}(\text{SR})_{14}$ clusters.

| # Ag atoms | HL, eV |
|------------|-------------|
| 0 | 1.48 |
| 1 | 1.59 |
| 2 | 1.60 |
| 3 | 1.67 |
| 4 | 1.65 |
| 5 | 1.64 |
| 6 | 1.70 |
| 7 | 1.74 |
| 8 | 1.68 |
| 9 | 1.64 |
| 10 | 1.63 |

Table 2. First peaks their oscillator strength and contribution from HOMO-LUMO transition of studied clusters.

| # Ag atoms | Peak energy | Oscillator strength | HOMO->LUMO (% contribution weight) |
|------------|-------------|---------------------|------------------------------------|
| 0 | 1.6671 | 0.018 | 85.60 |
| | 1.8550 | 0.047 | |
| 1 | 1.7711 | 0.015 | 87.70 |
| | 1.9710 | 0.057 | |
| 2 | 1.7948 | 0.020 | 86.00 |
| | 1.9912 | 0.080 | |
| 3 | 1.8633 | 0.026 | 79.40 |
| | 2.0254 | 0.042 | |
| 4 | 1.8517 | 0.043 | 65.70 |
| | 1.9255 | 0.061 | |
| 5 | 1.8772 | 0.071 | 73.60 |
| | 1.8944 | 0.034 | |
| 6 | 1.9095 | 0.074 | 56.48 |
| | 1.9575 | 0.042 | |
| 7 | 1.9284 | 0.075 | 69.40 |
| | 2.0547 | 0.041 | |
| 8 | 1.8791 | 0.088 | 81.90 |
| | 2.180 | 0.059 | |
| 9 | 1.8676 | 0.114 | 83.80 |
| | 1.9121 | 0.135 | |

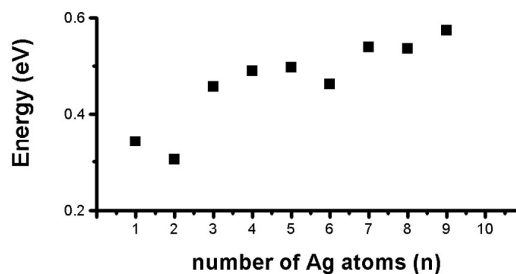


Fig 4. energy of the substitution reaction for Ag doping structures. Lowest value indicates the optimal structure.

$\text{Au}_{16}\text{Ag}_2(\text{SCH}_3)_{14}$ cluster.

Noteworthy is that during the revision of this manuscript, it has published the experimental structure of the $\text{Au}_{15}\text{Ag}_3(\text{SR})_{14}$ cluster.³³ The obtained $n=3$ structure seems to contradict the calculated high reaction energy for $n=2$. However, we think that the obtained preference for the $n=3$ structure can be ascribed to the high

Boltzmann weight (0.98) associated with the most stable isomer of a set of 40 isomers, while when $n=2$ structure two isomers showed Boltzmann weights greater than 0.10. Moreover, looking at the Figure 3 and the first intense peak for $n=3$, that is comparable in intensity with the HOMO-LUMO peak of the monometallic cluster (indicated as a dotted line), is evident that this peak is located at high energy among all studied compositions.

Calculated optical absorption spectrum of parent thiolated Au_{18} cluster displays characteristic peaks located at 1.98, 2.18 and 2.75 eV, while calculated spectrum shows corresponding peaks located at 1.86, 2.17 and 2.64 eV, respectively (Figure 3, left panel).

Spectral line shapes are qualitative different for each n , and new sharp peaks evolve according as the Ag doping increases ($n > 4$), this result coincides with a previous work related to the thiolated Au_{25} cluster. However, in the case of the silver doping of the anionic thiolated Au_{25} cluster, no enhancement of the oscillator strength was found.⁸ In contrast, in this report is found that starting from four Ag atoms, doped structures show more defined peaks with higher oscillator strengths (circa 7.5 times for $n=10$). Regarding the first peak (HOMO- LUMO transition) found in all spectra, it shifts toward higher energies, with a maximum change of circa 0.3 eV for $n=3$ (see reported oscillator strengths in Table 2 and Table S2). This behaviour agrees with the trend obtained in the HL gaps discussed above and shown in Table 1.

The proximity in the relative energies of the calculated isomers may affect the population of possible structures at ambient temperature. We estimate individual contributions by a weighted Boltzmann distribution, in such a manner that the computed intensities of absorption spectra should be multiply by the Boltzmann weight (BW(i)) of each isomer. The number of isomers included in each set for specific composition n is included in the denominator of the following formula:

$$BW(i) = \frac{e^{-E_i/kT}}{\sum_j e^{-E_j/kT}}$$

Where k is the Boltzmann constant (8.6173324×10^{-5} eV/K), T the temperature (298 K), and E_i is the relative energy of the isomer. Table S1 shows the Boltzmann weights and the averaged absorption spectra for isomers of each n . From that Table S1 is concluded that lowest energy isomers are contributing more significantly to the absorption spectra and mainly to those peaks due to the HOMO-LUMO transitions. For example, for $n=3$, the calculated Boltzmann weight is circa 0.99, which mean that only the more stable isomer contributes to the absorption spectrum.

On the other hand, a recent study of the enhancement in the fluorescence of a silver doped rod-shaped Au_{25} cluster has been reported by Muniz-Miranda et al.²⁸ They have attributed the enhancement to an intense lower energy peak (large oscillator strength) that is shifted toward high energies in the adsorption spectrum after silver doping. Moreover, they proposed that the fluorescence occurs due to the high oscillator strength of the HOMO- \rightarrow LUMO transitions. Worthy of note is that several of the silver doped clusters studied in this report show enhanced peaks related to HOMO- \rightarrow LUMO transitions. For example, by doping with more than four Ag atoms, the first lowest peak of absorption spectra is intense with respect to the un-doped thiolated Au_{18} cluster. Experimental work by Zhou group has established that ligand type protecting the thiolated Au_{25} core are important because some ligands can enhance the quantum yield.²⁹ Worthy of note is that the mechanism to fluorescence in thiolated gold cluster is not clear but

there exist some important proposals.^{30,31}

Regarding chiroptical properties of silver doped clusters, Jin group has reported that thiolated Au_{18} cluster is non-chiral because there exists a symmetry plane along the dimer motif.^{21b} We agree that by considering only the Au-S framework could be viable to determine the thiolated Au_{18} cluster as non-chiral, but including ligands and their relative orientations (steric hindrance) may change the symmetry. We built a C_s structure (Fig. S5) covered with $-\text{SCH}_3$ as ligand and compared it against the C_1 isomer. Interestingly, C_s isomer is 3.06 eV less stable than the C_1 structure. This result indicates that Au_{18} protected with $-\text{SCH}_3$ is chiral as previously was reported by Tsukuda et al.³² A further comparison of the experimental absorption spectra confirms that Tsukuda and Jin group have reported similar UV data (see the comparison on Fig. S3). Along this report we have used Tsukuda CD data of parent Au_{18} cluster for comparison against the silver doped clusters.

The analysis of the calculated CD spectra suggests the inherent chirality of silver doped structures. Our results can be summarized as follow:

- (1) The CD spectrum of the calculated $\text{Au}_{18}(\text{SR})_{14}$ features more intense peaks located at: 2.79(+), 2.95 (-), 3.10 (-), and one more intense peak located at 3.49 eV (+) (indicated with a dotted line). Last two peaks coincide with the reported CD data by Tsukuda (Fig. S4).
- (2) In general, it is observed that silver doping of the thiolated Au_{18} cluster results in less intense CD profiles, as can be verified in the right panel of Figure 3. For example, when one Ag atom is incorporated into the thiolated Au_{18} cluster, the obtained CD shows two less intense peaks located at 3.17 (-) and 3.49 (+) eV with respect to the un-doped cluster.
- (3) The CD spectrum of the thiolated Au_{18} cluster doped with two Ag atoms is similar in the position of peaks included in the range from 3.0 to 4.0 eV, but their intensity is clearly diminished.
- (4) Two distinct and positive peaks located at 3.08 and 3.65 eV are found for the $n=4$ structure. The profile of $n=3$ and $n=4$ are similar in the range from 3.0 to 4.0 eV.
- (5) In the case of $n=5$ and $n=6$ their profiles display three positive peaks in the range from 3.0 to 3.75 eV, being comparable in intensity in the case of the $n=6$ structure. However, $n=5$ has a negative intense peak located at 3.9 eV.
- (6) For $n=7$ cluster a positive and distinct peak is located circa 3.06 eV, and two negative peaks are located at 3.21 and 3.78 eV, respectively.
- (7) Doping with 8 and 9 silver atoms results in similar CD profiles, both curves present two positive peaks but their intensities are reversed. $n=8$ structure shows the positive intense peak located at 3.3 eV while $n=9$ has the intense positive peak around 3.03 eV.
- (8) In the case of the structure doped with 10 silver atoms, the curve shows three positive peaks located at 3.0, 3.33 and 3.58 eV, and one negative peak located at 3.17 eV.

Taking into account that in Figure 3 are depicted calculated CD profiles of more stable isomers for each composition. The obtained less intense CD peaks, when the monometallic $\text{Au}_{18}(\text{SR})_{14}$ cluster is doped, clearly demonstrate that the experimental observed less intense CD profile in silver doped $\text{Au}_{18}(\text{SR})_{14}$ clusters is not related neither to the presence of various isomers at each composition nor to a cancellation effect as was published by Kobayashi et al.³⁴

The analysis of calculated adsorption spectra (Figure 3) support our conclusion that the thiolated Au_{18} cluster displays an enhancement of

the peaks related to HOMO-LUMO transitions when more Ag atoms are incorporated. Regarding CD intensity, it is found that it varies accordingly with the number of doping Ag atoms, and a less intense peak located at 3.49 eV is displayed for all studied structures.

The importance of this study is based on the enhancement of the lower energy peak (HOMO-LUMO transitions) that is seen as necessary to improve the quantum yield of these structures.

Conclusions

In summary, in this communication we have carried out a systematically study of a total set of 180 silver doped structures. The structure, electronic, optical and chiroptical properties of the silver doped thiolated Au₁₈ cluster were studied. It was found that silver doped clusters show enhanced HL gap values with respect to the parent Au₁₈ cluster. Moreover, it was determined that when three and seven Ag atoms are incorporated into the structure, large HL gap values are obtained. However, the first intense band for n=3 is located at high energy in contrast to the n=7 structure. Our calculations show that the Ag doping of the thiolated Au₁₈ cluster disturbs its optical and chiroptical properties depending on the specific number of incorporated Ag atoms. Calculated absorption spectra show a lowest energy peak with enhanced oscillator strength for some specific compositions that will represent a challenge to synthesize them in order to let us verify its enhanced properties. Another interesting results is that CD profile of silver doped Au₁₈(SR)₁₄ cluster is less intense and the positive intense peak located at 3.49 eV is affected by the incorporation of Ag atoms.

These results can be seen as a manner to enhance the photoluminescence properties where is necessary to obtain structures with enhanced absorption in the optical region (1.5-3.0 eV).

Notes and references

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