Unraveling a generic growth pattern in structure evolution of thiolate-protected gold nanoclusters

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Unraveling a generic growth pattern in structure evolution of thiolate-protected gold nanoclusters†

Wen Wu Xu,a Yadong Li,a,b Yi Gao*a,c,d and Xiao Cheng Zengd,e

Precise control of the growth of thiolate-protected gold nanoclusters is a prerequisite for their applications in catalysis and bioengineering. Here, we bring to bear a new series of thiolate-protected nanoclusters with a unique growth pattern, i.e., Au32(SR)16 → Au36(SR)20, Au44(SR)28 → Au52(SR)32. These nanoclusters can be viewed as resulting from the stepwise addition of a common structural motif [Au8(SR)4]. The highly negative values of the nucleus-independent chemical shift (NICS) in the center of the tetrahedral Au4 units suggest that the overall stabilities of these clusters stem from the local stability of each tetrahedral Au unit. Generalization of this growth-pattern rule to large-sized nanoclusters allows us to identify the structures of three new thiolate-protected nanoclusters, namely, Au52(SR)32 → Au60(SR)36, Au68(SR)40, and Au76(SR)44. Remarkably, all three large-sized nanoclusters possess relatively large HOMO–LUMO gaps and negative NICS values, suggesting their high chemical stability. Further extension of the growth-pattern rule to the infinitely long nanowire limit results in a one-dimensional (1D) thiolate-protected gold nanowire (RS-AuNW) with a band gap of 0.78 eV. Such a unique growth-pattern rule offers a guide for precise synthesis of a new class of large-sized thiolate-protected gold nanoclusters or even RS-AuNW which, to our knowledge, has not been reported in the literature.

Introduction

Since the first successful crystallization of the thiolate-protected gold nanocluster Au102(SR)44 in 2007,1 research into the structural evolution and structure–property relationship of thiolate-protected gold nanoclusters has attracted considerable attention due to high potential of these nanoclusters for applications in electronics, catalysis and bioengineering.2–7 Significant advancement in structure determination has been made on the basis of X-ray crystallography,1,8–10 single-particle transmission electron microscopy (SP-TEM),21 as well as density-functional theory (DFT) computation22–25 in conjunction with the “divide and protect” formulation.4,31 Although the latter formulation can be very useful in seeking optimal ligand patterns for given gold-core structures, generic growth patterns of the gold nanoclusters are still largely unknown, which hinders the development of large-sized ligand-protected gold nanoclusters for optical and electronic applications.

In this communication, we report a growth-pattern rule that has been revealed based on previously known1 (via X-ray crystallography) and/or theoretically predicted structures of a series of ligand-protected gold nanoclusters, i.e., Au20(SR)16 → Au28(SR)20, Au36(SR)24 → Au44(SR)28, and Au52(SR)32 → Au60(SR)36.11,14 These clusters can be viewed as structural evolutions from the starting cluster Au20(SR)16 via sequential addition of a [Au8(SR)4] motif, i.e., Au20(SR)16 + [Au8(SR)4] → Au28(SR)20 + [Au8(SR)4] → Au36(SR)24 + [Au8(SR)4] → Au44(SR)28 + [Au8(SR)4] → Au52(SR)32. Fig. 1 illustrates the structural evolution of the face-centered-cubic (FCC) type of Au kernels in these clusters via sequential addition of the “boat-like” Au8 motif.

Computational methods

All clusters were optimized using the DFT method implemented in the Dmol3 7.0 code.34,35 To this end, the generalized gradient approximation in the Perdew–Burke–Ernzerhof (PBE)36 form was employed together with the double numeric polarized (DNP) basis set and the semi-core pseudopotential. In all our computations, the R group in the ligands is simplified as a methyl group or hydrogen atom. All the optimized structures of the nanoclusters are presented in ESI Fig. S1.† On basis of the optimized structures (R = hydro-
Table 1 A summary of literature results for a series of ligand-protected gold nanoclusters from Au_{20}(SR)_{16} to Au_{76}(SR)_{44}. \( \sqrt{\text{v}} \): structure determined from X-ray crystallography; p: theoretical prediction; ?: structure unknown; †: different in crystallization, prediction not yet confirmed.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au_{20}(SR)_{16} ( \sqrt{\text{v}} )</td>
<td>p (ref. 25)</td>
</tr>
<tr>
<td>Au_{28}(SR)_{20} ( \sqrt{\text{v}} )</td>
<td>( \sqrt{\text{v}} ) (ref. 41)</td>
</tr>
<tr>
<td>Au_{36}(SR)_{24} ( \sqrt{\text{v}} )</td>
<td>( \sqrt{\text{v}} ) (ref. 9)</td>
</tr>
<tr>
<td>Au_{44}(SR)_{28} ( \sqrt{\text{v}} )</td>
<td>p (ref. 28 and 42)</td>
</tr>
<tr>
<td>Au_{52}(SR)_{32} ( \sqrt{\text{v}} )</td>
<td>?</td>
</tr>
<tr>
<td>Au_{60}(SR)_{36}</td>
<td>This work</td>
</tr>
<tr>
<td>Au_{68}(SR)_{40}</td>
<td>This work</td>
</tr>
<tr>
<td>Au_{76}(SR)_{44} ( \sqrt{\text{v}} )</td>
<td>This work</td>
</tr>
</tbody>
</table>

The results of this study are also compared with other published results for a series of ligand-protected Au nanoclusters from Au_{20}(SR)_{16} to Au_{76}(SR)_{44}.

Results and discussion

As shown in Table 1, the atomic structures of Au_{20}(SR)_{16}, Au_{36}(SR)_{24}, and Au_{52}(SR)_{32} nanoclusters have been determined via X-ray crystallography. Note that Au_{20}(SR)_{16} may have two isomeric structures. The theoretically predicted structure was well reproduced by the optical absorption spectrum of Au_{20}(PET)_{16} (PET = SCH_{2}CH_{2}Ph), and it has a distinct Au kernel of the crystallized Au_{20}(TBBT)_{16} (TBBT = SPh-t-Bu) cluster.

A similar situation was reported in the cases of Au_{40}(o-MBT)_{24} and Au_{40}(PET)_{24}. The structure prediction of Au_{44}(SR)_{28} was based on the structural rules derived from the crystallization of Au_{28}(SR)_{20} and Au_{36}(SR)_{24}, i.e., Au_{28}(SR)_{20} + [Au_{8}(SR)_{4}] \rightarrow Au_{36}(SR)_{24} (Fig. 1(b)) + [Au_{8}(SR)_{4}] \rightarrow Au_{44}(SR)_{28} (Fig. 1(c)). The excellent agreement between experimental and computed optical absorption spectra of Au_{44}(SR)_{28} validates the predicted structure of Au_{44}(SR)_{28}, which is solely based on the growth-pattern rule derived from Au_{28}(SR)_{20} and Au_{36}(SR)_{24}.

Additional evidence comes from the crystallization of the Au_{52}(SR)_{32} nanocluster, whose structure can be viewed as adding the [Au_{8}(SR)_{4}] motif to the predicted structure of Au_{44}(SR)_{28} (Fig. 1(d)). It should be noted that the recently reported Au_{28}(S-c-C_{6}H_{11})_{20} (where c-C_{6}H_{11} = cyclohexyl) cluster exhibits a similar Au_{20} kernel structure to crystallized Au_{28}(TBBT)_{20} (ESI Fig. S2†). Therefore, the two crystallized structures of Au_{28}(SR)_{20} can be evolved from Au_{20}(SR)_{16} (Fig. 1(a)). Besides the different surface-protecting ligands, the two isomeric structures have different staple motifs.

According to the “divide and protect” formulation, Au_{20}(SR)_{16}, Au_{28}(SR)_{20}, Au_{36}(SR)_{24}, and Au_{52}(SR)_{32} can be divided into Au_{14}[Au_{8}(SR)_{4}]_{4} + Au_{14}[Au_{8}(SR)_{4}]_{4} + Au_{14}[Au_{8}(SR)_{4}]_{4} + Au_{14}[Au_{8}(SR)_{4}]_{4}. Au_{28}(Au_{8}(SR)_{4})_{6}, Au_{28}(Au_{8}(SR)_{4})_{6}, Au_{28}(Au_{8}(SR)_{4})_{6}, and Au_{28}(Au_{8}(SR)_{4})_{6}, respectively. The Au_{20} kernel clusters Au_{20}(SR)_{16}, Au_{28}(SR)_{20}, Au_{36}(SR)_{24}, and Au_{52}(SR)_{32} which are comprised of tetrahedral Au_{4} units, can be derived by removing the [Au_{8}(SR)_{4}] staple motifs, as shown in Fig. 2. It is known that NICS values have been commonly used as an index to measure the local aromaticity of fullerene cages or small metal clusters. In addition, NICS analyses have been applied successfully to evaluate the stabilities of gold fullerene structures, such as Au_{13}, 48 and Au_{13}. 49 Recently, NICS analyses of the Au_{36}(SR)_{24} cluster were performed to support the concept of a superatom-network (SAN) theory to explain the stability of thiolate-protected gold nanoclusters. Thus, it is sensible to examine the stabilities of Au_{20}(SR)_{16}, Au_{28}(SR)_{20}, Au_{36}(SR)_{24}, Au_{44}(SR)_{28}, and Au_{52}(SR)_{32} based on the computed NICS values corresponding to the center of the tetrahedral Au_{4} units of these clusters. It can be seen that the absolute NICS values (see Table 2) at the centers of the tetra-
hedral Au₄ units are large; larger than those at the centers of the total structures. The NICS results suggest notable aromaticity in the tetrahedral Au₄ units. As such, the overall stabilities of Au₂₀(SR)₁₆, Au₂₈(SR)₂₀, Au₃₆(SR)₂₄, Au₄₄(SR)₂₈, and Au₅₂(SR)₃₂ likely stem from the local stability of each tetrahedral Au₄ unit.

The unique growth-pattern rule derived among the series of clusters, Au₂₀(SR)₁₆, Au₂₈(SR)₂₀, Au₃₆(SR)₂₄, Au₄₄(SR)₂₈ and Au₅₂(SR)₃₂, suggests the possible existence of larger-sized clusters through continuously adding the motif [Au₈(SR)₄], e.g.,

\[
\text{Au}_{52}(\text{SR})_{32} + [\text{Au}_{8}(\text{SR})_{4}] \rightarrow \text{Au}_{60}(\text{SR})_{36} + [\text{Au}_{8}(\text{SR})_{4}]
\]

\[
\rightarrow \text{Au}_{68}(\text{SR})_{40} + [\text{Au}_{8}(\text{SR})_{4}]
\]

\[
\rightarrow \text{Au}_{76}(\text{SR})_{44}
\]

where the newly created Au₆₀(SR)₃₆, Au₆₈(SR)₄₀, and Au₇₆(SR)₄₄ all possess the FCC-type Au-kernels (Fig. 3). Fig. 4 presents the computed HOMO–LUMO gaps of the optimized nanoclusters from the small-sized Au₂₀(SR)₁₆ to large-sized Au₇₆(SR)₄₄, as well as the experimentally measured optical gaps of Au₂₀(SR)₁₆, Au₂₈(SR)₂₀, Au₃₆(SR)₂₄, and Au₄₄(SR)₂₈. The computed gaps reproduce the experimental gaps quite well except for Au₂₈(SR)₂₀. Nevertheless, the computed gap of Au₂₈(SR)₂₀ is consistent with a previous theoretical study.¹⁴ The HOMO–LUMO gaps of Au₆₀(SR)₃₆, Au₆₈(SR)₄₀, and Au₇₆(SR)₄₄ are all greater than 1.0 eV, comparable to those of Au₆₄(SC₆H₁₁)₃₂ ⁵¹ and Au₇₆(PET)₃₅.⁵² Double-helix structures made of tetrahedral Au₄ units can be seen in the three new structures (ESI Fig. S4†), and are also present in Au₂₀(SR)₁₆, Au₂₈(SR)₂₀, Au₃₆(SR)₂₄, Au₄₄(SR)₂₈ and Au₅₂(SR)₃₂ clusters. Furthermore, the NICS analyses (ESI Table S1 and Fig. S6†) also show that the overall stabilities of Au₆₀(SR)₃₆, Au₆₈(SR)₄₀, and Au₇₆(SR)₄₄ are likely due to the local stability of each tetrahedral Au₄ unit. The large HOMO–LUMO gaps and the negative NICS values suggest high stability of the newly predicted structures.

It should be noted that the Au₇₆(4-MEBA)₄₄ (4-MEBA = 4-(2-mercaptoethyl)benzoic acid) nanocluster has been synthesized recently by Takano et al.⁵³ Although Au₇₆(4-MEBA)₄₄ has the same number of Au atoms and ligands as Au₇₆(SR)₄₄, a comparison of the computed and experimental X-ray diﬀraction (XRD) and optical absorption spectra suggests that the two clusters may have diﬀerent structures in their Au-kernels (ESI Fig. S5†). It is known that surface-protecting thioclates can have significant eﬀects on the structures of gold nanoclusters even with the same number of Au and S atoms. For example, the marked differences in their absorption spectra indicate that

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**Table 2**  Computed nucleus-independent chemical shift (NICS) values of Au₂₀(SR)₁₆, Au₂₈(SR)₂₀, Au₃₆(SR)₂₄, Au₄₄(SR)₂₈, and Au₅₂(SR)₃₂. “0” denotes the NICS values at the centers of the total structures. “1–10” denote the NICS values at the centers of tetrahedral Au₄ units of these clusters (ESI Fig. S3)

<table>
<thead>
<tr>
<th>Cluster</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au₂₀(SR)₁₆</td>
<td>–7.5</td>
<td>–28.2</td>
<td>–28.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au₃₆(SR)₂₄</td>
<td>–10.8</td>
<td>–24.5</td>
<td>–26.2</td>
<td>–23.4</td>
<td>–23.1</td>
<td>–24.2</td>
<td>–25.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au₄₄(SR)₂₈</td>
<td>–17.3</td>
<td>–25.6</td>
<td>–23.5</td>
<td>–23.5</td>
<td>–23.6</td>
<td>–23.8</td>
<td>–23.5</td>
<td>–25.6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Fig. 2  The structures of Au₈ in Au₂₀(SR)₁₆, Au₁₄ in Au₂₈(SR)₂₀, Au₂₀ in Au₃₆(SR)₂₄, Au₂₆ in Au₄₄(SR)₂₈, and Au₃₂ in Au₅₂(SR)₃₂. Au atoms are both olive and wine.

Fig. 3  The optimized structures of Au₆₀(SR)₃₆, Au₆₈(SR)₄₀, and Au₇₆(SR)₄₄, where the methyl groups are omitted for clarity. Au and S atoms are in gold and red, respectively.
Au_{40}(o-MBT)_{24}^{43} and Au_{40}(PET)_{24}^{44} have different structures, and so do Au_{20}(PET)_{16}^{32} and Au_{20}(TBBT)_{16}^{38}, as well as Au_{28}(TBBT)_{20}^{13} and Au_{28}(S-c-C_{6}H_{11})_{20}^{40}. Moreover, even with the same ligands, different Au_{38}(PET)_{24} isomers have been detected.^{15,54}

Lastly, if the growth-pattern rule is extended to the infinitely-long nanowire limit by repeatedly adding [Au_{8}(SR)_{4}] units in one direction, the thiolate-protected gold nanowire (RS-AuNW) can be obtained, as shown in Fig. 5(a) and (b). The present RS-AuNW also exhibits a double-helix structure made of tetrahedral Au_{4} units, which is very different from that of previously proposed vertex- and face-sharing icosahedral thiolated Au nanowires^{55} and crystallized [Au_{25}(SBU)_{18}]_{n}^{n} nanowires.^{56} Fig. 5(c) shows the computed total density of state (DOS) of the present RS-AuNW, which shows an electronic band gap of 0.78 eV, suggesting that the present RS-AuNW is semiconducting. The vertex-sharing thiolated gold nanowire can be made either semiconducting or metallic by tuning the charge. The face-sharing nanowire is always metallic. The non-magnetic ground state of [Au_{25}(SBU)_{18}]_{n}^{n} has a band gap of 0.12 eV, suggesting that [Au_{25}(SBU)_{18}]_{n}^{n} could behave as a narrow-gap semiconductor. It is also found that the valence band of the present RS-AuNW is mainly contributed to by the Au(5d), S(3p) Au(6s), and Au(6p) atomic orbitals, while the conduction band is mainly due to the Au(6sp) atomic orbitals.

Conclusions

In conclusion, a generic growth-pattern rule is identified based on the series of nanoclusters Au_{20}(SR)_{16}, Au_{28}(SR)_{20}, Au_{36}(SR)_{24}, Au_{44}(SR)_{28}, and Au_{52}(SR)_{32}, which can be viewed as the sequential addition of [Au_{8}(SR)_{4}] units. The large negative nucleus-independent chemical shift (NICS) values in the centers of the tetrahedral Au_{4} units indicate that the integral stabilities of these clusters are determined by the local stability of each tetrahedral Au_{4} unit. Extension of the rule to larger-sized nanoclusters than the state-of-the-art gives rise to new structures of nanoclusters such as Au_{60}(SR)_{36}, Au_{68}(SR)_{40}, and Au_{76}(SR)_{44}. All three large-sized nanoclusters exhibit relatively large HOMO–LUMO gaps and negative NICS values, suggesting their high chemical stability. It is also found that the computed XRD and optical absorption spectra of Au_{76}(SR)_{44} are not the same as those of Au_{76}(4-MEBA)_{44} from experiments, suggesting the two nanoclusters may have different Au-kernel structures. Finally, extension of the growth-pattern rule to the infinitely long nanowire limit results in a 1D RS-AuNW with a band gap of 0.78 eV. The unique growth-pattern rule offers a guide for future synthesis of a new class of large-sized thiolate-protected gold nanoclusters or even RS-AuNW that has not been reported in the literature.

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