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

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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.*, Au₂₀(SR)₁₆, Au₂₈(SR)₂₀, Au₃₆(SR)₂₄, Au₄₄(SR)₂₈, and 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 Au₄ unit. Generalization of this growth-pattern rule to large-sized nanoclusters allows us to identify the structures of three new thiolate-protected nanoclusters, namely, Au₆₀(SR)₅₆, 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,^{1,8–20} single-particle transmission electron microscopy (SP-TEM),²¹ as well as density-functional theory (DFT) computation^{22–30} 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 known (*via* X-ray crystallography) and/or theoretically predicted structures of a series of ligand-protected gold nanoclusters, *i.e.*, Au₂₀(SR)₁₆,^{25,32} Au₂₈(SR)₂₀,^{13,40} Au₃₆(SR)₂₄,¹⁵ Au₄₄(SR)₂₈,^{28,33} and Au₅₂(SR)₃₂.¹² 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-

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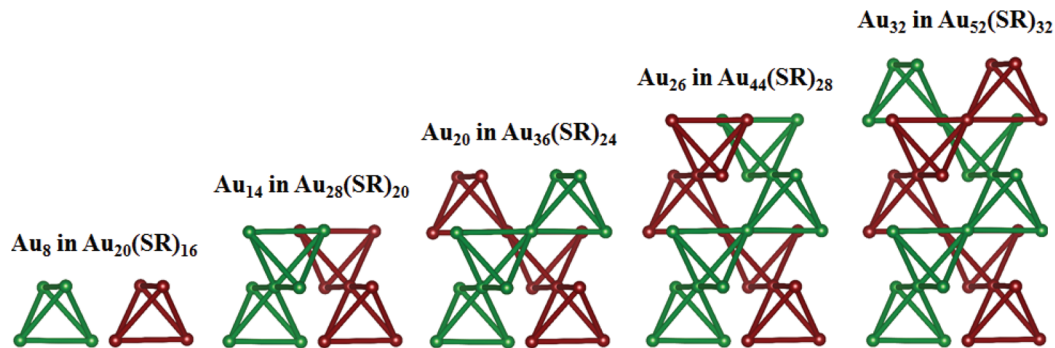


Fig. 2 The structures of Au_8 in $\text{Au}_{20}(\text{SR})_{16}$, Au_{14} in $\text{Au}_{28}(\text{SR})_{20}$, Au_{20} in $\text{Au}_{36}(\text{SR})_{24}$, Au_{26} in $\text{Au}_{44}(\text{SR})_{28}$, and Au_{32} in $\text{Au}_{52}(\text{SR})_{32}$. Au atoms are both olive and wine.

Table 2 Computed nucleus-independent chemical shift (NICS) values of $\text{Au}_{20}(\text{SR})_{16}$, $\text{Au}_{28}(\text{SR})_{20}$, $\text{Au}_{36}(\text{SR})_{24}$, $\text{Au}_{44}(\text{SR})_{28}$, and $\text{Au}_{52}(\text{SR})_{32}$. "0" denotes the NICS values at the centers of the total structures. "1–10" denote the NICS values at the centers of tetrahedral Au_4 units of these clusters (ESI Fig. S3)

	0	1	2	3	4	5	6	7	8	9	10
$\text{Au}_{20}(\text{SR})_{16}$	-7.5	-28.2	-28.7								
$\text{Au}_{28}(\text{SR})_{20}$	-12.4	-25.3	-26.3	-25.2	-26.5						
$\text{Au}_{36}(\text{SR})_{24}$	-10.8	-24.5	-26.2	-23.4	-25.1	-24.2	-25.7				
$\text{Au}_{44}(\text{SR})_{28}$	-17.3	-25.6	-23.5	-23.5	-25.6	-25.6	-23.8	-23.5	-25.6		
$\text{Au}_{52}(\text{SR})_{32}$	-12.7	-25.9	-25.1	-24.2	-22.1	-25.5	-26.0	-23.1	-23.0	-24.7	-25.7

hedral Au_4 units are large; larger than those at the centers of the total structures. The NICS results suggest notable aromaticity in the tetrahedral Au_4 units. As such, the overall stabilities of $\text{Au}_{20}(\text{SR})_{16}$, $\text{Au}_{28}(\text{SR})_{20}$, $\text{Au}_{36}(\text{SR})_{24}$, $\text{Au}_{44}(\text{SR})_{28}$, and $\text{Au}_{52}(\text{SR})_{32}$ likely stem from the local stability of each tetrahedral Au_4 unit.

The unique growth-pattern rule derived among the series of clusters, $\text{Au}_{20}(\text{SR})_{16}$, $\text{Au}_{28}(\text{SR})_{20}$, $\text{Au}_{36}(\text{SR})_{24}$, $\text{Au}_{44}(\text{SR})_{28}$ and $\text{Au}_{52}(\text{SR})_{32}$, suggests the possible existence of larger-sized clusters through continuously adding the motif $[\text{Au}_8(\text{SR})_4]$, 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 $\text{Au}_{60}(\text{SR})_{36}$, $\text{Au}_{68}(\text{SR})_{40}$, and $\text{Au}_{76}(\text{SR})_{44}$ 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 $\text{Au}_{20}(\text{SR})_{16}$ to large-sized $\text{Au}_{76}(\text{SR})_{44}$, as well as the experimentally measured optical gaps of $\text{Au}_{20}(\text{SR})_{16}$, $\text{Au}_{28}(\text{SR})_{20}$, $\text{Au}_{36}(\text{SR})_{24}$, and $\text{Au}_{44}(\text{SR})_{28}$. The computed gaps reproduce the experimental gaps quite well except for $\text{Au}_{28}(\text{SR})_{20}$. Nevertheless, the computed gap of $\text{Au}_{28}(\text{SR})_{20}$ is consistent with a previous theoretical study.¹⁴ The HOMO–LUMO gaps of $\text{Au}_{60}(\text{SR})_{36}$, $\text{Au}_{68}(\text{SR})_{40}$, and $\text{Au}_{76}(\text{SR})_{44}$ are all greater than 1.0 eV, comparable to those of $\text{Au}_{64}(\text{SC}_6\text{H}_{11})_{32}$ ⁵¹ and $\text{Au}_{67}(\text{PET})_{35}$.⁵² Double-helix structures made of tetrahedral Au_4 units can be seen in the three new structures (ESI Fig. S4†), and are also present in $\text{Au}_{20}(\text{SR})_{16}$, $\text{Au}_{28}(\text{SR})_{20}$, $\text{Au}_{36}(\text{SR})_{24}$, $\text{Au}_{44}(\text{SR})_{28}$ and $\text{Au}_{52}(\text{SR})_{32}$ clusters. Furthermore, the NICS analyses (ESI Table S1 and Fig. S6†) also show that the overall stabilities of $\text{Au}_{60}(\text{SR})_{36}$, $\text{Au}_{68}(\text{SR})_{40}$, and $\text{Au}_{76}(\text{SR})_{44}$ are likely due to the local stability

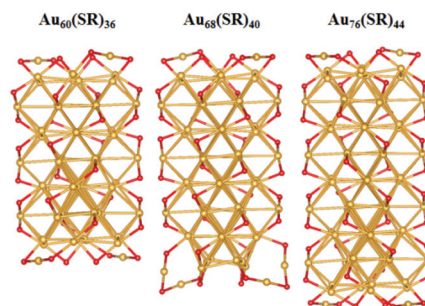


Fig. 3 The optimized structures of $\text{Au}_{60}(\text{SR})_{36}$, $\text{Au}_{68}(\text{SR})_{40}$, and $\text{Au}_{76}(\text{SR})_{44}$, where the methyl groups are omitted for clarity. Au and S atoms are in gold and red, respectively.

of each tetrahedral Au_4 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 $\text{Au}_{76}(4\text{-MEBA})_{44}$ (4-MEBA = 4-(2-mercaptoethyl)benzoic acid) nanocluster has been synthesized recently by Takano *et al.*⁵³ Although $\text{Au}_{76}(4\text{-MEBA})_{44}$ has the same number of Au atoms and ligands as $\text{Au}_{76}(\text{SR})_{44}$, 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 thiolates 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



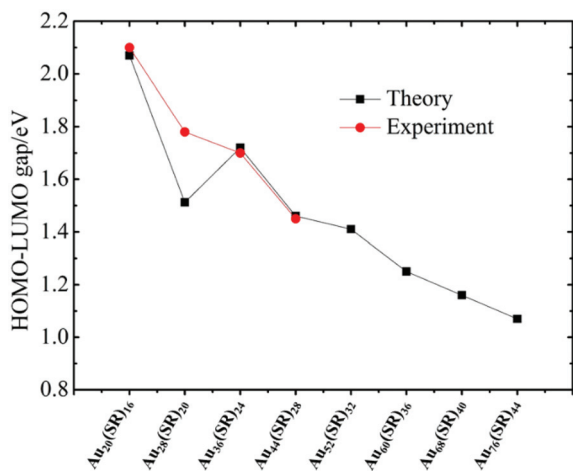


Fig. 4 The computed HOMO–LUMO gaps of the optimized nanoclusters from small-sized Au₂₀(SR)₁₆ to large-sized Au₇₆(SR)₄₄, and the measured optical gaps.

Au₄₀(*o*-MBT)₂₄⁴³ and Au₄₀(PET)₂₄⁴⁴ have different structures, and so do Au₂₀(PET)₁₆³² and Au₂₀(TBBT)₁₆,⁸ as well as Au₂₈(TBBT)₂₀¹³ and Au₂₈(S-c-C₆H₁₁)₂₀.⁴⁰ Moreover, even with the same ligands, different Au₃₈(PET)₂₄ isomers have been detected.^{15,54}

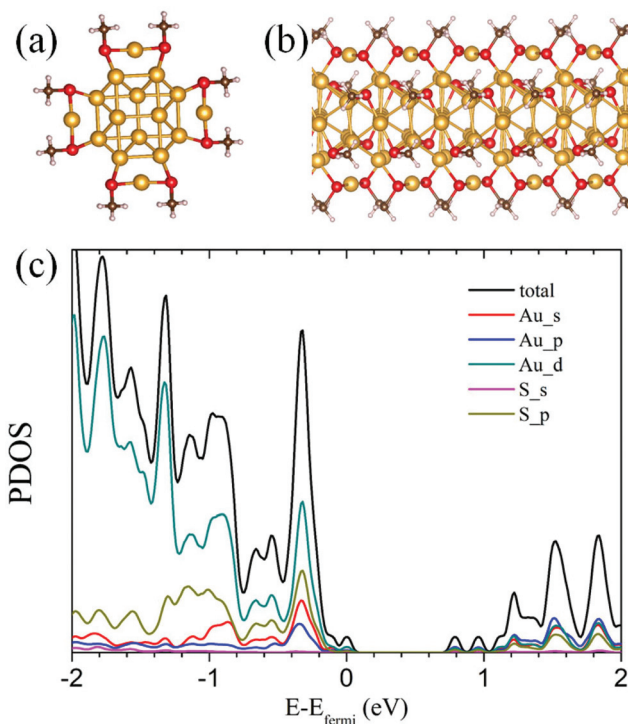


Fig. 5 The proposed structure of the thiolate-protected gold nanowire: (a) viewed along the wire; (b) side view. Au, S, C, and H atoms are in gold, red, dark gray, and white, respectively. (c) Computed projected density of state (PDOS) of the thiolate-protected gold nanowire. Au_s, Au_p, and Au_d denote the s, p, and d orbitals of Au atoms, respectively. S_s and S_p denote the s and p orbitals of S atoms, respectively.

Lastly, if the growth-pattern rule is extended to the infinitely-long nanowire limit by repeatedly adding [Au₈(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 Au₄ units, which is very different from that of previously proposed vertex- and face-sharing icosahedral thiolated Au nanowires⁵⁵ and crystallized [Au₂₅(SBu)₁₈⁰]_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 [Au₂₅(SBu)₁₈⁰]_n has a band gap of 0.12 eV, suggesting that [Au₂₅(SBu)₁₈⁰]_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 Au₂₀(SR)₁₆, Au₂₈(SR)₂₀, Au₃₆(SR)₂₄, Au₄₄(SR)₂₈, and Au₅₂(SR)₃₂, which can be viewed as the sequential addition of [Au₈(SR)₄] units. The large negative nucleus-independent chemical shift (NICS) values in the centers of the tetrahedral Au₄ units indicate that the integral stabilities of these clusters are determined by the local stability of each tetrahedral Au₄ unit. Extension of the rule to larger-sized nanoclusters than the state-of-the-art gives rise to new structures of nanoclusters such as Au₆₀(SR)₃₆, Au₆₈(SR)₄₀, and Au₇₆(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 Au₇₆(SR)₄₄ are not the same as those of Au₇₆(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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