From Monolayer-Protected Gold Cluster to Monolayer-Protected Gold-Sulfide Cluster: Geometrical and Electronic Structure Evolutions of \( \text{Au}_{60} \text{S}_n \text{(SR)}_{36} \) (\( n = 0 – 12 \))

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ABSTRACT: Thiolate-monolayer-protected gold clusters are usually formulated as \( \text{Au}_n \text{SR}[\text{Au}(1)-\text{SR}]_x \) where \( \text{Au}_n \) and \( \text{SR}[\text{Au}(1)-\text{SR}]_x \) \( (x = 0, 1, 2, ... \) ) are the inner gold core and outer protection motifs, respectively. In this work, we theoretically envision a new family of S-atom-doped thiolate-monolayer-protected gold clusters, namely, \( \text{Au}_{60} \text{S}_n \text{(SR)}_{36} \) \( (n = 0 – 12) \). A distinct feature of \( \text{Au}_{60} \text{S}_n \text{(SR)}_{36} \) nanoclusters (NCs) is that they show a gradual transition from the monolayer-protected metal NC to the \( \text{SR}[\text{Au}(1)-\text{SR}]_x \) oligomer-protected gold-sulfide cluster with the increase of the number of doping S atoms. The possible formation mechanism of the S-atom-doped thiolate-protected gold cluster is investigated, and the size-dependent stability and electronic and optical absorption properties of \( \text{Au}_{60} \text{S}_n \text{(SR)}_{36} \) are explored using density functional theory (DFT) calculations. It is found that doping of S atom significantly tails the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap and optical absorption properties of thiolate-protected gold cluster, representing a promising way to fabricate new monolayer-protected gold nanoparticles.

1. INTRODUCTION

The synthesis and characterization of thiolate-monolayer-protected gold nanoparticles (NPs) and nanoclusters (NCs) have aroused great research interest over the past few decades due to the unique physicochemical properties and promising applications of these gold nanomaterials in catalysis, nanotechnology, and chemical biology.\(^1–7\) With the improvement of synthesis method, to date wide-size spectra of atomically precise \( \text{Au}_n \text{(SR)}_m \) NCs with \( n \) ranging from a few tens of atoms to hundreds of atoms have been synthesized, and the structure of several NCs has been successfully characterized by single-crystal X-ray diffraction.\(^9–18\)

The discrete size and precise composition of \( \text{Au}_n \text{(SR)}_m \) NCs provided an ideal template to probe the structure and property relationships of gold nanoclusters. It has been demonstrated by a number of studies that the structure of any \( \text{Au}_n \text{(SR)}_m \) NC was composed of a symmetric \( \text{Au}_n \) core and the oligomeric \( \text{SR}[\text{Au}(1)-\text{SR}]_x \) \( (x = 0, 1, 2, 3, ... \) also denoted as the staple motif) ligand layer.\(^19–30\) For instance, Scheme 1 summarizes the already discovered Au cores in the \( \text{Au}_n \text{(SR)}_m \) clusters, which showed five types of polyhedral structures such as hexagonal close-packed (HCP),\(^31,32\) face-centered cubic (FCC),\(^33–43\) body-centered cubic (BCC),\(^44\) icosahedral (ICO),\(^45–49\) and decahedral (DEC) structures.\(^50–53\) On the surface of metal cores, the \( \text{SR}[\text{Au}(1)-\text{SR}]_x \) motifs had varied lengths depending on the size and atomic packing structure of the metal cores. The bridge SR unit \( (x = 0) \), oligomer \( \text{SR}[\text{Au}(1)-\text{SR}]_x \) \( (x = 1, 2, 3, 4, 6, \text{etc.}) \), and cyclic \( \text{[Au}(1)-\text{SR}]_x \) \( (x = 6 \text{ and } 8) \) have been found in the available NC crystal structures.\(^35,44,46,50,54–65\) Generally, the length of \( \text{SR}[\text{Au}(1)-\text{SR}]_x \) motif will become shorter with the increase of the size of the metal core or cluster. This kind of metal core plus \( \text{SR}[\text{Au}(1)-\text{SR}]_x \) motif assembly pattern has been denoted as the “divide-and-protect” scheme.\(^66–69\)

Scheme 1. Summarization of the Metal Core and Surface Motif Structures of the Thiolate-Monolayer-Protected Gold Nanoclusters

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Besides the well-defined thiolate-monolayer-protected gold NCs, a slightly different category of sulfur atom-doped thiolate-gold NC, which can be formulated as Au_{60}S_{12}(SR)_{36} (the symbol y represents the number of the sulfur atoms), was synthesized recently. Dass et al. reported the synthesis and structural characterization of Au_{60}S(S-{B}u)_{18} cluster, which was closely related to the “green gold” compound Au_{60}S(S-{B}u)_{18}. According to the crystal structure of Au_{60}S(S-Bu)_{18}, a sulfur atom (μ-S) was bonded with three Au atoms, and the remaining part of the Au-S skeleton was the same as that of Au_{60}S(S-Adm)_{19}. Liu et al. reported the bcc-structured Au_{60}S_{2}(S-Adm)_{20} (S-Adm = adamantanethiol) cluster, in which two sulfur atoms were found on the surface of the metal core. The third prototype Au_{60}S_{6}(Au(I)-SR), NC, Au_{61}S_{6}(SAdm)_{15}, was reported recently. The atomic structure of Au_{61}S_{6}(SAdm)_{15} NC is very similar to that of Au_{61}(SAdm)_{15} with the exception that Au_{61}S_{6}(SAdm)_{15} has an additional sulfur atom on the surface of the metal core. Tlahuice-Flores et al. proposed that the Au_{61}(S-Adm)_{15}(SH)_{10}(SCH_{2}CH_{2}S_{2})_{15} model involves disulfide bonds between the dithiolate ligands.

Based on the atomically precise metal NCs, recently, the atomic-level tailoring chemistry (replacing specific surface motifs and removing one or two metal atoms with the structure of the other parts unchanged) on the metal core or surface of metal nanoparticles has been developed. Wang et al. reported a strategy for shuttling a single Ag or Cu atom into a centrally hollow, rod-shaped Au_{60}S_{6} nanoparticle, forming AgAu_{54} and CuAu_{54} alloy nanoparticles in a highly controllable manner. Through a combined experimental and theoretical study, they mapped out the shuttling pathways of a single dopant into and out of the nanoparticles. The single dopant was shuttled into the hollow Au_{54} nanoparticle either through the apex or side entry, while shuttling a metal atom out of the Au_{54} to form the Au_{54} nanoparticle occurs mainly through the side entry. Li et al. reported a site-specific “surgery” on the surface motif of an atomically precise 23-gold-atom [Au_{23}(SR)_{16}] nanoparticle by a two-step metal-exchange method, which leads to the “resection” of two surface gold atoms and formation of a new 21-gold-atom nanoparticle [Au_{21}(SR)_{12}(Ph_{2}PCH_{2}PPh_{2})_{2}] without changing the structure of the other parts of the starting nanoparticle. These advanced experimental works constituted a major step toward the development of atomically precise, versatile nanochemistry for the precise tailoring of the nanocluster structure to control its properties. In particular, the surface single-atom tailoring of a gold nanoparticle, that is, adding, removing, or replacing one surface atom on a structure-resolved nanoparticle in a controlled manner is very exciting.

Very recently, a novel gold nanocluster, namely, Au_{60}S_{6}(SCH_{2}Ph)_{36}, was synthesized by Gan and co-workers. Different from all already known thiolate-monolayer-protected gold NCs in either the Au_{60}S_{6}(Au(I)-SR), or Au_{61}S_{6}(Au(I)-SR), form, the single-crystal X-ray crystallography (SCX) revealed a unique hierarchical structure in Au_{60}S_{6}(SCH_{2}Ph)_{36}. The Au_{60}S_{6}(SCH_{2}Ph)_{36} cluster can be divided into a metal core (Au_{60}), a middle layer of gold-sulfide (SAu_{4}), and a protection monolayer made of SR(Au(I)-SR), motifs. In the middle gold-sulfide layer, six S atoms were combined with 24 gold atoms, forming six SAu_{4} units. Shortly after the report of Au_{60}S_{6}(SCH_{2}Ph)_{36} cluster, Gan et al. reported the single-atom tailing of Au_{60}S_{6}(SCH_{2}Ph)_{36} NC, that is, an extra S atom was successfully introduced into the metal core by reacting the Au_{60}S_{6}(SCH_{2}Ph)_{36} NC with thiol molecule PhCH_{2}SH at an elevated temperature (473 K). The single-crystal X-ray diffraction characterization revealed that a new SAu_{4} unit was formed in Au_{60}S_{6}(SCH_{2}Ph)_{36} while the other parts of the NC remained unchanged compared with Au_{60}S_{6}(SCH_{2}Ph)_{36}. Although the introduction of a new dopant S atom only led to a local structure change of the cluster structure, the crystallographic arrangement of Au_{60}S_{6}(SCH_{2}Ph)_{36} cluster was greatly different from that of Au_{60}S_{6}(SCH_{2}Ph)_{36}. Unlike the case of 6HLH arrangement in Au_{60}S_{6}(SCH_{2}Ph)_{36} crystals, the “ABAB” arrangement was found in Au_{60}S_{6}(SCH_{2}Ph)_{36} crystal, which enhanced the solid photoluminescence of amorphous Au_{60}S_{6}(SCH_{2}Ph)_{36} and brought a slight red shift of the maximum emission.

The discovery of hierarchical structures in Au_{60}S_{6}(SCH_{2}Ph)_{36} and Au_{60}S_{6}(SCH_{2}Ph)_{36} NCs and their possible interconversion reactions encouraged us to explore the structural evolution and the electronic structure properties of the derivative Au_{60}S_{6}(SR)_{36} nanoclusters (n = 0–12). Based on the resolved structure of Au_{60}S_{6}(SCH_{2}Ph)_{36} and Au_{60}S_{6}(SCH_{2}Ph)_{36} it can be easily seen that with gradual decrease or increase of the number of S atoms inside the cluster, the gold cluster will gradually evolve into a thiolate-monolayer-protected gold cluster (Au_{60}S_{6}(SCH_{2}Ph)_{36} n = 0) or a novel thiolate-monolayer-protected gold-sulfide cluster (Au_{60}S_{12}(SCH_{2}Ph)_{36} n = 12). In other words, a gradual evolution from the thiolate-monolayer-protected gold cluster (n = 0) to the hierarchical gold clusters containing a [Au(I)-SR], monolayer, a gold-sulfide middle layer, and a center Au core (n = 1–11) and finally the thiolate-monolayer-protected gold-sulfide quantum dot (QD) (n = 12) is expected in the Au_{60}S_{6}(SR)_{36} nanocluster with the increase of the number of doping S atoms. To the best of our knowledge, there is neither an experimental nor theoretical study on the evolution from the monolayer-protected gold cluster to the monolayer-protected gold-sulfide clusters. Unraveling the structural evolution patterns and the size-dependent properties, as well as the doping mechanism of S atom into the monolayer-protected gold nanoclusters, will enrich our knowledge on the structural diversity and property of monolayer-protected gold nanoclusters.

Based on the above discussions, in this work, we systematically studied the structure and electronic structure evolution as well as the formation mechanism of S-atom-doped thiolate-gold nanoclusters using density functional theory (DFT) and time-dependent (TD)-DFT calculations. The article is organized into four parts: (1) the exploration of structural evolution of Au_{60}S_{6}(SR)_{36} (n = 0–12) NC based on the increase or decrease of S atom (or SAu_{4}) unit in two prototype NCs, Au_{60}S_{6}(SCH_{2}Ph)_{36} and Au_{60}S_{6}(SCH_{2}Ph)_{36}; (2) the simulation of S atom doping mechanisms based on two model reaction systems, i.e., the reaction between thiolate-gold NC and the free S atom or the mercaptan molecule such as PhCH_{2}SH, (3) the evolution of the electronic structure and optical absorption property of Au_{60}S_{6}(SR)_{36} NC, and (4) a comparison of the relative stability of the Au_{60}S_{6}(SR)_{36} (n = 0, 6, 12) NC isomers.

2. RESULTS AND DISCUSSION

2.1. Structure Evolution of Au_{60}S_{6}(SR)_{36} (n = 1–12).

Gan et al. suggested that the Au_{60}S_{6}(SR)_{36} NC was composed of a quasi-FCC Au_{60} core and a pair of giant Au_{20}S_{6}(SCH_{2}Ph)_{18} motifs. In the present study, as shown
in Figure 1, we show that the Au60S6(SR)36 cluster can be divided into a pair of Au30S3(SR)18 subunits. Each Au30S3(SR)18 subunit was composed of a Au10 core formed by three fused gold tetrahedrons and three μ4-S atoms. Each μ4-S atom was bonded with four Au atoms, forming a SAu4 unit. For the convenience of demonstrating the structural feature of the Au60S6(SR)36 cluster, the μ4-S atoms and other S atoms in the SR groups were labeled as 1, 2, and 3 and 1’, 2’, and 3’ in two sets of Au30S3(SR)18 subunits, and the six gold tetrahedrons were labeled as a, b, and c and a’, b’, and c’, respectively. It is worth noting that c, c’, a, a’, b, b’, c, and c’ are the end tetrahedrons of the tetrahedron chain and b, b’, and c are the middle tetrahedrons of the tetrahedron chain. Furthermore, we defined a two-dimensional distribution pattern for the six μ4-S atoms. The S atoms labeled 2, 2’, 3 were distributed in a transverse dimension and the S atoms labeled 1, 3, and 1’ were in the longitudinal dimension.

To assess the formation energy of the Au60S6(SR)36 cluster, we defined a cluster transformation equation using the Au60S6(SR)36 cluster as a reference, i.e., Au60S6(SR)36 + (n − 6)S → Au60S6(SR)36 (0 ≤ n ≤ 12). The averaged formation energy of any Au60S6(SR)36 cluster was defined as ΔE = [E(Au60S6(SR)36) − E(Au60S6(SR)36) − (n − 6) × E(S)]/ln − 6l, where the E(Au60S6(SR)36), E(Au60S6(SR)36), and E(S) represented the energy of the Au60S6(SR)36 cluster, Au60S6(SR)36 cluster, and single S atom, respectively. To reduce the computational cost, the SR ligand was mimicked by the CH3 group. As displayed in Figure S1 in the Supporting Information, even though the averaged formation energy values in the Au60S6(SR)36 (n = 0−12) series with R = CH2Ph and CH3 ligands were different, the trends in quality were the same. Moreover, geometrical analysis also indicates that the Au60S6(SR)36 (n = 0−12) series with R = CH2Ph and CH3 ligands share a very similar bonding pattern. These results show that the geometrical and electronic structures of the clusters change little when we use the simple methyl group (−CH3) to replace the real −CH2Ph group. Therefore, in all model calculations, the SR group was simplified by SCH3.

Beginning with the Au60S6(SR)36 cluster, the formation process of Au60S7(SR)36 clusters was first studied. As shown in Table S1, we considered six doping positions of single S atom. Due to the symmetry of the Au20 core, the a, a’, b, b’, c, and c’ were indeed three pairs of equivalent positions. The comparison of the relative energy of six isomer NCs, Au60S7(SR)36-Iso1 to Au60S7(SR)36-Iso6, confirmed that the optimal position for holding a new dopant S atom in the Au60S7(SR)36 NC was at the c or c’ site. Au60S7-Iso1 and Au60S7-Iso2 (inserting a S atom at the c and c’ site) were more favorable in energy than the other two sets of isomers (inserting a S atom at a, a’ sites or b, b’ sites) by 0.22 and 0.28 eV, respectively. The theoretically determined stable structure of Au60S7(SR)36 was in good agreement with the experimental crystal structure, indicating that the theoretical calculations can correctly predict the structural evolution of the Au60S7(SR)36 NCs.

The optimal structures of other Au60S7(SR)36 (n = 0−5 and 8−12) nanoclusters were determined by comprehensively sampling the doping position of S atom in the metal core. Taking Au60S8(SR)36 as an example, as shown in Table S1, the most favorable doping site of S atom was determined by either
randomly inserting a S atom into the Au₆₀S₇(SR)₃₆ NC or by adding two S atoms at one time into the Au₆₀S₆(SR)₃₆ NC. From Figure 2, in the most stable isomer structure of Au₆₀S₈(SR)₃₆, eight dopant S atoms adopted a symmetric distribution surrounding a compact Au₁₄ core. Using the same means, the optimal structures of Au₆₀S₉(SR)₃₆, Au₆₀S₁₀(SR)₃₆, Au₆₀S₁₁(SR)₃₆ and Au₆₀S₁₂(SR)₃₆ (n = 12), there is only one possible configuration. In particular, in Au₆₀S₁₂(SR)₃₆, all gold atoms were in Au(I) oxidation form. 

Figure 2 displays the Au−S framework of Au₆₀Sₙ(SR)₃₆ NC. A distinct trend of S atom doping that can be seen is that the S atom tended to first occupy the center of the outermost gold tetrahedron (c or c′). Then, a pair of gold tetrahedron in the transverse dimensional was doped by S atom. If we take a look at the reverse process of S atom doping, i.e., the evolution from Au₆₀S₇(SR)₃₆ to Au₆₀(SR)₃₆ NC, it can be found that two centroid μ₋S atoms were extruded first and then the middle and outer layer μ₋S atoms. This trend agreed with the recent experimental finding that during the conversion of the monolayer-protected silver quantum dot [Ag₆₂S₁₃(SBu)]⁴⁺ into silver metal NC [Ag₆₂(SBu)]⁴⁺ via the electrochemical reduction, a centroid S atom in the Ag₁₄ cubic core was extruded out.⁷⁵

To assess the relative stability of the Au₆₀Sₙ(SR)₃₆ (n = 0−12) series, we have defined two kinds of cluster formation processes. The first is a step-by-step NC transformation process by inserting μ₋S atoms originated from the template Au₆₀(SR)₃₆ NC, i.e., Au₆₀Sₙ₋₁(SR)₃₆ + S → Au₆₀Sₙ(SR)₃₆ (1 ≤ n ≤ 12). The second is a cluster formation process using the Au₆₀(SR)₃₆ cluster as a reference, i.e., Au₆₀(SR)₃₆ + nS → Au₆₀Sₙ(SR)₃₆ (1 ≤ n ≤ 12). Figure S2 plots the formation energy of Au₆₀Sₙ(SR)₃₆ cluster via two kinds of formation processes. Using the Au₆₀S₉(SR)₃₆ and Au₆₀S₁₀(SR)₃₆ cluster synthesized recently as the reference, it is found that Au₆₀S₉(SR)₃₆, Au₆₀S₁₀(SR)₃₆ and Au₆₀S₁₁(SR)₃₆ have more negative formation energy, suggesting their relatively high stabilities.

2.2. Doping Mechanism of S Atom into the Thiolate-Monolayer-Protected Gold Clusters. Although experimental studies⁷² have proved that S atom can be introduced into the metal core of Au₆₀Sₙ(SCH₂Ph)₃₆ cluster by reacting with a mercaptan molecule such as HSCH₂Ph at an evaluated temperature, the detailed mechanism of S atom doping into the monolayer-protected gold cluster is still unclear. In this part of the study, we studied two possible reaction processes, including the direct interaction of a S atom with the thiolatemonomer-protected gold NC and the reaction of the thiolatemonolayer-protected gold cluster with a mercaptan molecule such as HSCH₂Ph.

For the first model system, it was found that once a S atom approached the metal kernel of a thiolate-gold nanocluster such as Au₆₀S₇(SR)₃₆ it can spontaneously migrate into the metal kernel to form an SAu₄ unit. Figure 3 displays the process of gradual entering of a S atom into the metal kernel that included three stages: the S atom first adsorbed on the top of an Au₄ triangle unit and then broke the gold−gold bonds to enter the center of the Au₄ tetrahedron, forming an SAu₄ unit. The whole process was strongly exothermic with the reaction energy being as large as −6.75 eV.

The reaction between the thiolate-protected gold cluster and the mercaptan molecule such as PhCH₂SH was investigated based on a smaller size model thiolate-gold cluster, Au₁₅(CH₃)₁₃.⁷⁶,⁷⁷ Gan et al.⁷² found that the reaction of Au₆₀S₉(SCH₂Ph)₃₆ and PhCH₂SH produced a large number of PhCH₂SCH₂Ph side products. Based on the experimental observations, we proposed a three-step reaction mechanism, which consisted of three reaction steps (reactions 1−3)

\[
\begin{align*}
2\text{PhCH}_2\text{SH} & \rightarrow \text{PhCH}_2\text{S} + \text{SCH}_2\text{Ph} + 2\text{H}^+ + 2\text{e}^- \quad (1) \\
\text{PhCH}_2\text{S} + \text{SCH}_2\text{Ph} & \rightarrow (\text{PhCH}_2)_2\text{S} = \text{S} \quad (2) \\
\text{Au}_{15}(\text{CH}_3)_{13} + (\text{PhCH}_2)_2\text{S} & \rightarrow \text{PhCH}_2\text{SCH}_2\text{Ph} + \text{Au}_{15}(\text{CH}_3)_{13} \quad (3)
\end{align*}
\]

The first step was the dimerization of phenylmethane thiol. This reaction has been reported by several previous studies, which indicated that the disulfide bond was formed by coupling two mercaptan groups.⁸⁻⁸³ Then, PhCH₂S−
SCH$_2$Ph transformed into a (PhCH$_2$)$_2$S species by an intermolecular atomic rearrangement. This reaction mechanism has been observed by many previous experimental studies as well.$^{80,82-84}$ Lastly, the reaction of Au$_{15}$(CH$_3$)$_{13}$ NC with the (PhCH$_2$)$_2$S species resulted in a Au$_{15}$S(CH$_3$)$_{13}$ nanocluster.$^{80}$

Since the first reaction step has been confirmed by many experimental studies,$^{78-83}$ here we mainly focused on the second and the last reaction steps. As shown in Figure 4a, isomerization of PhCH$_2$S=SCH$_2$Ph to (PhCH$_2$)$_2$S=S proceeded via an intramolecular benzyl group migration by overcoming an energy barrier of 2.47 eV. Then, the Au$_{15}$(CH$_3$)$_{13}$ cluster can easily fetch a S atom of (PhCH$_2$)$_2$S=S species to form a SAu$_4$ unit by overcoming an energy barrier of 0.67 eV. The reaction was exothermic by $-1.35$ eV. Figure 4b shows an alternative reaction pathway in which the PhCH$_2$S=SCH$_2$Ph reacts directly with the gold cluster. The energy barrier of S atom transferring into the tetrahedron-Au$_4$ unit is 1.64 eV. In both reaction mechanisms, the dimerization of PhCH$_2$SH to form an active intermediate (PhCH$_2$)$_2$S=S is a key step. According to the DFT calculations, the energy barrier of the isomerization of PhCH$_2$S=SCH$_2$Ph to (PhCH$_2$)$_2$S=S is 2.47 eV, or 1.62 eV in the one-step reaction mechanism. This agrees with the previous experimental result$^{72}$ that the reaction was carried out at an evaluated temperature of 473 K.

2.3. Electronic Structure and Optical Absorption Property of Au$_{60}$S$_n$(SR)$_{36}$ ($n = 0-12$) NC. A distinct property of the Au$_{60}$S$_n$(SR)$_{36}$ NC was that with the increase of the dopant S atom, the NCs showed gradual evolution from the conversional monolayer-protected gold NC ($n = 0$) to the hierarchical gold clusters ($n = 1-11$) containing a middle layer of gold-sulfide and then to the monolayer-protected gold-sulfide quantum dot ($n = 12$). In the metal NC Au$_{60}$(SR)$_{36}$, the metal kernel was composed of 12 Au$_4$ tetrahedrons. The total valence electron number of Au$_{60}$(SR)$_{36}$ was 24 (24e). From the metal cluster Au$_{60}$(SR)$_{36}$ to Au$_{60}$S$_6$(SR)$_{36}$ and then to quantum dot Au$_{60}$S$_{12}$(SR)$_{36}$, the number of cluster valence electrons decreased from 24 to 0.
It is therefore important to explore the electronic structure evolution of the Au$_{60}$S$_n$(SR)$_{36}$ NC. Herein, the electronic structure property such as the highest occupied molecular orbital (HOMO)−lowest unoccupied molecular orbital (LUMO) gap, the component of the frontier molecular orbitals, as well as the singlet−single excitation energies of Au$_{60}$S$_n$(SR)$_{36}$ ($n = 0$−$12$) nanoclusters were carefully studied by DFT and TD-DFT. Figure 5 summarizes the HOMO−LUMO gaps of Au$_{60}$S$_n$(SR)$_{36}$ NC with $n$ changing from 0 to 12. An overall trend of the HOMO−LUMO gap in these NCs was that with the increase of the number of dopant S atoms, the HOMO−LUMO gap increased gradually. Au$_{60}$S$_{12}$(SR)$_{36}$ possessed the largest HOMO−LUMO gap (2.56 eV). In comparison, the metal NC Au$_{60}$(SR)$_{36}$ had the smallest HOMO−LUMO gap (1.30 eV). By investigating the evolution of HOMO−LUMO gaps, it was found that the “magic” stable 12e Au$_{60}$S$_{12}$(SR)$_{36}$ NC possessed the largest HOMO−LUMO gap among the first nine NCs ($n = 0$−9). Interestingly, the Au$_{60}$S$_{7}$(SR)$_{36}$, Au$_{60}$S$_{8}$(SR)$_{36}$, and Au$_{60}$S$_{9}$(SR)$_{36}$ NCs have much smaller HOMO−LUMO gaps than their adjacent NCs, although in three NCs the doping concentration of S atom was quite high.

Figures 5 and S3 displayed the energy level diagram of Kohn−Sham (KS) orbitals and the electronic density profiles of HOMO and LUMO of the Au$_{60}$S$_n$(SR)$_{36}$ clusters. It was found that with the increase of the dopant S atom, the HOMO energy level was almost unchanged, which was in a narrow range of −5.35 to −5.45 eV, whereas the LUMO energy level increased significantly from −4.04 to −2.89 eV. These suggest that the Au(6sp) orbitals significantly contributed to the Au−S

Figure 5. (a) HOMO−LUMO gap of Au$_{60}$S$_n$(SR)$_{36}$ NCs determined by DFT calculations. (b) Diagram of Kohn−Sham (KS) orbital energy level and the electron density profile of the HOMO and LUMO. Each KS orbital is drawn to indicate relative contributions (line length with color labels) of the atomic orbitals from Au(6sp) in dark cyan, Au(5d) in pale blue, μ$_4$-S(3p) in magenta, other S(3p) in purple and H in LT gray.

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bonding. On the other hand, the electronic density of Au$_{60}$S$_{n}$(SR)$_{36}$ ($n = 0 – 12$) showed a trend that from the metal NC Au$_{60}$(SR)$_{36}$ to the gold-sulfide QD Au$_{60}$S$_{12}$(SR)$_{36}$, the LUMO density distribution gradually changed from the local distribution on the Au core to the diffusion distribution on the Au–S($\mu_4$) skeleton. It was worth noting that in Au$_{60}$S$_6$(SR)$_{36}$, Au$_{60}$S$_7$(SR)$_{36}$, and Au$_{60}$S$_{10}$(SR)$_{36}$, the LUMO density showed a very concentrated distribution on the Au core. This implied a significant electronic transition from the Au–S($\mu_4$) skeleton to the metal core in these NCs.

The optical absorption properties of the Au$_{60}$S$_n$(SR)$_{36}$ ($n = 0 – 12$) NCs were further explored by means of TD-DFT. First, the theoretically simulated optical absorption curves of Au$_{60}$S$_6$(SR)$_{36}$ and Au$_{60}$S$_7$(SR)$_{36}$ were compared with the available experimental results in Figure 6. The shapes of UV–vis curve of Au$_{60}$S$_6$(SR)$_{36}$ and Au$_{60}$S$_7$(SR)$_{36}$ NCs were very similar to the previous experimental measurements. Two weak feature peaks centered at ~600 and ~345 nm were seen in the experimental curves. In this work, the TD-DFT calculations well reproduced the feature of the UV–vis curve of two NCs. The absorption peaks at ~674 and ~498 nm were predicted, which verified the feasibility and reliability of the theoretical method in this work. The theoretical optical curves of 12 Au$_{60}$S$_n$(SR)$_{36}$ NCs are summarized in the right panel of Figure 6, which showed a gradual blue shift of the absorption band of Au$_{60}$S$_n$(SR)$_{36}$ NC with the increase of the dopant S atom.

2.4. Relative Stability of Au$_{60}$S$_n$(SR)$_{36}$ Isomers. In the final part of this study, we studied the relative stability the Au$_{60}$S$_n$(SR)$_{36}$ cluster isomers. It was proposed that the Au$_{76}$(SR)$_{44}$ ($N = 7$) NC and the recently reported Au$_{52}$(SR)$_{32}$ ($N = 4$), Au$_{44}$(SR)$_{28}$ ($N = 3$), Au$_{36}$(SR)$_{24}$ ($N = 2$), and Au$_{28}$(SR)$_{20}$ ($N = 1$) belonged to a family of homologous Au$_{20+8N}$(SR)$_{16+4N}$ clusters, which showed unique one-dimensional growth of metal kernel along the crystal [001] direction. According to the evolution of Au$_{20+8N}$(SR)$_{16+4N}$ clusters, an isomer Au$_{60}$(SR)$_{36}$ NC containing an anisotropic metal core was predicted when $N$ was equal to 6, which is denoted as Au$_{60}$(SR)$_{36}$-IsoP in this work. As shown in Figure 7, Au$_{60}$(SR)$_{36}$-IsoP was composed of a metal core made of 12 Au$_4$ tetrahedrons. However, the structural pattern of the metal core and the ligand layer of Au$_{60}$(SR)$_{36}$-IsoP were totally different from those of the Au$_{60}$(SR)$_{36}$ cluster studied in the above sections. In Au$_{60}$(SR)$_{36}$-IsoP, 12 gold tetrahedrons formed a double-helical configuration. In comparison, in Au$_{60}$(SR)$_{36}$ eight gold tetrahedrons formed a double-helical tetrahedron chain in the middle and the additional four Au$_4$ tetrahedrons were systematically distributed at two sides of the tetrahedron chains.
Based on Au60(SR)36-IsoP, we further constructed the isomer NCs Au60S6(SR)36-IsoP and Au60S12(SR)36-IsoP by inserting 6 or 12 S atoms into the metal core (Figure 7). As shown in Table 1, it was found that Au60(SR)36-IsoP1 was more stable than Au60(SR)36 (R = CH3) by 0.81 eV. However, when 6 or 12 S atoms (n = 6 or 12) were doped into the metal core, all Au60Sn(SR)36-IsoP isomers have much higher relative energies (from 0.89 to 1.51 eV) than Au60S0(SR)36. These results indicated that the stable structure of Au60S6(SR)36 nanoclusters were sensitive to the dopant S atom. For the μ-S atom-free Au60(SR)36 cluster, it favored the elongated anisotropic structure. In comparison, if the S atoms were doped into the metal kernel, the Au60S6(SR)36 cluster favored the more “flat” structure displayed in Figure 1.

### Table 1. Relative Energies and HOMO–LUMO Gap of Au60Sn(SR)36-IsoP; the R Group Is Simplified into Methyl Group in Energy Calculationsa

| Au60S0(SR)36-IsoP     | ΔE (eV) | H–L gap (eV) |
|-----------------------|--------|-------------|
| Au60(SR)36-IsoP1      | 0.81   | 1.22        |
| Au60S1(SR)36-IsoP1    | 0.89   | 1.65        |
| Au60S1(SR)36-IsoP2    | 1.30   | 1.53        |
| Au60S1(SR)36-IsoP3    | 1.38   | 1.51        |
| Au60S1(SR)36-IsoP4    | 1.46   | 1.48        |
| Au60S1(SR)36-IsoP5    | 1.51   | 2.52        |

aΔE = E[Au60S0(SR)36-IsoP] − E[Au60S0(SR)36].

3. CONCLUSIONS

The structural evolution, S atom doping mechanism, and electronic and optical absorption properties of a novel family of Au60S0(SR)36 (n = 0–12) nanoclusters were studied by DFT and TD-DFT methods. Our studies revealed that the S atom tended to first dope into the outermost gold tetrahedron in the metal core of thiolate-protected gold NC, then doped into the gold tetrahedron in the inner part of NC. With increasing the number of doped S atoms, the Au60S0(SR)36 (n = 0–12) nanocluster gradually evolved from the ligand-protected metal NC (n = 0) to the hierarchical cluster contained a middle layer of gold-sulfide (n = 1–11) and finally to SR[Au(1)-(SR)]4 oligomer-protected gold-sulfide QD (n = 12). During this evolution process, the HOMO–LUMO gap of Au60S0(SR)36 NCs increased from 1.30 to 2.56 eV, and the absorption band of UV–vis curves showed a blue shift. The doping of S atom into the thiolate-protected gold NCs was a three-step reaction. The mercaptan molecule such as PhCH₂SH provided the S atom by a dimerization reaction to form a PhCH₂S–SCH₂Ph intermediate and then isomerized into (PhCH₂)₅S=S. Once the (PhCH₂)₅S=S was formed, the thiolate-protected gold NC fetched a S atom to form a SAu unit in the metal core. Finally, we also found that the stable structure of Au60S0(SR)36 was affected by the number of dopant S atoms. The μ-S-atom-free Au60(SR)36 cluster favored an anisotropic structure. However, when the S atoms were doped in the metal kernel, the Au60S0(SR)36 cluster (n = 6 and 12) favored a more “flat” configuration.

4. COMPUTATIONAL METHODS AND DETAILS

The geometric structure optimizations, energy calculation, and HOMO–LUMO gap evaluations are performed using the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE)95 functional, and the d-polarization included basis set (DND) was used for C, H, and S elements. The DFT semicore pseudopotential (DSPP) approximation with some degree of relativistic corrections was used for the Au element implemented in the Dmol3 package.92,93 The transition state (TS) method94 was computed using a combination of linear synchronous transit (LST)/quadratic synchronous transit (QST) algorithms with conjugated gradient optimization. The convergence criterion of the geometrical optimization was set to 1.0 × 10⁻³ Hartree for energy change, 4.0 × 10⁻³ Hartree/Å for the gradient, and 5.0 × 10⁻³ Å for the displacement.

The TD-DFT calculations were carried out using the Amsterdam density functional (ADF 2016) software packages.96 The optical absorption spectra were plotted based on the computation of the lowest 1000 singlet-to-singlet excitation energies of the lowest-energy isomer structure of Au60S0(SR)36 NCs (R = H) using GGA with PBE functional, and the triple-ζ polarized (TZP) basis set, d with the inclusion of the scalar relativistic effect, via the zeroth-order regular approximation (ZORA). The all-cluster structures were proven to be a local minimum by the frequency calculations.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02091.

Relative energies of Au60S0(SR)36 nanocluster with R = –CH₃, –Ph and –CH₃; the atomic structures of Au60S(n)(SR)(36) (n = 7–12, R = –CH₃) and the atomic structures of Au60S(n)(SR)(36) (n = 5–0, R = –CH₃); the Kohn–Sham (KS) orbital energy level diagram and distribution of electron clouds of Au60S(n)(SR)(36); the distances and angles of Au₄ units in Au60Sₙ(SR)(36) clusters; two approaches to explain the gold core structure of Au₆₀Sₙ(SR)(36) clusters; two kinds of formation energy of the Au₆₀Sₙ(SR)(36) (n = 0–12) series; XYZ coordinates of lowest-energy isomer structure of Au₆₀Sₙ(SR)(36) (n = 0–5 and 8–12) (PDF)

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Notes
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