Assembling Au₄ Tetrahedra to 2D and 3D Superatomic Crystals Based on Superatomic-Network Model

Chen Yan, Jiuqi Yi, Peng Wang, Dan Li,* and Longjiu Cheng*

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ABSTRACT: Thiolate-protected gold nanoclusters (denoted as Auₐₙ(SR)ₙ or AuₐₙLₙ) have received extensive attention both experimentally and theoretically. Understanding the growth mode of the Au₄ unit in Au₄ₙ(SR)ₙ is of great significance for experimental synthesis and the search for new gold clusters. In this work, we first build six clusters of Au₃₄(AuCl₃)₉, Au₃₅(AuCl₃)₉, Au₃₆(AuCl₃)₉, Au₃₇(AuCl₃)₉, and Au₃₈(AuCl₃)₉ with the Au₄ unit as the basic building blocks. Density functional theory (DFT) calculations show that these newly designed clusters have high structural and electronic stabilities. Based on chemical bonding analysis, the electronic structures of these clusters follow the superatom network (SAN) model. Inspired by the cluster structures, we further predicted an Au₄ two-dimensional (2D) monolayer and a three-dimensional (3D) crystal using graphene and diamond as templates, respectively. The computational results demonstrate that the two structures have high dynamic, thermal, and mechanical stabilities, and both structures exhibit metallic properties according to the band structures calculated at the HSE06 level. The chemical bonding analysis by the solid-state natural density partitioning (SSAdNDP) method indicates that they are superatomic crystals assembled by two electron Au₄ superatoms. With this construction strategy, the new bonding pattern and properties of AuₐₙLₙ are studied and the structure types of gold are enriched.

1. INTRODUCTION

Thiolate-protected gold nanoclusters (donated as Auₐₙ(SR)ₙ or AuₐₙLₙ) have become a research hotspot in the field of nanoscience owing to their unique physicochemical properties. Since the structure determination of Auₐₙ(SR)ₙ and AuₐₙLₙ, a large amount of Auₐₙ(SR)ₙ has been successfully characterized. Particularly, due to the relatively outstanding chemical stability of Auₐₙ(SR)ₙ, enormous efforts have been devoted to the study of Auₐₙ(SR)ₙ both experimentally and theoretically. On this basis, the structure evolution behaviors of Auₐₙ(SR)ₙ were further explored. According to X-ray single-crystal diffraction analyses of Auₐₙ(SR)ₙ, some gold atoms were arranged in an ordered Au core. The rest of the gold atoms were combined with the ligands to form a series of gold–thiolate protecting units (e.g., −RS−Au−SR− and −RS−Au−SR−Au−SR−, also called staple motifs) capping the Au core. As more Auₐₙ(SR)ₙ structures were acquired, it was found that these clusters possessed diverse configurations of core structures. In addition, the types and the numbers of staple motifs were extremely sensitive to the number of gold atoms and thiolate ligands.

The structure determination of thiolate-protected gold nanoclusters provides an effective theoretical model for understanding the relationship between their structures and properties. The “divide and protect” model was first proposed by Häkkinen et al. In this model, Auₐₙ(SR)ₙ can be viewed as an Au core protected by different staple motifs. Following the proposed structural partition formula, a low-energy isomer of Auₐₙ(SR)ₙ was acquired and written as [Auₐₘ(SR)ₙ]ₐ[Auₐₙ(SR)ₙ]ₐ[Auₐₚ(SR)ₙ]ₐ... where a, a’, b, c, d, ... were integers, which was first applied to the experimentally synthesized Auₐₙ(SR)ₙ. Following the proposed structural partition formula, a low-energy isomer of Auₐₙ(SR)ₙ was acquired and written as [Auₐₘ(SR)ₙ]ₐ[Auₐₙ(SR)ₙ]ₐ[Auₐₚ(SR)ₙ]ₐ... which was in good agreement with later experimental reports. Some Auₐₙ(SR)ₙ clusters with magic numbers were well explained by the superatom complex (SAC) concept based on the jellium model, such as Auₐ₈(SR)ₙ, Auₐ₉(SR)ₙ, and Auₐ₁₀(SR)ₙ having 2, 8, and 18 free valence electrons, respectively.

However, not all of the gold nanoclusters satisfy the framework of the SAC model. Cheng et al. developed the super valance bond (S VB) model to explain the electronic stability of nonspherical shells of Auₐₙ(SR)ₙ metal clusters. Nonetheless, the high stability of some low-symmetry ligand-protected gold nanoclusters also cannot be clearly explained. Subsequently, the superatom network (SAN) model was proposed by Cheng et al., combined with the adaptive natural density partitioning (AdNDP) method, to explain the
electronic stability. The Au core of these gold clusters can be viewed as networks of nonconjugated 4-center-2-electron (4c-2e) tetrahedral Au$_4$ superatoms. The experimentally synthesized Au$_{18}$(SR)$_{14}$, Au$_{20}$(SR)$_{16}$, Au$_{22}$(SR)$_{18}$, and Au$_{24}$(SR)$_{20}$ are compounds with four valence electrons, following the SAN model. Au$_{18}$(SR)$_{14}$ is composed of an Au$_9$ core and five staple motifs. According to the SAN model, the Au$_9$ core can be regarded as a unique combination of two fused superatom octahedral Au$_6$ units. The structure of Au$_{20}$(SR)$_{16}$ features a vertex-sharing bi-tetrahedral Au$_7$ kernel and a "ring" motif Au$_8$(SR)$_8$. The structure of Au$_{22}$(SR)$_{18}$ also has an Au$_7$ kernel, which is surrounded by one Au$_6$(SR)$_6$ and three Au$_3$(SR)$_4$ motifs. This Au$_7$ kernel is formed by two Au$_6$ units sharing vertices. The structure of Au$_{24}$(SR)$_{20}$ has a bi-tetrahedral Au$_9$ kernel protected by two pairs of tetrameric staples. According to the SAN model, the Au kernels of these three clusters can all be seen as networks of two Au$_4$ superatoms. In addition, Pei et al. reported many Au$_m$(SR)$_n$ clusters with face-centered-cubic (fcc) type of Au$_4$ kernel. These clusters have a unique growth pattern and grow into a double-helix structure through the Au$_4$ unit sharing the vertex, such as Au$_{16}$(SR)$_2$, Au$_{24}$(SR)$_2$, Au$_{44}$(SR)$_2$, Au$_{42}$(SR)$_3$, Au$_{50}$(SR)$_3$, and Au$_{60}$(SR)$_3$ clusters. The thiolate-protected gold nanowire (RS-AuNW) can be obtained by infinite growth according to its growth mode. Moreover, the Au$_{44}$(SR)$_2$ cluster was confirmed by Jin et al. Therefore, the developed theoretical models not only logicize the existing structures but also facilitate the design of new structures.

Because the synthesis and characterization of thiolate-protected gold nanoclusters remain challenging, density functional theory (DFT) calculations play a prominent part in structural prediction. The tetrahedral Au$_4$ unit is a basic block in thiolate-protected gold nanoclusters and is often used to predict new Au$_m$(SR)$_n$ clusters and crystal materials. In this work, we predicted five Au$_m$(SR)$_n$ clusters based on the SAN model, using the tetrahedral Au$_4$ unit as basic building blocks, including Au$_{10}$(SR)$_6$, Au$_{16}$(SR)$_8$, Au$_{18}$(SR)$_{12}$, Au$_{36}$(SR)$_{12}$, and Au$_{54}$(SR)$_{12}$. DFT calculations show that these clusters have high electronic and structural stabilities. Based on the growth patterns of these clusters, a graphene-like two-dimensional (2D) Au$_4$ monolayer and a diamond-like three-dimensional (3D) Au$_4$ solid were predicted to be stable. Both the 2D-Au$_4$ monolayer and 3D Au$_4$ solid have strong light absorption ability. This cluster assembly material based on cluster superatoms can be regarded as an extension of the SAN complexes.

2. COMPUTATIONAL METHOD AND DETAILS

Geometry optimizations, frequency analyses, and electronic properties calculations of all cluster structures were carried out at the PBE60 level of theory with the def2tzvp basis set as implemented in the Gaussian 09 package. Considering the computational cost, we used halogen (Cl) instead of thiolate.
chemical bonding pattern of the Au
isolobal ligands.

3. RESULTS AND DISCUSSION

Generalized gradient approximation (GGA)
(VASP) code.65

were performed in the Vienna ab initio simulation page

periodical structure, ab initio molecular dynamic (AIMD) was
carried out by the Nose–Hoover method.66

dispersion spectra. To assess the thermal stability of the

were performed with an energy of 10

were verified by frequency check
to be true local minimum on the potential energy surface. DFT

calculations of the Au4 monolayer and the Au4 bulk structure

were performed in the Vienna ab initio simulation page

by the projector-augmented plane-wave (PAW) method.67

were carried out by the AdNDP method. The results show that

indicate that Au

clusters have been successfully synthesized and
designed with the bi-tetrahedral Au

unit as a building block, such as Au20(SR)16, Au30(SR)16, and Au36(SR)20.78

Here, according to the SAN model, we build an Au7(AuCl3)3 cluster,

features a vertex-sharing bi-tetrahedral Au4 core

protected by three [Cl–Au–Cl] ligands. The optimized

Au8(AuCl3)3 cluster with a fairly large highest occupied

molecular orbital–lowest unoccupied molecular orbital

(HOMO–LUMO) gap (EHOMO) of 2.47 eV is shown in Figure

1a, indicating high electronic stability. The average Au–Au bond

length within the Au4 tetrahedrons is 2.70–2.77 Å. The

bond lengths of Au–Cl are 2.39 Å. Au (5d106s1) has one free

valence electron, and each Au atom of the three Au atoms in

the Au4 unit transfers 0.5 valence electrons to the surrounding

Cl atoms to satisfy the 8 electron rule. The remaining centered

Au atom contributes 0.5 valence electrons to each Au4 unit.

Thus, the whole Au4 unit has two valence electrons in total,
donated as the Au4 (2e) superatom. To clearly understand the

bonding mode of the monomer, chemical bonding analyses

were carried out by the AdNDP method. The results show that

Au8(AuCl3)2 has two 4c-2e Au4 σ bonds with the occupancy

numbers (ON) = 1.90 lel and twelve 2c-2e Au–Cl σ bonds

with ON = 1.97 lel.

Next, we adopt Au7(AuCl3) as a monomer to design a
dimer. The dimer is composed of four [Cl–Au–Cl] ligands

and an Au12 core, which is formed by two bi-tetrahedral Au4

units via sharing two Au atoms. Figure 1b shows that the

optimized dimer Au12(AuCl3)4 has an EHOMO of 1.86 eV, and the
dimer contains four 4c-2e Au4 σ bonds with ON = 1.90 lel. The

bond lengths of Au–Cl are 2.39 Å, and the Au–Au bond

lengths within the Au4 tetrahedra are in the range of 2.70–2.80 Å. Following a similar construction method, tetramer

Au12(AuCl3)6 and hexamer Au30(AuCl3)6 are designed and

shown in Figure 1c,d, respectively. Their Au–Au bond lengths

within the Au4 tetrahedra are in the range of 2.70–2.83 Å, and

the Au–Cl bond lengths are 2.41 Å. The AdNDP results

indicate that Au12(AuCl3)6 and Au30(AuCl3)6 clusters have

eight 4c-2e σ bonds with ON = 1.82 lel and twelve 4c-2e σ

bonds with ON = 1.81 lel, respectively.

The nucleus-independent chemical shift (NICS) method79

is widely used to measure the aromaticity of delocalized bonds.

It has been successfully used to confirm many Au4 superatomic

3.1. Geometric and Electronic Characters of

Au7(AuCl3)3, Au12(AuCl3)4, Au12(AuCl3)6, and

Au30(AuCl3)6 Clusters. It is well known that a series of

Au4(SR)m clusters have been successfully synthesized and
designed with the bi-tetrahedral Au4 unit as a building block,

as well as Au30(AuCl3)6 clusters. The optimized

unit has two valence electrons in total,
donated as the Au4 (2e) superatom. To clearly understand the

bonding mode of the monomer, chemical bonding analyses

were carried out by the AdNDP method. The results show that

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The nucleus-independent chemical shift (NICS) method79

is widely used to measure the aromaticity of delocalized bonds.

It has been successfully used to confirm many Au4 superatomic
systems. Here, we perform a NICS method to further prove the existence of Au$_4$ superatoms. We take the Au$_{4}(\text{AuCl}_3)_8$ cluster as a test. The NICS scan points are located at the geometric center of Au$_4$ units, and the corresponding NICS values are both $-28.8$ ppm, which is much more negative than that of benzene ($-9.7$ ppm). This strong aromaticity indicates electron delocalization with shell closure in the Au$_4$ core, which confirms the presence of Au$_4$ superatoms.

3.2. Geometric Structure, Stability, and Electronic Character of the Au$_4$ Monolayer. The cyclic hexamer Au$_{40}(\text{AuCl}_3)_8$ has a similar structure to benzene and can be extended to a graphene-like Au$_4$ monolayer. As shown in Figure 2a, the space group of the monolayer is P6/mmm (number 191, $a = b = 5.45$ Å, and $c = 15$ Å), where one unit cell is composed of eight Au atoms. Similar to the clusters, adjacent Au$_4$ units are connected by a shared Au atom. The structure of the Au$_4$ monolayer is a three-layered sandwich structure, similar to the recently discovered AlB$_6$ monolayer with high stability, unique motif, and superconductivity. The average length of the Au–Au bond in this monolayer is 2.77 Å. For the Au$_4$ monolayer, we use the SSAdNDP method to analyze its bond patterns. According to the results, there are five d-type localized lone pairs (LPs) on each Au atom with ON = 1.91–2.00 Å as shown in Figure S1. Therefore, it is implied that they are not involved in the bonding process. Figure 2b shows the 4c-2e Au$_4$ σ bonds (ON = 1.82 Å) in each Au$_4$ unit. Similar to the previously predicted Cu$_4$Si and Cu$_4$Ge monolayers, their special 4c-2e bonds lead to strong connections between atoms, thereby enhancing the stability of the structure.

Although the Au$_4$ monolayer has rather intriguing structural properties, the stability of the structure is still unknown. To assess the relative stability of this material, we first calculate the cohesive energy $E_{\text{coh, Au4 monolayer}} = (mE_{\text{Au-atom}} - E_{\text{Au4 monolayer}}) / m$, where $m$, $E_{\text{Au-atom}}$ and $E_{\text{Au4 monolayer}}$ are the atom number, the total energies of a single Au atom, and one unit cell of the Au$_4$ monolayer, respectively. The cohesive energy of the Au$_4$ monolayer is 2.63 eV per atom, indicating that the Au$_4$ monolayer has a strongly bonded network. To verify the kinetic stability of the Au$_4$ monolayer, we perform phonon dispersion calculations for its geometric configuration (Figure 2c). All positive frequencies in the first Brillouin zone indicate kinetic stability. Moreover, we perform AIMD simulations with a supercell (containing 4 × 4 × 1 primitive cell involving 144 Au atoms) to examine its thermal stability, where the time step and time duration are 1.0 fs and 5 ps, respectively. As shown in Figure 3a, the Au$_4$ monolayer can maintain its structural integrity at 300 K in AIMD simulations, indicating its thermal stability. Moreover, it can be seen from Figure S2 that the structure of the Au$_4$ monolayer can maintain its integrity, whereas the structure breaks at 1000 K. Therefore, the melting point of the Au$_4$ monolayer is between 700 and 1000 K. We also study the mechanical properties of the Au$_4$ monolayer by calculating the elastic constants, Young’s modulus ($E$), and Poisson’s ratio ($\nu$), and the results are listed in Table 1. For this monolayer, the elastic constants satisfy $C_{11}C_{22} - C_{12}^2 > 0$ and $C_{66} > 0$, suggesting its mechanical stability.

Table 1. Calculated Elastic Constants ($C_{ij}$ in N m$^{-1}$), Young’s Modulus ($E$, in N m$^{-1}$), and Poisson’s Ratio ($\nu$) for the Au$_4$ Monolayer

| structure | $C_{11}$ | $C_{12}$ | $C_{66}$ | $E$ ($\text{N m}^{-1}$) | $\nu$ |
|-----------|---------|---------|---------|----------------|------|
| 2D-Au$_4$ | 71.06   | 29.34   | 20.86   | 58.95          | 0.41 |

Generally speaking, mechanical and liquid striping techniques are widely used to prepare most 2D materials. Here, the process of mechanical striping is studied theoretically. The cleavage energy ($E_{cl}$) is the minimum energy required during the exfoliation process. We first constructed a five-layer slab, four layers of which were fixed with the monolayer being removable. As shown in the schematic of Figure 3b, d is the separation distance between the exfoliated top layer and the remnant four layers, and $d_0$ (2.70 Å) is the original interlayer distance of bulk. The cleavage energy is defined as $E_{cl} = E_d - E_{\text{Au4 monolayer}}$, where $E_d$ and $E_{\text{Au4 monolayer}}$ are the separation distance d and no separation energy between the exfoliated top layer and the remnant four layers, respectively. It can be seen that as the separation distance increases, the cleavage energy gradually increases, and finally converges to a constant value of 0.91 J m$^{-2}$, which has the same order of magnitude as the experimentally measured value of graphene (0.37 J m$^{-2}$).79 Therefore, the results indicate that it is possible to exfoliate Au$_4$ monolayer by the mechanical method from its bulk structure experimentally.

We further investigated the electronic properties of the Au$_4$ monolayer by calculating the band structures and projected density of states (PDOS) at the HSE06 level. As shown in Figure 4a, there is a valence band (VB) passing through the
Fermi level, and the monolayer exhibits metallic properties. It is also worth noting that the valence band maximum (VBM) is slightly separated from the conduction band minimum (CBM), so there is a tendency to open the band gap. The projected density of states (PDOS) show that the valence band (VB) energy states are mainly contributed by the d orbitals of Au atoms.

The unique optical properties of gold nanomaterials make it of great application value in surface plasmon optics, information storage, surface-enhanced Raman scattering (SERS), and sensing devices. We further calculated the optical absorption spectrum of the Au₄ monolayer by the HSE06 method as shown in Figure 4b. The area within the dotted line is in the visible-light range. The Au₄ monolayer has no anisotropy in x- and y-directions, so we analyze the optical properties in the x- and z-directions. The Au₄ monolayer has very obvious light absorption in the infrared, visible, and ultraviolet regions in the z-direction, while it only has strong absorption in the visible and ultraviolet regions in the x-direction. The intensity of light absorption in the visible region is particularly important because visible light contains almost half the energy of sunlight. In the visible-light region, the absorption coefficients in both the x- and z-directions reach $10^5 \text{ cm}^{-1}$, indicating a high absorption efficiency of solar energy. Moreover, it can be seen that the Au₄ monolayer has a stronger light absorption ability in the ultraviolet region.
Therefore, the Au₄ monolayer has a large absorption coefficient in the visible and ultraviolet regions and may be a very promising optoelectronic material in the future.

### 3.3. Geometric and Electronic Characters of the Au₁₆(AuCl)₆ Cluster

In a similar approach, we build an Au₁₆(AuCl)₆ cluster, which is composed of six [Cl–Au–Cl] ligands and an Au₁₆ core. To highlight the Au core, we used a different color (blue) for the ligand Au atoms to distinguish them. The core of the Au₁₆(AuCl)₆ cluster consists of five vertex-sharing Au₄ units, which are protected by six [Cl–Au–Cl] stable motifs. The optimized geometric configuration of Au₁₆(AuCl)₆ with a large Eₜₙₙ of 2.47 eV is shown in Figure 5. The average Au–Au bond length is 2.72–2.75 Å. There are two types of Au–Cl bonds with bond lengths of 2.39 Å (connected with the Au unit) and 2.32 Å (connected with the ligand Au atom). The chemical bonding pattern of Au₁₆(AuCl)₆ clusters is studied by the AdNDP method. As shown in Figure 5, there are five 4c–2e Au–Cl σ bonds with ON = 1.86 eV. In addition, two different Au–Cl σ bonds with ON = 1.97 eV are also shown.

### 3.4. Geometric Structure, Stability, and Electronic Character of the Au₄ Crystal

The Au₁₆ core of the Au₁₆(AuCl)₆ cluster is similar to an sp³ hybrid C atom. Motivated by sp³ hybrid C atoms in diamond, a super-tetrahedral structure can be designed by replacing C atoms with regular tetrahedral units, and some previous theoretical works have proved this.90–92 Therefore, we use the diamond lattice as a template where all carbon atoms are substituted by Au atoms, then connected all of the Au₄ units by sharing vertices to design a diamond-like Au₄ crystal. The fully optimized structure of the designed Au₄ crystal is shown in Figure 6a. One unit cell of the Au₄ cluster contains 16 Au atoms, the space group is Fd3m (number 227) and the lattice constants are a = b = c = 7.76 Å. All of the Au–Au bond lengths are 2.74 Å, slightly shorter than the average Au–Au bond length (2.77 Å) in the Au₄ monolayer. To gain insight into the chemical bonds in the Au₄ crystal, the SSAdNDP method was used. The SSAdNDP results indicate that there are five lone pairs of electrons on each Au atom (Figure S3), and another valence electron forms 4c-2e σ bonds in the Au₄ unit (Figure 6b). Thus, the Au₄ crystal can be viewed as a superatomic crystal stacked by Au₄ (2e) superatoms.

As shown in Table 2, compared with the gold in the classic fcc phase, the density of the Au₄ crystal is much smaller due to its larger pore size. The cohesive energy is calculated by $E_{\text{coh}} = (mE_{\text{Au}} - mE_{\text{Au-bulk}})/m$, where $m$, $E_{\text{Au}}$, and $E_{\text{Au-bulk}}$ are the atom number, the total energies of a single Au atom, and one unit cell in the Au₄ crystal, respectively. The cohesive energy of the Au₄ crystal is 2.75 eV atom⁻¹, which is slightly smaller than that of the fcc-phase Au of 3.11 eV atom⁻¹. The Au₄ crystal has a higher strain strength and lower plasticity compared with the fcc-phase Au from the results of Young's modulus and Poisson's ratio value. Moreover, the Vickers hardness calculated with the same empirical formula also illustrates this point. The computed phonon spectra of the Au₄ crystal exhibit all positive phonon frequencies (Figure 6c), confirming its dynamic stability. To test the thermal stability of the Au₄ crystal, we carry out AIMD simulations under an NVT ensemble with the temperature controlled at 300, 700, and 1000 K. Here, a supercell containing a 4 × 2 primitive cell (involving 128 Au atoms) was adopted as the initial configuration. The AIMD simulations lasted for 5 ps with a time step of 1 fs. As shown in Figure S4, after 5 ps simulations at 1000 K, the structure is still intact and the total energy remains almost unchanged, which suggests its high thermal stability. The Au₄ crystal can be used at extremely high temperatures.

In comparison with the fcc-phase Au, the Au₄ crystal presents different structural properties and bonding patterns that may lead to unexpected physical properties. We calculated the band structure of the fcc-phase Au and the Au₄ crystal at the HSE06 level. As shown in Figure 7, both structures are metallic. The VB and conduction band (CB) of the fcc-phase Au are slightly overlapped, while the VB and CB of the Au₄ crystal phase are clearly separated, and there is a tendency to form a semiconductor. This may be due to the partial electronic localization in the Au₄ unit resulting from the special geometric structure of the Au₄ crystal. Similarly, we calculated the light absorption coefficients of the Au₄ crystal and fcc-phase Au by the HSE06 method, as shown in Figure S5. The area within the dotted line is in the visible-light range. We can clearly see that the Au₄ crystal and the fcc-phase Au have great light absorption in the visible and ultraviolet regions, and their absorption coefficients in the ultraviolet region reach 10⁶ cm⁻¹. The large absorption coefficient of the Au₄ crystal makes it a potential material for photovoltaic solar cells and optoelectronic devices.

### 4. CONCLUSIONS

To summarize, we first adopt the Au₄ unit and [Cl–Au–Cl] as basic building blocks to construct Au₄(AuCl)₆ clusters. DFT calculations show that each cluster is a real local minimum on the potential energy surface and has a large HOMO–LUMO gap.
energy gap. In particular, the HOMO–LUMO energy gap of the Au₅(AuCl₄)₃ cluster is 2.47 eV. AdNDP and NICS analyses reveal that all of the structures follow the SAN model. Based on Au₅₀(AuCl₄)₆ and Au₆₅(AuCl₄)₆ clusters, we use the graphene and diamond as templates to design a graphene-like Au₅ monolayer and a diamond-like Au₅ crystal. The computational results demonstrate that both Au₅ monolayer and Au₅ crystal have a high dynamic, thermal, and mechanical stability. The Au₅ crystal can remain stable even at 1000 K. The cleavage energy of the Au₅ monolayer is similar to that of graphene, indicating that the exfoliation of its bulk form to achieve freestanding monolayers is very feasible. The calculated band structures of both the Au₅ monolayer and the Au₅ crystal at the HSE06 level show metallicity. The optical properties show that the Au₅ monolayer has a large light absorption coefficient. The SSAdNDP analyses indicate that these two structures are composed of Au₄ (2e) units, thus they can be viewed as superatomic crystals. All these findings provide new insights for the study of thiolate-protected gold nanoclusters. In addition, we predicted two new types of superatom crystal gold, enriching the structure types of gold.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c04391.

SSAdNDP chemical bonding patterns of the Au₅ monolayer and the Au₅ crystal; AIMD simulation of the Au₅ monolayer and the Au₅ crystal; optical absorption spectra of the Au₅ crystal and the fcc-phase Au₅ and xyz coordinates of all structures after optimization (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Dan Li – Department of Chemistry, Key Laboratory of Functional Inorganic Materials of Anhui Province, Anhui University, Hefei, Anhui 230601, P. R. China; Email: ahulidan@aliyun.com

Longjiu Cheng – Department of Chemistry, Key Laboratory of Functional Inorganic Materials of Anhui Province, Anhui University, Hefei, Anhui 230601, P. R. China; Key Laboratory of Structure and Functional Regulation of Hybrid Materials, Anhui University, Ministry of Education, Hefei 230601, P. R. China; orcid.org/0000-0001-7086-6190; Email: clj@ustc.edu

Authors

Chen Yan – Department of Chemistry, Key Laboratory of Functional Inorganic Materials of Anhui Province, Anhui University, Hefei, Anhui 230601, P. R. China

Jiuqi Yi – Department of Chemistry, Key Laboratory of Functional Inorganic Materials of Anhui Province, Anhui University, Hefei, Anhui 230601, P. R. China

Peng Wang – Department of Chemistry, Key Laboratory of Functional Inorganic Materials of Anhui Province, Anhui University, Hefei, Anhui 230601, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c04391

Notes

The authors declare no competing financial interest.

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