Gold tetrahedra coil up: Kekulé-like and double helical superstructures

Chenjie Zeng, 1* Yuxiang Chen, 1* Chong Liu, 2 Katsuyuki Nobusada, 3, 4 Nathaniel L. Rosi, 2 Rongchao Jin 1†

Magic-sized clusters, as the intermediate state between molecules and nanoparticles, exhibit critical transitions of structures and material properties. We report two unique structures of gold clusters solved by X-ray crystallography, including Au40 and Au52 protected by thiolates. The Au40 and Au52 clusters exhibit a high level of complexity, with the gold atoms in the cluster first segregated into four-atom tetrahedral units—which then coil up into a Kekulé-like ring in the Au40 cluster and a DNA-like double helix in Au52. The solved structures imply a new “supermolecule” origin for revealing the stability of certain magic-sized gold clusters. The formation of supermolecular structures originates in the surface ligand bonding–induced stress and its propagation through the face-centered cubic (FCC) lattice. Moreover, the two structures reveal anisotropic growth of the FCC lattice in the cluster regime, which provides implications for the important roles of ligands at the atomic level. The rich structural information encoded in the Au40 and Au52 clusters provides atomic-scale insight into some important issues in cluster, nanoscale, and surface sciences.

INTRODUCTION

Metal clusters containing tens to hundreds of metal atoms constitute an important regime that bridges molecular materials (typically <1 nm) and nanoparticle materials (typically >3 nm). Because of their intermediate state, metal clusters often exhibit distinct properties in catalysis, optics, electronics, and magnetism, and thus hold great potential as functional materials (1–4). On the other hand, clusters might share some features with molecules and nanoparticles: they can be viewed as the miniature of nanoparticles, or the “maxiatom” of molecules. Important molecular and nanoscale information may be encoded inside the cluster, and many fundamental issues (for example, the origin of magic sizes and the structural evolution pattern) and real-world applications require the knowledge of atomic structures of clusters.

The thiolate-protected gold clusters referred to as Au_n(SR)_m have emerged as a new frontier in cluster research, not only because of their high stability, atomic precision, and wide size tunability (5) but also for the rich gold thiolate chemistry—which is broadly used in surface functionalization of nanoparticles and two-dimensional (2D) films (6). It is these merits of Au_n(SR)_m clusters that bestow on them the potential to shed light on some issues in the cluster, nanoscale, and surface sciences. The recent research efforts in structural characterization of ultrasmall Au_n(SR)_m clusters with n ≤ 38 and n ≥ 102 have revealed some common features: (i) the inner cores of clusters are constructed from various polyhedra and their derivatives; (ii) the surfaces of clusters are protected by the Au-SR oligomeric staple or ring motifs (5, 7); and (iii) their stability is often interpreted by the shell-closing “superatom” model with stable electronic structure [for example, Au25(SR)18 as an 8e superatom and Au102(SR)44 as a 58e superatom] (8, 9), which is similar to other ligand-protected metal clusters and gas-phase clusters (10–15). However, certain Au_n(SR)_m clusters do not conform to the superatom category, such as Au38(SR)24 (16). The polyhedron-based kernels, Au-SR surface oligomeric motifs, and superatom model have been serving as the basis for analysis and prediction of Au_n(SR)_m cluster structures (7, 17–19).

However, despite the advances in Au_n(SR)_m cluster research, several basic and critical issues remain to be addressed. First, the origin of the stability of magic sizes in solution-phase clusters is still unclear. This issue lies in the center of cluster research. Although the well-known superatom model can explain the stability of a few magic sizes (8–14), it cannot accommodate the newly discovered magic sizes. Second, the crystal structural information of medium-sized gold clusters (between Au38 and Au102) is still missing (8, 16) except for some theoretical work (18–21), and most of the solved structures are concentrated on the smaller end (5). This knowledge gap precludes the understanding of the growth pattern of clusters. Third, the thiolate bonding and patterning structures on the gold crystalline facets remain largely unknown. We have recently revealed the formation of anisotropic “helical-striped” patterns of -S-Au-S- motifs on the curved surface of Au_{133}(SR)_{52} nanoparticles (22); however, it remains to be seen whether the same protecting mode exists on gold crystalline surfaces.

In an effort to gain insight into these issues, we herein report two unique structures of Au_n(SR)_m clusters, that is, Au_{40}(SR)_{24} and Au_{52}(SR)_{32}. The rich structural information encoded in these two clusters provides atomic-scale insight into some major issues, including the origin of magic sizes in clusters, the shape control of nanocrystals, and the self-assembled monolayers of thiolates on gold crystalline facets. Significantly, unlike the previously reported superatom or close-shell clusters (8–14), Au_{40} and Au_{52} exhibit a high level of complexity, with the gold atoms in the cluster first segregated into four-atom tetrahedral units, which then coil up into a Kekulé-like ring in the Au_{40} cluster and a DNA-like double helix in Au_{52}. These structures are better viewed as “supermolecules” rather than superatoms. Also, the Au_{40} and Au_{52} structures reveal the construction of clusters in a manner similar to the anisotropic growth of nanocrystals, reflecting the early stage of “shape control” in the cluster regime. Moreover, the anisotropic growth patterns of Au_{40} and Au_{52} lead to the exposure of the extended Au(111) and Au(100) facets on clusters, which provide valuable crystallographic information on thiolate bonding and patterning on gold crystalline surfaces.
RESULTS AND DISCUSSION

The Au_{40} and Au_{52} clusters were synthesized by a two-step “size-focusing” method (1). The key aspects involve careful control of reaction kinetics and a proper selection of protecting thiolates (SR); see Materials and Methods for details. The Au_{40} was synthesized with 2-methylbenzenethiolate (o-MBT), formulated as Au_{40}(o-MBT)_{24} (23), whereas the Au_{52} was synthesized with 4-tert-butylbenzenethiolate (TBTT), formulated as Au_{52}(TBTT)_{32}. Both Au_{40} and Au_{52} are highly stable because they were thermodynamically selected through harsh size-focusing processes (1, 23). Their structures were determined by single-crystal x-ray crystallography (tables S1 to S4). Both clusters are chiral, and the unit cells of Au_{40} and Au_{52} single crystals comprise a pair of enantiomers for each cluster (Figs. 1, A and B, and 2, A and B).

Supermolecular view of Au_{40}(SR)_{24} and Au_{52}(SR)_{32} clusters
The structure of Au_{40}(SR)_{24} has long been a puzzle since the first isolation of this magic size from a mixture with the Au_{38}(SR)_{24} cluster (24). Density functional theory (DFT) predicted bi-icosahedron–based core structures for Au_{40}(SR)_{24} (18, 19), which are similar to the structure of Au_{38}(SR)_{24}. Here, we found that the overall structure of Au_{40}(o-MBT)_{24} is a unique oblate shape (that is, a hexagonal prism; Fig. 1, A and B), which is drastically different from the previous theoretical prediction.

An anatomy of the structure reveals a 25–gold atom kernel resembling a snowflake (Fig. 1C) and nine surface-protecting staples (Fig. 1, D and E). Significantly, we found that the gold atoms in the kernel are segregated into eight tetrahedral Au_{4} units, evidenced by the Au-Au bond length differences (vide infra). Two of the tetrahedral units form the central bi-tetrahedral antiprism (Fig. 1C, green), and the remaining six tetrahedra form a Kekulé-like external ring with alternatively facing-up-and-down arrangement of the tetrahedra (Fig. 1C, blue). The Kekulé ring is protected by six Au(SR)_{2} monomer staples (Fig. 1D), whereas the central bi-tetrahedron is protected by three Au_{3}(SR)_{4} trimer staples (Fig. 1E). The kernel adopts achiral D_{3d} symmetry, but the overall Au_{40}S_{24} framework has chiral D_{3} symmetry (Fig. 1F), which is due to the rotative arrangement of the surface staple motifs.

The discovery of the Kekulé-like Au_{40} structure indicates molecular complexity in this cluster, as opposed to a simple superatom-dimer as predicted on the basis of the Au_{38}(SR)_{24} structure (18, 19).

The segregation of tetrahedral Au_{4} units and the formation of an elegant superstructure are also observed in another magic-sized cluster, Au_{52}(TBTT)_{32} (Fig. 2). This indicates certain generality of the supermolecular complexity in clusters. The Au_{52} cluster has a 32–gold atom kernel, which is segregated into 10 tetrahedral units (Fig. 2C). The tetrahedra are assembled into a double helical superstructure resembling the...
The elegant patterns observed in Au40 and Au52 are not existent in Au32. Notably, the tetrahedral configuration is also favored in gas-phase gold clusters, for example, the Au20 tetrahedral cluster (15). This supermolecular picture from the Au40 and Au52 clusters provides a more complex origin of stable magic sizes in gold clusters than the superatom picture, and it reveals the assembly of “atoms” into “molecules” in the cluster regime. The supermolecular picture is expected to accommodate more magic sizes in the future.

**Anisotropic growth of the clusters and origin of supermolecular structures**

An intriguing question is what drives the formation of the supermolecular patterns of tetrahedra in the Au40 and Au52 clusters. To answer this question, we first need to have the overall pictures of the two structures without considering the differences in the Au-Au bond lengths. Specifically, when viewed as an entity, the 40 gold atoms in the Au40(o-MBT)24 can all be fit into a face-centered cubic (FCC) lattice with some distortions (Fig. 4, A to D). Three layers of gold atoms are stacked along the [111] direction in an a-b-c manner, forming a hexagonal prism. For the Au52(TBBT)32, 48 of the 52 gold atoms can also be
fit into the FCC lattice, with the atoms assembled in the [100] direction, forming a tetragonal rod enclosed by {100} facets (Fig. 4, E to H). Correspondingly, the surface-protecting Au$_x$(SR)$_x$+1 staples are decomposed into simple bridging thiolates (fig. S4). This alternative view of the Au$_{40}$ and Au$_{52}$ clusters reveals the anisotropic layer-by-layer construction mode of magic-sized gold clusters, similar to the anisotropic growth of 2D nanoprisms and 1D nanorods in shape-controlled nanocrystals (30, 31). It also provides atomic-scale insight into the effect of selective surface passivation in tailoring the particle shape (32).

The segregation of Au$_4$ tetrahedral units in the FCC lattice is due to the surface-protecting thiolates or, more specifically, the directional covalent bonds between thiolates and gold atoms. The bonding of the sulfur atom in the thiolate adopts the tetragonal configuration, with two orbitals bonded to two gold atoms, one bonded to the carbon tail, and one for the lone-pair electrons (Fig. 5, A and B). The three atoms in the Au-S-Au bridge form a triangle, with an Au-S bond length of ~2.33 Å and an average Au-S-Au angle of 87.4 ± 3.6° in Au$_{40}$ and 92.6 ± 7.3° in Au$_{52}$. Because of the geometric restriction of the Au-S-Au triangle, the two Au atoms underneath the sulfur bridge are pushed apart, with an average Au-Au bond length of 3.21 Å in Au$_{40}$ and 3.35 Å in Au$_{52}$, longer than the bulk Au-Au bond length of 2.88 Å (Fig. 5, A and B).

This thiolate bonding effect can be easily viewed on the 2D surface of the clusters, as reflected in the inhomogeneous distribution of Au-Au bond lengths (Fig. 5, C and D). As discussed above, the overall anisotropic growth of the Au$_{40}$ and Au$_{52}$ clusters leads to the exposure of

---

Fig. 4. Anisotropic growth of the gold FCC lattice into a hexagonal prism in Au$_{40}$(o-MBT)$_{24}$ and a tetragonal rod in Au$_{52}$(TBBT)$_{32}$. (A to C) Model of a 48–gold atom hexagonal prism composed of three layers (green, orange, and blue) stacked along the [111] direction in an a-b-c manner (the three arrows indicate the three missing gold atoms in the real Au$_{40}$ cluster). (D) Au$_{40}$(o-MBT)$_{24}$ as a hexagonal prism. (E to G) Model of a 48–gold atom tetragonal rod composed of six layers stacked along the [100] direction. (H) Au$_{52}$(TBBT)$_{32}$ as a tetragonal rod. The four gold atoms not included in the FCC lattice are indicated by arrows.

Fig. 5. Thiolate bonding and patterning on the crystalline facets of Au$_{40}$ and Au$_{52}$. (A) Tetragonal configuration of sulfur atom of o-MBT in the Au$_{40}$ cluster. (B) Tetragonal configuration of sulfur atom of TBBT in Au$_{52}$. (C) Twelve–gold atom (111) facets on the Au$_{40}$ cluster. (D) Twelve–gold atom (100) facets on the Au$_{52}$ cluster. Orange/magenta, Au; yellow, S; gray, C.
the extended gold crystalline facets, that is, the 12-atom \{111\} facets in the Au40 hexagonal prism (Fig. 5C) and the 12-atom \{100\} facets in the Au52 tetragonal rod (Fig. 5D). Every two gold atoms on the facet are bridged by one thiolate ligand (Fig. 5, C and D). With the thiolates bridging onto the gold crystalline facets, the Au-Au distance underneath the bridging S is expanded to meet the coordination requirements of the S bridge. On the other hand, the Au-Au pairs adjacent to the bridging thiolates are squeezed together by the forces from different directions, resulting in shorter Au-Au distances (Fig. 5, C and D, bottom). Such a demonstration of inhomogeneous distribution of Au-Au distances in 2D surface can be applied in the 3D nanoclusters because the thiolate bonding force can further penetrate into a few layers of gold atoms (fig. S5). Together, the surface thiolate bonding causes a stress, and this stress propagates into the anisotropic-shaped FCC cluster to induce segregation of Au4 tetrahedra and their further coiling up into hierarchical patterns.

**CONCLUSION**

Here, we have presented two novel structures of thiolate-protected gold clusters. The implications of the Au40 and Au52 structures are manifold. First, the two clusters illustrate the supermolecular complexity, and such a view can explain more magic-sizes of clusters than the early superatom model. The supermolecular picture is reminiscent of the fact that an unlimited number of stable molecules can be assembled from a limited number of atoms. Second, they reveal an anisotropic growth of FCC lattice at the atomic level, as reflected in the 2D hexagonal prism of the Au40 and the 1D tetragonal rod of the Au52 structure. The two structures imply the important roles of ligands in the anisotropic growth at the atomic level. Third, the new structures add a new dimension in constructing highly stable clusters in an anisotropic fashion other than the isotropic shell-by-shell growth (22) or polyhedron-fusion mode (24, 33, 34). The new supermolecular picture is expected to advance further understanding of the cluster structure and stability, and the Au40 and Au52 cluster materials will provide more insights into shape and surface-dependent properties and applications.

**MATERIALS AND METHODS**

**Chemicals**

The following chemicals were used: tetrachloroauric(III) acid (HAuCl4·3H2O, 99.99% metals basis, Sigma-Aldrich), tetraoctylammonium bromide (TOAB, 98%, TCI), TBBT (97%, Alfa Aesar), sodium borohydride (NaBH4, 99.9%, Sigma-Aldrich); N,N-dimethylethylbenzyldithiocarbamate (MBT) (97%, TCI), TBBT (97%, TCI), pentane (HPLC grade, 99.9%, Sigma-Aldrich), methanol [high-performance liquid chromatography (HPLC) grade, 99.9%, Sigma-Aldrich]; toluene (HPLC grade, 99.9%, Sigma-Aldrich), toluene (HPLC grade, 99.9%, Sigma-Aldrich), and tetrahydrofuran (HPLC grade, 99.9%, Sigma-Aldrich). All chemicals were used as received.

**Synthesis**

The Au40(ω-MBT)24 cluster was synthesized by a two-step size-focusing method (23). In the first step, 0.25 mmol of HAuCl4 was reduced by 1.27 mmol of ω-MBT to form Au(I)-ω-MBT polymers in a toluene solution containing 0.29 mmol of TOAB. The Au(I)-ω-MBT polymers were further reduced to size-mixed Auω(ω-MBT)5 clusters by 2.5 mmol of NaBH4 (dissolved in 5 ml of water). In the second step, the polydispersed Auω(ω-MBT)5 clusters were reacted with excess of ω-MBT thiol at 90°C for 48 hours. The Au52(TBBT)32 cluster was synthesized by a similar process. In the first step, 0.125 mmol of HAuCl4 was reacted with 0.625 mmol of TBBT in 10 ml of tetrahydrofuran, followed by reduction to size-mixed Auω(TBBT)5 clusters by 1.25 mmol of NaBH4 (in 5 ml of water). In the second step, the Auω (TBBT) mixture was reacted with excess TBBT thiol at 90°C for 24 hours. Both clusters were separated from the reaction mixture by precipitation with methanol and crystallized in the pentane/CH2Cl2 solvents.

**X-ray crystallography**

Data of both Au40(ω-MBT)24 and Au52(TBBT)32 were collected on a Bruker X8 Prospector Ultra equipped with an Apex II charge-coupled device detector and an IμS microfocus CuKα x-ray source (λ = 1.54178 Å) under cold N2 flow at 150 K.

For Au40(ω-MBT)24, a piece of brown crystal with dimensions of 0.16 × 0.10 × 0.01 mm was mounted onto a MiTeGen MicroMeshes with fluorolube. A triclinic unit cell with dimensions a = 18.9983(5) Å, b = 19.0751(5) Å, c = 35.625(5) Å, α = 81.5670(17)°, β = 81.4980(16)°, and γ = 60.9600 (15)° was derived from the least-squares refinement of 9930 reflections in the range of 2.66 < θ < 55.122. Centrosymmetric space group P1 was determined on the basis of intensity statistics and the lack of systematic absences. The data were collected to 0.94 Å. After integration of the data by the Bruker SAINT program, empirical absorption correction was applied using the program SADABS. The maximum and minimum transmittance (Tmax and Tmin) values were 0.6319 and 0.0455, respectively. The structure was solved with a direct method using the Bruker SHELXTL program. All the Au and S atoms were located, and all the C atoms were generated through subsequent difference Fourier syntheses. Idealized atom positions were calculated for all hydrogen atoms [with d-(Cmethyl-H) = 0.979 Å and d-(Cphenyl-H) = 0.95 Å]. All the Au, S, and C atoms were refined anisotropically, and all the H atoms were refined isotropically.

For Au52(TBBT)32, a piece of black crystal with dimensions of 0.20 × 0.08 × 0.02 mm was used for data collection. A triclinic unit cell with dimensions a = 24.3807(9) Å, b = 24.8559(10) Å, c = 39.7532(10) Å, α = 97.027(4)°, β = 98.189(4)°, and γ = 117.673(2)° was derived from the least-squares refinement of 9938 reflections in the range of 2.365 < θ < 51.159. Centrosymmetric space group P1 was determined on the basis of intensity statistics and the lack of systematic absences. The data were collected to 0.99 Å. The Tmax and Tmin values were 0.5367 and 0.0531, respectively. The structure was solved with a direct method using Bruker SHELXTL. All the Au and S atoms were located; all phenyl C and most t-butyl C atoms were generated through subsequent difference Fourier syntheses. However, some of the t-Bu C atoms were difficult to locate because of disordering of t-Bu groups as well as interference of surrounding solvent electron density, so a rigid TBBT fragment was used in these cases. Idealized atom positions were calculated for all hydrogen atoms [with d-(Cmethyl-H) = 0.979 Å and d-(Cphenyl-H) = 0.95 Å]. All the Au, S, and phenyl C atoms were refined anisotropically, and all the H atoms were refined isotropically.

**DFT simulations**

To gain insight into the electronic structures of the newly observed Au40 (ω-MBT)24 and Au52(TBBT)32 nanoclusters, we performed DFT calculations with the RI (resolution of the identity) approximation. In the calculations, the structures of the clusters are exactly the same ones observed by the single crystal x-ray crystallography, taking full account of each ligand, ω-MBT, or TBBT. The TURBOMOLE version 6.6 package
of ab initio quantum chemistry programs was used in all the calculations. The double-$\zeta$ valence quality plus polarization basis in the TURBOMOLE basis set library was adopted in the calculations along with a 60-electron, relativistic, effective core potential for the gold atom.

## SUPPLEMENTARY MATERIALS

### Supplementary Material for this article is available at http://advances.sciencemag.org/cgi/content/full/1/9/e1500425/DC1

Materials and Methods

- **Fig. S1.** The left- and right-handed isomers of the chiral double helical Au$_{32}$ kernel in Au$_{52}$(TBBT)$_{32}$.
- **Fig. S2.** DFT-simulated HOMO distribution of Au$_{40}$(o-MBT)$_{24}$.
- **Table S1.** Crystal data and structure refinement for Au$_{40}$(TBBT)$_{24}$.
- **Table S2.** Atomic coordinates (×10$^4$) and equivalent isotropic displacement parameters (Å$^2$ × 10$^3$) for Au$_{40}$(TBBT)$_{24}$.
- **Table S3.** Atomic coordinates (×10$^4$) and equivalent isotropic displacement parameters (Å$^2$ × 10$^3$) for Au$_{52}$(TBBT)$_{32}$.
- **Table S4.** Atomic coordinates (×10$^4$) and equivalent isotropic displacement parameters (Å$^2$ × 10$^3$) for Au$_{52}$(o-MBT)$_{24}$ and Au$_{52}$(TBBT)$_{32}$ clusters.
- **Fig. S5.** Penetration of surface bridging forces into the kernel, leading to the segregation of tetrahedral units.

### REFERENCES AND NOTES

1. H. Qian, M. Zhu, Z. Wu, R. Jin, Quantum sized gold nanoclusters with atomic precision. Acc. Chem. Res. 45, 1470–1479 (2012).
2. S. Yamazoe, K. Koyasu, T. Tsukuda, Nonsoluble oxidation catalysis of gold clusters. Acc. Chem. Res. 47, 816–824 (2014).
3. N. Barrabès, B. Zhang, T. Bürgi, Racemization of chiral Pd$_2$Au$_{10}$SC$_2$H$_4$PPh$_{12}$ Doping increases the flexibility of the cluster surface. J. Am. Chem. Soc. 136, 14361–14364 (2014).
4. S. H. Yau, O. Varnavski, T. Goodson III, An ultrafast look at Au nanoclusters. Acc. Chem. Res. 46, 1506–1516 (2013).
5. R. Jin, Atomically precise metal nanoclusters: Stable sizes and optical properties. Nanoscale 7, 1549–1565 (2015).
6. C. A. Mirkin, R. L. Letsinger, R. C. Mucic, J. J. Storhoff, A DNA-based method for rationally synthesizing metal nanoparticles. Science 289, 104–107 (2000).
7. B. Nikoobakht, M. A. El-Sayed, Preparation and growth mechanism of gold nanorods (NRs) using seed-mediated growth method. J. Phys. Chem. Lett. 4, 3186–3192 (2013).
8. C. Zeng, H. Qian, T. Li, G. Li, N. L. Rosi, B. Yoon, R. N. Barnett, R. L. Whetten, U. Landman, R. Jin, Structural and electronic properties of the gold nanocrystal Au$_{52}$(o-MBT)$_{24}$. Angew. Chem. Int. Ed. 51, 13114–13118 (2012).
9. D. M. Chevrier, A. Chatt, P. Zhang, C. Zeng, R. Jin, Unique bonding properties of the Au$_{52}$(o-MBT)$_{24}$ nanocluster with FCC-like core. J. Phys. Chem. Lett. 4, 3186–3191 (2013).
10. C. Zeng, C. Liu, Y. Chen, N. L. Rosi, R. Jin, Gold-thiolate ring as a protecting motif in the Au$_{52}$(o-MBT)$_{24}$ nanocluster and implications. J. Am. Chem. Soc. 136, 11922–11925 (2014).
11. L. Cheng, Y. Yuan, X. Zhang, J. Yang, Superatom networks in thiolate-protected gold nanoclusters. Angew. Chem. Int. Ed. 52, 9035–9039 (2013).
12. R. Jin, Y. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz, J. G. Zheng, Photoinduced conversion of silver nanospheres to nanoprisms. Science 294, 1901–1903 (2001).
13. B. Nikoobakht, M. A. El-Sayed, Preparation and growth mechanism of gold nanorods (NRs) using seed-mediated growth method. Chem. Mater. 15, 1957–1962 (2003).
14. M. L. Personick, C. A. Mirkin, Making sense of the mayhem behind shape control in the synthesis of gold nanoparticles. J. Am. Chem. Soc. 135, 18238–18247 (2013).
15. B. K. Teo, H. Zhang, Clusters of clusters: Self-organization and self-similarity in the intermediate stages of cluster growth of Au-Ag supraclusters. Proc. Natl. Acad. Sci. U.S.A. 88, 5067–5071 (1991).
16. E. G. Mednikov, L. F. Dahl, Nanosized Pd$_{37}$(CO)$_{28}$(P(C$_6$H$_5$)$_3$)$_2$ containing geometrically unprecedented central 23-atom interpenetrating tri-icosahedral palladium kernel of double icosahedral units: Its postulated metal-core evolution and resulting stereochemical implications. J. Am. Chem. Soc. 130, 14813–14821 (2008).

**Funding:** R.J. received financial support from the Air Force Office of Scientific Research (AFOSR) under AFOSR Award no. FA9550-15-1-0099 (FA9550-15-1-0154) and the Camille Dreyfus Teacher-Scholar Awards Program. K.N. received financial support from Elements Strategy Initiative for Catalysts and Batteries and a Grant-in-Aid for Scientific Research (no. 25288012) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. R.J. received financial support from the Air Force Office of Scientific Research (FA9550-15-1-0099) and the Camille Dreyfus Teacher-Scholar Awards Program. K.N. received financial support from Elements Strategy Initiative for Catalysts and Batteries and a Grant-in-Aid for Scientific Research (no. 25288012) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

**Author contributions:** C.Z., Y.C., and R.J. were responsible for synthesis and crystallization and for the design of the project. C.L. and N.L.R. conducted the x-ray crystallographic analysis. K.N. carried out DFT calculations. All authors contributed to the writing of the manuscript.

**Competing interests:** The authors declare that they have no competing interests. Data and materials availability: All data is available in the manuscript and the Supplementary Materials.

Submitted 4 April 2015
Accepted 6 August 2015
Published 9 October 2015
10.1126/sciadv.1500425

**Citation:** C. Zeng, Y. Chen, C. Liu, K. Nobusada, N. L. Rosi, R. Jin, Gold tetrahedra coil up: Kekulé-like and double helical superstructures. Sci. Adv. 1, e1500425 (2015).