

# Structure of Au<sub>15</sub>(SR)<sub>13</sub> and Its Implication for the Origin of the Nucleus in Thiolated Gold Nanoclusters

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**S** Supporting Information

**ABSTRACT:** Au<sub>15</sub>(SR)<sub>13</sub> is the smallest stable thiolated gold nanocluster experimentally identified so far, and its elusive structure may hold the key to the origin of the nucleus in the formation of thiolated gold nanoclusters. By an extensive exploration of possible isomers by density functional theory, we arrive at a novel structure for Au<sub>15</sub>(SR)<sub>13</sub> with high stability and whose optical absorption characteristics match those of the experiment. Different from the previous structures and the prevailing working hypothesis about the construction of thiolated gold nanoclusters, the Au<sub>15</sub>(SR)<sub>13</sub> model features a cyclic [Au(I)-SR] pentamer interlocked with one staple trimer motif protecting the tetrahedral Au<sub>4</sub> nucleus, together with another trimer motif. This structure suggests that Au<sub>15</sub>(SR)<sub>13</sub> is a transitional composition from an [Au(I)-SR]<sub>x</sub> polymer such as Au<sub>10</sub>(SR)<sub>10</sub> to larger Au<sub>n</sub>(SR)<sub>m</sub> ( $n > m$ ) clusters that have only the staple motifs and that the nucleation process starts from the Au<sub>4</sub> core.

Tremendous progress has been made in the field of thiolated gold nanoclusters, Au<sub>n</sub>(SR)<sub>m</sub>, ever since the accurate identification of many precise compositions from the product mixture in 2005<sup>1</sup> and the report of the first crystal structure, Au<sub>102</sub>(SR)<sub>44</sub>, in 2007.<sup>2</sup> This was followed by the crystal structure of Au<sub>25</sub>(SR)<sub>18</sub><sup>-</sup> in 2008.<sup>3</sup> Application of size-focusing synthesis<sup>4</sup> further delivered the structures of Au<sub>38</sub>(SR)<sub>24</sub> in 2010<sup>5</sup> and Au<sub>36</sub>(SR)<sub>24</sub> in 2012.<sup>6</sup> The experimental progress has been well matched by the parallel theoretical efforts based on density functional theory (DFT) which explained the cluster's stability by the superatomic complex concept<sup>7</sup> and, more impressively, by correctly predicting the structures of Au<sub>25</sub>(SR)<sub>18</sub><sup>-8</sup> and Au<sub>38</sub>(SR)<sub>24</sub>.<sup>9</sup> The success of the DFT method in understanding and predicting the structures of thiolated gold clusters has been truly inspiring.<sup>10</sup>

One outstanding challenge in the field of thiolated gold clusters in particular and in nanoscience in general is to determine the detailed, atomic-scale mechanism of the nucleation and growth process. Like the ultimate question in biology—what is the origin of life?—one asks, what is the origin of thiolated gold nanoclusters? Intuitively, this should start with the formation of the first Au–Au bond (that is shorter than the Au–Au nearest-neighbor distance in bulk, 2.88 Å) and a nucleus. In the commonly adopted or modified Brust synthesis<sup>11</sup> of Au<sub>n</sub>(SR)<sub>m</sub> clusters, this is achieved by reduction

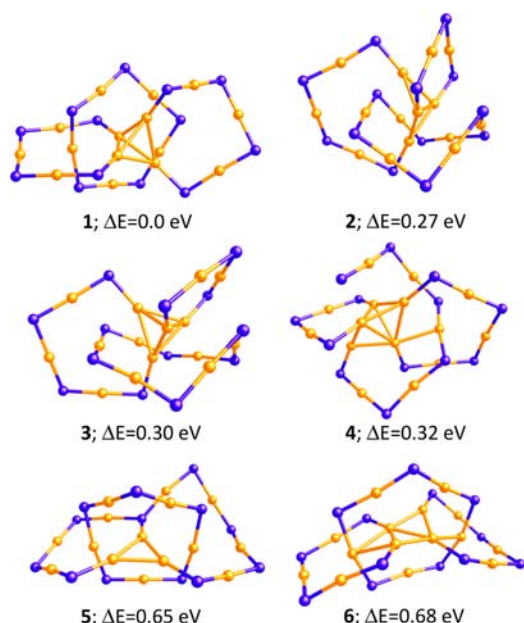
of [Au(I)-SR]<sub>x</sub> oligomers or polymers by NaBH<sub>4</sub>. The structure of the smallest thiolated gold cluster could shed light on the origin of the nucleus. This Au<sub>n</sub>(SR)<sub>m</sub> cluster, where  $n$  is greater than  $m$ , should have the smallest  $n$  possible. This reasoning led us to identify Au<sub>15</sub>(SR)<sub>13</sub> as our target which has been experimentally identified as the smallest Au<sub>n</sub>(SR)<sub>m</sub> cluster in a relatively large yield and high stability.<sup>1,12</sup> Below this size, only [Au(I)-SR]<sub>x</sub> oligomers were isolated in large yields, including Au<sub>10</sub>(SR)<sub>10</sub>, Au<sub>11</sub>(SR)<sub>11</sub>, and Au<sub>12</sub>(SR)<sub>12</sub>.<sup>1,12a,b</sup> Hence, we reason that the structure of Au<sub>15</sub>(SR)<sub>13</sub> may hold the key to the origin of the nucleation of a gold core in the thiolated gold clusters. Pursuing this idea, here we propose a promising structure for Au<sub>15</sub>(SR)<sub>13</sub> which not only possesses novel features but also sheds light on the likely pathways of the nucleation process during the initial formation of a gold nucleus in the synthesis of thiolated gold nanoclusters.

Structure prediction for thiolated gold nanoclusters remains a challenge, evident from the fact that the number of identified Au<sub>n</sub>(SR)<sub>m</sub> compositions without a structural model dwarfs that of the solved ones.<sup>10b</sup> The prevailing hypothesis or guiding principle, inspired by the known structures, has been that the structure of Au<sub>n</sub>(SR)<sub>m</sub> is composed of a gold core protected by staple motifs or more generally speaking, [RS-(Au-SR)<sub>m</sub>] oligomers.<sup>9a,13</sup> Does this hypothesis apply to Au<sub>15</sub>(SR)<sub>13</sub>? We think not. We reached this conclusion by exploring many isomers (over 50) including those from applying the staple hypothesis above, optimizing their structures, and comparing their energies by DFT (see the Supporting Information, SI, for computational details).

The structures of the 55 initial guesses are shown in Table S1 in SI together with their energies after geometry optimization. We used three strategies to construct the initial guesses: (i) derivation from the models of other clusters such as Au<sub>24</sub>(SR)<sub>20</sub><sup>14</sup> and Au<sub>12</sub>(SR)<sub>9</sub><sup>15</sup> by either adding or pruning off Au atoms and –SR ligands; (ii) the staple hypothesis in five scenarios (Table S2 in SI); and (iii) learning from the isomer energies from the first two strategies until a new hypothesis was developed. Nine scenarios of the new hypothesis were considered (Table S3 in SI). Six low-energy isomers out of 55 and their relative energies are shown in Figure 1. The most stable structure (isomer 1) in fact adopts a novel feature: a cyclic [Au(I)-SR] pentamer together with two staple trimer motifs<sup>16</sup> protecting a Au<sub>4</sub> nucleus or core. This feature is new and interesting in several aspects: (a) it is the first example that

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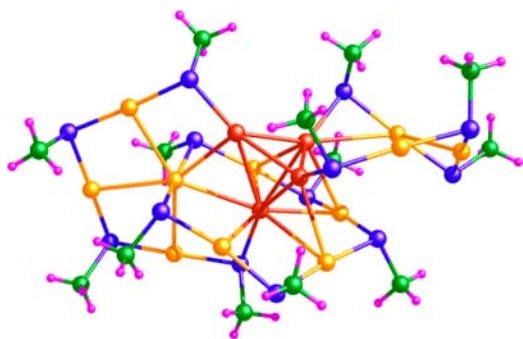
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**Figure 1.** Several low-energy isomers (out of 55) of  $\text{Au}_{15}(\text{SCH}_3)_{13}$  and their relative stability. Au, orange; S, blue;  $\text{CH}_3$  and some Au–Au bonds are not shown for clarity.

a cyclic  $[\text{Au}(\text{I})\text{-SR}]_x$  complex participates in the bonding of a  $\text{Au}_n(\text{SR})_m$  cluster together with the staple motifs; (b) it suggests that  $\text{Au}_{15}(\text{SR})_{13}$  is a hybrid between a homoleptic cyclic  $[\text{Au}(\text{I})\text{-SR}]_x$  complex and a “regular”  $\text{Au}_n(\text{SR})_m$  cluster; (c) the hybrid nature suggests that  $\text{Au}_{15}(\text{SR})_{13}$  is a transitional composition from  $[\text{Au}(\text{I})\text{-SR}]_x$  complexes to regular  $\text{Au}_n(\text{SR})_m$  clusters, matching well with the fact that  $\text{Au}_{15}(\text{SR})_{13}$  is the smallest  $\text{Au}_n(\text{SR})_m$  cluster identified in the experiment.

The core–ligand environment of isomer **1** can be better visualized in Figure 2 at a viewing angle slightly different from

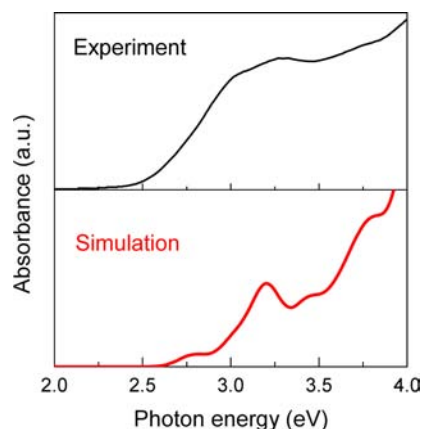


**Figure 2.** The most stable structure (isomer **1**) found for  $\text{Au}_{15}(\text{SCH}_3)_{13}$ . Au nucleus, red; Au in the ligand shell, orange; S, blue; C, green; H, pink.

that of Figure 1, and where the  $\text{Au}_4$  nucleus is highlighted in red and Au–Au bonds are shown. One can see that one of the two trimer motifs and the cyclic pentamer are interlocked. This catenane-like structure is a unique feature of homoleptic  $[\text{Au}(\text{I})\text{-SR}]_x$  complexes, such as  $\text{Au}_{10}(\text{SR})_{10}$ ,<sup>17</sup>  $\text{Au}_{11}(\text{SR})_{11}$ ,<sup>18</sup> and  $\text{Au}_{12}(\text{SR})_{12}$ ,<sup>17</sup> and low Au/S ratio  $\text{Au}_n(\text{SR})_m$  clusters such as  $\text{Au}_{24}(\text{SR})_{20}$ .<sup>14,19</sup> Figure 2 also shows that the  $\text{Au}_4$  core is well settled in and interacting with the interlocking cyclic-pentamer and trimer motifs. This interlocking structure between a cyclic  $[\text{Au}(\text{I})\text{-SR}]_x$  unit and an open, staple-like  $[\text{RS}-(\text{AuSR})_x]$  unit is

a common feature among the low-energy isomers of  $\text{Au}_{15}(\text{SR})_{13}$  shown in Figure 1. This is dictated by the low Au/S ratio (at 1.15) in  $\text{Au}_{15}(\text{SR})_{13}$ , but instead of using much longer staple motifs, the system now prefers a ring structure in the ligand layer. In addition, we found that the ring has a significant role in stabilizing cluster: the computed interaction energy between the cyclic pentamer and the rest of the cluster is at 2.1 eV, quite strong.

How do we know that isomer **1** is a viable structure for  $\text{Au}_{15}(\text{SR})_{13}$ ? First, this structure is the most stable one among the many isomers (over 50) we explored and far more stable (by 1.9 eV) than a recently proposed model.<sup>12a</sup> Second, we can compare the simulated optical absorption (Figure 3) of this



**Figure 3.** Simulated optical absorption spectrum of isomer **1** of the  $\text{Au}_{15}(\text{SCH}_3)_{13}$  cluster in comparison with the experimental spectrum of  $\text{Au}_{15}(\text{SG})_{13}$  (ref 1; SG = glutathionate).

isomer against the experiment.<sup>1</sup> The simulated spectrum shows an onset of absorption around 2.6 eV and a major peak at 3.2 eV, in good agreement with the measured onset at 2.55 eV and main peak at 3.28 eV.<sup>1</sup> Third, we can compare the relative stability of  $\text{Au}_{15}(\text{SR})_{13}$  against those of nearby compositions, in order to evaluate if isomer **1** of  $\text{Au}_{15}(\text{SR})_{13}$  is stable enough. This relative stability is measured by the energetics of transformation of  $\text{Au}_{15}(\text{SR})_{13}$  into  $\text{Au}_{10}(\text{SR})_{10}$  and a larger cluster (Table 1). The advantage of this measure is that

**Table 1.** Stability of Isomer **1** of  $\text{Au}_{15}(\text{SR})_{13}$  against Several Other Larger Ones, As Measured by the Transformation of  $\text{Au}_{15}(\text{SR})_{13}$  into  $\text{Au}_{10}(\text{SR})_{10}$  and a Larger Cluster

transformation of $\text{Au}_{15}(\text{SR})_{13}$ <sup>a</sup>	$\Delta E$ (eV)
$\text{Au}_{15}(\text{SR})_{13} \rightarrow \frac{3}{5} \text{Au}_{10}(\text{SR})_{10} + \frac{1}{2} \text{Au}_{18}(\text{SR})_{14}$ <sup>b</sup>	0.057
$\text{Au}_{15}(\text{SR})_{13} \rightarrow \frac{1}{2} \text{Au}_{10}(\text{SR})_{10} + \frac{1}{2} \text{Au}_{20}(\text{SR})_{16}$ <sup>c</sup>	0.020
$\text{Au}_{15}(\text{SR})_{13} \rightarrow \frac{3}{10} \text{Au}_{10}(\text{SR})_{10} + \frac{1}{2} \text{Au}_{24}(\text{SR})_{20}$ <sup>d</sup>	−0.315
$\text{Au}_{15}(\text{SR})_{13} \rightarrow \frac{67}{70} \text{Au}_{10}(\text{SR})_{10} + \frac{1}{7} \text{Au}_{38}(\text{SR})_{24}$ <sup>e</sup>	−0.526

<sup>a</sup>R =  $-\text{CH}_3$ . <sup>b</sup>Ref 20. <sup>c</sup>Ref 16a. <sup>d</sup>Ref 14. <sup>e</sup>Ref 5.

$\text{Au}_{10}(\text{SR})_{10}$  has a known structure<sup>17</sup> and exists in a large yield and high stability together with  $\text{Au}_{15}(\text{SR})_{13}$  and other larger clusters.<sup>1,12a,b</sup> We compared the relative stability of  $\text{Au}_{15}(\text{SR})_{13}$  against  $\text{Au}_{18}(\text{SR})_{14}$ ,<sup>1,12,20</sup>  $\text{Au}_{20}(\text{SR})_{16}$ ,<sup>16a,21</sup>  $\text{Au}_{24}(\text{SR})_{20}$ ,<sup>14,19</sup> and  $\text{Au}_{38}(\text{SR})_{24}$ ,<sup>5</sup> based on either the most viable structure from the computational modeling or the experiment. One can see that although isomer **1** of  $\text{Au}_{15}(\text{SR})_{13}$  is less stable than the larger  $\text{Au}_{24}(\text{SR})_{20}$  and  $\text{Au}_{38}(\text{SR})_{24}$ , it is slightly more stable than the closer compositions,  $\text{Au}_{18}(\text{SR})_{14}$  and  $\text{Au}_{20}(\text{SR})_{16}$ ,<sup>21</sup> which

coexist with  $\text{Au}_{15}(\text{SR})_{13}$  and  $\text{Au}_{10}(\text{SR})_{10}$  in the product mixture.<sup>1,12a,b</sup> This suggests that isomer **1** is a very viable model for  $\text{Au}_{15}(\text{SR})_{13}$ , as Table 1 shows that it is as stable as the best models of  $\text{Au}_{18}(\text{SR})_{14}$  and  $\text{Au}_{20}(\text{SR})_{16}$ .

When comparing the simulated optical absorption of  $\text{Au}_{15}(\text{SCH}_3)_{13}$  and the experimental optical absorption of  $\text{Au}_{15}(\text{SG})_{13}$  in Figure 3, we assumed that changing from  $-\text{SCH}_3$  to  $-\text{SG}$  (glutathionate) will not affect the optical absorption. This assumption, made out of necessity due to the large and flexible tripeptide  $-\text{SG}$  ligand that hampers simulation of the optical absorption of the  $\text{Au}_{15}(\text{SG})_{13}$  cluster at the B3LYP level, is reasonable in our opinion for several reasons. First, the experimental UV-vis absorption of  $\text{Au}_{25}(\text{SG})_{18}^-$  is very similar to those of  $\text{Au}_{25}(\text{SC}_6\text{H}_{13})_{18}^-$ <sup>22</sup> and  $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}^-$ ,<sup>3b</sup> and the computed optical spectrum of  $\text{Au}_{25}(\text{SH})_{18}^-$  agrees well with the experimental spectrum of  $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}^-$ ,<sup>3b</sup> indicating that changing from  $-\text{SG}$  to other commonly used  $-\text{SR}$  ligands does not affect the UV-vis absorption of  $\text{Au}_n(\text{SR})_m$ . Moreover, the  $-\text{SG}$  ligand itself has an optical absorption onset at much higher energy ( $>4$  eV).<sup>1</sup> Previously, Grönbeck et al. simulated the ligand effect on the optical absorption of  $\text{Au}_4(\text{SR})_4$  for  $-\text{R} = -\text{CH}_3$ ,  $-\text{C}_6\text{H}_5$ , and  $-\text{SG}$ .<sup>23</sup> To further test the effect of  $-\text{SG}$  on optical absorption while keeping the increase in the computational cost manageable, we replaced one  $-\text{SCH}_3$  of  $\text{Au}_{15}(\text{SCH}_3)_{13}$  with  $-\text{SG}$  and found that the computed optical absorption of  $\text{Au}_{15}(\text{SCH}_3)_{12}(\text{SG})_1$  is very similar to that of  $\text{Au}_{15}(\text{SCH}_3)_{13}$  (Figure S1 in SI), indicating that changing from  $-\text{SCH}_3$  to  $-\text{SG}$  does not seem to change the optical absorption of  $\text{Au}_{15}(\text{SR})_{13}$  much.

What does the structure of isomer **1** of  $\text{Au}_{15}(\text{SR})_{13}$  imply for the origin of a nucleus in thiolated gold cluster? The answer lies in the close similarity between isomer **1** and the experimental structure of  $\text{Au}_{10}(\text{SR})_{10}$  which comprises two interlocking cyclic pentamers. It is commonly assumed that reduction of  $[\text{Au}(\text{I})-\text{SR}]$  oligomers by  $\text{NaBH}_4$  leads to formation of  $\text{Au}_n(\text{SR})_m$  clusters during the Brust synthesis. Although this presumed mechanism has been challenged in the two-phase method, there is a consensus that it happens in the one-phase method.<sup>24</sup> Reduction by  $\text{NaBH}_4$  happens fast and is difficult to control; this fact coupled with the almost zero knowledge of the structure of the  $[\text{Au}(\text{I})-\text{SR}]$  precursor prior to reduction makes detailed experimental determination of the growth mechanism challenging. Recent theoretical efforts<sup>25</sup> have targeted the initial reduction process of  $\text{Au}(\text{III})$  to  $\text{Au}(\text{I})$  and of cyclic  $[\text{Au}(\text{I})-\text{SR}]$  tetramer. For the latter,<sup>25b</sup> hydride addition was suggested as a likely reduction channel, leading to (a) liberation of a free HSR and (b) anionic precursors such as  $\text{Au}_4(\text{SR})_3^-$  to  $\text{Au}_n(\text{SR})_m$  formation. On the experimental side, analysis of <sup>197</sup>Au Mössbauer spectroscopy suggests that  $\text{Au}_{15}(\text{SR})_{13}$  is the critical size where a  $\text{Au}_3$  nucleus likely forms.<sup>26</sup> Our examination of isomers with the  $\text{Au}_3$  core found them to be less stable than isomer **1**. In situ time-resolved quick X-ray absorption fine-structure spectroscopy suggested  $\text{Au}_4$  as a possible small nucleus during the initial reduction of  $\text{HAuCl}_4$  by  $\text{NaBH}_4$ .<sup>27</sup> Our prediction of the structure of  $\text{Au}_{15}(\text{SR})_{13}$  supports this suggestion and further indicates that the initiation of the smallest,  $\text{Au}_4$  nucleus might be achieved by controlled reduction of a smaller cyclic  $[\text{Au}(\text{I})-\text{SR}]$  complex such as a tetramer or pentamer.  $\text{Au}_4(\text{SR})_4$  has been crystallized before,<sup>28</sup> so it might be an ideal precursor. The choice of a reductant would be the key to control the speed of the reduction. The recent finding that slow reduction of  $[\text{Au}(\text{I})-\text{SR}]$  polymeric

precursors by carbon monoxide also leads to formation of  $\text{Au}_{25}(\text{SR})_{18}^-$  suggests a possibility of controlling the reduction speed by tuning the reductant.<sup>29</sup> Hopefully, the structure of isomer **1** can be confirmed experimentally; then a nucleation mechanism can be probed by controlled reduction of small cyclic  $[\text{Au}(\text{I})-\text{SR}]$  complexes such as the tetramer that can lead to formation of  $\text{Au}_{15}(\text{SR})_{13}$ . And then the growth of the nucleus can be further examined as  $\text{Au}_{15}(\text{SR})_{13}$  is converted to larger clusters such as  $\text{Au}_{18}(\text{SR})_{14}$ .<sup>12b</sup>

The structure of  $\text{Au}_{15}(\text{SR})_{13}$  also sheds new light on another topic, the smallest superatomic  $\text{Au}_n(\text{SR})_m$  cluster.  $\text{Au}_{25}(\text{SR})_{18}^-$  and  $\text{Au}_{102}(\text{SR})_{44}$  correspond to the magic numbers 8 and 58, respectively, according to the superatom complex concept.<sup>7</sup> Previously,  $\text{Au}_{12}(\text{SR})_9^+$  and  $\text{Au}_{10}(\text{SR})_8$ , two hypothetical formulas,<sup>15,16b</sup> have been proposed to be candidates for the magic number 2.  $\text{Au}_{12}(\text{SR})_9^+$  has an octahedron core with three dimer motifs;<sup>15</sup> however, in the reducing environment of  $\text{NaBH}_4$ , it is unlikely to survive as a cation.  $\text{Au}_{10}(\text{SR})_8$  has a tetrahedral core with two interlocking trimer motifs.<sup>16b</sup> Comparing  $\text{Au}_{10}(\text{SR})_8$  with  $\text{Au}_{15}(\text{SR})_{13}$ , the latter has one more cyclic pentamer in the structure. In other words, one can consider a reaction of  $\text{Au}_{10}(\text{SR})_8$  with 0.5 mol of  $\text{Au}_{10}(\text{SR})_{10}$  to form  $\text{Au}_{15}(\text{SR})_{13}$ . The DFT energetics of this reaction is  $-0.57$  eV, indicating that  $\text{Au}_{15}(\text{SR})_{13}$  is in fact much more stable than  $\text{Au}_{10}(\text{SR})_8$ . Since  $\text{Au}_{15}(\text{SR})_{13}$  also has an electron count of 2 according to the superatom complex concept,<sup>7</sup> isomer **1** is therefore now the best candidate for the smallest superatomic  $\text{Au}_n(\text{SR})_m$  cluster.

In sum, we have found a novel structural model for  $\text{Au}_{15}(\text{SR})_{13}$ , the smallest thiolated gold nanocluster identified experimentally in high enough yield and stability. The structure features a cyclic  $[\text{Au}(\text{I})-\text{SR}]$  pentamer in the ligand shell, together with two regular trimer motifs, protecting a  $\text{Au}_4$  nucleus. The computed optical absorption spectrum agrees well with the experiment, and the stability of this model is comparable with those of nearby compositions identified experimentally, indicating its viability. This structure suggests a probable pathway of the origination of the  $\text{Au}_4$  core, the smallest nucleus, from the  $[\text{Au}(\text{I})-\text{SR}]$  oligomers, and it is also the best candidate so far for the smallest superatomic  $\text{Au}_n(\text{SR})_m$  cluster.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Computational details, initial structures of the 55 isomers and their absolute energies after geometry optimization, strategies to create the isomers, simulated optical absorption of  $\text{Au}_{15}(\text{SCH}_3)_{12}(\text{SG})_1$ , and coordinates of isomer **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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spectrum of Au<sub>15</sub>(SG)<sub>13</sub>. This research used resources of the National Energy Research Scientific Computing Center (NERSC), which is supported by the Office of Science of the U.S. Department of Energy under contract no. DE-AC02-05CH11231.

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